

Summary of FY 2002 Geosciences Research

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FORWARD

The Department of Energy supports research in the geosciences in order to provide a sound foundation of fundamental knowledge in those areas of the geosciences that are germane to the Department of Energy's many missions, and those which provide stewardship for geosciences research capabilities, primarily 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, academic institutions, and other governmental agencies. 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. Within these areas, topics of research interest include Earth dynamics, properties of Earth materials, rock mechanics, seismic, electromagnetic and radar underground imaging, geochemistry, biogeochemistry, rock-fluid interactions, hydrogeology, coupled reactive fluid flow and transport, resource exploration and evaluation, and geomagnetic solar-terrestrial interactions. All such research is related either directly or indirectly to 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: Improving geophysical interrogation of the Earth's crust through better collection and analysis of seismic and electromagnetic data; improving understanding of geophysical signatures of fluids and fluid-bearing reservoirs; and characterizing geologic structures better.

Geochemistry: Investigating geochemistry of mineral-fluid interactions through 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 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

Mineral-Fluid Reactions: Synchrotron Radiation Studies at the APS

Principal Investigator: Paul Fenter, fenter@anl.gov, (630) 252-7053

Collaborator: Neil C. Sturchio, (now at) sturchio@uic.edu, (312) 355-1182

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 layering of fluid 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, including real-time measurements of the pH-dependent dissolution process of orthoclase cleavage surfaces and the systematic variation of dissolution kinetics with temperature, and measurements of the surface hydration structures of various mineral surfaces (e.g., muscovite, quartz).

LAWRENCE BERKELEY NATIONAL LABORATORY

Colloid Transport in Unsaturated Fractured Rocks and Porous Media

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

Collaborator: Tetsu K. Tokunaga, tktokunaga@lbl.gov, (510) 486-7176

Research Objectives: The earth science community has identified environmental nanoscience as an important emerging field. This project is to provide the first survey of mobile nanoparticle inventories for sediments from a variety of subsurface environments. The research will also provide systematic studies of subsurface nanoparticle transport, and its dependence on geochemical parameters.

Approaches: Quantification of the potentially mobile nanoparticle inventory requires separation of nanoparticle size fractions. In this study, particles in the < 100 nm size range are defined as nanoparticles. Flow-through columns, batch extractions in water, and batch extractions with a dispersant (sodium hexametaphosphate) are used. Thus, operationally defined measures of mass and specific surface areas associated with different particle fractions will be obtained in several sediment types from DOE facilities across the country. Nanoparticle transport quantification will be done through laboratory column experiments, with three main variables. These are natural versus synthetic (glass bead) sediments, natural versus synthetic (polystyrene latex) particles, and saturated versus unsaturated conditions. The validity of filtration theory predictions for nanoparticles will be tested through these experiments.

Results: Mobile nanoparticle inventories for two types of sediments, one from the Hanford Site and another from Oak Ridge National Laboratory, are being studied. Our results show that the release of mobile nanoparticles depends strongly on solution chemistry, including pH, ionic strength, and anion type. The maximum particle release occurred at the lowest ionic strength condition. Alkaline pH favors particles release. For example in the Oak Ridge sediments, the measured nanoparticle mass fractions (< 0.1 μm) were 0.98% at pH 12.0, and the maximum release obtained with hexametaphosphate solution is 1.72%. The nanoparticle fraction is about 7% of the total clay fraction (< 2.0 μm) released in this sediment. We have also found that U(VI) nanoparticles are more stable in the pore solutions of contaminated sediment than we had expected. U(IV) nanoparticles have been found in the mine drainage waters, resulting from microbial reduction. However, U(VI) species have previously been considered highly soluble under our test conditions. The mobility of U(VI) nanoparticles is currently being tested.

Computation of Seismic Waveforms in Complex Media

Principal Investigator: Valeri Korneev, vakorneev@lbl.gov, (510) 486-7214

The main goal of this project is to develop new processing technologies, which will improve the quality and resolution of seismic images for complex media, as well as understanding their connections with physical processes in rocks.

A significant part of the project helps to improve our understanding of seismic wave propagation in an active fault zone. Specific features of the recorded waves are attributed to the structural and physical properties of the fault, which allow extraction of more detailed information from the data. This includes extensive numerical modeling of seismic wave propagation in the fault zones and analysis and interpretation of recorded data. We use the Parkfield data as one application of the new forward modeling techniques developed in this work in a crustal scale. This study shows that fault-zone guided waves can be used for amplitude tomographic inversion giving high resolution images of the narrow low velocity layers. The resulting image includes several significant features in the fault zone - the region of shallow velocity change in the Vibroseis monitoring, high seismicity, the largest earthquakes and associated high slip rate, the 1966 M6 hypocenter, and the transition from locked to creeping behavior.

A unique data set was recorded in Weyburn field (Canada) for horizontal crosswell time-lapse survey. An innovative inverse scheme for guided wave tomography allowed to obtain first of the kind high-resolution images of thin low velocity target layer.

Another component of the project includes studies of the frequency dependence of seismic reflections from a thin fluid-saturated layer. Laboratory and field data were analyzed and interpreted. Reflections from a thin, water-saturated layer have increased amplitude and delayed travel time at low frequencies if compared with reflections from a gas-saturated layer. This effect was observed for both ultrasonic lab data and seismic field data. We compared the results of laboratory modeling with a diffusion-viscous theoretical model and found that low (< 5) values of the attenuation parameter Q and its approximate proportionality to frequency can explain the observations. The frequency dependent amplitude and phase reflection properties can be used for detecting and monitoring thin fluid-saturated layers.

Imaging Shear in Rocks

Principal Investigator: Seiji Nakagawa, snakagawa@lbl.gov, (510) 486-6792

Shear stress can have a significant impact on the mechanical and hydraulic properties of rocks containing fractures and faults. In particular, shear-induced slip along fractures and faults can cause rock failure at many scales, including instability of geological formations

during oil and gas production and CO₂ injection, and earthquakes induced by seismically active faults. Sheared fractures are also believed to be beneficial for enhancing the permeability of fractures in geothermal reservoir rocks while clay (shale)-smeared faults can serve as hydraulic barriers. The objective of this research is to understand the dynamic mechanical properties of sheared fractures and faults for their improved detection and characterization using geophysical (seismic) methods. Previously, we have shown that a fracture subjected to shear stress can exhibit anomalous conversion of seismic waves that indicates both the magnitude and orientation of the shear. In this research, we are conducting both experimental and numerical studies to examine the quantitative relationships between fracture geometry, stress state, and the resulting behavior of seismic waves. A two-dimensional fractured rock analogue has been built in the laboratory using an acrylic plate containing a rough fracture subjected to in-plane shear stresses, and seismic wave scattering measurements are being conducted. Numerical simulations of the experiment are conducted using the Discrete Particle Scheme (a variant of discrete element method) that can model both the nonlinear behavior of a statically sheared fracture and seismic wave propagation within the fractured medium. Also, an analytical model for seismic wave scattering by single fractures and faults with a heterogeneous distribution of surface compliance distribution was developed and implemented in a numerical code. This new model allows us to compute frequency dependent, three-dimensional scattering of seismic waves for a given distribution of fracture and fault compliances. Further, for studying the seismic attenuation characteristics of fault gouge materials at crosshole to borehole logging frequencies, a sonic frequency (1 kHz~ 10 kHz) acoustic resonance device has been built that can measure the seismic properties of small core samples (1.5 inches in diameter, near zero to a few inches in length).

Investigation of Scattering and Intrinsic Attenuation in Rock with Heterogeneous, Multiphase Fluid Distributions

Principal Investigator: Kurt T. Nihei, ktnihei@lbl.gov, (510) 486-5349

Research during this year focused on the development of an efficient seismic full-waveform inversion scheme for imaging frequency-dependent, viscoelastic moduli. Because the model updates in the inversion require repetitive numerical computations of the frequency response (phase and magnitude) of seismic waves propagating in heterogeneous, anisotropic, viscoelastic media, an efficient modeling scheme is required. The modeling approach that is being developed computes the frequency response at all locations in the model by running an explicit memory variable, staggered grid finite difference time domain code (MV-SG-FDTD) with a harmonic wave source out to steady-state, and then extracting the magnitude and phase from the transient data using a phase sensitive detection algorithm (PSD). The PSD algorithm requires integration over only several cycles of the waveform to obtain accurate phase and magnitude estimates. Because this integration is performed "on-the-fly", there is no need to store waveforms at the grid locations, as would be required if a Fourier Transform was used. Preliminary

tests demonstrate that it is possible to superimpose multiple frequencies at the source and extract the magnitude and phase at each frequency using the PSD algorithm. This opens up the potential for obtaining the multi-frequency response of a heterogeneous, anisotropic, viscoelastic medium with a single FDTD run. With a multi-frequency PSD, the response from multiple sources can also be obtained from a single FDTD run by "encoding" each source with a different frequency. These results form the basis for an efficient numerical modeling scheme for computing the multi-frequency, multi-source response of a heterogeneous, anisotropic, viscoelastic medium in a single FDTD run.

Investigator Symposium - Multiscale Reservoir Processes

Principal Investigator: Ernest Majer, elmajer@lbl.gov, (510) 486-6709

“Multiscale Reservoir Investigations and Applications to Terrestrial CO₂ Sequestration,” hosted by Lawrence Berkeley National Laboratory in Dec of 2001, was the ninth in a series of Geosciences Research Program Symposia dating from 1995. These symposia are topically focused meetings for principal investigators in the program and provide opportunities for our investigators to give presentations to one another and to discuss their Office of Basic Energy Sciences’ supported research. The presentations focused on the projects within Geosciences that are developing fundamental knowledge key to understanding critical issues surrounding geologic sequestration of CO₂ in the subsurface. This included imaging technologies, rock fluid interactions and flow and transport properties in the subsurface. In addition to the recognition the symposium gives to all of the investigators, we traditionally also recognize one outstanding contribution from a DOE Laboratory Project and one from a University Project. The outstanding contributions are selected by our session chairpersons. We were fortunate to have as guest session co-chairs Prof. John Logan, Emeritus Professor from Texas A&M University, Dr. Robert Burruss of the U.S Geological Survey, Professor Bob Benson of Colorado School of Mines and Professor Tony Kavscek of Stanford University. They join our Principal Investigator co-chairs Dr. Grant Garven of Johns Hopkins University, Dr. Laura Pyrak-Nolte of Purdue University, Dr. Kevin Knauss of Lawrence Livermore National Laboratory, and Dr. Greg Newman of Sandia National Laboratory.

Joint Inversion for Subsurface Imaging

Principal Investigator: Ki-Ha Lee, khlee@lbl.gov, (510) 486-7468

Hydrological properties such as fluid electrical conductivity and porosity cannot be directly obtained with conventional geophysical imaging techniques. The electromagnetic (EM) field propagating in the subsurface is a function of bulk conductivity, which in turn may be empirically related to porosity, pore fluid conductivity, saturation, and temperature. Similarly, the amplitude, phase and velocity of seismic wave depend on several factors such as porosity, density, elastic constants, temperature, and pressure. The

objective of this study is to develop methodologies for directly mapping hydrological parameters using joint inversion of different geophysical data, along with the use of empirical relationships between geophysical and hydrological parameters. To assess the feasibility of deriving hydrological properties directly, we introduced a joint inversion technique using EM and seismic traveltimes data (Tseng, H.-W., and Lee, K.H., Joint inversion for mapping subsurface hydrological parameters, Expanded abstracts, SEG International Exposition and 70th Annual Meeting, San Antonio, TX, 1341-1344, September 9 - September 14, 2001). Because of the limited capability inherent to the inversion techniques used, we began investigating advanced inversion schemes for the improved joint inversion. Most of EM inversion studies in the literature is full waveform, however, there is a lack of similar studies in the seismic area. Full waveform inversion of seismic data is difficult partly because of poor source information. Since currently available approaches involve some form of approximations to the source, inversion results are subject to the quality and the choice of the source information used. Exploiting the useful property of the normalized wavefield, we have developed a full waveform inversion scheme (Lee, K.H., and Kim, H.J., 2003, Source-independent full waveform inversion of seismic data, accepted for publication in Geophysics, published electronically May 20, 2003, LBNL-49934). A gather of seismic traces is first Fourier-transformed into the frequency domain and a normalized wavefield is obtained for each trace in the frequency domain. Normalization is done with respect to the frequency response of a reference trace selected from the gather. The source spectrum is eliminated during the normalization procedure. The inversion algorithm minimizes misfits between measured and computed normalized wavefields.

Prediction and Evaluation of Coupled Processes for CO₂ Disposal in Aquifers

Principal Investigator: Karsten Pruess, K_Pruess@lbl.gov, (510) 486-6732

The purpose of this research is to develop a systematic, rational, and mechanistic understanding of the coupled processes that would be induced by injection of CO₂ into saline aquifers. This is being 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. Three interrelated numerical simulation codes have been developed that address, respectively, issues of fluid dynamics (TOUGH2/ECO₂), reactive chemical transport (TOUGHREACT/ECO₂), and geomechanics (TOUGH-FLAC). TOUGH2/ECO₂ has been used to study immiscible displacement of brine by supercritical CO₂ for a range of scales and hydrogeologic conditions. Buoyancy effects tend to drive CO₂ towards the top of the permeable interval. This is found to reduce storage capacity, but also has the favorable effect of reducing interference between CO₂ and the aqueous phase, thus reducing injection pressures. CO₂ leakage through faults has a potential to be self-enhancing. The TOUGHREACT code has been used to analyze mineral alteration, CO₂ sequestration by secondary carbonates, and reservoir porosity changes in sandstones

modeled after Gulf Coast sediments. The amount of CO₂ that may be sequestered as solid carbonates is found to be roughly comparable to what may be held in aqueous solution. Geomechanical aspects of CO₂ sequestration have been studied using a simulator TOUGH-FLAC that was newly developed in this project. Increasing fluid pressure due to CO₂ injection will reduce the vertical effective stress, inducing vertical expansion of the aquifer. Our modeling studies suggest that these effects 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. 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.

Air-Derived Noble Gases in Sediments

Principal Investigator: B. Mack Kennedy, bmkenedy@lbl.gov, (510) 486-6451

Collaborator: Thomas Torgersen, thomas.torgersen@uconn.edu, (860) 405-9094

The goal of this project is to isolate and identify the various air-derived noble gas components in sediments, particularly, but not exclusively, those sediments associated with hydrocarbons. The project is designed to address how noble gas elemental patterns are acquired and retained, how they are transferred to basin fluids in which they have been measured, and to improve the 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 smooth mass dependent abundance patterns have led to adsorption hypotheses, three observations argue against single stage 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) Laboratory heating experiments suggests the enriched component is tightly bound, counterintuitive to a simple adsorption history. And (3) many sedimentary rocks (~half) and some oil field gases contain excess Ne in conjunction with excess Xe.

We are examining diffusive filling and emptying of angstrom-scale half-spaces in lithic grains as an explanation for the observed absolute and relative abundances sedimentary rocks. Since physical properties of the noble gases are strong functions of atomic mass, the individual diffusion coefficients, adsorption coefficients and atomic diameters combine to impede heavy noble gas transport relative to the lighter noble gases. Filling of lithic grains/half-spaces thus produces Ne enrichments in the early and middle stages of the filling process, emptying lithic grains/half-spaces produces a Xe-enriched residual in the late stages of the process, and both Ne and Xe enrichments can be produced by

incomplete emptying of the half-spaces followed by incomplete filling. A system of labyrinths-with-constrictions when combined with simple adsorption results in stronger diffusive separation and non-steady-state enrichments that persist for longer times. Laboratory work is currently underway to better evaluate noble gas absolute and relative abundances in sediments by isolating and identifying carrier phases and trapping mechanisms.

Center for Isotope Geochemistry

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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.

Clay Mineral Surface Geochemistry

Principal Investigator: Garrison Sposito, GSposito@lbl.gov, (510) 643-8297

Because of their ubiquitous presence in natural earth materials and their strong surface reactions with cations and organic molecules, clay minerals figure importantly in a broad range of phenomena, from global climate change to contaminant management. Our research is designed to provide molecular-scale information about the mechanisms of these surface reactions based on computer simulation using tested codes and realistic models of clay mineral interactions with liquid water and a variety of dissolved chemicals (e.g. cations).

The model clay mineral that we have studied is based on natural Wyoming montmorillonite (MMT). The unit cell structure, $M_{0.75}[Si_{7.75}Al_{0.25}](Al_{3.5}Mg_{0.5})O_{20}(OH)_4$, was used in a simulation slab consisting of 8 unit cells with six charge-balancing counterions. We have investigated the counterions Li^+ , Na^+ , Mg^{2+} , and Ca^{2+} . Monte Carlo (MC) simulations to determine equilibrium structure were performed on supercomputers at NERSC using the code MONTE. Isobaric-Isothermal ensemble (1 atm and 300K) MC simulations were carried out at 1 atm for interlayer water contents up to 10 molecular layers (i.e. 320 water molecules per simulation slab). Layer spacing was monitored to characterize swelling behavior.

We observed the layer spacing of Mg^{2+} to be greatest for $0 < N_{water} < 100$ (N_{water} = number of water molecules). The other bivalent cation, Ca^{2+} showed a similar swelling pattern over the same hydration range but less swelling than Mg^{2+} . Monovalent cations (Li^+ and Na^+) showed smaller swelling effects than the bivalent cations. A difference in layer spacing between Li^+ -MMT and Na^+ -MMT occurred between $N_{water} = 30$ and 50. We obtained water O density profiles at $N_{water} = 24$ and 54. The Na^+ -MMT hydrate exhibited a monolayer of water at $N_{water} = 24$, whereas Li^+ -MMT showed two layers of water at both $N_{water} = 24$ and 54. This difference may be due to size of the Li^+ being smaller than Na^+ . For $N_{water} > 160$, the layer spacing profile of Li^+ was virtually the same as that of Na^+ .

Development of Isotope Techniques for Reservoirs

Principal Investigator: B. Mack Kennedy, bmkenedy@lbl.gov, (510) 486-6451

This project develops noble gas isotope techniques for characterizing fluid sources, fluid flow paths, reservoir filling and compartmentalization, flow in homogenous versus fractured media, and water-rock interaction. This project also seeks to merge isotope techniques with structural and imaging information provided by geophysical techniques.

Successful sequestration of CO₂ will require reliable characterization of the storage potential of geologic formation reservoirs and aquifers and a better understanding of the multiple processes that affect the fate and transport of CO₂ in the subsurface. Groundwater aquifers and oil and gas reservoirs are complexly partitioned. Quantifying leakage to overlying strata and hydrodynamic processes such as advection, dispersion, and mixing/dilution, as well as chemical processes such as diffusion into low permeability matrix rocks, phase partitioning, dissolution/precipitation of carbonate minerals, and water-rock interaction bear directly on prediction of transport efficiency and the fate of injected CO₂. We seek to maximize CO₂ sequestration efficiency by addressing these and similar issues related to reservoir and aquifer characterization.

In collaboration with Drs. D. R. Cole and J Horita, Oak Ridge National Laboratory and M. Morea, ChevronTexaco, gas and isotope chemistry were monitored during the CO₂/Water injectivity tests conducted in the Belridge Diatomite of the Monterey Formation in the Lost Hills Oil Field, CA. Sampling was conducted periodically from Aug. 2000 through Oct. 2002. The contribution of CO₂ injectate to the production stream sampled at the monitoring wells can be quantified by mass balance modeling of the trends in the CO₂ concentration, carbon isotope composition of the co-produced CO₂ and CH₄, and the noble gas chemistry and isotopic composition. This approach demonstrates that increases in CO₂ and more depleted ¹³C values correlate with periods of CO₂ injection. During water flood events, the CO₂ contents decrease and the ¹³C values return to more reservoir-like in magnitude. Trends in noble gas chemistry and isotopes confirms mixing between indigenous reservoir fluids and injected CO₂ and under more controlled conditions would have provided a quantitative measure of the injected CO₂ return rate.

Kinetic Isotope Fractionation

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The mass-dependant fractionation of stable isotopes can occur during a number of physical processes, only some of which are well understood theoretically and well investigated experimentally. In particular, the kinetic fractionation of isotopes during diffusion, though understood for gaseous systems, is not well characterized and understood for condensed systems such as liquid water or silicate melts. We undertook experiments in aqueous solutions and silicate melts to better understand the phenomenon of kinetic fractionation during diffusion. Results could provide a signature for diffusion in geochemical and biological systems, as well as add to fundamental understanding of the structure and behavior of ion complexes in aqueous solutions. The experimental setup consists of a glass flask immersed in a larger (~300x) volume container. The flask is filled with a solution of the element of interest and communicates with the larger container via a thin tube. The experiments reported here used a lithium chloride solution

in the flask and high purity water in the surrounding container. Pairs of flasks and containers were allowed to exchange for periods ranging from 31 to 99 days. At the end of an experiment, we measured the concentrations of Li remaining in the flask and built up in the container. Lithium isotopic compositions ($^7\text{Li}/^6\text{Li}$ ratios) were measured by multiple-collector ICP mass spectrometry (MC-ICPMS) in the CIG at LBNL. Though fractionation was observed, about 7 ‰, it was not as great as would be expected from our experiments using other solvents. A portion of the difference probably results from Li^+ diffusing as a hydrated complex, diluting the ^6Li - ^7Li mass difference. Observations and models by others suggest a sphere of four to six water molecules surrounds Li^+ ions. But for an exponent of 0.5, as for a gas, a sphere of 11 waters would be required, an improbable number. If the hydration sphere consists of four waters, then an exponential factor of ~ 0.2 reproduces the data. This may reflect the inelastic nature of interactions between water molecules and the Li^+ hydrated complex. Further experiments are being conducted to better understand and independently constrain the exponential factor and the hydration number.

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

Principal Investigator: Glenn A Waychunas, GAWaychunas@lbl.gov, (510) 486-2224

Nanoscale coating formation on quartz wafers placed in wells at the Cape Cod USGS field site show the development of both iron-aluminum oxides and Ca-rich phases. Studies of the coatings via synchrotron-based total reflection x-ray fluorescence (TRXRF) show that areas of the wafers containing high Ca content have much less oxide formation. Analysis of the oxide coatings suggest a ferrihydrite or poorly crystalline phase with no obvious evidence of orientational ordering. Fundamental studies on the (0001) quartz surface included measurement of six crystal truncation rods (surface x-ray diffraction) under wet conditions, and evaluation of the ordering of water in the first molecular layer via SFVS (sum frequency vibrational spectroscopy). The CTR measurements suggest that the (0001) surface differs significantly from the bulk termination structure, but is not consistent with the "dense surface" structure predicted by simulations of the vacuum interface. The SFVS measurements show that the first water layer has more ordered components with tetrahedral bonding than observed for the wet vitreous silica surface, resulting in a red shift of the lowest frequency water vibrational band. In addition, the phase of the absorption between this low frequency ("ice-like") and next higher frequency ("water-like") band is found to be reversed near the PZC for quartz. This suggests that at low pH values the surface structure enhances the ordering of the first contact water layer, resulting in a dipole moment that is then partially cancelled by less-bonded water molecules. Far from the PZC the phase difference disappears, suggesting that the high overall surface charge dominates over any local molecular ordering effects. CTR work on the (0001) hematite surface has suggested a structural mechanism for the heightened reactivity of this face compared to the nominally isostructural sapphire (0001) surface. The hematite (0001) surface consists of a partially

occupied FeO_6 octahedral layer having favorable attachment sites for sorption, while the sapphire (0001) surface is fully occupied with AlO_6 octahedra. Further CTR work has examined the (0001) surface with silica and arsenate sorption complexes, the latter case also studied via grazing incidence EXAFS analysis. This work confirms the surface structure predicted by the CTR measurements.

Reactive Chemical Transport in Structured Porous Media

Principal Investigator: Tetsu K. Tokunaga, tktokunaga@lbl.gov, (510) 486-7176

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

Objectives: In subsurface reactive transport, large differences in chemical composition can be sustained in boundary regions such as sediment-water interfaces, interior regions of soil aggregates, and surfaces of fractured rocks. Studies of reactive transport in such boundary zones require information on chemical speciation with appropriate spatial and temporal resolution.

Project Description: Predicting transport of trace elements between various environmental compartments is currently often unsuccessful, partly due to lack of relevant information at compartment boundaries. Without in-situ, spatially- and temporally-resolved chemical information, transport between compartments can only be described with system-specific, nonmechanistic, mass transfer models. In this project, the synchrotron x-ray microprobe and micro-XANES techniques are used to obtain such measurements in a variety of critical microenvironments. Past efforts in this project focused on reactive transport of selenium and chromium in two types of microenvironments, the surface water-sediment boundary, and soil aggregates. In FY 2002, the project's focus shifted to the problem of uranium transport. Like Se and Cr, transport of U is strongly influenced by redox dependent solubility. However, the much stronger and highly pH-dependent sorption of U(VI) makes its transport more difficult to predict in systems exhibiting rapid changes in pe and pH. The current efforts are aimed at reconciling differences between measured U(VI) diffusion into sediments and predictions based on standard diffusion models and sorption isotherms.

Results: Measurements were obtained on U(VI) diffusion into two different soil types, under acidic and alkaline conditions. Periodic measurements of redox potential profiles within the soil columns, and of pH and U concentrations in the boundary reservoirs were obtained. Profiles of the total U and U(VI) distribution in the sediment column were obtained by micro- x-ray absorption near-edge structure (micro-XANES) spectroscopy at the GSECARS (APS) and X26A (NSLS) microprobe facilities. Micro-XANES analyses confirm that U remains as oxidized U(VI) forms in systems with low organic carbon availability. Strong pH-dependent apparent U(VI) diffusivities are obtained in transient experiments. These measured apparent diffusivities are significantly greater than values predicted from aqueous phase U(VI) diffusivities, soil porosities, and pH-dependent

sorption isotherms. The discrepancies have motivated new studies on surface diffusivities of adsorbed U(VI).

Unsaturated Fast Flow in Fractured Porous Media

Principal Investigator: Tetsu K. Tokunaga, tktokunaga@lbl.gov, (510) 486-7176

Objectives: The nature of unsaturated fast-flow in fractured rocks needs to be understood in order to obtain reasonable constraints on vadose zone transport. Water films along unsaturated fractures have been shown to be capable of supporting fast flow and transport, and revealed limitations of existing aperture-based models. Our latest studies compare unsaturated hydraulics of fractured rocks and gravels.

Project Description: The concept of film flow was introduced as a process by which preferential flow could occur along truly unsaturated fractured rock. Our work concerns water films on fracture surfaces under near-zero matric potentials, and examines the possibility of fast, unsaturated flow under tension. Thus, the thickness and connectivity of pendular film regions are important in controlling film flow on individual fracture surfaces. For similar reasons, films and pendular ring connectivity determine the hydraulic properties of unsaturated gravels. The current studies examine limits of capillary scaling and necessary conditions for removal of capillary hysteresis in gravels.

Results: Capillary models and unsaturated hydraulic scaling were used to predict conditions necessary for removal of hysteresis. A predicted grain-size limit of 10.4 ± 0.5 mm was obtained by applying Miller-Miller scaling to a conceptual model of Haines. More generally, hysteresis is predicted to also depend on surface tension, fluid densities, and the acceleration. Disappearance of hysteresis was tested through measurements of drainage and wetting curves for sands and gravels. The influence of surface tension was tested through measurements of $S(y)$ in gravel, without and with a surfactant (SDBS). Measurements showed that hysteresis loops remain well defined for grain-sizes up to 7 mm. At a grain-size of 9 mm, hysteresis is barely detectable. For grain-sizes equal to or greater than 10 mm, hysteresis is not observed. All results support our general analysis that predicts elimination of hysteresis based on fluid densities, acceleration, grain-size, and surface tension. These parameters combine to yield the dimensionless Haines number, with a critical value of 14.8 ± 1.4 . Above this value, capillary hysteresis is not possible. Thus, hysteresis is not a fundamental feature of unsaturated porous media. The behavior of unsaturated media containing surfactants and/or in centrifuges can violate classical capillary scaling.

LAWRENCE LIVERMORE NATIONAL LABORATORY

Analysis of Physical Properties for Heterogeneous Rocks Containing Fluids

Principal Investigator: James G Berryman, berryman1@llnl.gov, (925) 423-2905

Earth materials are notoriously heterogeneous, and at almost any scale of observation that one might choose to study them. Yet, the theoretical tools traditionally available for studying these effects introduced by Biot and Gassmann, in what is now often Biot-Gassmann theory of poroelasticity, originally treated only homogeneous (even microhomogeneous!) media. It has been one main purpose of this continuing project to extend this theory and incorporate first heterogeneity and then multi-scale heterogeneity in order to make the theory useful to realistic earth sciences problems in both oil and gas exploration contexts, and also in earthquake analysis. This effort has been a long process, but we have made significant progress on the heterogeneous extensions throughout the 1980s and 1990s. Since about 1994, we have also been studying (with H. F. Wang and others) the double-porosity (or sometimes multi-porosity) extensions for multi-scale heterogeneous media (especially those relevant to oil reservoir exploration and exploitation). We believe that significant progress has been achieved. In particular, some exact results for two-component systems are now available for both heterogeneous and double-porosity systems. Furthermore, very recent publications with S. R. Pride and others have incorporated sensible models of attenuation into the same formalism, so now velocity and attenuation can both be treated within the same theoretical framework. The double-porosity scheme is very natural for reservoir analysis, and in fact the concept was originally developed for fluid flow calculations in geomechanically rigid reservoirs. So the recent work has successfully extended that earlier work to incorporate seismic wave velocity, attenuation, and possibly also a means of estimating fluid permeability from seismic data as well. But some of this work as well as various extensions and elaborations thereof are still in progress at this time.

Application of Geophysical Tomographic Imaging

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Subsurface imaging technology, such as electric resistance tomography (ERT), may be useful for characterizing some soil properties of the near-surface hydrologic regime that are related to electrical conductivity. However, an image of the subsurface soil distribution gives little or no information concerning how the site will respond to groundwater flow or contaminant transport. There is even some question that tomographic imaging of soils alone can actually provide meaningful values of hydrologic

properties. The goal of this work is to utilize imaging not just as a means to characterize the soil structure by mapping different soil types but also as a way of obtaining quantitative information about how a site will respond hydrologically to an infiltration event. In the modeling component of this project, we have been looking at how Bayesian statistical approaches in conjunction with ERT imaging studies can be used to "soft condition" model domains of hydrologic systems that must already satisfy "hard constraints" associated with borehole logs and coring. During FY02 we used hydrologic data from the Vadose Zone Observatory (VZO) field study area at Lawrence Livermore to develop a range of initial lithologic descriptions of the hydrologic domain. Numerical simulations of infiltration are obtained using these domains and the results are in the process of being compared to ERT images of changes in the electrical conductivity associated with infiltration. The ability to soft condition the hydrologic properties of model domains will depend on the accuracy of linking saturation changes to conductivity changes, which is also a continuing aspect of our research. In the laboratory phase of this project (#458), a study has been carried out in collaboration with Rensselaer Polytechnic Institute (RPI) to investigate the merits of using single versus multiple current sources in ERT studies. Electrode array models similar to those used at the VZO have been employed in both saline- and soil-filled tanks. Results obtained show that target distinguishability in a domain characteristic of a hydrologic regime is greater for the multi-source current approach. This suggests that single-source, geophysical imaging may benefit by using multiple current sources. A paper describing this work is in progress.

Electrical Properties of Rocks

Principal Investigator: Jeffery J. Roberts, roberts17@llnl.gov, (925) 422-7108

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. The focus is on samples from active regions of geophysical interest.

The first year of this project has focused on experimental design and measurements of dielectric constant, electrical resistivity, and zeta potential of clay-water mixtures. Both swelling and non-swelling clays were mixed with a variety of saturating fluids. Preliminary results indicate that fluid salinity strongly affects surface conduction of swelling and non-swelling clays differently. Electrical conductivity measurements were also performed on rocks from the Miocene Monterey formation and the Parkfield

syncline leading to an alternate explanation of an anomalously conductive region identified by a high resolution magnetotelluric profile across the San Andreas fault. A previous interpretation attributed the conductive region to fractured rock saturated with brines, and our laboratory measurements suggest that the anomalous region could result from conductive sedimentary rocks in a plunging syncline that is adjacent to the fault. If correct, the current surface trace of the San Andreas fault at Middle Mountain does not form the boundary between the Salinian block and the North American plate, but is ~1 km west and collocated with current seismicity. This work has helped develop a strong collaboration with Steve Park of UC Riverside and resulted in two journal publications.

Geophysical Monitoring of Carbon Dioxide Sequestration Using Electrical Resistance Tomography (ERT)

Principal Investigator: Robin L. Newmark, newmark1@llnl.gov, (925) 423-3644

If geologic formations are used to sequester carbon dioxide (CO₂) for long periods of time, it will be necessary to verify the containment of injected CO₂ by assessing leaks and flow paths. The objective of this work is to develop a quantitative understanding of the effects of CO₂ migration on the electrical properties of these geologic materials, and our ability to detect and monitor them. Numerical and physical studies have been carried out to evaluate the sensitivity of electrical resistance tomography (ERT) to electrical resistivity changes caused by CO₂ injection and sequestration in geologic reservoirs. We chose the Maljamar CO₂ flood as a basis for our numerical modeling study. Physical models consisting of blocks of various materials inserted in a water tank are used to evaluate some of the conclusions of the numerical study. This study quantifies the effects of a variety of factors that affect the resolution and accuracy of the ERT method, under realistic conditions of scale, contrast, and measurement error. Scenarios where vertical arrays of point electrodes are used and where metal-cased boreholes are used as long electrodes are considered. Long electrode tomographs provide information such as the shape, location, and lateral extent of the flood. When point electrode arrays or horizontal wells are available, the approximate vertical extent of the flood and coarse estimates of sequestered CO₂ volume may be deduced. Results from physical models support trends observed in the numerical study, and suggest that the ERT method can help confirm the containment of CO₂. Based on our numerical and experimental results, we have conducted field trials in an oil field undergoing CO₂ flood to evaluate the effectiveness of using well casings as very long electrodes with the goal of producing images of CO₂ migration at very low cost, with no interruption to field operations and without the need for additional drilling. Initial time-lapse casing ERT survey results show changes consistent with operational changes across the survey areas, and are consistent with independent measurements (i.e., production records).

Three Dimensional Analysis of Seismic Signatures & Characterization of Fluids & Fracture in Anisotropic Formations

Principal Investigator: Patricia A. Berge, berge1@llnl.gov, (925) 423-4829

Collaborators: Gary Mavko, mavko@stanford.edu, (650) 723-9438; Ilya Tsvankin, ilya@dix.mines.edu, (303) 273-3060

Seismic anisotropy caused by layering, foliation, or aligned fractures is pervasive in sediments and rocks such as silty sands, clay-bearing sandstones, shales, and fractured igneous rocks. Earth materials with interconnected pores or fractures can behave mechanically as poroelastic media. Recent advances in laboratory and field techniques allow measurement of all the constants needed to characterize mechanical behavior of some earth materials that are either anisotropic or poroelastic. Current research efforts in the oil industry and university collaborations may provide ways to measure the many anisotropy parameters and poroelastic constants needed to characterize poroelastic, anisotropic sediments and rocks. These earth materials are important in many environmental cleanup, energy resource, and civil engineering applications. The availability of reliable lab and field data gives incentive for developing better theoretical methods for analyzing poroelastic, anisotropic earth materials. Some models do exist but they have significant limitations. Incorporating fluid effects into some of the common anisotropy models yields insight into the implicit assumptions in the models as well as into material behavior.

Our major objective is to obtain constraints on lithology in fluid-filled anisotropic rocks by using rock physics theories for anisotropic and poroelastic media. We are collaborating with investigators on related OBES projects at the Colorado School of Mines and Stanford University, who are developing techniques for obtaining anisotropy parameters from seismic reflection data (CSM) and relating laboratory measurement information to modeling and field data (Stanford). By using our theoretical methods to model the anisotropy parameters recovered from seismic data, we can find ways to improve analysis of seismic reflection data collected in areas where the geology is complicated by anisotropy and heterogeneity.

Experimental Investigation into the Role of Water During the Thermal Maturation of Sedimentary Organic Matter

Principal Investigator: Roald Leif, leif1@llnl.gov, (925) 422-2469

Generation of oil by geological maturation of sedimentary organic matter is primarily a thermal process involving a complex mix of hydrocarbon cracking reactions. The presence of water has been identified as a chemically reactive component during the oil formation process. The purpose of this study is to investigate aqueous-organic chemical reactions important for understanding the role of water in petroleum generation. High temperature/high pressure hydrous pyrolysis reactions are performed using Dickson-type

flexible gold bag rocking autoclaves. This approach is used to identify reaction pathways between water and sedimentary organic matter. The results of these experiments are applied to lower temperature organic geochemical processes that occur over geological time. Key reaction mechanisms between water and hydrocarbons have been identified. Elucidation of reaction pathways is aided by the use of isotopic labeling. Detailed identification of reaction products and mass balance measurements provide information for mechanistic and kinetic evaluations.

In-Situ CO₂ Sequestration

Principal Investigator: Susan Carroll, carroll6@llnl.gov, (510) 423-5694

We experimentally measured labradorite dissolution rates using a mixed flow reactor from 30 to 130°C as a function of dissolved carbon dioxide (3 mM and 0.6 M), and aluminum (0.001 to 1 mM) at pH 3.2. Over these experimental conditions, labradorite dissolution can be described with a single rate expression that accounts for observed increases in dissolution rate with increasing temperature and decreases in dissolution rate with increasing dissolved aluminum:

$$\text{Rate}_{\text{Si}} (\text{mol Labradorite cm}^{-2} \text{ s}^{-1}) = k'' \times 10^{(-E_a/2.303RT)} [(a^{3n\text{H}^+}/a^{n\text{Al}^{3+}})K/(1+K (a^{3n\text{H}^+}/a^{n\text{Al}^{3+}}))].$$

where the apparent dissolution rate constant, $k'' = 10^{-5.69}$ (mol Labradorite cm⁻² s⁻¹) and the net activation energy, $E_a = 10.06$ (kcal/mol). This temperature dependent rate expression is partly based on the model proposed by Oelkers and co-workers in which the dependence of silicate dissolution rates on dissolved aluminum in acidic solutions is attributed to H⁺ - Al³⁺ exchange at the mineral surface and formation of silica rich surface complexes. For this exchange reaction, regression of the experimental data yield a stoichiometric coefficient $n = 0.31$ and a enthalpy of reaction $\Delta H = 0.54$ (kcal/mol). The temperature dependence of the silica rich surface complex formation constant, K , was estimated from the van't Hoff equation and yielded $K = 4.49$ to 5.61 from 30 to 130°C. The affect of CO₂(aq) on mineral dissolution is accounted for by changes in solution pH, because elevated CO₂(aq) did not directly effect dissolution. At temperatures below 100°C, labradorite dissolves incongruently with preferential dissolution of Na, Ca and Al over Si.

Investigation of the Physical Basis for Biomineralization

Principal Investigator: James DeYoreo, deyoreo1@lbnl.gov, (925) 423-4240

Collaborator: 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. 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.

Kinetic Isotope Fractionation

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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 $^{44}\text{Ca}/^{40}\text{Ca}$ by more than 6‰, and for $^7\text{Li}/^6\text{Li}$ 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 $^{26}\text{Mg}/^{24}\text{Mg}$) 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 $^7\text{Li}/^6\text{Li}$ 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.

Mineral Dissolution and Precipitation Kinetics

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Collaborator: Carrick Eggleston, carrick@uwyo.edu, (307) 766-6769

Plug Flow Reactor (PFR) macroscale reactive transport experiments were performed to scale up from the Hydrothermal Atomic Force Microscope (HAFM) experiments that we have conducted to date. Our first PFR experiment was 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, and subsequent X-ray Diffraction (XRD) post-mortem of the reacted solids show that significant amounts of a high-Ca strontianite were precipitated and coated the calcite grains in the first half of the column. Vertical Scanning Interferometric (VSI), Scanning Electron Microscopic (SEM), and AFM examination of reacted grains show that the armoring crust of strontianite did not impede calcite dissolution. We noted etch pits underneath a thick crust of strontianite crystals. Elsewhere underneath the strontianite crust it is clear that some reprecipitation of calcite has occurred, displayed as new growth hillocks, suggesting that locally solution compositions reached calcite saturation, in spite of an incoming fluid that was considerably undersaturated with respect to calcite

solubility. The bulk fluid exiting the core was essentially at calcite saturation. Analyses continue on the solids and fluids recovered during this experiment. These results, and others from the continuing series of runs, will provide a vehicle for benchmarking our reactive transport simulators by comparing them to the a priori simulations made using the code CRUNCH. This is a critical undertaking, given that a wide variety of DOE programs depend upon the results obtained from reactive transport simulators, which are largely unvalidated with respect to coupled dissolution and growth processes. We will also relate the macroscopic and microscopic results obtained at LLNL, U of Wyoming and Wright State University in the effort to up-scale from our nanoscale dynamic measurements.

Reactive Transport of CO₂ Rich Fluids

Principal Investigator: William Durham, durham1@llnl.gov, (925) 422-7046

The project entails reacting fluids with rock in the laboratory setting. Experiments and simulations are to be done on rock samples containing a single laboratory-made or natural fracture. Detailed imaging of the fracture aperture before and after alteration are coordinated with measurements of fracture deformation, permeability, dispersivity, and effluent composition, all as functions of pressure, temperature, temperature gradient, time, rock composition, fluid velocity, and fluid composition. For the most part we work with simple but relevant systems in order to maximize our understanding and impact: samples are monomineralic rocks with low porosity and low bulk permeability (such as marble), under fully saturated, single-phase flow conditions. We will attempt measurements in undersaturated, dual-porosity, and more chemically complex settings as success dictates. Recent results of flow simulations show flow patterns with high precision. The simulations have the additional advantage that transport of dissolved minerals and surface reaction can be included, and that work is in progress. Along with reactive flow experiments being carried out on Carrara marble, additional experiments are underway in analog KDP (potassium di-hydrogen phosphate) fractures. This material not only reacts at convenient rates in the laboratory, but it is sufficiently transparent that imaging of the fracture is possible during the fluid flow experiment. This allows direct measurement of fracture apertures during reactive flow experiments using light transmission techniques.

Testing Deep Saline Aquifers

Principal Investigator: Gregory J. Nimz, nimz1@llnl.gov, (925) 423-2766

The ultimate objective of this project is to develop techniques based on noble gas isotopes to test deep saline aquifers for long-term leakage of gases. Such aquifers are suggested as repositories for industry-derived CO₂, effectively sequestering this

"greenhouse" gas. Some noble gas nuclides, notably 4He , 21Ne , 40Ar , and $134,136\text{Xe}$, are produced in-situ in aquifers, and accumulate in measurable abundances. If CO_2 is capable of leaking, these gas nuclides would likely also be affected, and their full accumulation would not be observed. In-situ production of most noble gas nuclides is due directly or indirectly to aquifer uranium and thorium through spontaneous fission and radioactive decay. Knowing effective average concentration of U and Th allows estimation of equilibrium concentrations of in-situ noble gas isotopes - required for this technique. Since the integrated history of U and Th "exposure" for saline waters is important, U and Th concentrations in any one aquifer rock is insufficient. Rather, we are investigating ^{36}Cl and ^{129}I as indicators of integrated U-Th exposure. Magnitudes of $^{36}\text{Cl}/\text{Cl}$ ratios will reflect integrated neutron flux resulting from U-Th decay, and $^{129}\text{I}/\text{I}$ ratios will reflect magnitudes of U spontaneous fission. Derived integrated values of U-Th exposure can then be used to estimate equilibrium concentrations of noble gas isotopes. This assumption was investigated through combined analysis of ^{36}Cl and ^{129}I in a variety of aquifer lithologies. For example, we analyzed a suite of Gulf Coast carbonate brines for $^{36}\text{Cl}/\text{Cl}$ that had previously been analyzed for $^{129}\text{I}/\text{I}$ (Moran et al, 1995). Carbonate aquifers are a low U-Th environment, providing an endmember case. The suite produced $^{36}\text{Cl}/\text{Cl} = 5.2\text{E}-15$. Assuming the aquifer $\text{Th}/\text{U} = 2$, common for carbonates, the $^{36}\text{Cl}/\text{Cl}$ ratio implies $[\text{U}] = 1.35$ and $[\text{Th}] = 2.70$. This U concentration produces a calculated $^{129}\text{I}/\text{I}$ ratio of $30\text{E}-14$, using a spontaneous fission half-life of $\sim 7\text{E}+15\text{a}$ and a fission yield of 0.04%. This calculated $^{129}\text{I}/\text{I}$ ratio compares well with the measured values of $27\text{E}-14 \pm 6\text{E}-14$, suggesting that the $^{36}\text{Cl}/\text{Cl}$ and $^{129}\text{I}/\text{I}$ ratios accurately reflect aquifer U and Th concentrations. Other lithologies of saline aquifers were also investigated with similar results.

LOS ALAMOS NATIONAL LABORATORY

Fast 3D Seismic Modeling

Principal Investigator: Michael Fehler, fehler@lanl.gov, (505) 667-1925

Collaborator: Ru-Shan Wu, wrs@earthsci.ucsc.edu, (831) 459-5135

Objectives: Our objectives are to use wave equation migration to improve the quality of information that can be obtained from seismic images. We also seek exploit the natural advantages of our methods for providing reflection amplitude vs. angle information that can be used to infer in situ parameters like rock properties and fluid type and content. In addition, we are investigating wave propagation in heterogeneous media with the intent of developing new methods for characterizing the Earth's heterogeneity on scales that cannot be determined using deterministic approaches.

Results: One area we have investigated is the applicability of using wave-equation migration for imaging using cross-well data. We have compared the image of a field dataset obtained using wave-equation imaging with that obtained using both ray-based Kirchhoff migration and a method called mapping, which has been used for cross-well data. We find that wave-equation and Kirchhoff migration provide images that have more information than can be found by using mapping. We have also developed a new migration imaging condition that combines common-angle images for different incidence/reflection angles using an angle-dependent weight. The method uses a new common-angle imaging approach that we have also developed. The output volume after application of the new imaging condition will be three dimensional for 3D cases, rather than four- to five-dimensional. The new image is the normal-reflection image that is proportional to the normal-reflection coefficients at interfaces for amplitude-preserving migration. This method provides the ability to obtain robust information that may be interpreted to infer material properties at an interface in the Earth. We have also developed a method for characterizing the spectrum of the heterogeneous structure of a medium.

Nonlinear Dynamics of Fluid/Contaminant

Principal Investigator: Bryan J. Travis, bjtravis@lanl.gov, (505) 667-1254

Collaborator: David Yuen, davey@krissy.geo.umn.edu, (612) 624-1868

This project is a collaborative effort between researchers at the University of Minnesota and the Los Alamos National Laboratory (LANL). The goal is to explore use of particle-

based and continuum-based numerical algorithms for analysis of fluid flow in the Earth's crust at different length and time scales, and for coupling across scales. At LANL we have focused on fluid flow at these two scales: (1) large (macro) scale whole-Earth mantle dynamics, and (2) localized, pore (micro) scale/field scale flow in porous media. An important fluid flow problem for whole-Earth dynamics requires the ability to solve inverse problems, that is, given present-time observations of the Earth's interior, what must the state of the Earth's interior have been 100 million years ago to allow it to evolve to the present conditions? This is an example of inversion for initial conditions in a fluid flow system, given boundary and end-time conditions. A generalized inverse formulation using adjoints to compute the functional derivatives of the full-Earth 3-D numerical model (employing 10s of millions of nodes) makes the large-scale inversion feasible in 4-D (3-D space plus time). For localized (field scale or smaller) complex flow and transport in porous media, we created a hybrid lattice-Boltzmann/continuum model of fluid transport and biofilm growth in porous media, using lattice Boltzmann to solve flow equations in an explicit pore-scale representation of a porous medium, and continuum methods to solve the microbial metabolic reaction model of biofilm growth on pore grains. For coupling across scales, we adapted fractal interpolating functions (fif) to field-scale 1-D porous media flow and transport equations as a proof of principle, providing solutions that capture dynamics at all scales. In addition, we can integrate fif representations exactly to provide a sub-grid-scale homogenization that can be used in more traditional finite difference or finite element solutions of porous flow and transport. The U. Minnesota and LANL PIs have organized sessions in nonlinear geophysics at A.G.U. Fall Meetings (2000, 2002, 2003), to promote cross-disciplinary efforts in the geosciences.

Nonlinear Elasticity in Rocks

Principal Investigator: Paul A. Johnson, paj@lanl.gov, (505) 667-8936

The basic premise of this work is the modern theory of critical phenomena can be applied to the description of the nonlinear elastic behavior of all or most geomaterials. We submit that geomaterials represent a nonlinear elasticity universality class. Our work entails testing for universality based on unique, experimentally-derived scaling relations indicating anomalous nonlinear elastic behavior. For instance, in dynamic resonance wave experiments the scaling of the resonance peak shift on the fundamental wave strain amplitude is always one. A type of characteristic strain memory called slow dynamics is another example. Establishing a universal description offers a vast simplification in describing nonlinear elasticity over a huge number of length scales, in a huge range of dissimilar materials. We believe that all earth materials will one day be characterized by their nonlinear elastic response. The materials in this class are remarkably disparate in their physical, meso-geometrical and chemical makeup. These are materials that owe their elastic behavior to a fabric of elastically soft material within a hard matrix ("the bond system") that exists within a small fraction of the total material volume. It contains nanoscopic-to-mesoscopic scale elastic features, as yet unidentified, that are responsible

for the unique behavior. This is a set of ideas for which we had only preliminary evidence. The purpose of our work is to undertake their full development. Recently, (1) we have demonstrated that the class is universal; not in the sense of critical phenomena but as in other universal classes such as thermal conductivity in glasses as described in a paper in review. (2) We have broadened the class significantly to include certain ceramics and metals, all damaged material and rocks, to date. A compilation is in press. (3) We have advanced our analytical/numerical description for characterizing the elastic behavior markedly as is described in two recent papers. (4) We have carefully analyzed the effects of fluids in the porous members of the class as described in a recent publication. (5) We have very recently discovered an important physical link between fast and slow dynamics that can be used to show their origin is linked.

Space Plasma Physics

Principal Investigator: S. Peter Gary, pgary@lanl.gov, (505) 667-3807

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 plasma microinstabilities on the large-scale models of space plasmas that describe the solar-terrestrial interaction, 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. Particle velocity distributions and parameters observed by Los Alamos plasma and energetic particle instruments on various spacecraft as well as computer simulations are used to carry out fundamental studies of plasma instabilities and associated transport in and near the solar wind, the Earth's bow shock, and the terrestrial magnetosphere. Our most important accomplishment in 2002 was the demonstration of the close relationship between the deformation of the magnetosphere, caused by the solar wind, and the formation of a thin electric current sheet inside the geomagnetic tail, which becomes unstable and drives geomagnetic activity. The self-consistent kinetic structure of thin current sheets also implies the presence of electric potentials, which map along magnetic field lines toward the Earth and may drive parallel electric fields through closure across the magnetic field. The acceleration of electrons from such parallel electric fields is a crucial element in enhanced precipitation into the atmosphere and the generation of auroral activity.

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

Principal Investigator: Michael Murrell, mmurrell@lanl.gov, (505) 667-4299

The goal of our project is to apply mass spectrometric methods to answer basic questions in quaternary dating and geochemistry using uranium-series disequilibria techniques. In the last year we have studied 1) the temporal and spatial evolution of MORB at the Northern Gorda Ridge and the East Pacific Rise, 2) the chronology of glacial ice, 3) the dating of hot springs deposits, and 4) we have contributed a chapter to a new book – Uranium Series Geochemistry. This work provides information on the recent evolution of magmatic systems and also has application to natural hazard risk assessment, paleoclimate studies, and the carbon cycle.

We have emphasized integrating our new multi-collector ICP mass spectrometer into current research. This new instrument comes with a steep learning curve but it has greatly improved our sensitivity for the U-series members. One project that has benefited from these new capabilities involves dating of hydrothermal calcite, opal and quartz hot spring deposits from Dixie Valley, Nevada. This is an active geothermal system located 160 km NE of Fallon in west-central Nevada within the Basin and Range tectonic province that is fed by geothermal fluids arising from about 3000m depth. Samples were purified by handpicking, and were separated into calcite, quartz or opal-rich fractions. Many of the measurements were obtained with our GV Isoprobe MC-ICP in the "soft extract" mode using the Cetac Aridus nebulizer. We observe a cluster of relatively young ages close to 5 ka that are consistent with expectations based on the presence of active fumaroles that indicate a current heat source, as well as geologic observations for recent faulting that has provided conduits for fluid flow. The observed older ages in excess of 100 ka for travertine deposits are also consistent with expectations, as cold seeps and the absence of fumaroles indicate a lesser degree of hydrothermal activity in these areas. These results show that U-series chronology is an important tool for understanding the longevity of hydrothermal systems and the time-scales of fluid-flow in the crust. In addition, the new ICP demonstrated its greatly improved sensitivity and accuracy relative to previous studies.

Biogeochemical Processes

Principal Investigator: Larry E. Hersman, hersman@lanl.gov, (505) 667-2779

Collaborator: Patricia Maurice, pmaurice@nd.edu, (574) 631-9163

Objective: Our overall objective is to determine the mechanisms of iron release during microbially enhanced iron oxide dissolution by an aerobic microorganism. The results of several of our experiments performed in our first funding cycle lead us to believe that aerobic microorganisms used a reductive dissolution process to acquire iron from Fe

oxides. We therefore use a combination of biochemical and analytical techniques to determine the compounds and conditions responsible for the microbially enhanced dissolution. We report here the progress of our work to date, at LANL.

Project Description: The purpose of this research is to investigate the mechanisms used by aerobic microorganisms to obtain Fe for growth. Understanding these mechanisms is fundamental to a wide range of bio-geo-chemical processes. For example, Fe oxides sorb a variety organic and inorganic pollutants, therefore understanding the mechanisms of dissolution is important to understanding pollutant transport phenomena.

Results. This past year we have concentrated on determining the metabolic response (siderophore, reductants) of *P. mendocina* to Fe supplied as two different preps of 1) hematite, 2) goethite, and 3) ferrihydrite, plus positive (FeEDTA) and negative (no Fe) controls, relative to energy consumption (i.e., succinate utilization).

Obviously this microorganism responded differently to different Fe sources. While a complete discussion of these results is beyond the scope of this report (and would be somewhat premature), there are some obvious observations that can be made. As expected, the no Fe control induced the production of siderophore, which resulted in a significant amount of Fe being used per cell, yet in the presence of Fe as Hematite 1, a similar amount of siderophore was produced at the expense of much less succinate.

Both of the ferrihydrite preparations resulted in significant amounts of Fe reductant (both cell free and membrane bound) in early log growth phase, yet nearly disappeared by late log growth phase.

We are currently interpreting the results of these series of experiments, and will publish the results by the end of the current FY.

OAK RIDGE NATIONAL LABORATORY

Experimental Studies of Fundamental Stable Isotope Exchange in Experimental Mineral-Fluid Systems

Principal Investigator: Juske Horita, horitaj@ornl.gov, (423) 576-2750

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 CO₂-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 CO₂ on a time-scale ranging from hours to thousands of years, ensuing from the injection of large volume of CO₂ into the subsurface. Our specific objective is to investigate the mechanisms, rates, and isotope fractionation during (1) slow and rapid precipitation of calcite from a CO₂-bearing solution at low temperatures (25-90°C) and (2) recrystallization and replacement of calcite and dolomite in CO₂-rich fluids at moderately elevated temperatures (100-300°C), as function of several key variables (temperature, pressure, pCO₂, ionic strength, microbial activity, etc.). Detailed monitoring and measurement of solution chemistry, coupled with mineralogic and crystallographic characterization of the solid phase, will allow us to determine reaction mechanisms and rates as a function of time. Carbon and oxygen isotope fractionation during the precipitation of carbonate minerals will provide crucial information on kinetic and equilibrium behavior of the isotopes during the precipitation in the subsurface. The results of the recrystallization and replacement experiments will provide information on the mechanisms and rates of isotope exchange needed for long-term modeling of the CO₂ injection.

Experimental Studies of Hydrothermal Fluid Speciation & Fluid/Solid Interactions Employing Potentiometric Methods

Principal Investigators: Pascale Benezeth, benezethp@ornl.gov, (865) 574-4960; David Wesolowski, wesolowskid@ornl.gov; (865) 574-6903

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.

Fundamental Research in Geochemistry of Geothermal Systems

Principal Investigator: Juske Horita, horitaj@ornl.gov, (865) 576-2750

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 and theoretical.

Ion Microprobe Studies of Fluid Rock Interactions

Principal Investigator: Lee Riciputi, riciputilr@ornl.gov, (865) 574-2449

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 km³. 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.

Mechanisms and Rates of Isotope Exchange in Mineral-Fluid Systems

Principal Investigator: David R Cole, coledr@ornl.gov, (865) 574-5473

The major goal of the research is to measure the equilibrium fractionations and rates of isotope exchange between minerals and fluids (gases) at elevated temperatures and pressures. Our primary focus has been on the experimental determination of rates of isotopic exchange controlled by one of two general mechanisms: surface reactions leading to recrystallization or mineral transformation and volume (lattice) diffusion. Results obtained during the current period have led to a quantitative understanding of the importance of solution composition, pressure, and mineral chemistry in controlling the mechanism and rate of exchange. Ion microprobe investigations of isotopic exchange resulting from diffusional transport demonstrate the influence crystallographic transport direction has on the diffusion rate, particularly hydrogen in hydrous silicates. Hydrogen diffusivities in single crystals and hydrogen isotope fractionation factors have been measured for the system epidote-water at temperatures between 200 and 600°C and pressures up to 200MPa. We have also investigated the isotopic exchange behavior in systems where chemical reaction and solid-state diffusion are coupled (e.g., cation exchange between alkali feldspars and salt solutions). The influence of pressure is one of our other themes wherein we have examined the rate of O and C diffusion in carbonates (calcite, dolomite) as a function of temperature and f_{CO_2} . This effort benefits from collaborations with T. Labotka, C. Mora, L. Anovitz and M. Fayek (Univ. Tenn., Knoxville), P. Larson (Wash. State Univ.), and T. Chacko (Univ. Alberta).

Volumetric Properties, Phase Relations and Reaction Kinetics of CO₂-CH₄-H₂-H₂O Fluids: Effects of Injecting CO₂ into Geological Reservoirs

Principal Investigator: James Guy Blencoe, blencoejg@ornl.gov, (865) 574-7041

Published thermophysical data for carbon dioxide-methane-hydrogen-water (CO₂-CH₄-H₂-H₂O) 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 CO₂ sequestered in geologic reservoirs.

To gain an improved understanding of the behavior of CO₂-CH₄-H₂-H₂O 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 CO₂-CH₄-H₂-H₂O 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 CO₂-CH₄-H₂-H₂O fluids over wide ranges of temperature, pressure and composition.

PACIFIC NORTHWEST NATIONAL LABORATORY

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

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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} [$\text{MO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{n+}(\text{aq})$; with $M = \text{Al(III)}$ for Al_{13} , $n = 7$; $M = \text{Ga(III)}$ for GaAl_{12} , $n = 7$; $M = \text{Ge(IV)}$ for GeAl_{12} , $n = 8$]. A partly dissociated, metastable intermediate molecule of expanded volume is necessary for exchange of both sets of $m_2\text{-OH}$ and that the steady-state concentration of this intermediate reflects the bond strengths between the central metal and the $\mu_4\text{-O}$. This mechanism explains the reactivity trends for oxygen-isotope exchange in $m_2\text{-OH}$ and $h\text{-OH}_2$ sites in the ϵ -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 $\mu_4\text{-O}$ in boehmite, α -, and $\gamma\text{-Al}_2\text{O}_3$ 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 $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, and $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})^+$, indicating that fluctuations in hydrolysis state can be viewed on a continuum with other solvent contributions to the reorganization energy.

Electron Transfer at the Fe(111) Oxide-Microbe Interface

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The iron biogeochemical cycle is integral to chemical and energy flux in near surface geochemical systems and involves oxidative and reductive valence transformations of Fe. Bacterial activity catalyzes the reduction of Fe(III) to Fe(II) in geochemical systems where Fe(III) exists in the oxide form. This project is investigating the transformation of poorly crystalline iron oxides (e.g., 2-line and 6-line ferrihydrite, lepidocrocite) by dissimilatory metal reducing bacteria (DMRB) as a model of a common process that occurs in soils, sediments, and subsurface systems. We seek to understand i.) the molecular rearrangements that occur as poorly crystalline Fe(III) oxides are utilized as electron acceptors by metal reducing bacteria and ii.) the kinetic and geochemical factors that control the pathways and identities of solid-phase transformation products. Key to this process is the molecular geochemical behavior of Fe(II) including its clustering, spatial distribution, and bonding environment in nanometer-sized ferrihydrite crystallites which are studied by X-ray diffraction, Mossbauer spectroscopy, scanning and transmission electron microscopy, scanning probe microscopy, and X-ray adsorption spectroscopy and scattering.

In FY02 we investigated the biotransformation of Ni- and Si-substituted 2-line ferrihydrites as examples of poorly crystalline secondary Fe(III) oxides found in metal contaminated environments and groundwater aquifers. The DMRB (*S. putrefaciens*) transformed the metal ferrihydrite into 6-line ferrihydrite (the first time such transformation has been documented) and nanometer-sized Ni-substituted magnetite. The incorporation of Ni in octahedral magnetite sites (as determined by Mossbauer and X-ray absorption spectroscopy) significantly reduced Ni solubility. The Ni-magnetite exhibited a curious excess of Fe(II) that has yet to be adequately explained. Anoxic incubation of Si-ferrihydrite with DMRB in the presence of lactate yielded a carbonate green rust as the primary mineral product. Green rusts are highly reactive and reduce the oxidized forms of polyvalent metals such chromate, selenate, vanadate, and uranyl to lower valence, insoluble forms. Variations in phosphate concentration in the media were found to control the Fe(II)/Fe(III) valence ratio in the green rust. Our experiments demonstrate that bacteria may mediate the formation of green rusts with a wide Fe(II)/Fe(III) ratio (previously unrecognized), and that these compounds may be significant geochemical reductants.

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

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In this joint University of California, San Diego and Pacific Northwest National Laboratory (PNNL) research program, high temperature (pressure) electrolyte solutions thought to facilitate metal ion transport in hydrothermal environments will be studied using ab initio molecular dynamics (AIMD) methods. Much of our molecular understanding of these hydrothermal solutions has been provided by X-ray adsorption fine structure experiments, which observe increasing ion-pair formation at elevated temperatures. However, the interpretation of these measurements usually requires some structural information about the solvation shell around the ions. Our AIMD calculations will be used to probe the chemistry of the metal ion solvation shell as well as ion-pairing kinetics and stability as a function of temperature, pressure and concentration.

All the scientific problems proposed here have extremely large computational and memory requirements. The required performance can only be obtained in a parallel computational environment. However, performance on a parallel computer is dependent on the scaling of the required algorithms. In the PNNL portion of this research program, a new generation parallel algorithms will be developed to both improve the performance and generality of algorithms used in AIMD calculations. Many of the algorithms proposed to be developed in this project have an unusual structure that will require careful code development to obtain efficient and reliable simulations. PNNL will also assist in analyzing the large amount of electron and structural information from the proposed AIMD calculations.

Local Reactions of Carbonate Surfaces: Structure, Reactivity and Surface Effects

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This project involves an interdisciplinary theoretical and experimental effort designed to gain a fundamental, molecular level understanding of carbonate mineral surface structure and chemistry including the impact of surface sorbates and precipitates on the surface reactivity. Carbonate minerals are particularly important in the global CO₂ cycle and in subsurface contaminant migration processes. The program links theoretical and experimental research at two different levels. First, experimental measurements on single crystal surfaces in combination with empirical and first-principles quantum-mechanical calculations are used to build and test models of the structure and chemistry of the carbonate surface. Second, the structural and chemical information from well-defined

surfaces is linked with direct (site-specific) observations of more macroscopic properties of the surface, such as rates of step or pit movement during crystal dissolution or growth. The molecular level theoretical and experimental information is used to provide input parameters and boundary conditions for a kinetic Monte Carlo model description of step and pit evolution. These combined efforts provide both insight to the nature of the important processes and sites on carbonate surfaces and information relating the site-specific surface properties to the overall reactivity of these surfaces. In particular, specific dissolution rates for five types of sites on dissolving surfaces have been determined by a combined theory and experimental effort. This work has been extended to examine the influence of solution flow rate and contaminants on the sorption and desorption rates at these five sites. Experimental measurements have focused on the impacts of divalent Mn, Sr, and Co ions on the dissolution rates of the specific surface sites. A terrace-ledge-kink site blocking model has been used to explain the observed results. In FY 2002 a kinetic Monte Carlo model of surface of step reactions in flowing water was developed in relation to step morphologies and velocities during dissolution. In addition to the dissolution measurements, the heteroepitaxial growth of a secondary nano-phase of a manganese carbonate was observed and has been reported.

Molecular Basis for Microbial Adhesion

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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. A consistent molecular model for the mineral goethite has been designed for biomolecular simulations of our model of the microbial membrane. Molecular modeling studies have been carried out of the model of the rough LPS membrane of *P. aeruginosa*, specifically to analyze the structural and dynamical properties of the externally exposed polysaccharide surface. The inner core region of the membrane is fairly rigid, in part due to the nature of calcium coordination. Calcium-LPS interactions are the strongest interactions, which bind the LPS units together. The five outermost saccharides do show a much greater range of motion than all other saccharide groups, and have the ability to respond to an external perturbation within this time period, whereas the response of the inner core is slower and smaller in magnitude. Using the fragment model for goethite in a configuration that puts the mineral in close contact with the fully atomistic membrane model, and collected properties for the resulting system, molecular dynamics simulations have been performed. Of primary interest in these initial simulations is the response of the membrane to the presence of the mineral. Significant structural changes were observed for these outermost saccharide groups. Several saccharide groups were found to have

rotated with respect to the membrane-only simulation so that hydrogen bonds could be formed with the mineral surface. The structure of the inner core of the membrane is unchanged, and the corresponding integrity of the membrane, is thus maintained. The mineral surface dehydrates slightly in the presence of the membrane as saccharide hydroxyl groups compete with water molecules for hydrogen bonding sites on its surface.

SANDIA NATIONAL LABORATORY/ALBUQUERQUE

Interactions of Pore Fluid Pressure

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When subjected to non-hydrostatic, compressive stresses, some porous sandstones exhibit non-uniform compaction. The compaction occurs as a localization process, analogous to shear localization, but results in a thickening, tabular zone of compaction as opposed to culminating in a shear fracture. We reported the results of several triaxial compression experiments done at a confining pressure of 45 MPa on Castlegate sandstone, 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 produced by compaction localization, 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. Experimental results were reported that showed the evolution of effective permeability to be linear with respect to the distance the compaction fronts propagated as predicted by the model. 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.

Laboratory Investigation of Constitutive Property Upscaling

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Rarely can petrophysical data be acquired at the desired scale of analysis. The resulting disparity between the scale at which data are measured and the desired scale of analysis necessitates the application of averaging or upscaling models. Unfortunately, the complexity inherent to geologic materials and the accompanying flow and transport

processes requires simplifying assumptions to achieve tractable solutions. Here, we use systematic physical and numerical experimentation to test current models of upscaling and the conceptual framework on which they are predicated. In the current phase of studies, upscaling in the context of solute transport was explored. Using X-ray absorption imaging we quantitatively visualized solute transport in an exhaustively characterized slab of rock. Specifically, experiments were conducted on a 30 by 30 by 2.5-cm thick slab of cross-stratified sandstone exhibiting nested scales of heterogeneity. Transport experiments were conducted under steady-state flow conditions using a conservative tracer. Tests were conducted parallel, normal, and diagonal to stratification with both point and line sources subject to slug and continuous tracer injection. Two-dimensional digital images of the solute concentration fields at select times during the tracer experiments were acquired in addition to conventional breakthrough curves. Results show solute pathways to be strongly influenced by the spatial permeability/porosity patterns of the sandstone slab. Specifically, solute dispersion was found to scale linearly with distance when flow was oriented parallel to stratification while complex, non-linear scaling relations were encountered when flows were forced to cross the stratification. Additionally, the calculated dispersion coefficients vary spatially and by the orientation and mode of injection.

Additionally, the relationship between pore-scale heterogeneity and permeability for a slab of Massillon Sandstone was investigated. Petrographic and scanning electron microscopy analyses were conducted on thin sections taken from one-inch diameter core samples, while permeability data were collected with a gas minipermeameter from the same cores. Results suggest surprisingly poor correlation between the measured pore characteristics and the calculated permeability. We ascribe this poor correlation to the diagenetic history of the rock sample. Specifically, the interplay between cement precipitation and secondary porosity dissolution appears responsible for the complex relationship between permeability and pore scale characteristics.

Micromechanical Processes in Porous Geomaterials

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This project focuses on systematic investigation of the microscale characteristics of natural earth materials and how these characteristics control macroscopic deformation and transport behavior. We use an integrated approach consisting of experimental rock mechanics, quantitative microscopy, and theoretical and numerical analyses.

In the current year, we extended the scope of prior investigations of microstructural evolution during brittle faulting and compactive failure of well-indurated sandstones to include weakly-cemented sandstones. High-resolution field-emission scanning electron

microscopy was performed to elucidate the micromechanics of compaction in Castlegate sandstone deformed under triaxial compression loading conditions. The microscopy revealed that compaction proceeds in two phases: an initial stage of porosity decrease that is accomplished by breakage of grain contacts and grain rotation, and a second stage that is accommodated by intense grain breakage and rotation. This sequence contrasts with that observed in more strongly indurated rocks, where grain fragmentation coincides with the onset of inelastic compaction. Quantitative stereological measurements corroborate the decrease in intergrain spacing and increase in grain boundary contact area that the microscopy suggests occur during the first stage. Acoustic emission (AE) measurements are consistent in that rotation and breakage of grain contacts in the first compaction stage are marked by diffuse AE whereas the regions of intense grain breakage and subsequent compaction are indicated by intensely concentrated AE. In another study to investigate the influence of pore geometry on permeability, we applied 3D image data acquired during synchrotron computed microtomography experiments conducted at the GSECARS beamline at the Advanced Photon Source to numerical fluid flow simulations conducted using the Lattice Boltzmann (LB) method. The permeability of cores with porosities from 5 to 35 percent was measured in the laboratory using the steady-state technique. The data exhibit the classic power law relationship between permeability and porosity (with evolving exponent) observed in natural sandstones. The LB simulations using subvolumes of $\sim 1\text{mm}^2 \times 3\text{mm}$ predict the macroscopic permeability as measured in the laboratory with over four orders of magnitude variation in permeability, including a sample that lies well below the point at which permeability versus porosity relationship departs from a power law relationship with exponent 3.

Modeling of Mesoscale Phenomena During Sequestration of Carbon Dioxide in Porous Reservoirs

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Processes for the sequestration of carbon dioxide in porous reservoirs involve several components of multiphase flows. If hydraulic fracturing is used to develop local "sweet spots" (zones of high permeability), the flow and resulting distribution of the proppant can have a large impact on the subsequent sequestration process. Even without hydraulic fracturing, the creation of precipitates can drastically alter the characteristics of the porous formation itself. Furthermore, emulsions can form and fingering can take place at the supercritical CO_2 /brine interface. In order to be of use in designing effective CO_2 sequestration processes, significant enhancements to currently available continuum-level suspension flow models are required. Both experimentation and high performance computing at the mesoscopic level are used to obtain microstructural information that is necessary for the development and refinement of the continuum models.

The continuum models originally developed by Phillips et al. (1992) and Nott and Brady (1994) have been improved and implemented into a general-purpose finite element computer code. Results show good agreement with experimental measurements based on nuclear magnetic resonance (NMR) imaging in idealized three-dimensional flows. Massively parallel computing has allowed particle level simulations, based on the boundary element method (BEM), with up to three thousand particles. Volume averaging of the stress tensor has been added to the codes to allow prediction of average macroscopically observed transport properties from particle scale simulations. This work is complemented by experimental work to provide insights and benchmarks. A study of apparent particle slip in confined geometries has been performed. It was found that there exists markedly non-Newtonian wall effects in concentrated suspensions in which the volume fraction of particles is greater than 0.2. At these higher concentrations, wall effects are much larger and extend further into the suspension than in Newtonian fluids.

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

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This work continues a previous study of dispersion at fracture junctions, by adding a set of laboratory experiments and advanced numerical modeling. Coupled flow/kinetics/dissolution experiments in single fractures will be performed at Sandia, and dissolution/precipitation experiments in fracture intersections will be performed at New England Research. Sandia provides numerical modeling of the experiments, via the lattice Boltzmann (LB) method.

Several environmental or commercial processes depend on dissolution or precipitation in fracture networks. Acid-fracturing, to enhance oil and gas recovery in carbonate and silicate reservoirs, ideally assumes uniform etching of the surfaces of all fractures in a network. Similar processes are employed for solution mining of copper deposits. However, the positive-feedback mechanism of selective dissolution, and sidewall porosity, can serve to create an undesirable focussing of flow through just a few fractures, greatly reducing the effectiveness of the treatments. Similarly, models for the transport of radionuclides in Yucca Mountain, and particularly for precipitation of actinides, assume near uniform spreading of contaminant plumes throughout the fractured tuff. However, the NRC speculated that fracture intersections may actually focus flow through a few channels, and precipitation, once begun, may further constrain flow.

We proposed experiments to (1) test the validity of single fracture dissolution/precipitation models; and (2) investigate the extent of channeling that occurs at intersections among fractures, due to selective dissolution and precipitation. Upcoming dissolution experiments will use flat walls of high-density (low porosity) dental plasters and machined gypsum surfaces, and porous quartz; these flat walls will be mated to

transparent rough “fracture” walls to provide a varied velocity field. Initial rotating disk experiments were completed, and establish limits on the dissolution rates of the dental plaster.

The 3D LB models use flexible surface kinetics and options for controlling specific surface area as functions of solution chemistry and precipitation history. Initial simulations are for single fractures with one flat dissolvable surface, opposed by a textured non-dissolving surface. The 3D reaction models have a much broader application, and have also been applied to the growth of artificial bone, and the formation of clots in arteries.

Three Dimensional Transient Electromagnetic Inversion

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Inversion of transient electromagnetic (TEM) data sets to image the subsurface three-dimensional electrical conductivity and magnetic permeability properties can be done directly in the time domain. The technique, first introduced by Wang et al. (1994) for causal and diffusive electromagnetic fields, is based upon imaging methods originally developed for seismic wavefields (Claerbout, 1971; Tarantola, 1984), but was not correctly formulated for the full treatment of 3D TEM fields. In our work we modify the original theory of Wang et al. (1994), to overcome this limitation as well as extend the method to treat non-causal TEM fields. Our algorithm uses a conjugate-gradient search for the minimum of an error functional involving EM measurements governed by Maxwell’s equations without displacement currents. Treatment for magnetic field, voltage (time derivative of the magnetic field) and electric field data are given. The functional can be computed by propagating the data errors back into the model in reverse time along with a DC field, sourced by the integrated data errors over the measurement time range. By correlating these fields, including the time-integrated back-propagated fields, with the corresponding incident field and its initial value at each image point, efficient computational forms for the gradients are developed. The forms of the gradients allow for additional efficiencies when voltage and electric field data are inverted. In such instances the combined data errors can be back-propagated jointly, significantly reducing the computation time required to solve the inverse problem. The inversion algorithm has already been applied to the long offset transient electromagnetic measurement (LOTEM) configuration thereby demonstrating its capability in inverting non-causal field measurements of electric field and voltage, sourced by a grounded wire.

Transport Visualization for Studying Mass Transfer and Solute Transport in Permeable Media

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Our project, collaborative between Sandia National Laboratories, MIT, and Oregon State University, investigated two fundamental questions in hydrogeology with applications to carbon sequestration, energy production, waste disposal and remediation. (1) Under what conditions is solute spreading best modeled by Fickian dispersion and versus mobile-immobile domain mass transfer? (2) How do chemicals mix so that they react in natural porous media? These questions are intimately connected, as pore-scale mixing, reaction and large-scale spreading profoundly affect one another. We used a combination of transport visualization experiments where we obtained real-time quantitative maps of concentration in 2D and numerical simulation to answer the questions. The following are some of the key results to date. (1) The connectedness of permeability is a critical parameter to solute transport and reaction. The connectedness of geologic media influences parameters for flow and transport models, and also determines the most appropriate form of the transport model itself. (2) Solute transport may be divided into three regimes, each with a different appropriate transport model – macrodispersion, diffusion-controlled mass transfer, and advection-controlled mass transfer. The regime depends on the connectivity, permeabilities, length scales, diffusivity, and hydraulic gradient. Experimental confirmation of these regimes can be seen at http://web.mit.edu/harvey-lab/www/Regimes_Page/movs.html. (3) Mass transfer timescales for use in transport models are strongly correlated to residence time and experimental duration, a fact that is consistent with multiple timescales of mass transfer present in most natural materials. (4) The conventional coupling of chemical reaction equations with the convective-dispersive equation may overpredict chemical reaction. Experimentally observed dispersion inaccurately represents pore-scale mixing because at the pore-scale, reactants may remain separated. (5) When flow velocities are low, reaction can create density fingering that greatly increases mixing and enhances reaction, creating an important feedback that has not been noted before. The phenomenon is similar to mixing from double-diffusive convection but also occurs

Two-Phase Immiscible Fluid Flow

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The objective of this project is to develop a quantitative understanding of the critical processes controlling two-phase flow and transport in fractures. Fundamental understanding may subsequently be abstracted for application to large-scale problems in petroleum extraction, radioactive waste isolation, subsurface remediation, and CO₂

sequestration. We explore fundamental physical processes through a combination of detailed physical experiments and numerical simulations. 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 facilitate concurrent model development.

Highlights:

A depth-averaged model for dissolution of non-aqueous phase liquid (NAPL) within a variable aperture fracture: The model explicitly couples fluid flow, transport of dissolved NAPL, inter-phase mass transfer and NAPL-water interface movement. When compared to high resolution experimental data, the model accurately predicted both the change in overall NAPL saturation with time and the evolution of the entrapped phase geometry. This is perhaps the first instance where close agreement between simulations and experiments on NAPL dissolution was achieved without empirical treatment of inter-phase mass transfer. Results were published in *Water Resources Research* [37(12) 3115-3130, 2001].

A 3-D particle-tracking simulator to explore solute transport through a variable aperture fracture containing an entrapped fluid phase: In comparison to experiments, the model was able to predict 85% of the increase in dispersion over single-phase conditions. It also reproduces the experimentally observed nonlinear relationship between solute dispersion and Peclet number, which suggests that Taylor dispersion effects are significant even in partially saturated fractures. Results were published in *Geophysical Research Letters* [29(8) 10.1029/2001GL013508, 113-1 – 113-3, 2002].

Demonstration of the importance of local head loss in predicting solute transport through single fractures: An ad hoc correction to the Reynolds equation was used to demonstrate that underestimation of local head loss in regions of changing aperture can artificially smooth the predicted flow field. Subsequent prediction of solute transport is affected in terms of both the mean velocity and longitudinal dispersion. Results were published in *Geophysical Research Letters* [28(23) 4351-4354, 2001].

Molecular Simulations of Layered Minerals & Their Interactions with Hazardous Materials

Principal Investigator: Randall T. Cygan, rtcygan@sandia.gov, (505) 844-7216

A molecular mechanics forcefield developed for modeling hydrous phases was used to simulate the bulk structure of various layered phases, and to examine the swelling behavior of smectite clays such as montmorillonite and beidellite. Molecular dynamics results are in excellent agreement with crystal structure refinements, and with several quantum optimizations. The CLAYFF forcefield offers a computationally efficient

approach for simulating large molecular configurations relating to environmentally important systems such as clays, hydroxides, oxyhydroxides, double layered hydroxides, their interlayers and external surfaces, and aqueous solutions. Most noteworthy is the dynamics of water at the clay-water interface in the interlayer region that will ultimately control the swelling behavior of the clay and the ability of the clay to intercalate various cations, anions, and molecular compounds. Our ability to understand these complex processes at the atomic level is provided by a few experimental and analytical methods such as X-ray absorption, vibrational, and NMR spectroscopies. However, due to complexities in the structure and composition of clays and other hydrated minerals, and the inherent uncertainties of the experimental methods, it is important to apply theoretical molecular models for a fundamental understanding and interpretation of these phenomena.

The swelling of two smectite clays (montmorillonite and beidellite) and pyrophyllite were examined using molecular dynamics methods and the CLAYFF forcefield. No constraints on the simulation cell and atomic positions were imposed, thereby allowing complete relaxation of the structure. The MD simulations incorporated an NPT canonical ensemble to evaluate the equilibrium configuration for each clay-water system for simulation times up to 100 ps. Equilibrated structures and energies suggest the stabilization of distinct layering of waters within the interlayer near the siloxane surfaces. Montmorillonite, characterized by a layer charge residing primarily in the octahedral sheet, exhibits somewhat greater expansion for a given water content. Beidellite exhibits a more dynamically structured water layer at the siloxane surface due to the localization of layer charge on the tetrahedral sheet. Solvation of the interlayer sodium ions locally affects the water molecule distribution, especially at low water contents. Pyrophyllite has no interlayer ions and expands readily with the artificial introduction of water molecules.

PART II: OFF-SITE

ARIZONA STATE UNIVERSITY

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

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The objective of this research is to use chemical and light stable isotopic variations of diagenetic minerals and organic compounds in hydrocarbon bearing sedimentary basins to address the chemical dynamics of fluids interacting with host rocks. Our first goal in 2002 was to measure B-isotopes in organic matter. We conducted a survey of B isotopic ratios for 28 coal and kerogen samples. Our analyses were obtained using secondary ion mass spectrometry (SIMS) on pressed pellets of the size fractionated coal material. The bulk coal analyses were compared to analyses of kerogen from Type I, II and III source rocks that we analyzed in polished sections. The second goal of our project was to determine the timing (temperature) of the release of B from organic matter, relative to the release of N, S and O compounds. The importance of NSO compounds in kerogen is that they represent elements that are actively released during thermal maturation. For example, oil generation is at its peak when N is released from kerogen, but N is commonly affected by variations in the oxidation state of the reservoir and therefore may not be preserved in the rock record. Unlike nitrogen, boron is unaffected by oxidation state and is potentially a better tracer of hydrocarbon related fluids. Experiments to measure the change in boron isotopic composition of coexisting coal and clay minerals are underway. The results of our survey showed that coal and kerogen are isotopically lighter than most crustal material (-1 to -70‰). Boron occurs in silicate and organic hosts, but is primarily associated with organic material. The N, S and B compounds in coal all show a gradual change in isotope ratio with increasing thermal maturity. The range of isotope variations for B ($\sim 70\text{‰}$) is 3 times greater than the range of N and S ($\sim 20\text{‰}$). Therefore, the release of B from kerogen during thermal maturation would introduce a significantly light B-isotope signature to pore fluids that could be used to trace migration of generated hydrocarbons and other organic contaminated fluids.

ARIZONA STATE UNIVERSITY

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

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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.

BOSTON UNIVERSITY

Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes

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Research under this project is focused on the analysis of crustal deformation processes in 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

Infrared Spectroscopy and Stable Isotope Geochemistry of Hydrous Silicate Glasses

Principal Investigator: Edward Stolper, ems@expet.gps.caltech.edu, (626) 395-6504

Objectives: This project focuses on the application of experimental petrology and stable isotope geochemistry to the study of volatile components dissolved in silicate melts and glasses and CO₂ in the atmosphere, especially as it relates to air quality issues in the Los Angeles basin.

Project Description: *Parts 1 and 3* involve equilibration of volatiles with silicate melts to determine fractionations and/or diffusion rates: CO₂ in *Part 1* and H₂O in *Part 3*. *Part 2* involves equilibrating forsteritic olivine with a 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 CO₂ in the atmosphere of the Los Angeles basin, especially as it relates to sources of pollution and changes through time.

Results: *Part 1:* We published an easily accessible model of CO₂ and H₂O dissolved in silicate melts (*Newman S, JB Lowenstern (2002) VOLATILECALC: a silicate melt-H₂O-CO₂ solution model written in Visual Basic for Excel®, Comput. Geosci.-UK 28 (5): 597-604*) and prepared our work on Na-melilitic melt (*Appora, I, JM Eiler, A Mathews, and EM Stolper (2003) Experimental determination of oxygen isotope fractionations between CO₂ vapor and soda-melilite melt. Geochim. Cosmochim. Acta 67: 459-471*).

Part 2: We prepared a related paper on mineral/melt partitioning of trace elements (*Gaetani, GA, AJR Kent, TL Grove, ID Hutcheon, and EM Stolper (2003) Mineral/melt partitioning of trace elements during hydrous peridotite partial melting. Contrib. Mineral. Petrol. (in press)*).

Part 3: We are developing protocols for experiments, using rhyolitic glasses before working with more difficult basalts. Experimental problems include preparation of large samples with homogeneous water contents, preparation of diffusion couples, and perfection of techniques using TZM bombs to produce diffusion profiles.

Part 4: Our daily to bi-daily analyses in 2000-2002 revealed that the CO₂ concentration increased by ~50 ppm since a similar data set was collected in 1972-73. The isotopic composition of the heaviest endmember became ~0.5‰ heavier, but the light, pollutant, endmember looks very similar, because changes in the provenance of oil consumed compensated for the change in proportions of fuel types burned.

CALIFORNIA INSTITUTE OF TECHNOLOGY

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

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^{238}U , ^{234}U , ^{232}Th , ^{226}Ra , ^{228}Ra , ^{224}Ra , and ^{222}Rn were measured in groundwaters of the Ojo Alamo aquifer in New Mexico an arid area with annual precipitation of ~22 cm. We investigated transport of U-Th series nuclides in an old, slow-moving groundwater mass to compare results with a temperate zone aquifer. It was found that ^{232}Th is at saturation and supports the view that Th is precipitated irreversibly upon weathering, leaving surface coatings of ^{232}Th and ^{230}Th on aquifer grains. Uranium in the aquifer waters has very high [$^{234}\text{U}/^{238}\text{U}$] ~ 9 and low ^{238}U concentrations due to low weathering rates in the aquifer ($w_{238\text{U}} \sim 2 \times 10^{-18}$ to $2 \times 10^{-17} \text{ s}^{-1}$) using a continuous flow, water-rock interaction model. The Ra isotopes are roughly in secular equilibrium despite very different lifetimes. ^{222}Rn and ^{228}Ra in the aquifer correspond to ~10% of the net production rate of the bulk rock. Coatings of Th on aquifer minerals provides Ra and Rn to the aquifer waters. Waters feeding the aquifer today have low [$^{234}\text{U}/^{238}\text{U}$] and high ^{238}U concentrations. It is not possible to obtain the high [$^{234}\text{U}/^{238}\text{U}$] and low [^{238}U] values in the aquifer from a source like the present input. This requires a major change in water input with much larger rainfall several thousand years ago and may represent a climatic change in the Southwest. We also studied lateritic soils and ground and river waters in southern Cameroon, Africa. The Nd of the river waters was much more radiogenic than the parent rocks and is carried by different components that are not isotopically homogenized. Nd transported in the river is not representative of the parent rock but reflects differential weathering of constituent minerals and the re-deposition of REE in phosphates. The concentration of Nd in the tropical river water is far above that found in temperate climate rivers and may play a dominant role in the marine Nd and REE budget. The upper laterite profile shows large depletions in all REE below Tb and enrichment above, while the complementary behavior pattern was found in the lower section.

CALIFORNIA, UNIVERSITY OF BERKELEY

Collaborative Research: Studies for Surface Exposure Dating in Geomorphology

Principal Investigator: Kunihiko Nishiizumi, kuni@ssl.berkeley.edu, (510) 643-9361

Objective: An experimental and theoretical program to fully develop the systematics of *in situ* produced cosmogenic nuclides in terrestrial surface samples and to apply their measurement to the dating of surface features and processes.

Project Description: Surface exposure dating utilizing cosmogenic nuclides is now acknowledged as a successful means with which to date many terrestrial surfaces. This project will focus on chemical isolation of cosmogenic nuclides from geologic and artificially exposed samples such as olivine; on implementation of surface exposure dating methods using new radionuclides such as *in situ* ^{14}C and pure spallation ^{36}Cl ; on measurements of proton and neutron cross sections and on improvement of theoretical production rate calculations.

Results: We are developing a reliable measurement system for *in situ* produced ^{14}C extraction from quartz, based on a step-wise heating technique. The extraction line consists of three sub-systems: carrier and flow gas measurement and aliquotting, sample heating, and CO_2 purification. The total background in blank quartz that was collected from deep in the Homestake mine in South Dakota, is 1.5×10^5 ^{14}C atoms (1-6 g of quartz). A preliminary estimate of extraction efficiency of greater than 90% was obtained by using quartz collected from the Transantarctic Mountains in Antarctica. These samples must contain ^{14}C activity in saturation, based on ^{10}Be and ^{26}Al concentrations.

Although quartz is the best mineral for studies of cosmogenic nuclide surface exposure dating, it is rare in many geological settings. We are developing a method for separating *in situ* produced ^{10}Be from meteoric ^{10}Be in olivine using stepwise leaching methods as well as determination of ^{26}Al . The ^{10}Be and ^{26}Al concentrations in olivines taken from continental lava samples (Oregon and New Mexico) are $0.04\text{-}1 \times 10^6$ atom/g and $0.05\text{-}3 \times 10^6$ atom/g, respectively. Exposure ages based on these concentrations are, in general, consistent with those based on cosmogenic ^3He . We have measured ^{10}Be in recently erupted volcanic olivine from Hawaii (Kilauea) and Iceland, where we don't expect to find ^{10}Be from subduction or *in-situ* production. The high ^{10}Be concentration in olivines from both volcanoes suggests that unexpected reactions between basaltic magma and hydrothermally altered oceanic crust may occur.

CALIFORNIA, UNIVERSITY OF BERKELEY

Diffusion/Dispersion Transport of Chemically Reacting Species

Principal Investigator: Harold Helgeson,
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Thermodynamic calculations and Gibbs free energy minimization computer experiments strongly support the hypothesis that kerogen maturation and oil generation are inevitable consequences of oxidation/reduction disproportionation reactions caused by prograde metamorphism of hydrocarbon source rocks with increasing depth of burial. These experiments indicate that oxygen and hydrogen are conserved in the process. If water is stable and present in the source rock at temperatures and pressures corresponding to a typical U.S. Gulf Coast geotherm, immature (reduced) kerogen melts congruently with increasing depth of burial in response to hydrolytic disproportionation of the kerogen to produce crude oil and CO₂ gas. However, in the water-absent region of the system CHO, any water in or entering the source rock is consumed by reaction with the lowest atomic hydrogen-to-carbon-ratio (H/C) kerogen it encounters to form CO_{2(g)} and a new kerogen with a higher H/C, which increases the oil generation potential of the source rock. In the absence of water, crude oil is generated by incongruent melting of immature kerogen with relatively high H/C to produce a metastable equilibrium assemblage consisting of a more mature (oxidized) kerogen with a lower H/C, together with crude oil and CO₂ gas. For example, computer experiments indicate that the overall incongruent melting process in the absence of water at 150 °C and ~5 km depth of an immature type-II kerogen with a bulk composition represented by C₂₉₂H₂₈₈O_{12(c)} to produce a mature (oxidized) kerogen represented by C₁₂₈H₆₈O_{7(c)}, together with a typical crude oil with an average composition corresponding to C₉H₁₇ (C₉H_{17(l)}) and CO₂ gas (CO_{2(g)}) can be described by writing



which corresponds to a disproportionation reaction representing the sum of a series of oxidation/reduction conservation reactions. The speciation of the oil generated by this reaction compares favorably with that of the API Project 6 Ponca City Crude. Reaction (1) is consistent with the observation that the relative abundance of mature kerogen increases, and that of immature kerogen decreases with increasing burial of hydrocarbon source rocks. It is also compatible with preservation of biomarkers during the incongruent melting process.

CALIFORNIA, UNIVERSITY OF BERKELEY

Dissolution of Fe(III) (hydr) Oxides by Aerobic Microorganisms

Principal Investigator: Garrison Sposito,
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During FY 02, we investigated the effects of a trihydroxamate siderophore, desferrioxamine B (DFO-B), and a common biological ligand, oxalate, on the steady-state dissolution of goethite at pH 5 and 25 C. The main goal of our study was to quantify the adsorption of the ligands and the dissolution of goethite they promote in a two-ligand system under oxic conditions.

In systems with one ligand only, at 80 μM the surface excess of oxalate was maximal at 40 mmol kg^{-1} whereas that of DFO-B was only 1.2 mmol kg^{-1} . In two-ligand systems, oxalate decreased DFO-B adsorption significantly. In systems containing oxalate only, goethite dissolution rates were very low below 200 μM , despite maximal adsorption of the ligand, and far-from-equilibrium conditions did not obtain. In systems containing DFO-B, goethite dissolution was always far from equilibrium, irrespective of the presence of oxalate. The dissolution rate promoted by DFO-B between 1 and 80 μM was approximately doubled when oxalate was also present at 40 μM concentration. The dissolution rate promoted by oxalate between 0 and 200 μM was increased by more than an order of magnitude when DFO-B was also present at 40 μM concentration.

These results were described by a far-from-equilibrium rate law containing a term proportional to the surface excess of DFO-B and a term proportional to that of oxalate, both surface excesses being determined in the two-ligand system. The first-order rate coefficient in the DFO-B term had the same value as measured for goethite dissolution in the presence of DFO-B only, while the rate coefficient in the oxalate term was unique to the two-ligand system, where far-from-equilibrium conditions obtain. This is because the siderophore is able to remove Fe from all Fe-oxalate complexes rapidly, leaving the uncomplexed oxalate in solution free to react again with the goethite surface. The synergy observed in the two-ligand system implies that the production of modest quantities of siderophore in the presence of very low concentrations of the ubiquitous ligand, oxalate, would be an extremely effective mechanism for microbes to induce the release of Fe from minerals.

CALIFORNIA, UNIVERSITY OF BERKELEY

Precipitation at the Microbe-Mineral Interface

Principal Investigator: Jillian Banfield, jill@seismo.berkeley.edu, (510) 642-9488

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.

CALIFORNIA, UNIVERSITY OF DAVIS

Electrochemical Measurements and Theoretical Predictions of the Thermodynamic Properties of Carbonate and Oxide Minerals

Principal Investigator: Peter Rock, rock@lsdo.ucdavis.edu, (530) 754-8919

Assessment of two of the proposed strategies for reducing the flow of carbon dioxide into the atmosphere, namely, disposal of carbon dioxide in geological media and acceleration of the carbon cycle in soil or oceans requires a detailed knowledge of the Gibbs energies of carbonate minerals. Carbonate mineral solubilities vary considerably with composition and sound thermodynamic data are the starting point for estimating the fate of carbonate in geologic strata.

We have devised a novel electrochemical double-cell technique that is used for the direct determination of the Gibbs energies of formation of metal carbonate solid solutions, mixed-metal carbonate minerals, hydroxycarbonates, disordered metal carbonates, and metal oxides. Additional electrochemical experimental experiments are in progress.

We have developed a novel theoretical method based on electrostatics for calculating lattice energies of calcite-structure metal carbonates, which we have extended to calcite-structure metal-carbonate solid solutions. The method also has been applied to metal oxides of the type M_2O_3 with the corundum structure.

Our lattice-energy calculation model for calcite-structure metal carbonates treats the lattice energy a sum of electrostatic, polarization, and repulsive components. The electrostatic contribution is evaluated by summing the energies of all pairwise point-charge interactions throughout the crystal, while the polarization contribution is determined via computation of all ion/dipole and dipole/dipole interactions in the crystal.

The repulsive energy contribution to the lattice energy is evaluated by using the Slater potential. Before the three components of the lattice energy can be evaluated, the parallel and perpendicular components of the oxygen polarizability in $MCO_3(s)$ must be determined along with the charge distribution of carbonate in metal carbonates. The calculation of the polarizabilities is accomplished by using the Lorentz Local Field Method which requires experimentally determined crystal refractive indices as input.

The method does not involve any adjustable parameters. We are presently extending our lattice-energy calculations to metal carbonates with the aragonite structure, which constitute a more difficult theoretical challenge because of the lower lattice symmetry. Theoretical work on metal oxides with the corundum structure has been completed, except for metal-oxygen cluster calculations designed to determine the charge on the metal ion in the oxide; these calculations are in progress.

CALIFORNIA, UNIVERSITY OF DAVIS

Tailored Crystal Growth and Impurity Control Using Nanocluster Adsorbates

Principal Investigator: William Casey, whcasey@ucdavis.edu, (916) 752-3211

The morphologies, growth rates and properties of crystals grown from solution are dramatically affected by adsorbates that poison the highly reactive steps on surfaces. As a consequence, impurity adsorption is a central issue in pharmaceutical design and manufacturing, corrosion, single crystal production, and mineralization in geochemical and biological environments. In nearly all of these processes, impurities are either an unavoidable feature of the system, or are intentionally introduced to modify the product. We are studying this problem systematically by conducting careful atomic-force microscopy (AFM) experiments on KDP (potassium dihydrogen phosphate) crystals coupled to a combination of inert and labile adsorbate complexes to affect growth. The results are complemented with ab initio-molecular dynamics calculations of the step energies and terrace morphologies on the growing KDP surfaces. The crystal growth rates and morphologies of KDP are extraordinarily well characterized.

Certain trivalent metals, such as Al(III) and Cr(III), when added to the aqueous growth solution, dramatically affect the growth rates and morphologies of KDP crystals by pinning elementary steps, causing step bunching and the formation of supersteps that can consist of hundreds of elementary steps. In experimental studies we are attempting to understand this chemistry by adding inert coordination complexes of specific geometries in order to reproduce the result. The fact that a fresh solution of Rh(III) additives in trace amounts does not affect the KDP growth morphologies, but causes profound step pinning if Rh(III) is allowed to age in the KDP growth solution, indicates that the step poisons are probably phosphato complexes, but of unknown structure. Although we understand that the step-pinning complex is a metal-phosphate molecule, we have been unable to synthesize this complex and a series of Co(III)-amminophosphate and Co(III)-amminopyrophosphate complexes show no effect. Because these complexes are large relative to the unit cell of KDP, we speculate that a mix of ligands bound to the inert metal but away from the phosphate is needed. Apparently, it is important that the step-pinning molecule be able to both accept and donate hydrogen bonds in order to pin elementary steps.

CALIFORNIA, UNIVERSITY OF DAVIS

The Aqueous Geochemistry and Kinetics of Reactions Involving Al (III)

Principal Investigator: William Casey, whcasey@ucdavis.edu, (916) 752-3211

Geochemists rely heavily on computer simulations of reactions because so many of the key environments are either in geologic settings that are impossible to sample or because the time scales are too large for experiment. Methods of computational chemistry are advancing rapidly but they simulate molecular-scale processes, not bulk reactions, and there is relatively little information on geochemically important molecular-scale reactions, yet understanding these processes is essential for improving our ability to predict toxicant chemistry and the fates of pollutants.

To extend this field, we determine the rates of isotopic exchange of oxygens in aqueous Al(III) molecules that span the range from monomers to nanometer-sized multimers that are close to colloidal dimensions (see review in Casey et al., 2001). We then compare these reaction rates and mechanisms to the results of computer simulations. Our motivation is a desire to understand reactions at the surfaces of the aluminum (hydr)oxide and aluminosilicate minerals that account for much of the reactivity of soil, since many of the reactions that cause metal contaminants to become relatively inert in soil are polymerization and hydrolysis reactions that form 1-5 nm sized multimers and hydroxy-bridged surface polymers.

Our understanding of these reactions is limited by the difficulty in synthesizing nanocluster molecules of metal-hydrolysates that can be separated cleanly from solution, purified, and back-dissolved into isotopically enriched water to create a monospecific solution for NMR study. For example, we recently completed work on the largest aluminum polyoxocation for which the structure is known, the $\text{Al}_{30} [\text{Al}_{30} = \text{Al}_2\text{O}_8\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{26}]^{18+}(\text{aq})$ molecule. The molecule is 2 nm in length and exposes oxygens in many different coordination environments to the aqueous solution. The structural complexity of this molecule is greater than that exposed at the surfaces of common soil minerals, like gibbsite, so that it presents a fair challenge to methods of simulation of the reaction.

Casey, W. H., Phillips, B. L., and Furrer, G. (2001) Aqueous aluminum polynuclear complexes and nanoclusters: a review. ch 5 in: Nanoparticles in the Environment (J. F. Banfield and A. Navrotsky, eds). Reviews in Mineralogy and Geochemistry 44, pp. 167-216.

CALIFORNIA, UNIVERSITY OF DAVIS

Thermodynamics of Minerals Stable Near the Earth's Surface

Principal Investigator: Alexandra Navrotsky,
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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 the jarosite – alumite series of hydrated sulfates, other phases related to acid mine drainage, uranyl minerals, phosphates, arsenates, and selenium minerals. New calorimetric approaches to the energetics of sulfide minerals are being developed.

CALIFORNIA, UNIVERSITY OF LOS ANGELES

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

Principal Investigator: T. Mark Harrison, tmh@argon.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 $^{40}\text{Ar}/^{39}\text{Ar}$ 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 $\delta^{18}\text{O}$ was measured by high spatial resolution ion microprobe. Both reveal surprising trends. $\delta^{18}\text{O}$ varies positively with temperature on both intra- and inter-annual timescales. On the inter-annual scale, $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ is responding to rainfall $\delta^{18}\text{O}$. Preservation of the annual rainfall $\delta^{18}\text{O}$ signal suggests that rainfall amount is recorded by speleothems in this region.

CALIFORNIA, UNIVERSITY OF SANTA BARBARA

Fluid Flow in Faults: Processes and Effects from Modern and Paleo Systems in a Transpressional Tectonic Setting, Southern California

Principal Investigator: James Boles, boles@magic.ucsb.edu, (805) 893-3719

Collaborator: Grant Garven, garven@jhu.edu, (410) 516-8689

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: the Wheeler Ridge Fault in the San Joaquin Basin and the Refugio Fault in the Transverse Ranges near Santa Barbara. 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.

Results: Manuscripts by Perez & Boles and Boles & others have been accepted by the AAPG Bulletin. In addition, a Perez & Boles manuscript on the kinetics of plagioclase albitization has been accepted by the American Journal of Science. These papers demonstrate the spatial distribution of fault cements, relate cementation patterns to hydrocarbon migration pathways and demonstrate that up to 2 km of vertical fluid movement has occurred along fault pathways at Wheeler Ridge. In addition, the albitization modeling predicts the dependence of this calcite-producing reaction on a critical burial temperature precipitation. A new study in an offshore Santa Barbara oil field (Boles & Horner, 2003) has calculated fault permeability from the rate of sea water influx into an underpressured reservoir. On the hydrogeologic modeling front, Garven & Stanislavsky (2002, 2003) published articles in Geophysical Research Letters and Earth and Planetary Science Letters that characterize fault-valve behavior and earthquake recurrence in a generic transpressional profile. Their calculations show that highly transient fluid flow is focused toward the thrust-fault zone where geomechanical failure occurs first near the basement-sediment interface. In addition, a finite element model has been prepared to simulate the migration of aqueous methane and mixing with meteoric groundwater in faulted, submarine reservoirs along coastal Santa Barbara, which provides a basis for ongoing studies of fault mineralization and reactive flow.

CALIFORNIA, UNIVERSITY OF SANTA BARBARA

Three-Dimensional Miscible Porous Media Flows with Viscosity Contrasts and Gravity Override

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High accuracy, three-dimensional numerical simulations of miscible displacements with gravity override in homogeneous porous media have been carried out for the quarter five-spot configuration. Special emphasis is placed on describing the influence of viscous and gravitational effects on the overall displacement dynamics in terms of the vorticity variable. Even for neutrally buoyant displacements, three-dimensional effects are seen to change the character of the flow significantly, in contrast to earlier findings for rectilinear displacements. At least in part this can be attributed to the time dependence of the most dangerous vertical instability mode. Density differences influence the flow primarily by establishing a narrow gravity layer, in which the effective Peclet number is enhanced due to the higher flow rate. However, buoyancy forces of a certain magnitude can lead to a pinch-off of the gravity layer, thereby slowing it down. Overall, an increase of the gravitational parameter is found to enhance mostly the vertical perturbations, while larger Pe values act towards amplifying horizontal disturbances. The asymptotic rate of growth of the mixing length varies only with Peclet number. For large Peclet numbers an asymptotic value of 0.7 is observed. A scaling law for the thickness of the gravity layer is obtained as well. In contrast to immiscible flow displacements, it is found to increase with the gravity parameter.

For heterogeneous displacements, regimes of viscous fingering, harmonic resonance and channeling are classified based upon the relative magnitudes of the viscous and permeability length scales of heterogeneous displacements and the natural viscous length scale of homogeneous displacements. A change in either the density difference or the permeability variance can influence the effective path resistance by changing the local coupling between the viscous and permeability fields. For random permeability displacements, the displacement efficiency is very sensitive to individual random realizations due to the importance of the selective harmonic resonance and effective path resistance.

CALIFORNIA, UNIVERSITY OF SANTA CRUZ

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

Principal Investigator: Ru-Shan Wu, wrs@earthsci.ucsc.edu, (831) 459-5135

Collaborator: Michael Fehler, fehler@lanl.gov, (505) 667-1925

The purpose of this project is to further develop and apply the new theories/methods of multi-domain one-way wave propagation to imaging and parameter estimation of reservoir structure and properties in 3D complex environments, such as the Gulf of Mexico. This efficient wave-equation based method can generate excellent modeling/imaging results and high-fidelity local parameter estimation compared with the widely used ray-based methods.

Major results:

- I. Anisotropic one-way propagator: We developed the theory and methods for VTI (vertically transversal isotropy) and oblique TI media. We apply the perturbation correction based on the method of generalized screen propagator. The wide-angle performance of the new propagator is far superior to other anisotropic propagators.
- II. True-reflection imaging and local AVO analysis: We have developed the theory and methods of evaluating the effects of acquisition-aperture combining with the overburden path influence to the imaging in angle-domain. We decompose the wavefield at each step into angle-domain by Gabor-Daubechies transform and define the imaging condition in angle-domain. We define the image matrix and derived the formulations for calculating the directional illumination and acquisition dip response (ADR). We also start to study the theory and techniques for the corresponding amplitude corrections. We apply the method to the imaging of subsalt steep reflectors of the SEG salt model. From the ADR map for reflectors with different dips, We can see clearly the subsalt shadow zones are drastically different for different dips. After a preliminary correction based on the ADR map, the improvement on images of steep reflectors are significant. We have done also some work on local AVA (amplitude vs. angle) analysis based on the amplitude-preserving imaging in angle-domain.
- III. Fast elastic wave modeling by thin-slab method: We incorporated quality factors (Q_p and Q_s) into the thin-slab propagator to model waves in visco-elastic media. With this enhancement, we have studied AVO responses of reservoirs with complex overburden structures and random heterogeneities. The method is 2 to 3 orders of magnitude faster than the full-wave finite difference method.

CALIFORNIA, UNIVERSITY OF SAN DIEGO

First Principles Simulation of the Supercritical Behavior of Ore Forming Fluids

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In this program we apply advanced simulation tools to the analysis of the processes that lead to the concentration of metal species in natural waters and deposition of ore-rich formations. It is widely accepted that the chemical properties of concentrated brines at high temperatures and pressures are responsible for the transport of metals via the formation of metal ion (e.g., Fe^{3+} , Zn^{2+} , etc.) associations with highly concentrated anions (e.g., Cl^- and HS^-). To predict the properties of metal ions in hydrothermal solutions, we are developing dynamic simulation methods based on first-principles density functional calculations of the forces between atoms in solution (ab-initio molecular dynamics, AIMD). These methods accurately account for properties such as changes in forces in the water molecules due to interactions with ions or transfers of protons in acid/base reactions. These processes play an essential role in the chemistry of aqueous solutions and cannot be treated by conventional molecular dynamics. This year we worked on the analysis of the solvation properties of Al^{3+} ions. Our AIMD results agree well with the measured octahedral structure of the 1st solvation shell. The properties of the 2nd solvation shell of the ions are poorly determined. Data from X-ray measurements have been interpreted using a highly coordinated model with two water molecules in the second shell coordinating each of the six 1st shell waters. The $G(r)$ calculated from our AIMD simulations shows a second shell peak with roughly 12 water molecules hydrogen bonded to the first shell waters, which is consistent with X-ray measurements. The calculated shell radius is in excellent agreement with the measured radius of 4.02Å. However, more careful analysis of the simulations shows that there is also a liquid-like contribution in the second shell. This is the first evidence of liquid behavior in this shell. At high temperatures, and less frequently at lower temperatures, hydrolysis reactions (proton exchanges) are evident in the dynamical simulations and calculated $G(r)$. While various hydration species ($\text{Al}(\text{OH})_n(3-n)^+$) have been postulated from modeling solution solubility data, evidence of their existence at neutral pH is indirect. The AIMD method is essential to simulate such proton transfers.

CHICAGO, UNIVERSITY OF

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

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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, redox chemistry of metals at the root-soil interface, chemical nature of hydrothermal fluids, and structures of and chemical reactions at mineral-water interfaces. Since FY99, a total of 324 beam time proposals have been received, 284 outside users (25% students) have conducted experiments, and 160 publications have been produced. Results include: (1) First direct spectroscopic evidence for vapor-phase Cu speciation in fluid inclusions suggesting copper is transported in the vapor phase as a neutral chloride complex (with J. Mavrogenes and A. Berry, Australian National University). (2) Arsenic budget within upper wetland sediments of the Wells G&H site (Woburn, MA) was dominated by cattail root sequestration (with N. Keon - MIT and colleagues) and the As(III) content was significant. (3) Pb(II) sorption on the (0001) and (1-102) surfaces of α -Al₂O₃ supported previous suggestions of sorption at ordered surface sites (with G. Brown, Jr – Stanford University, G. Waychunas – Lawrence Berkeley National Laboratory). (4) Soil aggregates with higher available organic carbon absorbed greater amounts of Cr(VI) and reductively precipitated Cr(III) within shorter diffusion distances, suggesting the spatial distribution of microbial activity is related to the creation of redox gradients (with T. Tokunaga – Lawrence Berkeley National Laboratory). (5) Measured hydraulic properties of unsaturated porous media were found to depend on drainage flow rate suggesting interference from dynamic phenomena such as air entrapment, pore-water blockage, and solid/liquid-gas contact angle (with D. Wildenschild - Tech. Univ., Denmark).

CHICAGO, UNIVERSITY OF

Kinetic Isotope Fractionation by Diffusion in Liquids

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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 $^{44}\text{Ca}/^{40}\text{Ca}$ by more than 6 per mil, and for $^7\text{Li}/^6\text{Li}$ 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 $^{26}\text{Mg}/^{24}\text{Mg}$) 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 $^7\text{Li}/^6\text{Li}$ 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. 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.

CHICAGO, UNIVERSITY OF

Synchrotron X-Ray Microprobe and Microspectroscopy Research In Low Temperature Geochemistry

Principal Investigator: Stephen R. Sutton,
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The project focuses on applications of the x-ray fluorescence microprobe on Beam Line X26A at the National Synchrotron Light Source (NSLS, BNL) for determinations of the compositions, structures, oxidation states, and bonding characteristics of earth and environmental materials with trace element sensitivity and micrometer spatial resolution. Research focused on actinide incorporation in minerals and sediments, biogeochemistry of metal contaminants, mineral surface site controls on metal uptake by minerals, and iron oxidation states in igneous petrogenesis. Research on surface site preferences for Cu(II), Co(II) and U(VI) uptake by calcite (with R. Reeder – SUNY Stony Brook) showed metal uptake by minerals is strongly dependent on the surface characteristics of the sorbent. Calcite single crystals grown in uranyl-containing solutions differentially incorporate uranium between nonequivalent vicinal surfaces, reflecting step-selective incorporation during growth. The distribution of Pb in the stems of EDTA treated samples (*Nicotiana tabacum*) was shown to be extensive and at a much greater concentrations than the stems of untreated samples (with M. Fuhrmann – Brookhaven National Laboratory). The distribution of Pb in the untreated stem showed very small, discrete localization of Pb suggesting that reactions at individual roots have mobilized small quantities of Pb. The variations in metal distributions in roots and shoots of plants exposed to recent magmatic degassing of CO₂ as a result of an earthquake in 1989 showed enhanced metal uptake since the degassing event (with S. C. B. Myneni, Princeton University). Iron oxidation state measurements in plagioclase from a middle Tertiary volcanic succession in the Atascosa Mountains of south-central Arizona provided direct evidence for a decrease in magmatic oxygen fugacity as the lava evolved (with M. D. Dyar – Mount Holyoke College and J. S. Delaney – Rutgers University). Clinopyroxene crystals in lavas from the East African volcano Satiman (adjacent to hominid locality, Olduvai Gorge, Tanzania) have dramatic oscillatory zoning correlated with oxygen fugacity variations as revealed by Fe oxidation state heterogeneity.

CLARK UNIVERSITY

Physics of Channelization: Theory, Experiment, and Observation

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We study the physical processes that create eroded channels and drainage networks. Common to many such systems is the regular spacing of drainage patterns. Depending on the particular setting, this preferred length scale has been observed to range from centimeters to hundreds of kilometers. The prediction of this length scale is one of the fundamental problems faced by any theory of landscape erosion. A major objective of our research is to understand how and why erosive dynamics not only selects the observed length scales but also acts to produce such rhythmic structures.

Our approach is to combine theoretical, experimental, and observational studies. The experiments shall consist of laboratory-scale analogs of regularly spaced channels formed by seepage erosion. Using modern laser-aided data-acquisition and digital imaging techniques, we obtain detailed time-dependent two-dimensional topographic data. Our preliminary experiments have already yielded periodic channels. By combining three-dimensional simulations, physical reasoning, and mathematical analysis we expect to obtain a thorough understanding of the phenomena observed in the laboratory. The prediction of the distance between regularly spaced channels will be but one of the products of this analysis.

The laboratory-scale component of this project is performed so that at least one manifestation of channelization may be completely understood. To better understand where our theories and experiments apply in the natural world, we also perform simple observational studies of natural channels found on beaches.

COLORADO SCHOOL OF MINES

Inversion of Multicomponent Seismic Data and Rock Physics Interpretation for Evaluating Lithology, Fracture and Fluid Distribution in Heterogeneous Anisotropic Reservoirs

Principal Investigator: Ilya Tsvankin, ilya@dix.mines.edu, (303) 273-3060

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Objectives: The goal of the CSM group is to develop a methodology for characterizing heterogeneous fractured reservoirs using 3-D multicomponent seismic data. The results are used for high-resolution evaluation of the position, orientation, spatial density and connectivity of fractures and other reservoir heterogeneities.

Project description: CSM investigators are working on an efficient approach to the anisotropic inversion and processing of 3-D wide-azimuth PP and PS (mode-converted) reflection data. Stacking-velocity tomography followed by multicomponent depth imaging produces an accurate heterogeneous, anisotropic model of the reservoir. Interpretation of the anisotropic parameters in terms of the physical properties of natural fractures is the main focus of collaborative research with LLNL and Stanford University.

Project results: *Construction of SS-wave traveltimes from PP and PS data.* To overcome difficulties in processing of PS (mode-converted) data, a method was devised for computing SS-wave reflection traveltimes from PP and PS data without precise knowledge of the velocity model.

Multicomponent stacking-velocity tomography for TI media. A joint tomographic inversion of the normal-moveout (NMO) ellipses and zero-offset traveltimes of PP- and SS-waves was developed and applied to layered transversely isotropic (TI) media with an arbitrary tilt of the symmetry axis.

Anisotropic processing of multicomponent data from the North Sea. The method of constructing SS-wave traveltimes and anisotropic multicomponent stacking-velocity tomography were successfully applied to a 2-D line acquired over the Lower Tertiary Siri reservoir in the North Sea.

Seismic inversion for the parameters of two orthogonal fracture sets. Inversion of wide-azimuth reflection moveout of PP- and PS(or SS)-waves was used to find the orientation of two orthogonal vertical fracture sets embedded in a TI matrix and estimate (in combination with the vertical velocities) the differences between the normal and shear weaknesses of the fracture sets.

Characterization of micro-corrugated vertical fractures. The parameters of realistic vertical fractures with micro-corrugated surfaces were estimated

COLORADO SCHOOL OF MINES

Possible Vertical Migration of CO₂ Associated with Large-Scale Injection into Subsurface Geologic Formations

Principal Investigator: Ronald Klusman, rklusman@mines.edu, (303) 273-3617

Measurements of carbon dioxide and methane soil gas concentrations and exchange with the atmosphere were made at a large-scale carbon dioxide enhanced oil recovery (EOR) operation at Rangely, Colorado, USA. The EOR has been operating since 1986, producing 16,000 bbl of oil per day from a depth of 2000 m. The interpretation was complemented by both stable and radiogenic isotopic measurements of carbon.

Strong seasonality in both carbon dioxide and methane fluxes into the atmosphere was found. The average summer, 2001 fluxes were 3.80 g carbon dioxide and 3.59 mg methane per square meter per day. During the winter of 2001/2002, fluxes averaged 0.33 g carbon dioxide and 17.8 mg methane per square meter per day. These measurements suggested a strong biological contribution to the summer carbon dioxide flux, and a summer maximum in methanotrophic oxidation of methane.

The results have demonstrated an estimated microseepage to the atmosphere of approximately 400 metric tonnes of methane per year from the 78 square km area of the field. Preliminary estimates of carbon dioxide seepage were in the range of 170-3800 metric tonnes per year. Carbon-14 measurements and computer modeling of methanotrophic oxidation rates necessitated a revision to <170 metric tonnes per year. The rate constants for methanotrophic oxidation were less in the winter than in the summer. Methanotrophic oxidation in the unsaturated zone will be the most important component of amelioration of microseepage from overpressure reservoirs undergoing carbon dioxide injection. Methane measurements are as important as carbon dioxide measurements.

An evaluation of historic produced water quality from the Rangely reservoir demonstrated an increase in some parameters, particularly calcium and bicarbonate, indicating a dissolution of ferroan carbonate cements. Computer modeling suggested carbonate mineral sequestration was possible within the constraints of produced water quality. X-ray analysis of well scales did not support the presence of mineral sequestration. The bulk of the 23+ million tonnes of carbon dioxide that has been injected since 1986 is stored as dissolved carbon dioxide. Precipitation of anhydrite and reduced iron minerals, such as FeS, and possibly siderite, will contribute to a loss of permeability and injectivity in sequestration systems.

COLORADO, UNIVERSITY OF

Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crystal Deformation Processes

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Research under this project is focused on the analysis of crustal deformation processes in 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 3 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 Aperature Radar Interferometry data, which are other new types of crustal deformation data. In addition to these major results, we also have determined that 1) there are several classes of earthquakes, each with a distinct set of scaling exponents; 2) the evolution of earthquake seismicity patterns can be described with (surprisingly) a linear theory over short times, since the nonlinear clusters in the patterns have very small amplitude; and 3) the non-equilibrium, driven, meanfield earthquake fault system in southern California has many characteristics (again, suprisingly) of equilibrium systems.

COLORADO, UNIVERSITY OF

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

Principal Investigator: Hartmut Spetzler,
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We are 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 the (1) onset of contaminant leakage at buried waste sites, (2) progress of contaminant remediation, and (3) progress of water flooding or steam injection during enhanced petroleum recovery

Last year marked the initial phase of our feasibility study in the field, where we seek to detect changes in recorded strain signals (attenuation) in response to local changes in the fluid saturation conditions in the vadose zone. Rather than employing manmade sources, which are very expensive and invasive, we are exploring the use of natural sources of strain and seismic waves, specifically Earth tides and globally-recorded, natural microseisms, respectively. The field site is operated by the University of Arizona, and has sophisticated facilities for controlled water irrigation and a comprehensive, dense array of instruments used for measuring water saturations and flow. We plan to change the saturation conditions by irrigating at the site with water in October '03, with water plus a biosurfactant in late spring '04 and again with water late in '04. First background data over a 9 months period from three tiltmeters and 3 seismometers are encouraging.

We measured the wettability hystereses of clean and diesel-coated quartz crystals by water, diesel, and oil-reducing bacteria solution. The purpose of this work was to see if there are differences in the wettability hystereses, which result in differences in low-frequency seismic attenuation. When the diesel-coated quartz was dipped in and out of the bacterial solution, we observed significant changes in hystereses that did not occur with the other fluid constituents. These results suggest that we ought to be able to monitor bioremediation progress using low-frequency seismic attenuation data.

COLORADO, UNIVERSITY OF

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

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The objective of this project is to develop a quantitative understanding of the critical processes controlling two-phase flow and transport in fractures. Fundamental understanding may subsequently be abstracted for application to large-scale problems in petroleum extraction, radioactive waste isolation, subsurface remediation, and CO₂ sequestration. We explore fundamental physical processes through a combination of detailed physical experiments and numerical simulations. 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 facilitate concurrent model development.

Highlights:

A depth-averaged model for dissolution of a non-aqueous phase liquid (NAPL) within variable aperture fractures: The model explicitly couples fluid flow, transport of dissolved NAPL, inter-phase mass transfer and NAPL-water interface movement. When compared to high resolution experimental data, the model accurately predicted both the change in overall NAPL saturation with time and the evolution of the entrapped phase geometry. This is perhaps the first instance where close agreement between simulations and experiments on NAPL dissolution was achieved without empirical treatment of inter-phase mass transfer. Results were published in *Water Resources Research* [37(12) 3115-3130, 2001].

A 3-D particle-tracking simulator to explore solute transport through a variable aperture fracture containing an entrapped fluid phase: In comparison to experiments, the model was able to predict 85% of the increase in dispersion over single-phase conditions. It also reproduces the experimentally observed nonlinear relationship between solute dispersion and Peclet number, which suggests that Taylor dispersion effects are significant even in partially saturated fractures. Results were published in *Geophysical Research Letters* [29(8) 10.1029/2001GL013508, 113-1 – 113-3, 2002].

Demonstration of the importance of local head loss in predicting solute transport through single fractures: An ad hoc correction to the Reynolds equation was used to demonstrate that underestimation of local head loss in regions of changing aperture can artificially smooth the predicted flow field. Subsequent prediction of solute transport is affected in

terms of both the mean velocity and longitudinal dispersion. Results were published in Geophysical Research Letters [28(23) 4351-4354, 2001].

CONNECTICUT, UNIVERSITY OF

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

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The goal of this project is to isolate and identify the various air-derived noble gas components in sediments, particularly, but not exclusively, those sediments associated with hydrocarbons. The project is designed to address how noble gas elemental patterns are acquired and retained, how they are transferred to basin fluids in which they have been measured, and to improve the 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 smooth mass dependent abundance patterns have led to adsorption hypotheses, three observations argue against single stage 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) Laboratory heating experiments suggests the enriched component is tightly bound, counterintuitive to a simple adsorption history. And (3) many sedimentary rocks (~half) and some oil field gases contain excess Ne in conjunction with excess Xe.

We are examining diffusive filling and emptying of angstrom-scale half-spaces in lithic grains as an explanation for the observed absolute and relative abundances sedimentary rocks. Since physical properties of the noble gases are strong functions of atomic mass, the individual diffusion coefficients, adsorption coefficients and atomic diameters combine to impede heavy noble gas transport relative to the lighter noble gases. Filling of lithic grains/half-spaces thus produces Ne enrichments in the early and middle stages of the filling process, emptying lithic grains/half-spaces produces a Xe-enriched residual in the late stages of the process, and both Ne and Xe enrichments can be produced by incomplete emptying of the half-spaces followed by incomplete filling. A system of labyrinths-with-constrictions when combined with simple adsorption results in stronger diffusive separation and non-steady-state enrichments that persist for longer times. Laboratory work is currently underway to better evaluate noble gas absolute and relative abundances in sediments by isolating and identifying carrier phases and trapping mechanisms.

DELAWARE, UNIVERSITY OF

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

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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.

FLORIDA, UNIVERSITY OF

Evolution of Surface Morphology During Dissolution of a Rough Fracture

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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, CO₂ 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. Therefore one of the technological requirements of the sequestration initiative are well-validated simulation tools to study the mechanisms underlying the time dependence of fracture permeability. 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. In this work we are developing this model further, to account for the transport of products as well as reactants, and to modify the erosion model to take account of the local concentrations of reactants and products. Our initial focus was on simple model systems, which were used to develop and validate the numerical algorithms. We are now concentrating on CO₂ dissolution in narrow fractures, where surface profile data has been obtained for samples of Carrara marble. This work supports Geosciences objectives aimed at developing a fundamental understanding of transport and reactive processes in rock-fluid systems, and specifically aids the goals of the CO₂ sequestration initiative by providing numerical algorithms for a reactive flow and transport model.

GEORGE WASHINGTON UNIVERSITY

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

Principal Investigator: H. Henry Teng, hteng@gwu.edu, (202) 994-0112

Etch pits occur ubiquitously on dissolved or weathered mineral surfaces and have a saturation-dependent nature for nucleation. However, conventional dissolution studies often ignore the controls of saturation by conducting experiments in distilled water. This study attempts to examine the dependence of pit formation on solution undersaturation using calcite as a model system. Experiments were conducted at various undersaturations to explore the behavior of mineral surfaces using in situ fluid cell Atomic Force Microscopy. The goal is to determine when pit formation dominates the dissolution process.

Three dissolution modes were observed. When saturation index $\Omega > 0.541$, no pits were seen and dissolution primarily occurred at existing steps. When Ω decreased to $\Omega_c = 0.541 - 0.410$, the first visible pits appeared and the pit density slowly increased with continuous reduction in Ω . Finally, when Ω fell below $\Omega_{max} = \sim 0.007$, a precipitous increase in pit density took place that sharply contrasted to the ordered fashion of pit formation at $W > W_{max}$. These observations are interpreted to be 2-D unassisted pit formation at $W < \sim 0.007$, defect-induced dissolution in between $W = 0.541$ and 0.007 , and existing step-assisted dissolution for $W > 0.541$.

The values of W_c are in good agreement with the dislocation theory's predicted critical undersaturations for pit formation at line dislocations. The occurrence of W_{max} is not directly predicted but is a logical consequence of dissolution thermodynamics. These findings suggest that (1) near-equilibrium ($W > W_c$) dissolution is not controlled by pit formation; (2) dislocation-induced pit formation should strongly impact dissolution kinetics in $W_{max} < W < W_c$; (3) at far from equilibrium ($W < W_{max}$), 2-D surface nucleation, instead of crystal defects, is largely responsible for surface pitting.

These findings may provide explanations for several well-observed geochemical relationships, including the weak dependence of dissolution rate upon dislocation density in distilled water, the non-linear dependence of dissolution rate upon chemical affinity of dissolution reactions, and the 'plateau' behavior of dissolution kinetics both near and far from equilibrium. The occurrence of W_{max} suggests that an accurate 'general' rate law describing universal dissolution processes has yet to be developed.

GEORGIA STATE UNIVERSITY

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

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This project began in September 1, 2002, and the proposed work is detailed in this summary. The proposed work is aimed at testing the hypothesis that remnant magnetization constrains the timing of diagenetic events in select diagenetic environments (thrust-sheet burial and burial metamorphism). Our specific work includes these four areas of investigation: laboratory simulation of the synthesis of diagenetic illite and magnetite at diagenetic temperatures at low to medium diagenetic temperatures (62 °C and 98°C) to identify the process by which magnetic minerals are forming on smectite-illite particles (adsorbed iron or iron released during the conversion of smectite to illite); measurement of CRM and K-Ar ages of illite in shales and bentonites affected by thrust-sheet burial in the Disturbed Belt, Montana; the timing of CRM in relation to progressive burial and maturation of organic matter in the Mississippian Desert Limestone in Utah; and the study of remagnetization and clay diagenesis of Jurassic age sediments in Skye, Scotland. The results from the studies detailed above are expected to provide information about the formation of authigenic magnetic minerals and diagenetic illite in relation to prominent geologic processes of such as thrust sheet burial, burial metamorphism, maturation of hydrocarbons and the movement of fluids and heat due to contact metamorphism which, in turn, increase our knowledge of the diagenetic processes marking the time-temperature window for the generation of oil and gas.

GSY-USA, INC.

The Magnetotelluric Data Simulation Project

Principal Investigator: Randall Mackie, randy@gsy-usa.com, (415) 469-8649

By computing synthetic magnetotelluric (MT) responses for realistic resistivity models of important crustal features, this project will provide a basis for validating research claiming improved MT imaging of similar features. Researchers will also be able to more thoroughly investigate fundamental resolution issues such as the degree to which knowledge of MT impedance transfer functions at particular noise levels can constrain the 1, 2, or 3D character of the resistivity distribution that produced them. Impedance transfer functions will be computed and distributed in an easily accessed standard format for most types of geologic targets currently receiving significant MT research funding, facilitating the transfer of new MT technology among research and industry groups. Massively parallel computers at Sandia National Laboratories, otherwise unavailable to the academic and industry MT communities, will be used to compute 3D MT responses from resistivity models that will be far more realistically detailed than any previously used in such studies. Recognized MT research leaders and industry experts have been recruited to provide representative detailed 3D models for a wide variety of models, many of which are designed to apply details available from industry to enhance the shallow sections of models of importance to academic researchers investigating more fundamental properties and processes of the Earth's crust. The 3D models that will be synthesized in this project include, for example, geothermal reservoirs, on-shore over-thrust petroleum models, sub-salt ocean bottom models, and mining models. The results will be incorporated into a database program and GUI (to run under Windows) for extracting the responses into standard EDI format.

HAWAII, UNIVERSITY OF

Growth of Faults, Scaling of Fault Structure, and Hydrologic Implications

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Strike-slip faults several kilometers long in the granite of Sequoia National Park, California, developed from pre-existing igneous dikes. The dikes are opening-mode fractures, and they dictated the position, size, and shape of the eventual faults. Field observations show that the dikes sheared and became faults after becoming highly fractured. Fractures localized in the dikes either because the dikes were weaker than the granite, or because tensile stresses were more concentrated in the dikes. The dikes are thin relative to their lengths, and hence material contrasts between the dikes and the granite can be ruled out as a potential cause for a tensile stress concentration in the dikes. Thermo-elastic analyses indicate that as dikes cool, tensile stresses will build in the dikes, whereas stresses become more compressive in the adjacent host rock. The character of cooling-induced fractures in dikes will reflect a balance between the regional stresses and the temperature difference between the dike and the host rock when the dike was intruded. Dikes intruded at different times during the cooling history of a granite body could fracture in markedly different ways. In Sequoia National Park, the thermo-elastic stresses might have been “locked” into the dikes for thousands of years before the dikes actually fractured. The field evidence is consistent with the dikes having faulted during a regional fracturing event. The resulting faults form part of a regionally connected fracture system that could serve as a regionally connected hydrologic system as well. The slip distribution measured on faults in this network is consistent with the faults interacting mechanically as they slipped and with contemporaneous slip on the faults in the network. In basalt of Hawaii, active normal faults several kilometers long grew by propagating up to the surface, rather than down from the surface. Systematic connected fractures developed on both sides of where a fault breaches the surface; some fractures have apertures of several meters. These fractures would readily permit the flow of fluids at prodigious rates parallel to the normal faults. Elastic analyses predict the locations of these fractures.

IDAHO, UNIVERSITY OF

The Interaction of Two Fluid Phases in Fractured Media

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The objective of this project is to develop a quantitative understanding of the critical processes controlling two-phase flow and transport in fractures. Fundamental understanding may subsequently be abstracted for application to large-scale problems in petroleum extraction, radioactive waste isolation, subsurface remediation, and CO₂ sequestration. We explore fundamental physical processes through a combination of detailed physical experiments and numerical simulations. 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 facilitate concurrent model development.

Highlights:

A depth-averaged model for dissolution of non-aqueous phase liquid (NAPL) within a variable aperture fracture: The model explicitly couples fluid flow, transport of dissolved NAPL, inter-phase mass transfer and NAPL-water interface movement. When compared to high resolution experimental data, the model accurately predicted both the change in overall NAPL saturation with time and the evolution of the entrapped phase geometry. This is perhaps the first instance where close agreement between simulations and experiments on NAPL dissolution was achieved without empirical treatment of inter-phase mass transfer. Results were published in *Water Resources Research* [37(12) 3115-3130, 2001].

A 3-D particle-tracking simulator to explore solute transport through a variable aperture fracture containing an entrapped fluid phase: In comparison to experiments, the model was able to predict 85% of the increase in dispersion over single-phase conditions. It also reproduces the experimentally observed nonlinear relationship between solute dispersion and Peclet number, which suggests that Taylor dispersion effects are significant even in partially saturated fractures. Results were published in *Geophysical Research Letters* [29(8) 10.1029/2001GL013508, 113-1 – 113-3, 2002].

Demonstration of the importance of local head loss in predicting solute transport through single fractures: An ad hoc correction to the Reynolds equation was used to demonstrate that underestimation of local head loss in regions of changing aperture can artificially smooth the predicted flow field. Subsequent prediction of solute transport is affected in

terms of both the mean velocity and longitudinal dispersion. Results were published in Geophysical Research Letters [28(23) 4351-4354, 2001].

ILLINOIS, UNIVERSITY OF

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

Principal Investigator: R. James Kirkpatrick, kirkpat@uiuc.edu, (217) 333-7414

The objectives of our molecular simulation efforts are: (1) the realistic modeling of the coupled dynamics of atomic motions between mineral substrate atoms and the interfacial aqueous phase, and (2) the development of computational tools for visualization and quantitative understanding of local structural, energetic and dynamic environments of aqueous species in mineral interlayers and at interfaces.

The interaction of anions with mineral surfaces and in mineral interlayers is less well understood than that of cations. In 2002, our extensive NMR and computational study of the structural and dynamical behavior of anions in a wide range of layered double hydroxide (LDH) phases was essentially completed (Hou et al., *Chem. Materials*, 14, 1195, 2002; Hou et al., *Chem. Materials*, 14, 2078, 2002; Hou et al., *Am. Mineral.*, 88, 167, 2003; Kalinichev and Kirkpatrick, *Chem. Materials*, 14, 3539, 2002). The results provide a comprehensive framework for molecular scale understanding of the effects of anion size, conformation, and charge and substrate composition and structure on the interlayer and surface structural environments of the anions, their reorientational dynamics, sorption/desorption behavior, and macroscopic interlayer expansion. Molecular modeling has proven highly effective in providing detailed nano-scale understanding of the interactions that lead to the observed phenomena.

LDH interlayer behavior is dominated by electrostatic and H-bonding interactions. Its low-frequency dynamics involves cooperative motion of many atoms. FIR spectra probing this dynamics are often difficult to interpret. Fourier transformation of the atomic velocity autocorrelation functions obtained by MD simulations allows interpretation of observed FIR bands. MD results for a variety of LDH phases show that interlayer motion is in many ways similar to the translational dynamics of aqueous fluids and involves distortion of the H-bonding network. For all phases investigated, motion of anions and water molecules parallel to the layers is dominated by H-bond bending, whereas motion perpendicular to the layers involves dominantly H-bond stretching (Wang et al., *Am. Mineral.*, 88, 398, 2003; Kirkpatrick et al., *Clay Minerals Society Workshop Lectures*, 2003, in print). The surprisingly good agreement between simulated and measured spectra provides strong support for our modeling approach and the CLAYFF force field used for the simulations.

ILLINOIS, UNIVERSITY OF

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

Principal Investigator: Craig Bethke, c-bethke@uiuc.edu, (217) 333-3369

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 chemical 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.

ILLINOIS, UNIVERSITY OF

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

Principal Investigator: Neil C. Sturchio, sturchio@uic.edu, (312) 355-1182

Collaborator: Paul Fenter, fenter@anl.gov, (630) 252-7053

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 glancing-incidence X-ray reflectivity, surface and thin-film diffraction, crystal truncation rods (CTR), and X-ray standing waves (XSW). We have performed experiments at the APS since late 1997. These experiments demonstrated the first uses of glancing-incidence 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, sulfates and phosphates).

ILLINOIS, UNIVERSITY OF

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

Principal Investigator: Kathryn Nagy, knagy@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, raised by our previous research. 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 aluminosilicate clays 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, cations, anions, and 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 are aging Fe-oxides and phyllosilicate clays in the presence of selected cations, anions, and organic molecules, and quantifying the effects of surface area, morphology, and phase proportions on the aging process.

INDIANA UNIVERSITY

Self-Organized Mega-Structures in Sedimentary Basins

Principal Investigator: Peter Ortoleva, ortoleva@indiana.edu, (812) 855-2717

A three dimensional finite element fault model that accounts for an incremental stress rheology, and fluid and heat flow is developed. In the model, mass and momentum balances for solid and fluid phases, and a total energy conservation equation are solved numerically along with a state and rate dependent friction law at the fault surface. The model allows one to study the effect of frictional heating, fluid influx from the deeper parts of faults, and effect of heterogeneities on the fault behavior at the crustal scale. Our preliminary results show that fluid flow can significant affect long and short time scale fault motion. Our finite element formulation allows one to simulate heterogeneous systems subjected to a complex far field velocity field. Permeability is shown to be an important factor in determining the fault behavior. As fault permeability during the seismic cycle changes significantly, fault models should take fracturing and fracture healing into consideration.

The volume of basin data, obtained at great expense, presents both a technical and economic challenge to the industry. What is needed is an automated procedure to derive value from these databases often available on a field or basin. From our research, we suggest that automated analysis can be achieved through model automated informatics. By definition, informatics is the science of deriving conclusions or otherwise deriving information from a vast and complex database. In our recent work, we suggest that this can be achieved with the use of comprehensive basin model to analyze available data using information theory. Our information theory approach also provides a natural platform for the integration of expertise. These expertise constraints include limiting the spatial and temporal scale of phenomena (e.g. maximum known rate of overall basin deformation, basement heat flux, etc.). When this above data/modeling integration is automated, a basin model in effect becomes the centerpiece of a database mining algorithm since differential equations of physics and chemistry are simply algorithms for processing information. In this sense, this procedure is the essence of a quantitative geoinformatics methodology.

INDIANA UNIVERSITY

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

Principal Investigator: Arndt Schimmelmann,
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Isotopically labile organic hydrogen occupies chemical positions that participate in isotopic exchange and in chemical reactions during thermal maturation. We monitor changes in the H-isotopic exchangeability and D/H ratio in maturing kerogens to evaluate their imprint on the diagenetic and/or paleoenvironmental significance of δD in different types of kerogen, and in oil as a maturation product. The D/H ratio of bulk coal kerogen is influenced by (1) the maceral composition, (2) the history of coal-water isotopic interaction along thermal maturation, and (3) the presence of isotopically exchangeable organic hydrogen. H_{ex} (= % of isotopically exchangeable, or labile organic hydrogen in total organic hydrogen) in coal kerogens was found to be highest in lignite (ca. 18%) and decreases to around 2.5% in coal with vitrinite reflectance R_o of 1.7 to ca. 5.7%. At still higher rank ($R_o > 6\%$), H_{ex} increases while the abundance of total hydrogen continues to decrease. The maceral composition influences H_{ex} up to the rank of high volatile bituminous coal and becomes irrelevant at higher ranks. δD_n (= the D/H ratio of non-exchangeable organic hydrogen expressed in ‰ versus VSMOW) is influenced by original biochemical D/H ratios and by thermal maturation in contact with water, and therefore δD_n does not show a globally consistent trend with maturity. A regional trend toward more negative δD_n values is observed for Illinois Basin and Appalachian Basin coals with increasing maturity from R_o of 0.55% to 1.4%. Kerogens prepared from a suite of samples from the New Albany Shale with R_o from 0.29 to 1.4% were characterized by ^{13}C -NMR, FTIR, and hydrogen stable isotope mass-spectrometry. All four independent analytical proxies for maturity showed mutually corroborating responses. NMR- and FTIR-based assessments of maturity do not rely on the presence of vitrinite and thus have special value for marine kerogens. The δD values of Australian bulk oils, fractions, formation waters and kerogens from source rocks demonstrate their usefulness for outlining oil families and for correlation between oil and source rocks. Lack of correlation of oil δD values with formation water δD values indicates that most organic hydrogen has not changed isotopically under reservoir conditions.

JOHNS HOPKINS UNIVERSITY

Fluid Flow in Faults: Processes and Effects from Modern and Paleo Systems in a Transpressional Tectonic Setting, Southern California

Principal Investigator: Grant Garven, garven@jhu.edu, (410) 516-8689

Collaborator: James Boles, boles@magic.ucsb.edu, (805) 893-3719

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: the Wheeler Ridge Fault in the San Joaquin Basin and the Refugio Fault in the Transverse Ranges near Santa Barbara. 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.

Results: Manuscripts by Perez & Boles and Boles & others have been accepted by the AAPG Bulletin. In addition, a Perez & Boles manuscript on the kinetics of plagioclase albitization has been accepted by the American Journal of Science. These papers demonstrate the spatial distribution of fault cements, relate cementation patterns to hydrocarbon migration pathways and demonstrate that up to 2 km of vertical fluid movement has occurred along fault pathways at Wheeler Ridge. In addition, the albitization modeling predicts the dependence of this calcite-producing reaction on a critical burial temperature precipitation. A new study in an offshore Santa Barbara oil field (Boles & Horner, 2003) has calculated fault permeability from the rate of sea water influx into an underpressured reservoir. On the hydrogeologic modeling front, Garven & Stanislavsky (2002, 2003) published articles in Geophysical Research Letters and in Earth and Planetary Science Letters that characterize fault-valve behavior and earthquake recurrence in a generic transpressional profile. Their calculations show that highly transient fluid flow is focused toward the thrust-fault zone where geomechanical failure occurs first near the basement-sediment interface. In addition, a finite element model has been prepared to simulate the migration of aqueous methane and mixing with meteoric groundwater in faulted, submarine reservoirs along coastal Santa Barbara, which provides a basis for ongoing studies of fault mineralization and reactive flow.

JOHNS HOPKINS UNIVERSITY

Predictive Single-Site Protonation and Cation Adsorption Modeling

Principal Investigator: Dimitri Sverjensky, sver@jhu.edu, (410) 516-8568

Research efforts this year have focussed on a thorough examination of defining standard states for species adsorbed on mineral surfaces in equilibrium with aqueous solutions. The most widely-used standard state in geochemical systems (the hypothetical 1.0 molar standard state) turns out to have undesirable practical consequences. In particular, the magnitudes of the equilibrium constants for surface reactions are directly dependent on properties of the solid, such as the site density, surface area, and even, for binuclear reactions, the amount of solid. As a consequence, these equilibrium constants cannot be directly compared with each other, even for different samples of the same solid. The theoretical basis for correcting such problems has been developed and published (Sverjensky, 2003, Standard states for the activities of mineral surface sites and species, *Geochimica et Cosmochimica Acta*, v. 67, pp. 17-28). The results of this study permit a reevaluation of predictive correlations for the adsorption of electrolytes on solid oxide surfaces. New correlations consistent with crystal chemical and solvation theory have been developed which enable all the parameters in the triple-layer model to be estimated. As a consequence, predictions of surface charge as functions of pH, ionic strength and electrolyte type can be made for many minerals in an internally consistent manner. A manuscript on this is in review. Research is also continuing on the adsorption of divalent and higher valence metals onto mineral surfaces, elucidating changes in surface speciation with solution chemistry and surface coverage. The overall objective is prediction of the acquisition of metals by fluids circulating through aquifers in the earth's crust.

JOHNS HOPKINS UNIVERSITY

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

Principal Investigator: David Veblen, dveblen@jhu.edu, (410) 516-8487

Collaborator: Eugene Ilton, (now at) Eugene.Ilton@pnl.gov, (509) 376-5022

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, most recently, sorbed to mineral surfaces. The project has three main components: experimental investigation of U reduction and sorption by micas; high-resolution transmission electron microscopy (HRTEM) characterization of grain boundaries and surfaces; 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.

Geochemical work has focused on the experimental and theoretical determination of the multiplet structures of Cr2p and Mn2p as a function of bonding environment. We have now documented strong bonding environment effects on the multiplet structures of Cr2p and Mn2p that complicate interpretations of the oxidation states of Mn(IV) and Cr(III) in environmentally important minerals. Theoretical calculations are focused on whether these observations can be explained by octahedral distortion or covalency effects. Mica composition, pH, time, and the type and concentration of aqueous alkali cations play important roles in heterogeneous reduction of uranyl at mica surfaces. Addition of NaCl to solution dramatically increases the reduction of U(VI) over the pH range 4.5 to 9.5. We have correlated the appearance of low binding energy (BE) U4f peaks with an increase in the U5f valence band, proving that low-BE energy peaks do record reduction of uranyl, and not just a change in uranyl speciation. We can also track low sensitivity satellite features that are diagnostic of U(VI), U(V), and U(IV). We have discovered the first evidence for U(V) on mineral surfaces in environmentally relevant, aqueous experiments. This is a particularly surprising result because U(V) is known to be extremely unstable in solution.

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. Imaging and electron energy-loss spectroscopy (EELS) of U phases and sorption products currently centers on development of a nano-scale valence determination technique.

LEHIGH UNIVERSITY

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

Principal Investigator: Eugene Ilton, (now at) Eugene.Ilton@pnl.gov, (509) 376-5022

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LOUISIANA STATE UNIVERSITY

3D Sedimentological and Geophysical Studies of Clastic Reservoir Analogs: Facies Architecture, Reservoir Properties, and Flow Behavior within A Delta Front

Principal Investigator: Christopher David White, cdwhite@lsu.edu, (225) 578-6039

Collaborator: Janok P. Bhattacharya, janokb@utdallas.edu, (972) 883-2449

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.

MARYLAND, UNIVERSITY OF

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

Principal Investigator: Steven Lower, lower.9@osu.edu, (614) 292-1571

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

This project is a collaboration between the University of Maryland (Dr. Steven Lower) and Virginia Tech (Dr. Michael Hochella, Jr.). The goal is to probe nanoscale forces and proteins at the interface between a dissimilatory metal reducing bacterium and an iron oxyhydroxide mineral. In this first phase of research, biological force microscopy (BFM) was combined with two-dimensional (2D) gel electrophoresis to identify outer membrane proteins from *Shewanella oneidensis* that are involved in the reduction of Fe(III). BFM-derived force curves between *S. oneidensis* and goethite (FeOOH) suggested that two proteins (~83 kDa and ~150 kDa) were targeted to the cell-mineral interface under anaerobic conditions. Protein expression patterns from 2-D gel electrophoresis revealed that two proteins of the same molecular weight were expressed almost exclusively under anaerobic conditions. Further, BFM measurements showed that these outer membrane proteins possess a strong affinity towards goethite but not diaspore (AlOOH), despite the fact that diaspore and goethite have very similar surface properties. Taken together, these results suggest that these two proteins are synthesized by *S. oneidensis* under anaerobic conditions to function in iron hydroxide binding and/or the reduction of Fe(III). In the future, this situation could be exploited to create genetically modified bacteria that selectively bind to particular mineral phases.

MARYLAND, UNIVERSITY OF

Theoretical Studies of Heavy Metal Species in Solution

Principal Investigator: John Tossell, tossell@chem.umd.edu, (301) 405-1868

Our research group utilizes the techniques of computational quantum chemistry to study the structures, energetics and properties of various metal species in solution, as components of mineral glasses, or absorbed on mineral surfaces. The focus in Fiscal Year 2002 has been on complexes of Cu(I) with thioarsenite ligands, on the energetics of the oxidation of Sb (III) species in sulfidic solutions, and on the speciation of Si in solutions containing polyalcohols and other organic ligands. In collaboration with Professor George Helz (UMCP) we recently identified a Cu thioarsenite complex which contributes greatly to the solubility of both Cu and As in sulfidic solutions in equilibrium with Cu and As sulfide minerals. A detailed discussion of the properties of this compound has now been published. Our studies of speciation in arsenite and thioarsenite solutions have been extended to a study of their UV spectra, to assess the capability of UV spectroscopy for species identification and quantification. Recently Helz, et al. (*Environ. Sci. Technol.*, 36, 943, 2002) reported the existence of two new Sb sulfide species, Sb₂S₅₋₂ and Sb₂S₆₋₂, in alkaline sulfidic solutions in equilibrium with stibnite, Sb₂S₃, and orthorhombic S. We have calculated from first principles of quantum mechanics the energetics for the oxidation of the Sb(III) sulfide dimer Sb₂S₄₋₂ to the mixed Sb(III,V) dimer Sb₂S₅₋₂ and then to the all Sb(V) dimer, Sb₂S₆₋₂. Negative free energy changes are calculated for the oxidation of the dianion of the III,III dimer to the III,V dimer by both small polysulfides, like S₄H⁻¹, and elemental S, modeled as S₈. For the further oxidation of the III,V dimer to the V,V dimer the reaction free energies are calculated to be close to zero. These results are thus consistent with the recent identification of Sb₂S₅₋₂ and Sb₂S₆₋₂ species by Helz, et al. In collaboration with Prof. Nita Sahai, Dept. of Geology, Univ. of Wisconsin, we are continuing to explore the speciation of Si in solutions containing polyalcohols as ligands. Our results cast doubt on the original assignments of five- and six- coordinate species.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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

Principal Investigator: J. Brian Evans, brievans@mit.edu, (617) 258-0620

Collaborator: Wenlu Zhu, wzhu@whoi.edu, (508) 289-3355

Transport properties of rocks, including fluid permeability and electrical conductivity, can be altered by diagenetic, metamorphic, and tectonic processes. This project involved measurements of permeability and electro kinetic properties of synthetic sandstones with varying surface roughness and of evolution of permeability at 400 K and higher, in stagnant fluids, at pore pressures up to 200 MPa, and at confining pressures between 200-400 MPa. For example, a series of transient flow experiments were done on reacting synthetic sandstones while recording the electrical potential across the sample. The sample permeability was $8 \times 10^{-15} \text{ m}^2$, and pressure pulses decayed in a few seconds. During the first 8 days, the samples were subjected to three heating sequences up to 400 K. The experiment lasted 23 days, during which 58 transient flow tests were performed. The streaming potential demonstrated a complex hysteretic response that could not be interpreted by the standard electro kinetic theory and was influenced by the kinetics of alteration. The experiments illustrate some possible effects of chemical reactions during field tests, especially when cold water is injected into hot rock. In a second set of experiments we deformed Solnhofen limestone with initial porosity of 4.5% at 473, 523, 573 and 673 K, at confining pressures (argon) of 70 to 200 MPa, and a constant pore pressure (distilled water) of 50 MPa. Most of the limestone samples failed by dilatancy and localized deformation. The failure process is sensitive to both pressure and temperature. The stress required to cause dilatancy and localization increases with increasing pressure and decreasing temperature. At low pressures and temperatures, strain softening and an abrupt stress drops were observed during localization. However, at higher pressure and temperature, the localization process became progressive, with strain softening and dilatancy accumulating over large amount of axial strain (up to 6%). Following the localization model of Rudnicki and Rice (1975), we used the internal friction parameter, the dilatancy factor, and the hardening modulus to characterize the failure behavior. Both the internal friction parameter and the dilatancy factor depend on P and T.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Fluid Mobility Estimation from Electro seismic Measurements:
Laboratory, Field, and Theoretical Study

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A laboratory scale model was constructed to investigate the possibility of using crosswell seismoelectric data to identify and characterize fractures in the inter-well region of a reservoir. In this experiment we place a seismic source in one borehole and an electrode array in a second borehole. A seismic wave propagating in a fluid-saturated porous medium moves ions in the double layer between the fluid and solid and induces an electric field. When there is a discontinuity (such as a fracture), the seismic wave induces a radiating electromagnetic (EM) wave. Our results indicate that when the seismic wave hits the fracture, fluid flow is initiated and a radiating electromagnetic wave is produced. This signal can provide information about the location and aperture of the fracture. Analysis of the results of these experiments show that the arrival time of the radiating EM wave can be used to determine the fracture location and dip angle in two dimensional models. By placing the acoustic source at a range of depths in one borehole and recording electric signals with real or synthetic arrays of acoustic and electric receivers in the second borehole, the position of a vertical or inclined fracture between two boreholes can be determined from the difference in arrival time between the acoustic and EM waves. Furthermore, the amplitude of the seismoelectric signal increases with increasing fracture aperture. Crosshole seismoelectric measurements may provide a new means for characterizing fractures between two boreholes. In a second experiment, the electrical signals generated during the fracturing of a cylindrical rock sample under pressure were measured. The results indicate that when the sample is wet, an electrical signal is generated due to motion of the charged fluid in the fracture. Signals related to piezoelectric effects are much smaller. These results indicate that seismoelectric/electroseismic measurements may be used during reservoir hydrofracturing as an indicator that fracturing has occurred. We have not yet studied the relationship between the signals and the geometry or flow capacity of the fractures.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Physics of Channelization: Theory, Experiment, and Observation

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We study the physical processes that create eroded channels and drainage networks. Common to many such systems is the regular spacing of drainage patterns. Depending on the particular setting, this preferred length scale has been observed to range from centimeters to hundreds of kilometers. The prediction of this length scale is one of the fundamental problems faced by any theory of landscape erosion. A major objective of our research is to understand how and why erosive dynamics not only selects the observed length scales but also acts to produce such rhythmic structures.

Our approach is to combine theoretical, experimental, and observational studies. The experiments shall consist of laboratory-scale analogs of regularly spaced channels formed by seepage erosion. Using modern laser-aided data-acquisition and digital imaging techniques, we obtain detailed time-dependent two-dimensional topographic data. Our preliminary experiments have already yielded periodic channels. By combining three-dimensional simulations, physical reasoning, and mathematical analysis we expect to obtain a thorough understanding of the phenomena observed in the laboratory. The prediction of the distance between regularly spaced channels will be but one of the products of this analysis.

The laboratory-scale component of this project is performed so that at least one manifestation of channelization may be completely understood. To better understand where our theories and experiments apply in the natural world, we also perform simple observational studies of natural channels found on beaches.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Transport Visualization for Studying Mass Transfer and Solute
Transport in Permeable Media

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Our project, collaborative between Sandia National Laboratories, MIT, and Oregon State University, investigated two fundamental questions in hydrogeology with applications to carbon sequestration, energy production, waste disposal and remediation. (1) Under what conditions is solute spreading best modeled by Fickian dispersion and versus mobile-immobile domain mass transfer? (2) How do chemicals mix so that they react in natural porous media? These questions are intimately connected, as pore-scale mixing, reaction and large-scale spreading profoundly affect one another. We used a combination of transport visualization experiments where we obtained real-time quantitative maps of concentration in 2D and numerical simulation to answer the questions. The following are some of the key results to date. (1) The connectedness of permeability is a critical parameter to solute transport and reaction. The connectedness of geologic media influences parameters for flow and transport models, and also determines the most appropriate form of the transport model itself. (2) Solute transport may be divided into three regimes, each with a different appropriate transport model – macrodispersion, diffusion-controlled mass transfer, and advection-controlled mass transfer. The regime depends on the connectivity, permeabilities, length scales, diffusivity, and hydraulic gradient. Experimental confirmation of these regimes can be seen at http://web.mit.edu/harvey-lab/www/Regimes_Page/movs.html. (3) Mass transfer timescales for use in transport models are strongly correlated to residence time and experimental duration, a fact that is consistent with multiple timescales of mass transfer present in most natural materials. (4) The conventional coupling of chemical reaction equations with the convective-dispersive equation may overpredict chemical reaction. Experimentally observed dispersion inaccurately represents pore-scale mixing because at the pore-scale, reactants may remain separated. (5) When flow velocities are low, reaction can create density fingering that greatly increases mixing and enhances reaction, creating an important feedback that has not been noted before. The phenomenon is similar to mixing from double-diffusive convection but also occurs where conventional models predict a stable interface.

MINERALOGICAL SOCIETY OF AMERICA

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

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Objectives: The project is the support of six short course and the companion *Reviews in Mineralogy and Geochemistry* volumes proposed to and accepted by the Mineralogical Society of America (MSA) and Geochemical Society (GS) to be held in 2001, 2002, and 2003.

Project Description: The support has two purposes: (1) keeping student registration fees affordable; and (2) producing the *Reviews* volumes. Speaker travel costs have become the most significant MSA and GS short course expense. Student fees were kept low indirectly through reimbursing speaker travel (Molecular Modeling, Nanoparticles) or using speaker stipends (Stable Isotopes). A portion of the editorial work for each *Reviews* volume was covered, but the most significant production support was for printing of the *Reviews* volume on nanocrystals. This allowed MSA and GS to publish one additional short course volume in 2001 which they could not otherwise do and move the nanoparticles course up to 2001 from its originally 2003 scheduled time. The course could thus be offered when research into nanocrystals and nanotechnology is just beginning to be a significantly new field of investigation.

Results: There were three short courses during 2001, each with a companion *Reviews* volume:

[1] "Molecular Modeling Theory and Applications in the Geosciences" was held in Roanoke, Virginia on May 18-20, 2001, preceding the 2001 Goldschmidt Conference in Hot Springs, VA. The organizers of the course were Randall T. Cygan of Sandia National Laboratories and James D. Kubicki of Pennsylvania State University. 75 people (17 students, 58 professionals) attended the course with participants from the United States, United Kingdom, Germany, Switzerland, Australia, and Japan.

[2] "Stable Isotope Geochemistry" was held in Boston, Massachusetts on November 3-4, 2001, preceding the 2001 Annual Meeting of the Geological Society of America in Boston, MA. The organizers of the course were John W. Valley of the University of Wisconsin and David R. Cole of the Oak Ridge National Laboratory. 79 people (34 students, 32 professionals, and 13 speakers) attended the course with participants from the United States, Germany, Austria, New Zealand, Denmark, and Venezuela.

[3] "Nanoparticles and the Environment" was held at the University of California, Davis, on December 7-9, 2001 immediately prior to the AGU meeting in San Francisco. The organizers of the course were Jillian F. Banfield of the University of Wisconsin-Madison and Alexandra Navrotsky of the University of California Davis. 92 people (31 students, 53 professionals, and 8 speakers) attended.

The three companion volumes are:

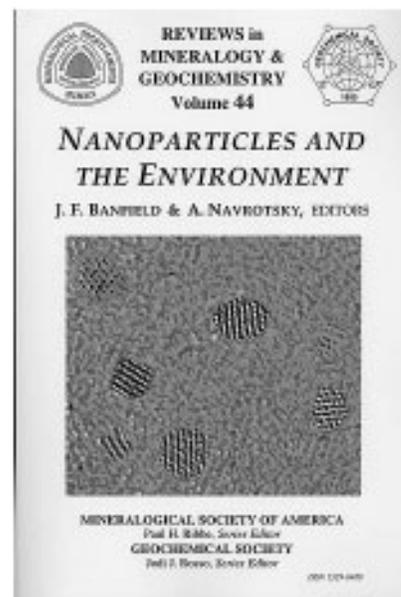
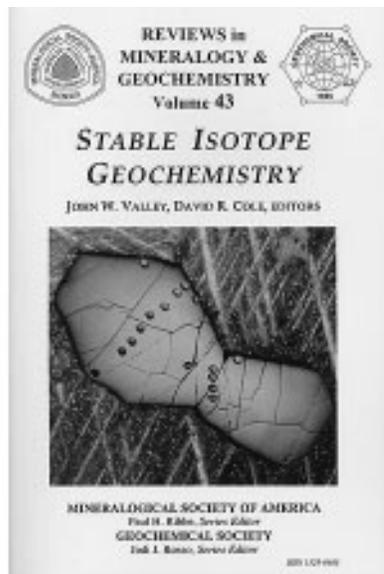
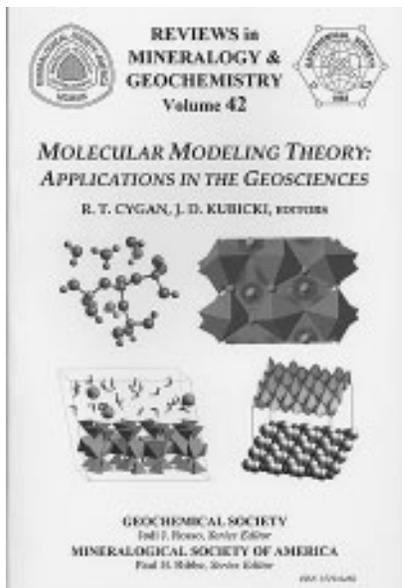
[1] "Molecular Modeling Theory: Applications in the Geosciences", edited by R. T. Cygan and J. D. Kubicki, *Reviews in Mineralogy and Geochemistry* volume 42, 14 chapters complete with references, 531 pages (ISBN 0-939950-54-5) \$32, \$24 for MSA, GSA and CMS members.

[2] "Stable Isotope Geochemistry", edited by J. W. Valley and D. R. Cole, *Reviews in Mineralogy and Geochemistry* volume 43, 13 chapters complete with references, 662 pages (ISBN 0-939950-55-3) \$32, \$24 for MSA, GSA and CMS members .

[3] "Nanoparticles and the Environment", edited by J.F. Banfield and A. Navrotsky, *Reviews in Mineralogy and Geochemistry* volume 43, 8 chapters complete with references, 349 pages (ISBN 0-939950-54-5) \$28, \$21 for MSA, GSA and CMS members

3,723 copies have been distributed thus far of the 3 volumes. Copies were distributed to all short course participants, 860 library subscribers to *American Mineralogist* (who are thought to include all library subscribers to *Geochemica et Cosmochimica Acta*), book reviewers, and by mail and meeting sales. The volumes have been on sale for differing lengths of time. That, and the fact that Volume 44 was unable to be included in the MSA membership renewals, account for the differing sales numbers. The breakdown:

Volume	number of volumes distributed to			mail/meeting sales	total
	short course	reviewers	libraries		
Volume 42	92	25	860	384 (since 5/10/01)	1361
Volume 43	79	35	860	340 (since 11/1/01)	1314
Volume 44	74	23	860	91 (since 12/7/01)	1048
				Total	3723



MINNESOTA, UNIVERSITY OF

Nonlinear Dynamics of Fluid and Contaminant Transport in Fractured Media and Crust from the Micro- to the Macro-scale

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Collaborator: Bryan J. Travis, bjtravis@lanl.gov, (505) 667-1254

We have focussed our efforts on several areas of computational and theoretical geophysics, which are relevant to bridging the physical scales in mesoscopic fluids. First, we have developed algorithms to solve Poisson-like equations over a large grid consisting of 25,000 x 25,000 grid points. Solution of these large-scale Poisson equations has a direct relevance in hydrological flows. Now we are forging ahead to solve Poisson-like equations with a grid of 200,000 x 200,00 points, using our newly developed in-core and out-of-core algorithm. These spectral-like methods can also be extremely useful for looking at surfaces of crystals. Second, we have used the spectral -finite difference method to solve very high Rayleigh number 3-D convection from one million to ten billion in Rayleigh number range, and with a grid configuration of 600 x 600 x 600 grid points. present and to visualize them using wavelet transforms. Wavelets allow us to pick out features not possible to be detected because of the multiple scale nature of the flow. We have also employed wavelets and threshold techniques to unveil coherent plume-like structures in high Rayleigh number convection. This type of localization techniques is also useful for detecting underlying coherent features in porous media. We have also developed fast visualization techniques for unveiling these kinds of mesoscopic structures.

NATIONAL ACADEMY OF SCIENCES

Board on Earth Sciences and Resources and Its Activities

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The Board on Earth Sciences and Resources provides the focal point for National Research Council activities related to the Earth sciences. Through its committees, panels, and working groups, it provides independent advice on a wide range of Earth science issues, including those involving basic and applied research, the environment, natural hazards, resources, data (from acquisition and archiving to dissemination and management) and education. It also provides guidance on U.S. participation in international Earth science programs. The members of the Board represent a breadth and depth of expertise necessary to address the most strategic Earth science issues facing the nation, ranging from identifying the frontiers of basic and applied research and improving use of scientific data to assessing resources, understanding environmental change and human interactions with the Earth, and evaluating breakthrough technologies. Many of the Board's activities are in response to requests from the federal government for information on specific technical or policy issues. Other activities are initiated by the Board to enhance the continued health of the Earth sciences. Through a combination of technical analysis, peer review and round-table discussions, the Board provides accurate and timely input to support wise decision-making in government, academia and industry. The Board, its committees, and staff recognize that one of the great tasks in the years ahead is to take advantage of the increased importance of the Earth sciences in a fast changing world by contributing more strongly than ever to the broad concerns of science and society. With this challenge in mind, the Board initiated in 1999 a continuous and formal planning process. This process is regarded as a complement to and an extension of the existing informal planning process. By making significant progress in these areas, the board will help to build and sustain the Earth sciences and their communities in the 21st century. Core support is requested for the Board's activities so that it can best serve the Office of Basic Energy Sciences, Department of Energy.

NEVADA, UNIVERSITY OF

Growth of Faults, Scaling of Fault Structure, and Hydrologic Implications

Principal Investigator: David A. Benson, dbenson@dri.edu, (702) 673-7496

Nearly all tracer tests conducted in fractured rock exhibit extreme transport behavior: dissolved solute particles travel either very far, very fast (preferential flow) or remain motionless for extended periods of time (retention). In general, traditional transport equations based on a classical Brownian motion model are not successful models of this type of transport, which is known as a continuous time random walk (CTRW).

First, we derive a governing equation for particles that travel very far and very fast in one-dimension (1-D). A fractional-order space derivative was well-suited to model both the accelerated growth rate and the early arrivals at downstream points. The formalism was extended to film flow in unsaturated fractures and within unsaturated soil. The parameterization of the fractional-order governing equation was directly tied to measurable aquifer properties at the well-studied, but previously poorly modeled MADE site. The analytic approach is very simple and accurate, and has been successfully compared to complex numerical experiments. An analytic extension of the fractional Laplacian operator in 2- and 3-D was made to model particles that undergo preferential flow in several directions, reasoning that fractured rock would certainly engender this behavior. The fractional Laplacian can also be related to measurable fracture properties such as fracture density, conductivity, orientation and length distributions.

Second, we derived the equation for particles that may stop for extended periods of time. The equation has a fractional time derivative and is similar to classical mobile/immobile formulations, but the fractional time derivative more accurately predicts the continual loss of mass into the immobile phase. Finally, we derived the governing equation for retention when it is coupled to (i.e., dependent on) the distance that particles move after release. This governing equation of the long-term limits of particle motion has fractional powers of coupled time and space operators and easily computes (in some cases with an analytic solution) the spreading rate of plumes in complex, structured media.

Software that computes the solutions of these equations is located on-line at www.hydro.unr.edu/homepages/benson/current/software.html.

NEW ENGLAND RESEARCH, INC.

Evolution of Fracture Permeability

Principal Investigator: Stephen Brown, sbrown@ner.com, (802) 296-2401

Collaborator: Harlan W Stockman, hwstock@sandia.gov, (702) 363-8522

Pore fluid flow and fluid composition within fractured rocks is a subject of primary importance to fields including hazardous waste isolation and remediation, oil and gas production, geothermal energy extraction, and formation of vein fillings and ore deposits. For these reasons, considerable effort has been directed toward the characterization and modeling of flow in fractures and fracture systems. We are investigating the complex active chemical interaction between pore fluid and fractures that causes the fluid composition and fracture surface topography of these systems 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 which are at a variety of flow rates are introduced to one end of the sample in order to actively alter the topography of the CaSO_4 surface. Using a laser profiler, we are able to quantitatively monitor the changing surface topography over time as it relates to the measured sample permeability and calcium saturation of the pore fluid. These methods allow us to create and analyze many features seen in natural fractures, including high-flow dissolution channels, plateaus, and caverns formed from precipitate. In addition, the laser profile of the sample surface can be used to produce a map of aperture across the sample. Using this information, we have applied numerical modeling via finite difference and lattice Boltzmann methods to calculate pore fluid flow direction and magnitude over the entire sample surface. This research is part of an integrated program using quantitative observations of fractures and veins in drill core as well as quantitative and visual observations of flow and chemical dissolution and precipitation within replicas of rough-walled fractures in order to refine our models and work toward a predictive capability.

NEW MEXICO INSTITUTE OF MINING & TECHNOLOGY

A Systematic Study of Heterogeneity, Instrumentation, and Scale
Using Physical and Numerical Experimentation

Principal Investigator: John Wilson, jwilson@nmt.edu, (505) 835-5308

Collaborator: Vincent Tidwell, vctidwe@sandia.gov, (505) 844-6025

Measurements are made at a variety of scales in aquifers and petroleum reservoirs, and model numerical grids are developed for even larger scales. Upscaling synthesizes these various scales. We explore fundamental understanding of upscaling through systematic physical and numerical experimentation. Our laboratory experiments employ a computer automated gas minipermeameter that collects highly resolved permeability data at a variety of scales on rock blocks and slabs. We've measured more than 250,000 permeability values on six different heterogeneous blocks of rock using six different scales of measurement, with new measurements and upscaling analyses on several of these rocks during FY02. We completed studies on the relationship between rock permeability and digital visual images of three rocks, analogous to images you would obtain with geophysical methods, and how such information might be used in aquifer/reservoir characterization. We found no significant direct correlation between the permeability measurements and any objective measure of corresponding images, despite the obvious resemblance of the permeability maps and the images. Although images can't give permeability itself, they can be used to estimate spatial statistics and to delineate the spatial pattern of permeability, especially to locate boundaries with sharp permeability contrasts. Instrument weighting functions are primary concept in our upscaling approach, which we've measured in the lab and simulated using adjoint equations. We continued simulation studies aimed at interpreting these results, especially by understanding the physical meaning of weighting functions. In collaboration with Fred Molz of Clemson we confirmed that the explanation lies in the fluid flow energy dissipation pattern, and continued studies on how spatial weighting functions depend on heterogeneity and are therefore non-unique. We continued solute transport experiments using X-ray absorption imaging, through which we quantitatively measured porosity and visualized solute transport in an exhaustively characterized slab of cross-stratified sandstone exhibiting nested scales of heterogeneity. Solute pathways were strongly influenced by the spatial permeability/porosity patterns. Macrodispersion scaled linearly with distance when flow was oriented parallel to stratification while complex, non-linear scaling relations were encountered when flows were forced to cross the stratification. Additionally, the calculated dispersion coefficients varied spatially, and with the orientation and mode of injection.

NEW MEXICO, UNIVERSITY OF

Modeling of Mesoscale Phenomena During Sequestration of Carbon Dioxide in Porous Reservoirs

Principal Investigator: Marc Ingber, ingber@me.unm.edu, (505) 277-6289

Collaborators: Lisa Ann Mondy, lamondy@sandia.gov, (505) 844-1755; Alan Graham, graham@lanl.gov, (806) 742-0451

Processes for the sequestration of carbon dioxide in porous reservoirs involve several components of multiphase flows. If hydraulic fracturing is used to develop local "sweet spots" (zones of high permeability), the flow and resulting distribution of the proppant can have a large impact on the subsequent sequestration process. Even without hydraulic fracturing, the creation of precipitates can drastically alter the characteristics of the porous formation itself. Furthermore, emulsions can form and fingering can take place at the supercritical CO₂/brine interface. In order to be of use in designing effective CO₂ sequestration processes, significant enhancements to currently available continuum-level suspension flow models are required. Both experimentation and high performance computing at the mesoscopic level are used to obtain microstructural information that is necessary for the development and refinement of the continuum models.

NEW YORK, CITY UNIVERSITY, CITY COLLEGE OF

Fluid and Particulate Transport in Self-Affine Fractures

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

We completed a study of studied permeability and dispersion in three-dimensional self-affine fractures. Effective medium approximations were able to predict permeability in 3d as well as in 2d, relating it to the fractal dimension and the characteristic correlation length of the surface. We studied local channeling effects in fluid transport, and related them to the dominance of geometric dispersion for tracer motion. For laterally shifted fracture surfaces our analytic estimate did not generalize, but the permeability can still be bounded by the two-dimensional result. In addition, a lateral shift leads to an obvious anisotropy in the shape of a dispersion front, which becomes elliptical with a long axis and higher-amplitude fluctuations normal to the shift, instead of the irregular circular shape seen without shift. The fractal dimension of the front was measured and was found to be equal to the Hurst exponent of the fracture surface and, remarkably, independent of any lateral shift. The front anisotropy and exponent universality are observed consistently in both simulations and experiments.

A doctoral thesis "Computer Simulations of Two-dimensional Granular Flow Past a Circular Obstacle" by Igor Baryshev, was completed. The goal of the research was to investigate whether granular flows exhibited a solid-body wake analogous to the familiar von Karman vortex street in ordinary fluids. Two major components of this work were the development of a numerical algorithm for event-driven simulations which incorporated a thermostat and which allowed insertion and removal of particles at the upstream and downstream ends of the simulation domain without numerical artifacts. For elastic collisions, we found transient swirl patterns behind the obstacle but no vortex street, and attributed contrasting claims in the literature to the presence of large density and temperature gradients. In the inelastic case, the granular system tends to cool rapidly without developing large-scale patterns, although we observe swirling flows similar to the elastic case and "dune" formation ahead of the obstacle, consistent with experiment.

NEW YORK, STATE UNIVERSITY OF STONY BROOK

An Inter-Disciplinary Study of the Surface Reactivity of Pyrite

Principal Investigator: Martin Schoonen,
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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 CO₂ sequestration), and sorbent of radionuclides and other constituents (e.g. gold).

NEW YORK, STATE U. OF ST BROOK

High Precision Dating of Sedimentary Material

Principal Investigator: Gilbert Hanson, gilbert.hanson@sunysb.edu, (631) 632-8210

Our original goal was to obtain radiometric ages for biostratigraphically controlled syn-sedimentary material with uncertainties of three million years or less to precisely date the times of sedimentation. We have shown that it is possible in some circumstances to obtain uncertainties of 1 Ma or less. Our focus has been on areas of rapid sedimentation from marine and terrestrial records where the duration of formation of the syn-sedimentary minerals is smaller than the age uncertainty. We have published high precision U-Pb ages for calcite in paleosols (caliche), in marine limestones and within siliciclastic fluvial facies. We have also been able to date calcite (altered from aragonite) that formed within an evaporite sequence, and as open marine cements. Additionally, a variety of lacustrine (lake) limestones have provided high precision ages. In order to get high precision ages it is necessary to have relatively high U/Pb ratios. In most cases this requires enrichment of the samples in uranium. In order to increase the probability of obtaining samples enriched in U for dating, we have sought to understand how U is fixed in dated minerals from different environments. For example, a caliche sample, dated at 298 +/- 1 Ma is highly enriched in organic material. The presence of organic material suggests that the sample formed under reducing conditions. Other lines of evidence for reducing conditions include pyrite lining fossil roots and bright orange luminescence indicating incorporation of Mn(II) in the calcite. XANES data indicate that U(VI) the oxidized species is dominant. Conversely, a sequence of lacustrine carbonates with ages from 15.28 +/- 0.29 to 16.25 +/- 0.22 Ma are without obvious organic matter but have elevated U abundances (100's of ppm). However, the U consists of the reduced species of U(IV). These samples formed at a lake margin, which presumably was at least suboxic. By working to determine how U is incorporated in precisely dated samples we will be able to make significant contributions to understanding the conditions that might immobilize and enrich U on geologic timescales. These studies are highly relevant to geochronology and to issues of nuclear waste management.

NEW YORK, STATE U. OF ST BROOK

Micromechanical Processes and Macroscopic Behavior in Porous Geomaterials

Principal Investigator: Teng-Fong Wong, teng-fong.wong@stonybrook.edu, (631) 632-8212

Collaborator: Joanne Fredrich, fredrich@sandia.gov, (505) 844-2096

This project focuses on the systematic investigation of the micro-scale characteristics of natural earth materials, and how these micro-scale characteristics control the macroscopic deformation and transport behavior. The research uses an integrated approach consisting of experimental rock mechanics testing, quantitative 2D and 3D microscopy and statistical microgeometric characterization, and theoretical and numerical analyses. The objective is to enhance fundamental understanding of failure and transport processes in geologic materials, and thereby strengthen the theoretical basis for the application of laboratory results to various technological operations of importance. Specifically these topics have been investigated: (1) Water-weakening effect on the strength of porous sandstones. (2) Triaxial compression experiments on three limestones (of initial porosities of 3%-14%) and detailed characterization of the failure envelopes in both the brittle and cataclastic flow regimes, as well as the micromechanics. (3) Damage evolution during the initiation and development of compaction localization.

NEW YORK, STATE U. OF ST BROOK

Pore Scale Geometric and Fluid Distribution Analysis

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High resolution, synchrotron X-ray CT tomography is used to study three dimensional pore space microgeometry in reservoir relevant rock and to study three dimensional fluid distribution within that pore space. Computational software, 3DMA-rock, has been developed to provide the analysis of the three dimensional images. Special capabilities of the software include the ability: 1) to segment grain from pore space; 2) in combination with appropriately doped fluids, to segment water, oil and air phases in the pore space; and 3) to identify pore throats. These capabilities allow identification of individual pores, and investigation of fluid saturation variation at the pore-by-pore level! We have characterized the pore microgeometry of Fontainebleau and Berea sandstones over a range of porosity. We are currently characterizing the oil/water distribution in the pore space of Berea sandstone (water wet) and artificial polyethylene cores (oil-wet) at residual fluid conditions as well as at fixed-fluid-ratio conditions. We are also investigating the effect of emplacement of water- and oil-based gels on the residual fluid distribution. This latter effort is also aimed at isolating the mechanism by which such gels induce disproportionate permeability reduction between oil and water phases.

We are using numerical modeling via lattice-Boltzmann and network flow models to relate the measured microgeometry characterization to core size "bulk" permeability and fluid saturation predictions. Measured fluid distributions based on the image analysis and laboratory based permeability measurements on bulk samples using the same cores that were imaged provide experimental validation for the numerical work. We have just completed a lattice-Boltzmann based computation for single phase flow in fractures to predict absolute permeability changes with mean fracture aperture.

NORTHWESTERN UNIVERSITY

Interactions of Propagating Compaction Fronts and Pore Fluids in Porous Rock

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Collaborator: W A Olsson, waolss@sandia.gov, (505) 844-7344

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 CO₂. 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.

Conditions for the formation of both shear and compaction localization have been addressed by determining whether the material behavior for homogeneous deformation permits a solution alternative to further homogeneous deformation, in particular, one which corresponds to localization in a planar band. This approach has shown that such solutions are indeed possible for material models of the type commonly used to describe weak porous rocks in which compaction bands have been observed. Such models involve inelastic compaction and a “cap” on the yield surface indicating a decrease in the shear stress needed to cause further inelastic deformation with increasing compressive mean stress.

A specific analysis for an elliptic yield cap applied to the standard triaxial test yields results that are consistent with experimental observations of compaction bands on relatively flat portions of the stress vs. strain curve and in a limited range of lateral confining stress. The analysis predicts that there is a particular value of the lateral confining stress at which a transition from compaction localization to shear localization occurs. As the lateral confining stress is decreased from the transition value, the predicted angle between the normal to the shear band and the maximum compression direction increases rapidly from 0° (for a compaction band) to 20 to 30°. This rapid increase provides an explanation for the infrequent observation of very low angle shear bands.

NOTRE DAME, UNIVERSITY OF

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

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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 NaClO₄, 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

OKLAHOMA, UNIVERSITY OF

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

Principal Investigator: R. Douglas Elmore, delmore@ou.edu, (405) 325-3253

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Field and laboratory studies have been conducted to test the hypothesis that remanent magnetization in sedimentary rocks can be used to constrain the timing of diagenetic events. Specifically, chemical remanent magnetizations (CRMs) resulting from the authigenesis of magnetic mineral phases were compared to the Apparent Polar Wander Paths for North America and Europe to constrain the timing of alteration processes. Diagenetic processes investigated include clay diagenesis (e.g. surface catalysis, illitization), kerogen maturation, fluid migration and structural deformation. Remagnetizations in Mesozoic age rocks from Skye, Scotland and from the disturbed belt, Montana are directly associated with clay mineral alteration. Simulation experiments conducted at low temperatures (62 and 98°C) resulted in the authigenesis of fine-grained magnetite on clay mineral surfaces, supporting our field observations. An alternative pathway for magnetite authigenesis in the Mississippian age Deseret Limestone (Utah) may be kerogen maturation, although clay diagenesis may have also been important. In all of these field studies, isotopic analyses indicate that the authigenesis of magnetic phases was probably not related to the migration of orogenic fluids. However, multiple CRMs occur in rocks along major fault zones in Scotland (e.g. Highland Boundary fault, Moine Thrust Zone) that, based on petrographic, isotopic and fluid inclusion analyses, appear to be related to fluid-flow events. The timing of these events has been established based on the Apparent Polar Wander Path. Similarly, it has been possible to verify the utility of this dating method by comparing the paleomagnetic age to the previously known age for sandstone dike emplacements associated with faults in early Proterozoic basement rocks, northwest Scotland.

OREGON STATE UNIVERSITY

Efficient Inversion of Multi-frequency and Multi-source Electromagnetic Data

Principal Investigator: Gary Egbert, egbert@oce.orst.edu, (541) 737-2947

This research project is focused on improving efficiency and practicality of three dimensional inversion of multi-frequency and multi-source electromagnetic (EM) data. The fundamental goal of the proposed work is to develop efficient but robust non-linear inversion schemes that take advantage of aspects of conjugate gradient (CG) approaches, as well as schemes that make use of at least some approximation to the Hessian of the penalty functional. The rationale for the proposed effort derives from the observation that for each search step in a straightforward application of CG, forward modeling is required for each frequency/source pair. These calculations provide multi-dimensional information about data sensitivity that can be used more effectively than in the standard CG approach, where they are used to define only a single additional search direction in the model space. To more readily explore a range of possible strategies, and to allow the algorithms developed to be applied to a wider range of EM geophysical field techniques, we are developing the inversion system in modules, using an object oriented computer programming paradigm. With this approach the inversion methodology can be developed independently of actual details of the specific EM problem, with only the forward modeling scheme and the action of the observation functionals on modeled EM fields changing between problems. At present we are completing development and testing of three-dimensional EM modeling modules. Initial inversion applications will be tested on two very different 3D problems: magnetotellurics (a multiple frequency problem) and cross-hole EM (a multiple source problem). For more rapid testing of algorithmic details and for initial exploration of novel approaches we will also use the 2D MT problem.

OREGON STATE UNIVERSITY

Transport Visualization for Studying Mass Transfer and Solute
Transport in Permeable Media

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Our project, collaborative between Sandia National Laboratories, MIT, and Oregon State University, investigated two fundamental questions in hydrogeology with applications to carbon sequestration, energy production, waste disposal and remediation. (1) Under what conditions is solute spreading best modeled by Fickian dispersion and versus mobile-immobile domain mass transfer? (2) How do chemicals mix so that they react in natural porous media? These questions are intimately connected, as pore-scale mixing, reaction and large-scale spreading profoundly affect one another. We used a combination of transport visualization experiments where we obtained real-time quantitative maps of concentration in 2D and numerical simulation to answer the questions. The following are some of the key results to date. (1) The connectedness of permeability is a critical parameter to solute transport and reaction. The connectedness of geologic media influences parameters for flow and transport models, and also determines the most appropriate form of the transport model itself. (2) Solute transport may be divided into three regimes, each with a different appropriate transport model – macrodispersion, diffusion-controlled mass transfer, and advection-controlled mass transfer. The regime depends on the connectivity, permeabilities, length scales, diffusivity, and hydraulic gradient. Experimental confirmation of these regimes can be seen at http://web.mit.edu/harvey-lab/www/Regimes_Page/movs.html. (3) Mass transfer timescales for use in transport models are strongly correlated to residence time and experimental duration, a fact that is consistent with multiple timescales of mass transfer present in most natural materials. (4) The conventional coupling of chemical reaction equations with the convective-dispersive equation may overpredict chemical reaction. Experimentally observed dispersion inaccurately represents pore-scale mixing because at the pore-scale, reactants may remain separated. (5) When flow velocities are low, reaction can create density fingering that greatly increases mixing and enhances reaction, creating an important feedback that has not been noted before. The phenomenon is similar to mixing from double-diffusive convection but also occurs where conventional models predict a stable interface.

PENNSYLVANIA STATE UNIVERSITY

Critical Chemical-Mechanical Couplings that Define Permeability Modifications in Pressure Rock Fractures

Principal Investigator: Derek Elsworth, elsworth@psu.edu, (814) 863-1643

This work is examining and quantifying the processes controlling rapid changes in the transport characteristics of natural fractures due to precipitation and dissolution mediated by coupled thermal-mechanical-chemical (TMC) effects. Water flow-through experiments are monitored for changes in fluid and mineral mass efflux and concurrently imaged by X-ray CT. These three independent measurements enable changes in fracture porosity to be monitored with the progress of dissolution, and constrain mechanistic models representing permeability change.

Tests have been completed on three rock types; Berea sandstone, Arkansas Novaculite, and Bellefonte Limestone; these specific materials were selected to observe contrasting behaviors of porous media, fractures alone, and carbonate systems, respectively.

Rapid reductions in permeability have been observed, even in silicate rocks under modest temperatures (c. 80°C) and stress levels (c. 3.5 MPa), and occur over durations as short as a month. Permeabilities have reduced by up to two orders-of-magnitude, despite continuous net removal of mineral mass from the samples. Observations are consistent with the stress-mediated dissolution of contacting asperities within the fracture, resulting in closure between opposing fracture walls. At constant stress, successive increases in temperature result in successively smaller reductions in fracture aperture as the fracture approaches a residual closure characteristic of the equilibrium temperature. This incremented closure is driven by the Arrhenius-type dependence of dissolution coefficients on temperature.

Isothermal tests on a fracture in limestone show a similar dependence of permeability on the dissolved mineral efflux from the fracture, in this case strongly moderated by the chemistry of the influent water. Permeability first decreases as asperities are dissolved, and then rapidly increases as dissolution localizes into a single dominant flow pathway.

For the contrasting rock types, changes in aperture are surprisingly large and rapid, even for modest changes in ambient temperatures, flowrates, or aqueous chemistry. This suggests that benign changes in the thermal, stress, or chemical environment may exert profound changes in transport characteristics of fractures.

PENNSYLVANIA STATE UNIVERSITY

Nanoscale Characterization of Corrosion at the Microorganism-glass Interface

Principal Investigator: Susan Brantley, sxb7@psu.edu, (814) 863-1739

Experiments to investigate the characteristics of microbial corrosion of silicate and apatite glass and crystal are underway, for comparison with abiotic dissolution. The effects of polymerization on dissolution of aluminosilicate glass under abiotic conditions has also been investigated to lay the groundwork for understanding controls on dissolution. Corrosion of the surface is being investigated in the presence of four microbes, a nitrogen-fixing bacterium (*Azotobacter vinelandii*), a dissimilatory iron-reducing bacterium (DIRB, *Shewanella putrefaciens*), a cyanobacterium (*Anabaena*), and a methanogen (*Methanobacterium thermoautotrophicum*). For example, we have utilized atomic force microscopy (AFM), X-Ray Photoelectron Spectroscopy (XPS), and Vertical Scanning Interferometry (VSI) to investigate iron-silicate glass surfaces after incubation with the siderophore desferrioxamine mesylate (DFAM) and after incubation with the soil bacterium *Bacillus* sp. We have also observed that *M. thermoautotrophicum* incubated with Ni-containing silicate glass increases the rate of nickel release to solution as compared to abiotic dissolution. The presence of biotic supernatant also enhances release of nickel. The enhanced nickel concentration in the presence of *M. thermoautotrophicum* over the abiotic control indicates that methanogens may have evolved a high affinity mechanism to enhance the release of nickel from nickel-containing minerals. Extraction of Mo from a silicate mineral analogue is similarly accelerated by a high-affinity ligand (a possible “molybdophore”) secreted by a nitrogen-fixing soil bacterium when Mo-limited. In contrast, experiments with *Anabaena*, a cyanobacterium, document that this organism, when grown with no P in the medium, produces excess extracellular polymeric material. The cells can extract P from the mineral apatite to extremely low concentrations. The mechanism of this solubilization may be related to lowered pH as well as the corrosive nature of the polymer. Although many bioessential elements such as Fe, Ni, Mo, and P are found only in low concentrations in rocks, soil solutions, and seawater, microbially enhanced extraction of trace elements from rocks and minerals remains poorly understood.

PRINCETON UNIVERSITY

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

Principal Investigator: Satish C. B. Myneni,
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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. Ni²⁺) 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 RESEARCH FOUNDATION

Mechanical Models of Fault-Related Folding

Principal Investigator: Arvid Johnson, gotesson@purdue.edu, (765) 494-0250

The research goals have been a unified, mechanical infrastructure of fault-related folding and computer programs with graphical users interfaces (GUIs) for structural geologists to model fault-related folds (FaRFs). (a) We have developed fault-dislocation theory to study fault-related folds associated with listric, antilistric and gang faults; (b) boundary-element theory to study growth of folds adjacent to faults that propagate or are stationary; (c) theory of forced folding above a rigid basement and (d) folding theory to describe mechanically décollement-ramp folding in isotropic and anisotropic, layered materials. See www.eas.purdue.edu/physproc. The GUI (a) SeDeRa FaRF produces folds by décollement ramps that are active sequentially; (b) SeGaLi FaRF models sequential or simultaneous activation of three-dimensional dislocation/fault elements and the folds, strains and displacement fields produced by such activity; (c) FoFo FaRF simulates forced folds and tri-shear deformation patterns. See www.eas.purdue.edu/fauxpli. We have completed three field projects. (a) Analysis of band faults in San Rafael Swell monocline. (b) Study of an earthquake rupture in Turkey. (c) Three-dimensional analytical structural geology of the Pitchfork anticline, Bighorn Basin, Wyoming. The form of the Pitchfork anticline was compared to forms produced ideally by mechanical models which suggest that the anticline formed by Kink-wedge and the Forced-fold mechanisms. The Kink-wedge form is characterized by increase of the width and amplitude of the fold upward toward the ground surface. The Forced-Fold form occurs over a rigidly displaced and rotated basement block. The fault trace of the 12 November 1999 earthquake in the Düzce-Bolu, Turkey region crossed the alignment of a 2.4 km viaduct at Kaynaplı. Resurvey of the viaduct piers, which were in effect a giant strain gage, showed that (a) the fault rupture is not a fault line or plane, but a zone (b) the structural damage within the zone was caused not by ground acceleration but by ground distortion. Theoretical analysis helps one understand why a broad zone of deformation rather than only a fault trace forms along a strike-slip fault. The manuscripts for the field research are available at the “physproc” website given above.

PURDUE RESEARCH FOUNDATION

Scaling of Seismic Wave Propagation Across Fractures Subjected to Time-Dependent Processes

Principal Investigator: Laura Pyrak-Nolte, ljpn@physics.purdue.edu, (765) 494-3027

Laboratory investigations were performed to examine the effects of time-varying, multi-scale, structural heterogeneity (specifically from non-welded interfaces, i.e. fractures) on seismic wave propagation through fractured rock, and how multi-scale heterogeneity potentially affects the interpretation of fracture properties from seismic data.

The specific stiffness of a given fracture is often assumed to be uniform. However, if the local stress field is non-uniform, the fracture specific stiffness will vary along the fracture plane. The effect of a non-uniform stress field on seismic wave propagation in fractured media was investigated using wavefront imaging. We have observed experimentally and shown theoretically that a radially symmetric distribution of fracture specific stiffness can cause seismic focusing of the wavefront. A single plane fracture with an axially symmetric stress distribution behaves as a seismic lens that focuses seismic energy to a beam "waist" at a focal plane. Both phase and amplitude effects on a seismic wave propagating across the fracture contribute to the lensing behavior. Radial gradients in the fracture specific stiffness cause wave refraction through a radially varying group time delay, while the fracture transmission amplitude approximates a Fresnel zone plate. This work demonstrates that a two-dimensional planar fracture, contrasted with three-dimensional geologic structures such as basins and domes, can focus seismic waves. Focusing of seismic waves by fractures should be considered in the interpretation of seismic data from fractured strata with heterogeneous stress distributions.

We have also performed experiments on the laboratory scale to image seismic wavefronts of compressional waves that are guided between parallel fractures. Two parallel fractures form a waveguide in an otherwise isotropic homogeneous medium and act as parallel displacement-discontinuity boundary conditions separated by a distance $d = 2$ wavelengths. The compressional wave is a leaky guided mode that sheds energy into the medium beyond the fractures. However, the fractures provide sufficiently strong energy confinement inside the central waveguide for the guided mode to be observed in a sample of length = 15 wavelengths. The existence of this leaky mode depends on the fracture spacing, fracture specific stiffness and the frequency of the signal.

RENSELAER POLYTECHNIC INSTITUTE

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

Principal Investigator: Jonathan Newell, newelj@rpi.edu, (518) 276-6433

Collaborator: Charles R. Carrigan, carrigan1@llnl.gov, (925) 422-3941

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.

RENSSELAER POLYTECHNIC INSTITUTE

Transport Properties of Fluid-Bearing Rocks

Principal Investigator: Bruce Watson, watsoe@rpi.edu, (518) 276-8838

The research supported by this grant addresses "fluid-assisted" chemical transport in the Earth's crust and upper mantle through systematic experimental investigations at appropriate high temperatures and pressures (500-900°C; 1 GPa). During FY 2002, efforts focused on two specific problems: 1) interdiffusion of CO₂ and H₂O in supercritical fluid; and 2) shape and grain-scale distribution of fluid-filled pores in deep-seated rocks as a means of constraining their permeability to fluid flow.

Interdiffusion of CO₂ and H₂O was investigated by quantifying the flux of CO₂ through a capillary connecting two fluid-filled chambers in a specially designed, solid-media, high-pressure cell. The two chambers, each containing the assemblage CaCO₃ + SiO₂ + CaSiO₃ + H₂O, were held at temperatures differing by ~100°C. Because of this T difference, the mole fraction of CO₂ in the fluid is buffered at different values in the two chambers by the solid assemblage. This causes a flux of CO₂ through the capillary that can be quantified by a change in proportion of the solid phases. At 550-700°C, the diffusivities calculated from these experiments fall in the range ~1 to 2x10⁻⁷ m²/s -- only about an order of magnitude lower than the thermal conductivity of crustal rock.

A two-step approach was used to address the pore geometry problem. Numerical experiments were conducted in which hypothetical pore shapes of various modified aspect ratio (MAR) were randomly sectioned in a computer to determine the distribution of apparent shapes in 2D section. These distributions were then compared with those in planar sections through experimentally produced samples having equilibrated microstructures. One experimental sample was serially sectioned to create a 3D digital image. The combined result of these approaches is that fluid is distributed primarily along grain edges in shapes approximating trigonal prisms. No tendency of fluid to localize in pockets at grain boundaries was noted, in contrast to previous speculations by other workers. The significance of our finding is that a single permeability-porosity relation ($k \propto \phi^3$) is likely to govern fluid behavior over the entire porosity range relevant to the Earth.

SOUTHERN CALIFORNIA, UNIVERSITY OF

Three-Dimensional Miscible Porous Media Flows with Viscosity Contrast and Gravity Override

Principal Investigator: Anthony Maxworthy, maxworth@usc.edu, (213) 740-5376

Collaborator: Eckart Meiburg, meiburg@engineering.ucsb.edu, (805) 893-5278

Applying a quantitative flow visualization technique, an experimental investigation of unstable, miscible-fluid displacement under the coupled effects of mobility (viscosity) contrasts and gravitational override has been performed in a Hele-Shaw cell that can be rotated both vertically, to allow filling with a initially plane interface, and horizontally, to vary the effective gravity. By means of image processing, properties such as perimeter and area of the injected fluid have been measured as functions of time at constant injection flow rate. The behavior of the displacement depends primarily on a dimensionless gravity number $G = g(\rho_2 - \rho_1) KHb / (Q\mu_1)$, where g is the acceleration due to gravity (m/s^2), ρ_1 is the density of the injected fluid (kg/m^3), ρ_2 is the density of the displaced fluid (kg/m^3), μ_1 is the viscosity of the injected fluid (kg/sm), K is the permeability (m^2), H is the width of the cell (cm), Q is the flow rate (m^3/s) and b is the thickness of the cell (cm). The experiments lay in the range $G = 0$ to $G = 270.5$ and covered the whole range from viscous fingering, at $G = 0$, through a transition regime to a regime where gravity override was predominant. It has been found that an unstable miscible displacement exhibited different growth rates of the interface between the initiation of the displacement and later time, in that both the interfacial length and the finger area increased piecewise linearly with time. The growth rate was independent of the Peclet number $Pe = Q/(bD)$, i.e., dimensionless flow velocity, where D is the molecular diffusion coefficient of the injected aqueous solute (cm^2/s), while the transition time between the linear regimes increased with the Peclet number. We also found that the recovery finger area and interfacial length, or perimeter, at breakthrough decreased with the gravity number, while the transition time and the area/perimeter slope increased with the gravity number.

STANFORD UNIVERSITY

Coupled Fluid Deformation Effects in Earthquakes and Energy Extraction

Principal Investigator: Paul Segall, segall@stanford.edu, (650) 725-7241

OBJECTIVES – To better understand the effects of coupled deformation and fluid flow in geologic systems with focus on mechanisms of deformation in volcanic and geothermal systems.

PROJECT DESCRIPTION – The focus of current research has been to develop new methods for assessing the causes of deformation in volcanic and geothermal areas. Models of distributed deformation sources are being developed to better determine the location, size, shape and nature of magma bodies. The case study is Long Valley caldera, which has experienced nearly 1 meter of uplift in the last two decades. State of the art geodetic data as well as repeated gravity measurements are available. Our previous results implied that intrusion of silicic magma rather than hydrothermal activity is responsible for the observed deformation.

RESULTS – We designed a model algorithm of distributed centers of dilatation, that inverts for the volume strain in discrete subsurface units. The estimation of the strain is generally non-unique. Solutions are sought that minimize a residual norm weighted by the data covariance and a regularizing functional that requires the source volume to be spatially compact. Compactness is realized by penalizing locations in the model space proportional to their distance from a “target” location. This compactness criterion distinguishes the modeling from the commonly used approach of spatial smoothing which would smear the source out over an unrealistically large volume, possibly implying a magma body too dispersed to be viable over long time periods. We applied the modeling algorithm to vertical and horizontal deformation data from Long Valley caldera between 1985 and 1999. The size of the discrete subsurface volumes is 2x2 km horizontally and 1 km vertically. We found an inflation source with a center depth of about 8 km, and with a vertical extent of about 4 km. The total volume increase over the 14 year time period is 0.06 km³. The estimated source depth is somewhat deeper than in previous models that assume a prolate ellipsoidal source, the total volume change is about 25 % smaller.

STANFORD UNIVERSITY

Inversion of Multicomponent Seismic Data and Rock Physics
Interpretation for Evaluating Lithology, Fracture and Fluid Distribution
in Heterogeneous Anisotropic Reservoirs

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Objectives: Conduct theoretical investigations into the effects of fluids and fractures on anisotropic elastic constants, and consequent constraints on lithology that may be obtained from seismic parameters.

Project Description: In this project, we are developing theoretical models to describe anisotropy in sediments and rocks. Seismic anisotropy, now widely recognized as a common feature of most subsurface formations, may lead to significant distortions in conventional seismic processing, such as errors in velocity analysis, mispositioning of reflectors, and misinterpretation of the amplitude variation with offset (AVO). Seismic anisotropy can arise from aligned fractures, stress-induced anisotropy, depositional textures, and intrinsic rock fabric anisotropy. Furthermore, geophysical characterization of fractured reservoirs via their elastic anisotropy is an extremely important economical problem. In tight formations often the only practical means to extract fluids is by exploiting the drainage provided by fractures. It is also important to understand the similarities and differences between fracture anisotropy and stress-induced anisotropy. Stress-induced anisotropy is specially important for less consolidated sediments. Results from last year: A major portion of our activity this year was focused on studying intrinsic seismic anisotropy resulting from stratification of poured sediments using laboratory measurement of seismic V_p . We also studied the effects of hydrostatic and non-hydrostatic stress on directional dependence of V_p in sands. Velocity anisotropy was observed even under isotropic stress revealing the importance of intrinsic, fabric-related anisotropy in the sand samples. We developed a method to determine textural anisotropy using optical images of the sand and glass bead packs. In this method we use the numerically computed spatial autocorrelation function and its variation with direction to characterize the stratification texture from images of the samples. To determine if there is a relation between V_p and the textural anisotropy, we compare laboratory measured velocity anisotropy and the estimated spatial autocorrelation function. We find that velocity anisotropy can reveal internal packing of sand deposits.

STANFORD UNIVERSITY

Metal Ion Sorption at Oxide Surfaces and Oxide-Water Interfaces: Spectroscopic Studies and Modeling

Principal Investigator: Gordon Brown,
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Sorption reactions of metal ions at mineral-water interfaces have been the subject of intensive study for many years because of their importance in sequestering trace metals in aquatic systems and soils, which impacts the biogeochemical cycles of these metals and the composition of natural waters as well as crystal growth and dissolution processes. Such interfaces are very complex and require a reductionist approach in which carefully controlled model systems of increasing complexity are examined using molecular-scale probes in order to characterize surface sites, reaction products, and the effects of time, ligands, and surface coatings on sorption reactions. Complex natural samples are studied in parallel to provide constraints on sorbent types and the types of precipitates formed. Molecular-level speciation of heavy metals and metalloids in such samples can be determined in favorable cases using an approach similar to that used in the model system studies. In addition, the geochemical processes responsible for metal(loid) sequestration reactions in natural systems can be unraveled based on simplified model system results. The objectives of our project are (1) to characterize sorption reactions by determining composition, molecular-scale structure, and bonding of the surface complexes produced using direct sorption measurements, synchrotron-based x-ray absorption fine structure (XAFS) spectroscopy and x-ray standing wave fluorescence spectroscopy, x-ray photoelectron spectroscopy (XPS), crystal truncation rod (CTR) diffraction, and UV/Vis/IR spectroscopy; (2) to investigate how these reactions are affected by the solid surface, the composition of the aqueous solution, the presence of simple organic ligands containing functional groups common in more complex humic and fulvic substances, the presence of microbial biofilms, and time; and (3) to develop molecular-level and macroscopic models of sorption processes. In FY 2002 we made good progress in each of these areas and have continued our grazing-incidence XAFS, X-ray standing wave (XSW), and CTR diffraction studies of the interaction of heavy metals with mineral surfaces and with biofilm-coated alumina and hematite surfaces. In addition, we have used the results of our model system studies to help determine the speciation of heavy metals in contaminated natural systems, including Pb- and Zn-contaminated soils from the U.S. and France.

STANFORD UNIVERSITY

Porous Reservoir Rocks with Fluids: Seismic and Transport Properties

Principal Investigator: Amos Nur, anur@stanford.edu, (650) 723-9526

Objectives: Earth sciences research is shifting from description of earth systems to process modeling, simulation, and visualization. This shift is challenging because many of the processes involved are nonlinear and coupled. In crustal rocks with fluids we are especially challenged with processes in strongly heterogeneous systems. To understand this complexity a numerically robust simulator of transport properties in realistic pore microstructures is needed.

Project Description: Our pore-scale effort is a computational rock physics framework that includes acoustic, elastic, electrical and NMR property simulators. This framework provides several: (1) prediction of bulk physical rock properties; (2) interrelations among the different rock properties, and (3) simulation of dynamic, coupled, and nonlinear physical processes in complex real pore spaces.

Results from last year: We have implemented a single-phase and a two-phase flow simulator using the Lattice-Boltzmann (LB) algorithm. In the single-phase flow simulator we calculate permeability from thin sections using a robust technique to construct 3D porous media from 2D thin sections. This technique accurately predicted permeability values of some 25 sandstone samples to date. We have also implemented a flow-dependent diagenesis code to model changes in transport properties associated with diagenetic processes in porous rocks.

Our two-phase LB flow simulator was used to accurately replicate two-phase flow phenomena in rocks. Specifically we accurately simulate intermittent flow and nonlinear relation between fluid flux and pressure gradient.

Plans for next year: We will numerically explore two-phase flow phenomena more rigorously, including the effect of wettability, capillary pressure and hysteresis, NMR response, elastic properties, and strength.

STANFORD UNIVERSITY

Structural Heterogeneities and Paleo Fluid Flow in An Analogue Sandstone Reservoir

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The principal objectives of this project are to develop conceptual models and predictive tools for the spatial distribution of permeability in subsurface sandstone aquifers and reservoirs as determined by structural heterogeneities. We are carrying out an integrated research plan to map structural heterogeneities (deformation bands, compactive and dilatant deformation bands, joints, sheared joints, and faults) in the Aztec sandstone, at the Valley of Fire, Nevada, in order to develop understand their effects upon groundwater and hydrocarbon flow in this analog aquifer or reservoir. The specific tasks of the current project are divided into three subprojects. (1) Paleo-hydrologic and geochemical fieldwork have revealed two distinct alteration and fluid flow events, the earlier event being correlated with the emplacement of Cretaceous Sevier thrusts, and the second event largely synchronous with Tertiary strike-slip faulting. The first alteration stage is inferred to result from the expulsion of reducing basinal fluids during thrusting. The second alteration stage is correlated with the migration of meteoric fluids and may be driven by topography. (2) Fault zone permeability upscaling based on field data and fluid flow modeling show that fault rock permeability is 1 to 3 orders of magnitude lower, and breakthrough pressures are 1 to 2 orders of magnitude higher than the median host rock permeability and capillary pressure, respectively. Calculated maximum sealable hydrocarbon column heights, using standard fluid properties, range between 10-69 m of gas, and 17-120 m of oil. Faults formed by shearing of joints in high permeability sandstone systems will act as barriers to flow during production and might be capable of sealing small to moderate hydrocarbon columns on an exploration time-scale. (3) In order to characterize and model compaction bands in sandstone and their fluid flow properties we have collected highly targeted field data and embarked on a program of laboratory experimentation in collaboration with scientists at Sandia National Laboratory, the University of Wisconsin, and the U.S. Geological Survey in Menlo Park, CA. The accumulating evidence supports our interpretation that compaction bands initiate and propagate as brittle “anti-cracks” within a nominally linear elastic medium.

TEMPLE UNIVERSITY

An Inter-Disciplinary Study of the Surface Reactivity of Pyrite

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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 CO₂ sequestration), and sorbent of radionuclides and other constituents (e.g. gold).

TENNESSEE, UNIVERSITY OF

Completion of Kr-81 and Kr-85 Analysis Development for Hydrogeology and Testing its Validity by Assessing Aquifer Recharge Rates

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Objectives: (1) Implement improvements to Kr-81 and Kr-85 RIMS analyses for hydrogeology, (2) validate with standards of known Kr-85 activity, (3) measure Kr-85 in samples from a hydrogeologically simple aquifer, and (4) apply Kr-85 to measure recharge in the outcrop region of a major confined aquifer.

Project Description: The Kr-81 and Kr-85 noble gas radioisotopes, having isotopic abundance and concentration in modern water of $\sim E-12$ and $\sim E-22$ are challenging to measure, but should lead to a better understanding of processes in the environment. Applications of Kr-81 include dating of polar ice and very old ground water, impacting long-term climate and waste-disposal studies, while Kr-85 elucidates pollution transport, recharge, and overall flow of modern groundwater. The analytical process consists of (1) collecting a groundwater sample, (2) degassing it, (3) separating Kr from the recovered gases, (4) isotopic enrichment reducing interfering isotopes by E5, (5) a second isotopic enrichment of E4, and (6) detection of the rare krypton isotope in a resonance ionization time-of-flight mass spectrometer. When fully operational, this technique will permit Kr-81 or Kr-85 measurements from 10 or 2 liter water samples.

Results: During FY2002, work focused on steps 4, 5 and 6, and completed deferred maintenance and repairs on the laser system, vacuum pumps and mass spectrometers. The First Enrichment System (step 4) gas recirculation lines were reconfigured for a miniature turbomolecular pump and reduced dead volume. Together with a redesigned gas-tight ion source, sample size for Kr-85 analyses should decrease by $\sim 4X$. The Second Enrichment System's (step 5) quadrupole filter assembly was replaced, bringing performance back to specifications. A new set of poles were fabricated with dimensions calculated for operation at 450 °C, which should reduce losses and memory effects from implantation into the poles. The main Nd:YAG pump laser and associated dye lasers were brought back to spec. Although the resonance ionization time-of-flight mass spectrometer sensitivity was sufficient for Kr-85 measurements, an extremely small leak (below any leak detector limit) allows atmospheric krypton to swamp the analyte signal. Repairs have been completed, but not yet tested.

TEXAS A&M UNIVERSITY

Fluid-Assisted Compaction and Deformation of Reservoir Lithologies

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The compaction and diagenesis of sandstones that form reservoirs to hydrocarbons depend on mechanical compaction processes, fluid flow at local and regional scales and chemical processes of dissolution, precipitation and diffusional solution transport. While the mechanical processes that govern grain-scale compaction of sedimentary rocks in the absence of reactive fluids are well documented, those that control time-dependent compaction and solution transfer in the presence of fluids are not. Our research has established the critical hydrostatic and triaxial loading conditions required for mechanical cracking of quartz aggregates under diagenetic conditions and rates of creep under sub-critical stress conditions. Our results include effects of grain size, presence of an aqueous fluid, and fluid flow rate. We have developed models that predict fluid chemistry on the basis of stress-induced solution transport and crack damage at grain contacts. Mechanisms of deformation at the experimental conditions have been identified unambiguously by monitoring acoustic emissions and by quantitative study of microstructures at grain contacts.

Our research has led to a significant reassessment of conditions that favor sub-critical cracking and strain-induced dissolution versus those that favor stress-induced solution transfer creep. Microstructural observations of our samples and acoustic emissions monitored during experiments show that fluid-assisted cracking is the predominant mechanism of deformation at effective stresses well below critical conditions ($Pe < 0.35 Pe^*$ where Pe is effective pressure or mean stress and Pe^* is the critical pressure for grain crushing and pore collapse). These results have implications for the range of natural conditions that favor fluid-assisted cracking, particularly as effective stresses required for this process will be even lower in the Earth as characteristic loading times are increased. They also have implications for non-equilibrium silica concentrations of percolating pore fluids, as elevated silica concentrations due to deformation are governed by increased surface areas following brittle failure rather than by stress heterogeneities and local interfacial values of pore fluid pressure.

TEXAS A&M UNIVERSITY

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

Principal Investigator: John Morse, jmorse@ocean.tamu.edu, (979) 845-9630

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. However, little is known regarding the kinetics of calcite dissolution by carbon dioxide, diffusion of carbon dioxide in natural gas, and displacement of natural gas by carbon dioxide 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. Calcite dissolution rates at 1 atm under high $p\text{CO}_2$ have been obtained in various synthetic brines. These solutions represent Ca^{2+} and Mg^{2+} concentrations ranging from seawater to a 3 km subsurface brine. Rates obtained in solutions modeled for 1, 2 and 3 km subsurface brines at 25°C are distinct from that of the simple seawater but remarkably consistent with each other ($n = 2.0 \pm 0.2$, $k = 0.13 \pm 0.04$). The reduced reaction order and increased rate constants of these concentrated brines are believed to be related to their greatly diminished carbonate carrying capacity resulting from their high calcium content. We have conducted experimental and analytical studies to evaluate the feasibility of displacing natural gas with supercritical CO_2 . Rate and composition of the produced gas were measured, enabling determination of mole fraction of produced CO_2 as a function of time. In addition, the core holder was CT scanned to determine core porosity, and CO_2 and methane saturation. Results indicate that some 73%-87% of the gas initially-in-place is recovered at CO_2 breakthrough. Analytical modeling results indicate a low CO_2 dispersion coefficient of 0.01-0.12 cm^2/min . Our results to-date indicate that CO_2 injection into depleted or abandoned gas reservoirs would not only sequester CO_2 but would also re-pressurize the reservoir, resulting in effective displacement of the gas.

TEXAS A&M UNIVERSITY

Time-Lapse Seismic Monitoring and Performance Assessment of CO₂ Sequestration in Hydrocarbon Reservoirs

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The goal this project is to assess the feasibility of time-lapse seismic monitoring of CO₂ sequestration in hydrocarbon reservoirs using coupled fluid flow, geochemical and seismic modeling. 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. We performed flow simulation followed by seismic modeling for both the liquid and supercritical fluid (SCF) phases of CO₂ to compare their influence on seismic data. These results show that the SCF will generally produce a larger change in seismic properties than liquid CO₂ because it has the larger contrast between its density and compressional wave velocity and the corresponding properties of brine. We have also examined the time-lapse amplitude variation with offset for both phases of CO₂, and the results show that this examination of the dependence of reflection amplitude on angle of incidence will also help to distinguish between the different phases of CO₂ in situ. For subsurface characterization, we have developed a hierarchical Bayesian approach to multiscale data integration using Markov Random Fields (MRF). Our method is computationally efficient and well suited to reconstruct fine scale spatial fields from coarser, multi-scale samples (e.g., based on seismic and production data) and sparse fine scale conditioning data (e.g., well data). We have applied our approach to a field example that utilizes seismic amplitudes and well log data to reconstruct 3-D distribution of porosity conditioned to well and seismic data.

TEXAS TECH UNIVERSITY

Continuum and Particle-Level Modeling of Concentrated Suspension Flows

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Processes for the sequestration of carbon dioxide in porous reservoirs involve several components of multiphase flows. If hydraulic fracturing is used to develop local "sweet spots" (zones of high permeability), the flow and resulting distribution of the proppant can have a large impact on the subsequent sequestration process. Even without hydraulic fracturing, the creation of precipitates can drastically alter the characteristics of the porous formation itself. Furthermore, emulsions can form and fingering can take place at the supercritical CO₂/brine interface. In order to be of use in designing effective CO₂ sequestration processes, significant enhancements to currently available continuum-level suspension flow models are required. Both experimentation and high performance computing at the mesoscopic level are used to obtain microstructural information that is necessary for the development and refinement of the continuum models. The continuum models originally developed by Phillips et al. (1992) and Nott and Brady (1994) have been improved and implemented into a general-purpose finite element computer code. Results show good agreement with experimental measurements based on nuclear magnetic resonance (NMR) imaging in idealized three-dimensional flows. Massively parallel computing has allowed particle level simulations, based on the boundary element method (BEM), with up to three thousand particles. Volume averaging of the stress tensor has been added to the codes to allow prediction of average macroscopically observed transport properties from particle scale simulations. This work is complemented by experimental work to provide insights and benchmarks. A study of apparent particle slip in confined geometries has been performed. It was found that there exists markedly non-Newtonian wall effects in concentrated suspensions in which the volume fraction of particles is greater than 0.2. At these higher concentrations, wall effects are much larger and extend further into the suspension than in Newtonian fluids.

TEXAS, UNIVERSITY OF DALLAS

3D Imaging of Top-Truncated Mixed Influence Delta Front Deposits, Cretaceous Wall Creek Member, Frontier Formation, Wyoming

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Sandstones of the Frontier Formation in the Powder River basin have been interpreted as being deposited as offshore bars, storm deposited prodelta sand sheets, and wave-dominated deltas. In the youngest Wall Creek member, seven major sandstones have been mapped. Our focus is primarily on sandstone 6 at two study sites. At Murphy Reservoir, sandstone 6 is a river-influenced delta lobe that grades upward from burrowed, to current rippled sandstones and mudstones into structureless to flat stratified and ripple cross-laminated sandstones interpreted as delta front turbidites. Cliff sections show inclined beds dipping southeast, in the same direction as paleocurrents, suggesting that they are delta front clinoforms. Farther south, at the Raptor Ridge site, shallow channelized units alternate with mud-draped tidally-formed dune-scale cross strata within an overall upward-coarsening unit that exhibits larger-scale, southward dipping clinoforms. This suggests both river and tide influence. The dipping beds are truncated by a regional transgressive surface of erosion, and we therefore interpret the Wall Creek as representing top-truncated lowstand delta deposits.

In the Raptor Ridge area two 2D GPR surveys (100 x 300 m and 160 x 200 m respectively) were acquired at a nominal frequency of 50 MHz. Also two 3D surveys (80 x 30 m and 12 x 12 m) were acquired at 100 MHz and 200 MHz respectively. The 12x12 m, 200MHz survey was collected specifically to image cemented zones at the top of the outcrop. Dip oriented GPR lines image the seaward dipping clinoforms whereas the strike-oriented GPR lines show bi-directional downlap, indicating the overlapping lens-shaped delta front sand body geometries.

At the Raptor Ridge site, 10 cores were drilled to an average depth of about 9 m within the GPR survey areas, and analyzed for porosity and permeability. In addition, we collected about 3.5 km of high resolution digital topography maps and digital photographs of the cliff faces at Raptor Ridge. These data sets will be merged to construct a 3D photorealistic image of the Raptor Ridge strata. This image will be imported into GoCAD so that we will be able to render key surfaces in the outcrop in 3D.

UTAH STATE UNIVERSITY

A Comparative Study of the Feasibility of CO₂ Sequestration in Faulted and Fractured Sandstone Reservoirs in Eolian and Fluvial Deltaic Deposits

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We characterize the sources, flow paths, and chemical evolutions of CO₂ gases and waters in a faulted and fractured CO₂ system using their isotopic and compositional chemistries. Six springs and geysers in both fault zones are very saline, with total dissolved solid values ranging from 13,848 to 21,228 mg/l, and all fall in the sodium-chloride chemical facies. Solute chemistries indicate that simple calcite and halite dissolution alone are not occurring. Hydrogen and oxygen isotopic compositions of the waters indicate a meteoric source. Values of $\delta^{13}\text{C}$ of total dissolved carbon for three locations are 0.0, 0.7 and 1.2‰. The gases emanating from all springs are CO₂ rich (95.66 to 99.41%) with minor amounts of N₂, O₂, and Ar, probably from the springs entraining slight amounts of atmospheric gases as they bubble or erupt. The average $\delta^{13}\text{C}$ value of the CO₂ gases is $-6.60\text{‰} \pm 0.13\text{‰}$. Helium isotopes for two locations have R/Ra values of 0.302 and 0.310, and CO₂/3He values of 1.75×10^{11} and 2.92×10^{11} . These values indicate crustal gas with a small amount of air. Comparison of carbon isotopes of gas, water, and calcite at the surface indicates that the three phases are in isotopic equilibrium. In this sedimentary basin, processes that can generate large amounts of CO₂ gas with carbon isotope values in the range mentioned above are diagenetic clay-carbonate reactions and/or thermal decarbonation of carbonates. Clay-carbonate reactions are probably the most likely source of the CO₂ gas. The thermal burial history of the basin indicates impure carbonates have achieved temperatures sufficient to produce CO₂ by clay-carbonate reactions. Our conceptual flow model depicts gas from depth (~>1 km) traveling upwards along the faults and entering shallower formation waters in the Navajo and Kayenta formations. Detailed mapping of the fault zone shows that the waters and gases discharge to the surface in the damage zones of the faults. At depth, clay-rich faults may be barriers to lateral migration to the gas, prompting discharge to the surface.

UTAH, UNIVERSITY OF

Comparative Study of the Feasibility for CO₂ Sequestration in Faulted/Fractured Sandstone Reservoirs in Eolian and Fluvial-Deltaic Deposits

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Sandstone aquifers are prospective targets for CO₂ sequestration. The presence of faults within an aquifer can impact the movement of injected CO₂. Low permeability faults may prevent access to regions of the aquifer while high permeability faults may lead to localized flow paths that bypass regions of the aquifer. In either case, additional injection wells may be required if the full aquifer volume is to be exploited for CO₂ sequestration. Detailed outcrop mapping, drillcore logging/testing, *in situ* hydraulic testing, and geophysical logging by our Utah State University collaborators provide the foundation for numerical simulations of CO₂ injection and migration in a faulted sandstone compartment using the commercial reservoir simulator ECLIPSE™. The sandstone compartment is 400 feet by 600 feet in plan and 200 feet thick. A single, vertical, fully penetrating injection well is located at one corner and a single, vertical fault is located 75 feet from the well. The simulation results using 500 mD sandstone as the host aquifer show how the evolving distribution of dissolved and free CO₂ is affected by the permeability structure of the fault. Although both free and dissolved gas spread together in the cases with high permeability faults, free gas is retained on the injection side of the low permeability fault. Dissociation of CO₂ leads to acidic conditions where the aquifer pores are not fully filled with free CO₂. Thus, the simulation results show how an acidic front moves through a faulted sandstone compartment. Using empirical evidence to vary the relative permeability and capillary pressure properties assigned to faulted material suggests that it is important to learn more about these properties of faulted rock in a CO₂ sequestration context. Separate, decoupled modeling of the chemical interaction between CO₂ enriched water and the host rock over a 500-year time period suggests that insufficient K-feldspar is available to produce significant change in porosity or permeability in the Navajo Sandstone through feldspar dissolution or precipitation of clay minerals. In other aquifer settings, however, fault zones may form key locales for changes in permeability and porosity that might affect migration of CO₂ away from the injection well.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Investigation of the Physical Basis for Biomineralization

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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.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Microbial Community Acquisition of Nutrients From Mineral Surfaces

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The objective of this research is to enhance our understandings of mineral-microbe interactions at the nanoscale by identifying how biomolecules are involved in solid-phase mineral reduction (e.g. mineral recognition, cellular adhesion, electron transfer) and quantitatively characterize these interactions. This involves using biological force microscopy (BFM) to study intermolecular forces between whole bacterial cells and minerals combined with proteomic techniques to identify the proteins involved; chemical force microscopy (CFM) to study interactions between biomolecules and mineral surfaces; and molecular modeling of interactions between functional groups on biological and mineralogical surfaces. The information gained from such research can be used to engineer biomolecules or microorganisms that selectively bind to a particular mineral or metal. Potential applications include environmental restoration/preservation, homeland security, and nanofabrication. BFM-derived force curves between the bacterium *Shewanella oneidensis* and goethite (FeOOH) collected under anaerobic conditions suggested that two proteins (~83 kDa and ~150 kDa) were targeted to the cell-mineral interface that possessed an affinity towards goethite but not diaspore (AlOOH). Protein expression patterns from two-dimensional gels showed that two proteins of the same molecular mass were expressed exclusively under anaerobic conditions. Taken together, these results suggest that these two proteins are synthesized by *S. oneidensis* under anaerobic conditions to function in iron oxide binding and/or Fe(III) reduction. CFM-derived force curves between the siderophore, azotobactin, and goethite or diaspore demonstrated an increased affinity for Fe over Al. This was also observed in molecular models simulating siderophore interactions with the minerals. These models showed that the association of the ligand with each surface was directed by steric forces within the molecule and coulombic interactions between the siderophore oxygens and the metals at the mineral surface. Backbone and amino acid side chain oxygen atoms coordinated with neighboring iron and aluminum atoms to form chelating ligand pairs. Upon simulated retraction of azotobactin from each surface, Fe-siderophore bonds persisted into higher force regimes than Al-siderophore bonds, and surface metals were removed from both minerals. Extrapolation of the model to more realistic hydrated conditions demonstrated that the presence of water energetically favors and enhances metal extraction, making this a real possibility in a natural system.

WISCONSIN, UNIVERSITY OF

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

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A numerical study was conducted to evaluate two different transient electromagnetic (TEM) acquisition scenarios. The first scenario involves surface TEM and the determination of how well 2-D geological structure can be imaged using 1-D TEM inversion, and the errors associated with such an interpretation. Models were constructed with layers dipping from 9 to 90 degrees for a resistor over a conductor and vice-versa. TEM responses were computed for these models using a 3D finite difference time domain algorithm and were then inverted with two different 1-D inversion schemes. Interpretation of the results show that structures with dips of 9, 14, and 27 degrees can be accurately imaged for a resistor over a conductor, where dips of 9 and 14 degrees can only be recovered for a conductor over a resistor. Although structures dipping at greater than 270 degrees are not correctly imaged for a resistor over a conductor, effects of the dip are localized. However, when dips exceed 14 degrees for a conductor over a resistor, they are imaged as being less than the true dip and the effects are seen far from the interface. This numerical analysis was verified with a data set collected at the Reclaimed Flambeau Mine in northern Wisconsin.

The second scenario evaluated the use of borehole TEM to monitor sub-surface carbon dioxide injection. Current densities, magnetic fields, and magnetic field sensitivities were analyzed for pre- and post-injection simulations. Interpretation of current density plots indicates that current density will be greater in conductive layers. The study also included analysis of magnetic fields for single and cross-well transmitter-receiver configurations located above and inside the injection zone. For the single-well case, a difference exists in pre- and post-injection fields when the transmitter is above the injection zone. Overall, a difference exists in the magnetic fields for all transmitter configurations and locations between the pre-and post-injection simulations indicating that TEM is sensitive to a resistive injection into a conductive layer.

WISCONSIN, UNIVERSITY OF

Deformation and Fracture of Poorly Consolidated Media: Borehole Failure Mechanisms in High-Porosity Sandstones

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During 2002 we concentrated our borehole breakout research on St. Peter sandstone from Wisconsin. It is aeolian, contains 100% quartz grains, and is held together primarily by sutured contacts. Porosity varies between 10 to 20%. Vertical drilling into rectangular prismatic blocks subjected to three principal stresses representative of crustal conditions, may result in compressive failure around the boreholes in the form of long and very narrow tabular breakouts perpendicular to the maximum applied horizontal principal stress (s_H) direction. The shape and width are virtually identical regardless of porosity or stress level. However, a striking difference exists in breakout formation mechanism between the low range (10-15%) and high range (16-20%) porosity. In both rocks breakouts appear to be the result of the emptying of compaction bands, created by the high stress concentration around the borehole along the least horizontal principal stress springline. The difference is that in the high porosity sandstone, grains are intact ahead of the breakout tip, while in the low porosity variety grains are cracked and crushed a long narrow band that appears to be the compaction band itself. This difference in mechanism was found to be related to the extent of grain suturing. In the high porosity rock the matrix is weak owing to narrow grain sutures, thus requiring relatively low stress magnitudes to debond the intact grains within the localized compaction band and make them available for the drilling fluid to flush them off creating the fracture-like breakout. The matrix of the low porosity sandstone is substantially stronger owing to the high degree of suturing between the grains. The resulting increase in strength causes the low porosity sandstone to remain stable at stresses that would cause breakouts to develop in the higher porosity rock. Moreover, since the sutures encompass much of the grain surfaces, they are nearly identical in strength to the grains themselves. Thus, the concentrated high compressive stress acting in the direction of s_H brings about cracking of both grains and grain sutures. Our research may explain why some compaction bands contain primarily intact grains, while other are dominated by crushed grains.

WISCONSIN, UNIVERSITY OF

Pore Scale Simulations of Rock Deformation, Fracture, and Fluid Flow in Three Dimensions

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A modified invasion percolation (MIP) model of two-phase flow in granular media has been implemented at the pore scale using nine parameters: permeability, porosity, mean coordination number, and three length-scale distributions (grain size, nonwetting fluid radius, and wetting fluid radius, each characterized by a mean value and standard deviation). Separate simulations to equilibrium of gradient-stabilized drainage and imbibition are used to quantify the inversion of the saturation-versus-height results (equilibrium height and fringe width) for the relevant granular medium properties (nonwetting fluid radius distribution function in the case drainage and wetting fluid radius distribution in the case of imbibition, although the imbibition case is complicated by the facilitation mechanism). Tortuosity estimates and residual saturation simulations are used to constrain estimates of the mean coordination number, suggesting a typical range of 3.0 to 4.5. Although extremely simplified, the residual-saturation MIP model results for both wetting and nonwetting fluid residual saturations compare well with a range of published literature on air-water and TCE-water systems. The capabilities of the MIP model have been extended to separate studies of gradient-destabilized flow conditions and a coupled percolation/continuum model of drying at the core scale. Computational results are in excellent agreement with experiments of single finger systems. Several other phenomena are observed experimentally that must be incorporated into the current MIP model, including re-imbibition, finger generation, and tandem growth. The re-imbibition mechanism can be incorporated into the MIP model as described by Glass and Yarrington (1996), and thus disconnected regimes can be simulated. The finger generation and tandem growth phenomena require the incorporation of a more accurate representation of the distribution of viscous forces, and represents one of the final stages of the MIP model development. The drying model builds on previous work by Prat (1993) and Prat (2002), providing a more detailed view of the drying process as a function of the granular medium properties and system boundary conditions. In addition, the results of the drying model demonstrate the ability of the MIP model to quantify the interface area during two-phase flow processes.

WISCONSIN, UNIVERSITY OF

Resolving Complex Hydrothermal/Magmatic Events in Caldera Environments: MicroAnalysis of Oxygen Isotope Ratios

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This study focuses on samples of altered volcanic rocks from several contrasting caldera complexes. New techniques allow analysis of oxygen isotope ratio in ultra-small samples; and $\delta^{18}\text{O}$ can now be contoured across single crystals. Mineral zonation patterns provide new insights into processes of water/rock and magma/rock interaction.

At Yellowstone, zircons and quartz have been analyzed from 24 units erupted over the past 2Ma. Zircon preserves the best record of primary magmatic oxygen isotope ratio. Extreme depletions of $\delta^{18}\text{O}$ occur after caldera forming eruptions. In contrast to earlier studies, analysis of zircons reveals periods of extreme disequilibrium in oxygen isotope fractionation that correlate to the periods of isotopic depletion. Diffusion modeling of $\delta^{18}\text{O}$ -zoned zircons provides time constraints ($500\text{y} < t < 5000\text{y}$) that support a new model of wholesale melting (Bindeman and Valley, 2000, 2001). Ion probe dating (U-Pb) of zircons confirm our predictions (Bindeman et al., 2001). At Long Valley, analysis of zircons and quartz from rhyolites characterize the long-lived magma chamber. Values of oxygen isotope ratio are homogeneous in Bishop tuff magmas and suggest longevity ($>100,000\text{ y}$) and convection of magmas, similar to other large volume rhyolite magma chambers (Bindeman and Valley, 2002).

At Timber Mountain/ Oasis Valley caldera complex, analysis of $\delta^{18}\text{O}$ (zircon) suggests that $\delta^{18}\text{O}$ was lowered by melting of altered wall rocks, but unlike Yellowstone, the volumes of low $\delta^{18}\text{O}$ rhyolite are large (to 1000 km^3) and the depletions are less extreme.

Zircons from Trench 14, Yucca Mtn, were analyzed from fault gouge and found to be magmatic, originating from adjacent rhyolites, supporting the hypothesis that crosscutting carbonates at Yucca Mountain are pedogenic in origin (Bindeman and Valley, 2003).

Tests of the Cameca 1270 multicollector ion microprobe show precision of $\delta^{18}\text{O}$ (quartz) better than 0.5 ‰ for sample volumes that are 100 times smaller ($<1\text{ ng}$) than by single collector ion probe and $10^6 - 10^9$ times smaller than possible by laser fluorination/ mass-spectrometry. A new ion probe has been funded and will be dedicated to stable isotope chemistry at the University of Wisconsin.

WOODS HOLE OCEANOGRAPHIC INSTITUTE

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

Principal Investigator: Wenlu Zhu, wzhu@whoi.edu, (508) 289-3355

Collaborator: J. Brian Evans, briefans@mit.edu, (617) 258-0620

The chemical and physical properties of partially molten regions of the crust and mantle are strongly influenced by the amount of melt present, and therefore the rate of magma segregation. Our current understanding is that melt migration in a typical mantle rock resembles fluid flow in a porous medium, and permeability is an intrinsic rock property that controls the flow rate (i.e., Darcy's law). Estimation of permeability in partially molten rocks requires knowledge of the melt phase distribution at the grain-scale. The melt distribution in an isotropic two-phase (solid+melt) system under equilibrium conditions is well defined. In such a system, all of the melt channels are identical and they are either interconnected or isolated depending upon the dihedral angle and the melt fraction. A simple power-law relationship between permeability, grain size and melt fraction, has been derived for such a system. However, several factors, such as non-hydrostatic stress, anisotropic interfacial energy, or the existence of a third phase, will alter this relationship. We developed a 3D network model to calculate permeability as a function of melt fraction for a system with a distribution of dihedral angles. This approach allows us to link the topology of melt phases and the geometry of individual melt channels to the bulk physical properties. The strength of our approach is that we can quantify the effects of grain-scale heterogeneities on melt transport by explicitly incorporating the distribution of melt (including dihedral angle, melt channel connectivity etc.) in the network models. In our model, each channel is treated as a prism with a length of the grain edges. The cross-sectional area of each prism is determined by a given dihedral angle and a melt fraction. By incorporating different dihedral angles into a network model, we are able to model permeability of partially molten rocks, taking the grain-scale heterogeneity of melt distribution into account. Our results show that the permeability of a heterogeneous system can be significantly smaller than the calculated permeability of an isotropic system with the same median dihedral angle.

WOODS HOLE OCEANOGRAPHIC INSTITUTE

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

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

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 are strongly dependent on redox. In the presence of mineral oxidants, stepwise oxidation of C²⁺ hydrocarbons causes rapid decomposition to produce a CH₄- and CO₂-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 CO₂ 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 CO₂. 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 CO₂. 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 INSTITUTE

Organic Geochemistry of Continental Margin and Deep Ocean Sediments

Principal Investigator: Jean Whelan, jwhelan@whoi.edu, (508) 289-2819

The objective of this program is 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. Current research focuses 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 long term goal is to understand the role of migrating gas on petroleum reservoirs. Research in collaboration with scientists at Cornell show that the oil and gas system in a 200 mile north to south transect across the northern Gulf of Mexico has been very dynamic - about 30 volumes of gas have passed through and altered oils to the north of the transect. Woods Hole geochemical data was combined with Cornell fluid flow modeling and 3D visualizations to support previous conclusions based on geochemical data alone that most of these oil reservoirs have recently or are in the process of being charging. Furthermore, the Cornell modeling results show that most earlier oil which entered these reservoirs has been flushed upward and out into the overlying water column. The total volume of upward-moving gas which has been involved in altering the transect oils decreases to the south so that the southernmost Green Canyon area wells show little or no alteration attributable to gas washing. However, significant gas migration is occurring now as shown by the complex communities of organisms which utilize the upward streaming petroleum gas as a primary food source. This gas also produces bubbles in the water column near the seafloor at 600m water depth. This gas streams through small fractures in the seafloor and also forms gas hydrates which look like ice and are formed from methane gas and water at the high pressure and low temperature conditions typical of the seafloor.

WYOMING, UNIVERSITY OF

Multiscale Reactive Transport in Processes Related to CO₂
Sequestration: Nanoscale Dynamics, Upscaling, and Non-Steady State
Kinetics

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Carbon sequestration in deep saline aquifers is one way of limiting carbon emissions from fossil fuel burning. In order to understand some of the consequences of such injection, our experiments were designed to produce a better understanding of the molecular level causes of, and macroscopic consequences of, silicate and oxide mineral dissolution and carbonate mineral growth processes that lead to the long term storage of carbon in a permanent mineral form. Some of our experiments utilize a novel hydrothermal atomic force microscope (HAFM), invented and enhanced as part of the research, that has been patented and that allows us to make molecular-level observations in-situ at the temperature and pressure conditions of the subsurface. Recent accomplishments include: 1) Macroscopic hydrothermal experiments designed to dissolve feldspar and precipitate calcite in some cases and dawsonite in other cases. Although precipitates formed, none were the intended carbonate mineral. Slow, rate-limiting silicate dissolution may obviate the more rapid precipitation of carbonates. Experiments were conducted on dawsonite dissolution because of a lack of kinetic data for this mineral. HAFM experiments on iron oxide dissolution reveal that well-known crystal growth theories do not apply to this mineral. 2) Plug Flow Reactor (PFR) macroscale reactive transport experiments were conducted to scale up from the HAFM experiments. Initial 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. Analysis of reacted solids reveal the precipitation of two distinct carbonate phases with the strontianite structure. The results provide a vehicle for benchmarking our reactive transport simulators. 3) Studies of the precipitation and dissolution of dolomite. The observations suggests a very important role for Mg²⁺ in limiting step edge kinetics, whereas step structure is primarily responsible for the step velocity differences for the end member calcite and magnesite. Dolomite does not grow continuously even at supersaturation [$S = \log(Q/K)$] as large as 3. However, growth does indeed occur for exactly one monolayer! This observation suggests the single layer has distinct structural and/or chemical properties that prevent additional multilayer growth.

YALE UNIVERSITY

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

Principal Investigator: Danny M. Rye, danny.rye@yale.edu, (203) 432-3174

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. We will extend our fluid/rock interaction numerical models that calculate geochemical transport of multicomponent aqueous or mixed volatile fluids, kinetic control of mineral reactions, dynamic changes of heterogeneous porosity and permeability, and thermal evolution. We will couple this to our model of isotope and trace element diffusion in grains.

Results:

Field-based studies of the interaction of fluids and metamorphosed carbonate rocks are providing important new constraints on crustal mass transfer and reaction kinetics. Morphological variations in garnets within the Orange-Milford belt provide a better understanding of the kinetics of mineral nucleation and growth. The preservation of high-pressure, low-temperature mineral assemblages adjacent to marble unit contacts on Tinos in Greece reveal that lithologic contacts are important conduits for retrograde metamorphic fluid flow at intermediate depths in subduction zones. Modeling of kinetically controlled metamorphic devolatilization reactions in siliceous carbonate rocks has elucidated the role kinetics can play in the reaction pathways. The trace element modeling has found a significant influence of kinetic effects even for high-temperature metamorphic to igneous sequences in the Himalayas. Modeling of black shale weathering in the vadose zone examined the feedback between atmospheric oxygen levels and oxidation of organic matter during uplift and erosion. Oxygen and hydrogen isotope exchange between water and orthosilicic acid was modeled using ab initio calculations. A review of fluid flow and chemical reaction in the deep crust has provided an integrated view of fundamental concepts including Darcy's Law, fracture flow, porosity, permeability, reaction kinetics, mass transport mechanisms, and field examples, which elucidates the importance of channelized flow regimes.

YALE UNIVERSITY

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

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During the year 2001-2002 we worked on the following topics:

1. The effect of changes in atmospheric O₂ on the fractionation of carbon isotopes during plant photosynthesis, and how this can be used to deduce ancient O₂ levels, has been studied. This has consisted of experiments at Sheffield University on growing plants under varying O₂/CO₂ ratios. In addition, carbon isotope determinations were made at Yale on fossil plants ranging in age from Devonian to Cretaceous. Combining these results with those from the laboratory experiments, we confirm the previous theoretical predictions of elevated O₂/CO₂ during the Permian and Carboniferous based on theoretical calculations.
2. Critical parameters were measured on the black shale that we are studying in terms of the role of O₂ and erosion in its weathering. This includes, SEM photomicrographs of the organic matter texture, permeability and porosity measurements, BET surface area, and determinations of the concentrations of organic carbon, nitrogen, sulfur and their changes with depth.
3. Burning experiments were initiated to test the role of varying O₂ on the intensity and spread of paleofires. This work was done at the fire labs at Ohio State University by Richard Wildman. He has done thermogravimetric analysis on the ignition of various natural forest fuels (leaves, bark, grass, peat, etc) as a function of O₂ concentration. He also followed, via elevated thermocouples, the spread of fires along a long track consisting of either pine dowels or pine needles as a function of fuel moisture content (0-61%) and O₂ concentration (8% to 35%). The only analogous previous experiments were severely limited by being based only on paper. It has been stated that at O₂ levels higher than 25%, at any past geological time, globally trees could not have survived burning even when wet, but this extrapolation is based only on the ignition of paper strips. Wildman's experiments with natural forest materials indicate that, at typical moisture levels, wood and pine needles will NOT burn at 30-35% O₂ which permits the possible existence of past O₂ levels this high.

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DOE/OBES Geosciences Research: Historical Budget Summary

(Thousands of dollars)

Insert new table 98-02

ON-SITE INSTITUTION	FY 96	FY 97	FY 98	FY 99	FY00
Argonne National Laboratory	600	620	620	740	438
Brookhaven National Laboratory	528	350	425	595	870
Idaho National Laboratory	65	40	40	0	0
Los Alamos National Laboratory	1960	2096	1509	1260	1235
Lawrence Berkeley National Laboratory	2197	2170	2320	2160	2332
Lawrence Livermore National Laboratory	1940	1915	1421	1445	1736
Oak Ridge Inst for Sci and Ed			85	110	155
Oak Ridge National Laboratory	1251	1195	1228	1235	1145
Pacific Northwest Laboratory	684	600	770	760	815
Sandia National Laboratory	1616	1725	1845	1635	1324
total, on-site published	10865	10826	10263	9940	10050
total, off-site published	8815 0	9705 0	11226	12851	10649
total, operating published	19680	20521	21489	22791	20699
total, equipment	1258	1450	1256	1235	1340
Total GEOSCIENCES- published	20938	21971	22745	24026	22039
OFF-SITE INSTITUTION					
AM. Mus. NY (Mathez)	69	85	98	87	
Arizona (Harpalani - Conf)					10
Arizona St. (Buseck)	132	139			

Arizona St. (Hervig/Williams)	59	74	83	70	
Boston Univ. (Klein)	74	77	123	129	116
Brown U (Yund)	152				
Cal Tech. (Stolper)	140	142	146	150	135
Cal Tech. (Wasserburg)	400	400	465	400	325
Calif, Univ. of Berkeley (Helgeson)	185	192	195	197	190
Calif, Univ. of Berkeley (Nishiizumi)		160	164	160	144
Calif, Univ of Berkeley (Sposito)		67	70	73	74
Calif. Univ. of Davis (Casey)	110	108	104	121	108
Calif, Univ of Davis (Navrotsky)		150		169	160
Calif, Univ. of Davis (Rock)	151	134	138		
Calif, Univ. of LA (Harrison)	111	119	123	124	126
Calif, Univ. of LA (McKeegan)	44				
Calif. Univ. of SB (Boles)	20	31	16		70
Calif. Univ of SM (Meiburg)					69
Calif. Univ. of SB (Spera)	75	76	89	92	82
Calif, Univ of Santa Cruz (Wu)			278	267	251
Calif, Univ of San Diego (DeGroot-Hedlin)		49	58		
Carnegie Inst of Wash (Hemley)			37		
Chicago, Univ. of (Richter)		183	141		
Chicago, Univ. of (Sutton/Rivers)	341	418	429	440	475
Chicago, Univ. of (Sutton)	159	131	137	299	
Colo, Univ. of (Ge)	13	86		120	101
Colo, Univ of (Nagy)				99	128
Colo, Univ. of (Rajaram)	79	124		60	54
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Colo, Univ. of (Rundle)	114	120	130	136	122
Colo, Univ. of (Spetzler)	132	152	161	168	

Col. Sch of Mines (Klusman)					159
Col Sch of Mines (Tsvankin)			230	240	216
Columbia Univ. (Broecker)	137	134	154	130	
Conn. Univ. of (Torgersen)	65	68	79	188	
Delaware, Univ. of (Wood)	109	111	124	236	
Desert Res. Inst. (Tyler)	80	148			
Duke Univ (Malin)			44		
Florida, Univ. of (Ladd)			85	70	63
Georgia Tech (Dove)	91	39	86	145	
Hawaii, Univ. of (Martel)	79	84	130		117
Illinois, Univ of (T. Johnson)		138			
Illinois, Univ. of (Kirkpatrick)					395
I.R.I.S. (Simpson)	211				
Indiana, Univ. of (Ortoleva)	102	108	141	124	112
John Hopkins Univ.(Garven)	67	70	77		77
Johns Hopkins Univ.(Sverjenski)	118	105	108	110	100
Johns Hopkins Univ.(Veblen)	156	163	110	110	99
Kent State Univ (Maurice)		33	34	69	
Lehigh Univ. (Ilton)	44	37	115	115	104
Lehigh Univ. (Moses)	123				
Maine Science & Tech (Shehata)		340			
Maryland, Univ. of (Tossell)	28	56	47	48	63
Michigan, Univ. of (Ballentine)	69	71	69		
Michigan, Univ. of (Halliday)	207	226	200		
Minn. Univ of (Yuen)	78	76	91	100	90
MIT (B. Evans)		185	188	198	185
MIT (Harvey)					35

MIT (Rothman)				134	135
MIT (Toksoz)			150	160	144
MIT (Toksoz)					240
NASA (Blankston)	113	95	113		
NAS/NRC (Schiffries/DeSouza)	100	100	100	100	90
Nevada, Univ of (Long)			106	106	96
New England Res (S. Brown)			211	372	
New Mexico Inst. Min. Tech.(Wilson)	30	64		72	65
New Mexico, Univ of (Ingber)			76	80	71
New Mexico, Univ. of (Miller)	100				
NY, City Univ. of CC (Koplik)	98	98	100	99	89
NY, State Univ. of SB (Hanson)	131		155	164	155
NY, State Univ. of SB (Lindquist)	33	35	50	95	
NY, State Univ. of SB (Schoonen)	48	51	54	65	60
NY, State Univ. of SB (Wong)	71	99	100	106	95
Northwestern Univ. (Rudnicki)		88	148	91	89
Notre-Dame, Univ. of (Maurice)					70
Notre Dame Univ (Pyrak-Nolte)	78	81	83		
Ohio St. Univ (Adler)	43				
Okla, Univ. of (Elmore)	158		219	131	127
Okla Sate (Nicholl)				40	36
Oregon St. Univ (Egbert)	41				
Oregon State Univ (Haggerty)					76
Penn St. Univ. (Barnes)	81	87	93		
Penn St. Univ. (Brantley)	117	107	200	142	110
Penn St. Univ. (Brantley) conf.	10				

Penn St. Univ. (Elsworth)					109
Princeton (Myneni)					102
Princeton Univ (Navrotsky)	150				
Purdue Univ. of (Johnson)			130	238	
Purdue Univ. (Pyrak-Nolte)				180	
Rensselaer Polytech. Inst. (Watson)	146		181	179	161
Rice Univ. (Mango)	105	109	111	213	
Rust Geotech, Inc. (Fukui)	87	35			
Rutger Univ (Cheney)		75	75		
Smithsonian Institution (Sorensen)					88
Southern Calif. Univ. of (Aki)	112				
Southern Calif. Univ of (Maxworthy)					85
Stanford Univ. (Brown)		247	259	268	
Stanford Univ. (Harris)	120	125			
Stanford Univ (Mavko)				115	104
Stanford Univ. (Nur)	193	196	211	219	200
Stanford Univ. (Nur)			150	150	135
Stanford Univ (Orr)				136	
Standard Univ. (Pollard)	232	250	195	199	179
Stanford Univ. (Segall)				93	97
Temple Univ. (Strongin)	76	49	52	60	60
Tennessee Univ. of (Thonnard)	82	69			
Texas, Univ of (Banner)			152	152	
Texas, Univ. of (Hardage)	175	175			
Texas, Univ of (Sharp)		61	58	59	
Texas, Univ of Dallas (McMechan/Bhattacharya)	164	124	162	137	124

Texas, A&M Univ. (Kronenberg)			184	350	
Texas A & M Univ (Datta-Gupta)					304
Texas A&M Univ (Morse)					259
Texas Tech Univ (Graham)			100	90	
Utah, Univ. of (Forster)					25
Utah, Univ. of (Tripp)	55	57	60	80	73
Utah St. (Hestir)	160	157	73	84	
Utah St (Evans)			129	147	85
VPI & SU (Bodnar)	100	104	122	118	108
VPI & SU (Dove)					202
VPI & SU (Hochella)				161	159
Washington, Univ. of (Booker)	116				
Washington, Univ of (Booker-conf)			8		
Washington, Univ. of (Unsworth/Booker)		96	97	205	
Washington Univ, St. Louis (Shock)	75	80	106	201	
Wisconsin (Alumbaugh)				52	50
Wisconsin (Alumbaugh - conf)					10
Wisconsin, Univ of (Banfield)	104	139	149	114	103
Wisconsin, Univ of (Haimson)			125	127	115
Wisconsin, Univ. of (Valley)		148	153	147	336
Wisconsin, Univ of (Wang)			50	95	
WHOI (Chave)	55				
WHOI (Eglinton)	135				
WHOI (Seewald)		130	79	134	120
WHOI (Whelan)	195	200	205	377	
WHOI (Zhu)					41

Wyoming, Univ. of (Eggleston)	81	56	56		95
Yale Univ. (Berner)	91	92	177	197	
Yale Univ. (Lasaga/Rye)	290	295	240	247	222
Other	90	244	222	316	505
OFF-SITE TOTALS	8815	9705	11226	12851	10649