

Summary of FY 2003 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 at the DOE National Laboratories. Excellent fundamental science that can improve and support DOE's mission needs will also provide basic knowledge applicable to many other areas of Earth science beyond DOE's borders. The Geosciences Research Program resides within the Division of Chemical Sciences, Geosciences and Biosciences, part of the Office of Basic Energy Sciences of the Office of Science. The participants in this program include researchers at Department of Energy laboratories and academic institutions. These activities are formalized by a contract or grant between the Department of Energy and the organization performing the work, providing funds for salaries, equipment, research materials, and overhead. Collaborative work among these institutions is encouraged. The summaries in this document, prepared by the investigators, describe the scope of the individual projects. The Geosciences Research Program includes research in the two broad areas of geophysics and geochemistry. Particular focus areas of interest include rock physics, flow and transport of geologic fluids through porous and fractured media, analytical geochemistry and experimental and theoretical geochemistry. The research is foundational to progress in the Department of Energy's long-range technological needs. Because of the variety of the research needs in the different applied DOE programs, fundamental approaches with multiple potential applications are favored. Further information on the Geosciences Research Program, including recent program activities and highlights, may be found on the Geosciences Programs home page at: <http://www.sc.doe.gov/production/bes/geo/geohome.html>.

THE GEOSCIENCES RESEARCH PROGRAM IN THE OFFICE OF BASIC ENERGY SCIENCES

The Geosciences Research Program is directed by the Department of Energy's (DOE's) Office of Science (SC) through its Office of Basic Energy Sciences (OBES). The Geosciences Research Program emphasizes research leading to fundamental understanding of Earth's natural processes and properties that will advance the forefront of scientific knowledge, as well as help solve geosciences-related problems in multiple DOE mission areas. Activities in the Geosciences Research Program are directed toward building the long-term fundamental knowledge base necessary to provide for energy technologies of the future. Future energy technologies and their individual roles in satisfying the nation's energy needs cannot be easily predicted. It is clear, however, that these future energy technologies will involve consumption of energy and mineral resources and generation of technological wastes. The Earth is a source for energy and mineral resources, and is also the host for wastes generated by technological enterprise. Viable energy technologies for the future must contribute to a national energy enterprise that is efficient, economical, and environmentally sound.

The Geosciences Research Program is divided into two broad categories, *Geophysics* and *Geochemistry*.

Geophysics: This sub-area focuses on innovative and improved approaches to interrogating the physical properties of Earth's crust through better collection and analysis of rock physics, seismic, and electromagnetic data and improving understanding of geophysical signatures of fluids and fluid-bearing reservoirs.

Geochemistry: This sub-area focuses on innovative and improved ways to interrogate the chemical properties of the Earth's crust through investigations of mineral-fluid interactions and studies of rates and mechanisms of reactions at the atomistic/molecular scale; studying coupled flow and reactivity in porous and fractured rocks; and tracking of mineral-mineral and mineral-fluid processes using isotopes.

The Geosciences Research Program evolves with time and progress in these and related fields. Individual research projects supported by this program at DOE national laboratories, academic institutions, research centers, and other federal agencies typically have components in more than one of the categories or subcategories listed. In addition, it is common for research activities to involve a high level of collaboration between investigators and different institutions. Cross-cutting issues include: improving understanding of basic properties of rocks, minerals, and fluids; determining physical, chemical, and mechanical properties of multi-phase, heterogeneous, anisotropic systems; improving analysis of rock deformation, flow, fracture, and failure, and characterization of fluid transport properties of large-scale geologic structures. Research progress, in addition, will be based on developing advanced analytical instrumentation and computational methods, including: higher-resolution geophysical imaging and inversion tools, angstrom-scale resolution analysis of heterogeneous minerals with x-ray and neutron methods, and advancing computational modeling and algorithm development.

PART I: ON-SITE

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

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The objective of this program is to advance the basic understanding of rock-fluid and soil-fluid interactions through experimental studies on atomic-scale processes at the mineral-fluid interfaces. This is crucial to establishing the relation between atomic-scale processes and macroscopic geochemical transport in natural systems. The principle approach is to observe single-crystal mineral surfaces in situ during chemically controlled reactions with fluids using X-ray scattering, standing wave and absorption techniques with high brilliance synchrotron radiation. Phenomena of interest include mineral-water interface structure (including mineral surface structure and the perturbations of near-surface water structure induced by the mineral), adsorption/desorption of metal ions and organic molecules, dissolution, precipitation and growth. Experiments are performed on common rock- and soil-forming minerals under conditions representative of geochemical environments near Earth's surface. Progress includes determination of the systematic variation of orthoclase dissolution kinetics with temperature and pH through *in-situ* and real-time measurements of dissolution at well-defined cleavage surfaces. Determinations of surface hydration structures of various mineral surfaces (e.g., orthoclase, fluorapatite, calcite) were also made. In particular, the structures of orthoclase (001) and (010)-water interfaces were found to be similar and do not explain differences in apparent activation energies for dissolution observed for these two surfaces. Direct measurements were also performed on cation adsorption sites (e.g., on muscovite). A new approach that directly reveals model-independent element-specified site density profiles with X-ray standing waves was demonstrated for the first time. The site distributions of impurities in muscovite (e.g., Fe, Mn, Ba) were used to illustrate the approach.

Consortium for Advanced Radiation Sources

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This project supports instrumentation for geoscience research conducted at GeoSoilEnviroCARS (Sector 13 at the Advanced Photon Source, Argonne, IL). The techniques being applied are particularly relevant to studies of processes involving geochemically and environmentally important cations and anions in earth materials under a wide range of conditions. A variety of analytical techniques are being brought to bear on geoscience problems including: (1) x-ray absorption fine structure spectroscopy; (2) powder, single crystal and interface diffraction, (3) x-ray fluorescence microprobe analysis; (4)

microtomography; (5) high-pressure crystallography using the diamond anvil cell; and (6) high-pressure crystallography using the large-volume press. The instrumentation is made available to the general scientific community through a proposal based review system. The user program has been in operation since FY1999 with more than 500 beam time proposals received, 350 users conducting experiments and 180 publications. Beam time is currently available for all techniques in experimental stations 13-ID-C, 13-ID-D and 13-BM-D. The 13-ID monochromator was modified for high-energy operation and beamline mirrors were commissioned on 13-ID and 13-BM. Scientific results are described in the accompanying abstract for GeoSoilEnviroCARS.

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Funding is requested to support research on geochemical processes using isotope ratios and trace element concentrations in natural materials. 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. A major focus of the proposed work involves using multi-collector ICP mass spectrometry to investigate natural isotopic variations of Fe, Ca and other elements. This work may provide new perspectives on the role of Fe and Ca in the carbon cycle and in weathering processes. Cr isotopic variations will also be investigated as a way to better understand the mobility and environmental effects of Cr contamination. Ca, Sr and U isotopes will be used to study *in situ* rates of weathering reactions in fluid-rock systems, and evaluated as measures of groundwater velocity and infiltration flux. U-Th-He geochronology will be investigated as a geochronologic tool for the Late Pleistocene and Holocene. Noble gas concentration measurements will be developed for continental paleo-temperature studies, and their use as a global change monitor explored. Modeling studies are aimed at relating isotopic variations to reservoir characteristics, atmospheric moisture transport, and drainage rates in deep soils of arid regions.

The primary research area of concern to the BCIG is the use of isotopic ratio measurements of natural materials to monitor geological processes. The impetus for our studies is the fact that most geological transport processes cannot be modeled accurately starting from first principles in the absence of observations to provide constraints. This limitation stems from heterogeneity on many scales and complex coupling between processes. The tracers provided by natural isotopic variations measure the net effects of these complex processes, and ultimately provide the critical calibration of models that can make the models useful for prediction. Our aim is to advance the state of the art of the isotopic approaches, partly by demonstrating or improving isotopic measurement methodology, and partly by advancing isotopic data analysis strategies.

Reactive Chemical Transport in Structured Porous Media

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Diffusion can exert strong and often unrecognized influences on subsurface solute transport and reactions. Many aspects of reactive chemical transport in diffusion-limited domains remain poorly

understood, despite the fact that the various possible reaction mechanisms are often known. Since the spectrum of microenvironments are coupled and stratified through diffusive mass transfer in interior regions of sediment blocks, soil aggregates, and even within sand grains, these diffusion-limited domains are the simplest systems within which the full range of geochemical transformations can occur. Moreover, when such stratification occurs, systems cannot be understood based on commonly employed bulk measurements that average across important geochemical gradients. This research proposal is directed at improving understanding of reactions within diffusion-limited domains. Two categories of reactions are considered, redox and sorption. For the redox case, the role of aqueous ferrous iron in reducing chromium(VI) will be examined. The hypothesis to be tested is that local Fe concentrations in diffusion-limited regions largely account for Cr(VI) reduction. For the sorption case, intragranular diffusion of uranium(VI) will be examined. The hypothesis for this part of the project is that intragranular diffusion accounts for most of the time-dependence observed in U(VI) sorption. The processes to be investigated require determination of chemical profiles with high spatial resolution. Therefore, key measurements will be obtained with spatially resolved synchrotron x-ray techniques including the x-ray microprobe, micro- x-ray absorption near-edge structure spectroscopy, and chemical microtomography.

Clay Mineral Surface Geochemistry

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The objective of this project is to characterize and elucidate the dual hydrophilic-hydrophobic properties of smectite clay mineral surfaces that figure in the attenuation of pollutant hydrocarbons and the sequestration of organic matter. This objective will be accomplished through state-of-the art computer simulations and spectroscopic experiments on molecular structure in the interlayer region between smectite particles where intercalation of organic compounds takes place. The simulations will involve tested codes, applying density functional theory, Monte Carlo or molecular dynamics techniques, and molecular mechanics methods, while making full use of the NERSC supercomputers. The results of the project will contribute directly to fundamental understanding of clay mineral structure and reactivity; the sequestration of carbon in gas hydrates or natural organic matter; and the fabrication of composite nanoparticles based on clay mineral-organic complexes.

Prediction and Evaluation of Coupled Processes

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The purpose of the research proposed here is to develop a systematic, rational, and mechanistic understanding of the coupled physical and chemical phenomena that would be induced by injection of CO₂ into aquifers. This will be accomplished by means of conceptual, mathematical, and numerical models that are based on rigorous continuum theories of fluid dynamics, coupled with detailed rock fracture mechanics and chemical speciation and reaction path analyses. By developing a mechanistic understanding of the relevant processes, this research will provide a sound basis for evaluating the feasibility of CO₂ disposal in different hydrogeologic environments, including fractured rock systems,

and will provide engineering tools for the design, implementation, and monitoring of CO₂ disposal systems in aquifers.

The analysis demonstrates how a large-scale CO₂ injection operation results in a gradual increase of aquifer pressure, which could reach close to the lithostatic stress after years of injection. Such aquifer pressure increase will induce a number of hydromechanical interactions and geomechanical responses through changes in the effective stress field in both the injection aquifer and the overlying semi-permeable caprock. A general reduction in the vertical effective stress induces vertical expansion of the aquifer, which can be significant and can be monitored on the ground surface. A relatively slow increase of the aquifer pressure during a typical constant rate injection will induce poroelastic stresses in the caprock which prevent catastrophic mechanical rock failure in the form of hydraulic fracturing through a caprock. Instead, the principal rock mechanics effect will be shear-slip along pre-existing faults and fractures occurring in the lower part of the caprock near the injection aquifer. The analysis shows that although shear-slip would be induced in the lower part of the caprock, it is not likely to propagate a rock failure zone through the upper part of the cap if preventive operational actions are taken. Thus, monitoring of seismic events in the lower part of the cap together with monitoring of ground surface movement are essential for controlling the hydromechanical responses during a CO₂ injection operation.

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

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This project's aim is to better describe the molecular chemistry, structure and reactivity at mineral-water interfaces by a combination of experiment and simulation techniques on important geochemical solids. An ultimate goal is to improve the level of molecular modeling to the point where the nature of sorption and surface precipitation are understood on the molecular level, and can be predicted for practically any system by tractable simulation methods.

The work focused on several types of experiments:

- (1) Surface diffraction, specifically "crystal-truncation-rod" or CTR diffraction, has been used to refine the structure of a hydrous interface together with sorbed complexes for the first time. This technique allows both the structure of the complexation arrangement and the surface relaxation to be determined, thus affording complete molecular-level information needed for MD simulations of hydrous interface reactions.
- (2) Grazing-incidence EXAFS, known as GIXAFS, has been used to determine complexation geometries on a range of mineral substrates. This method allows us to follow the very beginnings of complexation at surface coverages in the picomole range, and yields complementary information to the CTR studies (1). This work is presently being done with selenite, selenate and uranyl species on hematite and manganese oxide surfaces.
- (3) Investigation of precipitation processes on the surfaces of clean quartz samples placed in aquifers and withdrawn at six month intervals. Analysis by grazing-incidence x-ray absorption and fluorescence techniques sensitive to picomole quantities of sorbates. Results show development of reactive precipitate coatings within one year, with Ca-rich precipitates displacing Fe-containing precipitates. Initial work in this study was reported in Waychunas (2002). Work continuing in present year.

- (4) Studies of contaminant sorption on Fe oxides. We have been able to show how X-ray absorption near edge (XANES) spectroscopy can be used to determine sorption and precipitate geometry equivalent to EXAFS analysis, yet delivering about 10 fold improvement in sensitivity (Waychunas et al., 2003). This methodology is being applied to several types of surface precipitation processes.

Sum frequency generation (SFG) spectroscopy was used to study the structure of the overlying water on quartz substrates. Results show a dramatic increase in structured water as pH increases above the point of zero charge (PZC), and the existence of two types of water—"ice like" with tetrahedral bonding, and "liquid-like" with two or three hydrogen bonds. Analogous studies on vitreous silica surfaces show less structure, an indication that the crystalline surface "templates" the water structure.

Waychunas, G.A. Grazing Incidence x-ray spectroscopy of Mineral surfaces. Review in Mineralogy and Geochemistry 49, 267-315. (12/2002)

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

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

mechanism with nanoparticle size in the tens of nm regime, possibly from OA to diffusion-controlled growth.

Imaging Shear in Rocks

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The primary objective of the current project is to develop a basic understanding on the seismic properties of fractures and fault that are being subjected to and have been subjected to shear stress in the past. Fractures and faults define important subsurface permeability boundaries which influence the extraction of oil and gas from and the geological sequestration of CO₂ in a reservoir rock. In particular, a sheared fracture can exhibit enhanced permeability, and a fault can be either a fast path (conductive fault) or a seal (impermeable fault). Our research focus has been on (1) the anomalous seismic wave scattering off a sheared fractures and faults (Toomey and Nakagawa, 2003), (2) seismic wave scattering by a heterogeneous fracture and a fault (Nakagawa et al., 2004, in review), and (3) laboratory measurements on fractures and faults at field employed frequencies.

- (1) We have built discrete particle-based fracture models using self-affine surfaces that can be both statically and dynamically (wave propagation) loaded (Toomey and Nakagawa, 2003). A unique aspect of this numerical model is that the changes in the scattering characteristics of seismic waves can be examined as a function of applied stress. Using this tool we have been examining the anomalous shear-induced mode conversion of seismic waves observed in the laboratory. A paper has been prepared, which will be submitted to the Journal of Geophysical Research.
- (2) A plane wave theory has been built, and implemented in an efficient numerical code to simulate three-dimensional scattering of elastic waves off a heterogeneous fractures and faults. Using this theory, we have examined the apparent frequency-dependent compliance of fractures that has been observed in the laboratory. The theory and numerical modeling part of this work has been submitted to the Journal of the Acoustical Society of America. The paper has been accepted, and will be published soon.
- (3) A low-frequency (~1kHz) resonant bar device for rock fracture and fault property determination using a small core samples has been built, and a fracture within a Berea sandstone sample was tested under dry and water saturated conditions for a range of confining stress. Unique aspects of this measurement are that 1) unlike ultrasonic measurements, fracture (fault) properties can be measured without the effect of high-frequency wave scattering due to the heterogeneities, and 2) “intrinsic” attenuation due to the fracture can be measured.

-Nakagawa, S., K.T. Nihei, and L.R. Myer, 2003, Three-dimensional elastic wave scattering by a layer containing vertical periodic fractures, J. Acoust. Soc. Am., 3012-3023.

-Toomey, A.C. and Nakagawa, S., 2003, Seismic monitoring of shear stress on fractures/faults, Expanded Abstract, 73rd Annual Meeting for of Society of Exploration Geophysics, 2263-2266.

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

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The scientific objectives of the proposed research are: (1) to investigate the processes and relative contributions of intrinsic and scattering losses of seismic waves propagating in multiphase conditions, and (2) to explore a new method for using scattered energy to identify and monitor structure and fluid distributions in heterogeneous environments. The technical approach builds upon fundamental understanding of wave propagation in fractured rock. The applied focus is monitoring of the sequestration of CO₂ in geologic formations.

To test the performance of inversion schemes on non-synthetic data, we constructed a scanning stage that allows crosswell viscoacoustic measurements to be performed in the laboratory. The first test was performed in a water tank with three acrylic bars with diameters 0.5, 1.0, and 2.0 inches. We fabricated broadband P-wave sources and receivers from piezofilm cylinders. By driving the source below its first resonance with a pulse, we were able to acquire broadband crosswell data centered at 100 kHz for 16 sources and 31 receivers. The first attempt at full-waveform viscoacoustic inversion for velocity and intrinsic attenuation yielded the following. The velocity image shows a reasonable reconstruction of the three acrylic bars with characteristic artifacts (blue spots) resulting from limited illumination of the targets by the crosswell acquisition geometry. The intrinsic attenuation image recovers the locations of the three acrylic bars with the correct intrinsic attenuation (QI=30), however, with substantial smearing. We have noticed that a much sharper reconstruction of QI was obtained in the inversion of synthetic data, and are investigating possible reasons for this discrepancy.

As a first step towards full-waveform viscoelastic imaging, we have developed a 2D frequency domain staggered grid finite difference code that uses an iterative matrix solver (TFQMR). We have also developed a monofrequency time domain code that provides the magnitude and phase of the wavefield after running the code a prescribed time out to steady state. These codes are being integrated into a conjugate gradient full-waveform inversion scheme for the complex moduli of isotropic and anisotropic heterogeneous media.

Air-Derived Noble Gases in Sediments

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Measurements of noble gas abundances in hydrocarbon fluids, conducted under the previous grant, provide ample evidence that naturally occurring fluids within the Earth's crust contain at least three distinct 'air-derived' noble gas components. These components are: (1) water saturated with air (i.e. groundwater), (2) a heavy (Kr, Xe) noble gas enriched component believed to be associated with the hydrocarbon source rock and (3) a Ne-enriched component. With respect to component #1 (groundwater), identifying the source of components #2 and #3 and understanding the where, when, and how these components are added to the hydrologic system will provide important constraints to basin scale hydrogeology, such as fluid source, flow path, and re-charge temperature.

We propose a laboratory study to (1) identify and isolate the carrier phases of the various air-derived noble gas components in sedimentary rocks and minerals, (2) investigate the process(es) responsible for acquisition and subsequent trapping of the components in their sedimentary carrier phases, and (3) evaluate the mechanisms that release these noble gas components to the ambient hydrologic system under temperatures and pressures encountered in natural basin processes. We will investigate (i) young sediment recovered in DSDP/ODP drill holes, (ii) outcrop samples from the Monterey formation (<20 Myr), and (iii) drill core from the Elk Hills field (California State University, Bakersfield core repository) as well as specific samples of opportunity. Samples will be characterized with respect to compositions and geochemistry and a suite of chemically defined fractions will be used to investigate the fractions holding sorbed noble gas components. We will also investigate a suite of DSDP/ODP samples from various environments that have different initial compositions and have undergone different diagenesis patterns.

Colloid Transport in Unsaturated Fractured Rocks and Porous Media

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Although there is now a general appreciation for the importance of colloid transport in the subsurface, most of the fundamental understanding in this area is limited to the saturated zone, and most of that understanding is largely borrowed from filtration theory. The basic physics and chemistry unique to vadose zone colloid transport is a consequence of the existence of a second immiscible fluid phase, gas. Traditional filtration theory can not be directly applied in the vadose zone colloid transport because of the coexistence of air and water. The concept of particles being strained by becoming trapped within thin water films in unsaturated porous media, "film straining", was recently introduced. A clearer understanding for flow and transport in unsaturated fractures has also recently emerged with the identification of film flow. A quantitative method for measuring colloid partitioning between bulk water and the air-water interface has also recently been presented. These recent developments in combination provide the basis for understanding the physics and chemistry unique to colloid transport in the vadose zone. With this background, it now appears possible to make significant progress towards understanding vadose zone colloid transport in a thorough manner, encompassing both porous media and fractures, and accounting for differences in surface chemistry of different types of colloids. This research proposal is directed at reaching these goals.

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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.

Mineral Dissolution and Precipitation Kinetics

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Plug Flow Reactor (PFR) macroscale reactive transport experiments were begun to scale up from the 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 (Grier et al., 2002). Fluid chemistry pH changes were dominated by the dissolution of calcite in the PFR run, but subsequent post-mortem of the reacted solids show that significant amounts of at least 2 distinct strontianite compositions were precipitated and coated the calcite grains. Although under the investigated conditions aragonite (like calcite) should be unstable, we note that at lower temperatures it has been shown that aragonite-strontianite solid solutions show a significant miscibility gap (Plummer and Busenberg, 1987). Analyses continue on the solids and fluids recovered during this experiment. These results will provide a vehicle for benchmarking our reactive transport simulators.

Reactive Transport of CO₂ Rich Fluids

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The project entails reacting fluids with rock in the laboratory setting. Experiments and simulations are 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.

In-Situ CO₂ Sequestration

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Objectives: The objective of this research is to measure dissolution and precipitation rates important to the mineralization of dissolved carbon at conditions relevant to CO₂ sequestration. Determination of mineral dissolution and precipitation kinetics is fundamental to the successful disposal of greenhouse CO₂-rich gases in aquifers, because reservoir storage capacity is directly related to the conversion rates of CO₂ to carbonate minerals. The reaction of CO₂ and water with unstable silicate minerals to produce more stable silicates (e.g. clays) and solid carbonates is the natural weathering process which is a dominant part of the long-term global geochemical cycling process. Our kinetic research will feed

directly into promising reaction-transport codes that will evaluate aquifer storage of dissolved CO₂ and mineral carbonates, and resulting changes in porosity and permeability.

Project Description: Our approach is to conduct single and multi-mineral dissolution and precipitation experiments and reaction transport experiments in Ca-Al-Si-CO₂ and CaCO₃ systems as a function of pCO₂, pH and temperature. Supercritical CO₂ experiments simulate the reactive front of CO₂ plume and aquifer water and are designed to measure the available source of calcium for storage of CO₂ as carbonates and the source of aluminum and silica for the precipitation of secondary minerals that will effect aquifer porosity and permeability.

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 ⁴⁴Ca/⁴⁰Ca by more than 6‰, and for ⁷Li/⁶Li 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, MgCl₂) 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 MgCl₂ we found no measurable isotopic fractionation of Mg (<0.5‰ for ²⁶Mg/²⁴Mg) 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 ⁷Li/⁶Li 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.

Analysis of Physical Properties for Heterogeneous Rocks Containing Fluids

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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.

Geology, Geophysics & Earth Dynamics - Electrical Properties of Rocks

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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.

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

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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.

Application of Geophysical Tomographic Imaging

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A major environmental concern at many DOE sites is the degree to which the unsaturated or vadose zone acts as a barrier that prevents previously spilled or leaked contaminants from reaching the water table. The principal focus of this project has been to combine subsurface electrical imaging with numerical simulations to aid the understanding of vadose zone transport processes. However, linking field observations to field-scale models of subsurface flow and transport processes remains a significant challenge, particularly in the vadose zone. Previous LLNL Vadose Zone Observatory (VZO) experiments provide a source of Electrical Resistance Tomography (ERT) data obtained during the infiltration of water and brine from the near-surface to an 18-m deep water table. ERT observations suggested, surprisingly, that infiltrated contaminants might rapidly reach the water table within only hours, which is a concern where the vadose zone has been assumed to act as a barrier to contaminants. To better understand this behavior, we have integrated several LLNL 3-D computer models (listed in

parenthesis below) together to investigate the combined complexity of geologic heterogeneity (TSIM), variably saturated flow and transport (NUFT), flow of electrical current due to ERT (ParFlow), and ERT inversion (MultiBH). This integrated simulation approach, involving stochastic models, permits linkage between the ERT observations and 3-D flow and transport process models. While our simulations compare reasonably to some types of monitoring data (e.g. gypsum blocks), they do not exhibit rapid changes in electrical resistivity at the water table as indicated by the ERT observations. The models indicate that strong preferential pathways, such as fracturing or vertically oriented sand lenses, may be required to explain the rapid communication between the infiltration point and the water table. Alternatively, recent bench-scale lab experiments involving resistivity measurements in a partially saturated sand-filled test section performed as part of this project (Parekh, et al., 2004, Rensselaer Polytechnic Institute) suggest the existence of air-water interfacial conduction processes strongly decreasing the formation resistivity in the unsaturated zone during infiltration (Knight, Geophys., 56, p. 2139-2147, 1991) that are independent of resistivity decreases caused by the downward migration of a brine tracer.

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

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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).

Testing Deep Saline Aquifers

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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}Xe, are produced in-situ in aquifers, and accumulate in measurable abundances. If CO₂ 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 ³⁶Cl and ¹²⁹I as indicators of integrated U-Th exposure. Magnitudes of ³⁶Cl/Cl ratios will reflect integrated neutron flux resulting from U-Th decay, and ¹²⁹I/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 ³⁶Cl and ¹²⁹I in a variety of aquifer lithologies. For example, we analyzed a suite of Gulf Coast carbonate brines for ³⁶Cl/Cl that had previously been analyzed for ¹²⁹I/I (Moran et al, 1995). Carbonate aquifers are a low U-Th environment, providing an endmember case. The suite produced ³⁶Cl/Cl = 5.2E-15. Assuming the aquifer Th/U = 2, common for carbonates, the ³⁶Cl/Cl ratio implies [U] = 1.35 and [Th] = 2.70. This U concentration produces a calculated ¹²⁹I/I ratio of 30E-14, using a spontaneous fission half-life of ~7E+15a and a fission yield of 0.04%. This calculated ¹²⁹I/I ratio compares well with the measured values of 27E-14 ± 6E-14, suggesting that the ³⁶Cl/Cl and ¹²⁹I/I ratios accurately reflect aquifer U and Th concentrations. Other lithologies of saline aquifers were also investigated with similar results.

Experimental Investigation into Role of Water

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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.

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Fast 3D Modeling

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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 Elasticity in Rocks

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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. In short, we are testing whether or not geomaterials represent a nonlinear elasticity universality class, and determining the defining characteristics of these materials. Our work entails extracting experimentally-derived scaling relations indicating anomalous nonlinear elastic behavior. 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. The materials we are studying 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. They contain nanoscopic-to-mesoscopic scale elastic features that are responsible for the unique behavior. Recently, we broadened the class significantly to include certain ceramics and metals, all damaged material and rocks, to date. We have carefully analyzed the effects of fluids in the porous members of the class that strongly affect the elastic nonlinear response. We have developed a sophisticated model to describe these behaviors, and, over the past year we have carefully explored the transition behavior from (a) linear elastic, to (b) “classically” nonlinear elastic, to (c) “nonclassically” (hysteretic) elastic. It appears that slow dynamics appears only in tandem with nonclassical behavior. It seems, in fact, that nonclassical behavior could be the integral response induced by classical nonlinearity plus slow dynamics. In addition, we have begun to explore the linear and nonlinear elastic behavior of granular media. Granular media are extremely nonlinear in comparison to rock, but simpler to describe, by application of Hertz-Mindlin theory for instance. Further, we believe that the nonlinear response of granular material plays a significant role in earthquake processes, including earthquake triggering. We are currently exploring this role.

Lab Investigation on the Influence of Low Frequency Stress Waves on Multi-Phase Fluid Flow in Porous Media

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This project is investigating the effects of dynamic stress oscillations on the behavior of fluids and sub-pore-size particles (colloids) in porous media. It is important to understand this phenomenon because low-frequency (1 to 1000 Hz) stress waves have been observed to influence porous fluid-flow behavior in the Earth. Potential applications include enhanced oil production from depleted reservoirs, accelerated contaminant extraction from groundwater aquifers, and controlling colloid transport at waste facilities. The majority of observations to date have been mixed, unpredictable and anecdotal because the physics coupling stress waves to colloid and fluid-flow behavior in porous media is poorly understood. This project focuses on experimental basic research to advance our knowledge in this undeveloped intersection of three scientific fields: elastic-wave propagation, porous fluid-flow dynamics, and colloid electrokinetics. Improved understanding of the stress-stimulated-flow phenomenon will accelerate technology developments for application to numerous practical problems. Experimental approaches are being used to investigate the basic physics of coupled stress-wave and porous-flow phenomena. The major goals are 1) to obtain improved experimental data that will be used to validate and quantify proposed physical mechanisms, and 2) to define the hydrogeological, geophysical, and physicochemical conditions under which stress waves couple efficiently to porous fluid flow and colloidal transport. Experimental laboratory studies are being performed on fluid-flow and colloid behavior under the influence of applied stress oscillations. Two Los Alamos facilities are being used in these studies: The Dynamic Stress Stimulation Laboratory (DSSL) and the Automated Video Microscopic Imaging and Data Acquisition System (AVMIDAS). The DSSL is used to study low-frequency (1-1000 Hz) effects on core-scale fluid-flow and colloid behavior in porous material. AVMIDAS is used to visualize colloid behavior in parallel-plate glass cells and porous micro-models under the influence of high-frequency (10 kHz to 10 MHz) acoustic waves. Data from these two systems are compared to investigate possible scaling mechanisms that can be used to predict similar behavior in the Earth’s crust.

²³⁰Th-²³⁸U Disequilibrium Measurements

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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 3000 m 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 it's greatly improved sensitivity and accuracy relative to previous studies.

Biogeochemical Processes

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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.

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.

Space Plasma Physics

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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.

OAK RIDGE NATIONAL LABORATORY

CONTRACT: OR22725

PERSON IN CHARGE: D. Cole

Nanoscale Complexity at the Oxide/Water Interface

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This multi-institutional effort is focused on achieving a quantitative understanding of the interface between aqueous solutions and metal oxide nanoparticle and macrocrystal surfaces over a wide range of temperatures and solution chemistries. The pH- and temperature-dependent charging of oxide surfaces by reaction with water, and the association of solution counterions with the charged surface, form an interfacial domain termed the electrical double layer (EDL), which results from a complex interplay of electrostatic and van der Waals forces, quantum effects, lattice strain, ion hydration, hydrogen bonding, and specific binding of solute ions with the surface and one another. The experimental studies in this project are intended to quantify every aspect of the EDL for the selected solid phases and aqueous species, including degree of surface protonation and the total concentrations of counterions within the EDL, mineral surface structure, detailed geometrical information on ions and water molecules, and local bonding environments using non-perturbing, in situ measurements wherever possible. Principal investigators at Oak Ridge National Laboratory (D.J. Wesolowski, P. Bénézeth, A.A. Chialvo, B. Gu, W.A. Hamilton, D.A. Palmer), Argonne National Laboratory (P. Fenter), Penn State (J.D. Kubicki, S.N. Lvov), Northwestern (M.J. Bedzyk), Texas Tech (M.K. Ridley), Vanderbilt (P.T. Cummings), Illinois State Water Survey (M.L. Machesky) and their associates, employ a variety of unique approaches to elucidate the sub-angstrom-macroscopic structure and dynamics of the interfacial region, including: (1) surface pH titrations and ion adsorption studies to 300 degrees Centigrade using oxide powder suspensions, coupled with temperature-dependent multisite complexation modeling; (2) electrophoresis measurements of oxide powder suspensions to 250 degrees centigrade; (3) synchrotron x-ray standing wave, absorption and reflection studies on single crystal surfaces into the hydrothermal regime; (4) *ab initio* and molecular mechanics calculations, and large-scale molecular dynamics simulations, integrating the results of all experimental approaches; and (5) developmental studies of the use of neutron scattering and reflection for probing the interfacial structure. This research impacts a broad range of DOE mission areas, including catalysis, nanoscience, waste migration, energy production, and biological processes. The Geoscience Research Program within the Office of Basic Energy Sciences contributed an additional \$200,000 to support this effort.

Fundamental Research in Geochemistry of Geothermal Systems

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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

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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

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The major goal of the research is to determine the mechanisms and rates of isotope exchange between minerals and fluids (gases) over a broad range of 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 pressure and f_{CO_2} in controlling the diffusion mechanism and rate of exchange of carbon and oxygen between calcite and carbon dioxide. The influence of crystal growth on oxygen isotope exchange between magnetite-water and hematite-water has been examined from 0.1 to 100MPa at a temperature of 800°C. We have also investigated the oxygen isotope exchange behavior of systems where chemical reaction and solid-state diffusion are coupled (e.g., cation exchange between alkali feldspars and salt solutions). This latter effort will form the theme of our follow-on effort, which emphasizes new methods to image and/or quantify both the isotopic and chemical behavior during replacement rim formation. The use of neutron and X-ray scattering and NanoSIMS methods will

complement more conventional approaches such as scanning and transmission electron microscopy, and gas source isotope ratio mass spectrometry.

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

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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, sorbtive 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.

Volumetric Properties, Phase Relations & Reaction Kinetics

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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.

Fundamental Research In Isotopic Fractionation of Carbonate Systems Relevant to Subsurface CO₂ Sequestration

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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 time-scales ranging from hours to thousands of years, ensuing from the injection of large volumes of CO₂ into the subsurface.

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

PACIFIC NORTHWEST NATIONAL LABORATORY

CONTRACT: RL01830

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Electron Transfer at the Fe(III) 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.

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.

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

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The growth of ZnS nanoparticles with both water and mercaptoethanol was found to occur predominantly via crystallographically-specific oriented attachment (OA). The growth mechanism determines particle morphology and microstructure. Twins and stacking faults form in the coarsened mercaptoethanol-capped ZnS, whereas more complex, closely spaced twins, stacking faults, and polytypic intergrowths form in coarsened water-ZnS. At long reaction times, diffusion-controlled growth removes surface irregularities arising from OA to yield rounded particles with complex internal structures. The character of the surface ligands affects both phase transformation pathway and temperature of phase transformation. Methanol desorption and rewetting, and water binding cause structural changes, reversible in the case of methanol ligands. Aggregation and disaggregation also cause reversible structural modification. Dispersed nanoparticles in suspension have a more distorted internal structure than aggregated nanoparticles of the same size. Reversible switching between distorted and crystalline structures can be induced by changing the aggregation state at room temperature, implying a low activation energy for the transformation. The results are believed to be the first surface-driven room temperature transitions observed in nanoparticles. The results indicate that nanoparticle structure is not kinetically trapped, but responsive to environmental changes. The growth of goethite nanoparticles was explored with a variety of synthesis methods, including a flash annealing technique to create nanoparticles in the range from 5-80 nm with differing crystallinity, habit and surface properties.

TEM characterization shows aggregation in the more equant particles that is suggestive of initial face-to-edge impingement. This mode of aggregation was further suggested in large scale 10,000 atom MD simulations that showed positive charge buildup at the edges of goethite nanoparticles and negative charge buildup in the centers of the faces. We thus infer a possible mechanism for OA in these nanoparticles that mitigates the problem of particle-particle electrostatic repulsion. Other work has measured the growth of goethite nanoparticles in real time via synchrotron-based wide and small angle x-ray scattering (WAXS and SAXS, respectively). As with ZnS there is evidence for a change of mechanism with nanoparticle size in the tens of nm regime, possibly from OA to diffusion-controlled growth.

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 γ - Al_2O_3 and their Fe(III) analogs. The partial dissociation of these highly coordinated oxygens, coupled with simultaneous activation and displacement of neighboring metal centers, may be a fundamental process by which metals atoms undergo ligand exchanges at mineral surfaces.

A molecular model has been developed for ferrous-ferric electron transfer in a hydrolyzing solution. The model predicts that increasing pH reduces the potential of mean force between the ferrous and ferric ions. The magnitudes of the calculated contributions from the barrier heights and the potential of mean force nearly cancel each other at the canonical transfer distance of 0.55 nm. There is a surprising amount of overlap in electron transfer reorganization energies for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, 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.

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

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In this joint (UCSD, 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 of parallel algorithms will be developed to both improve the performance and generality of algorithms used in AIMD calculations. 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 2003 a kinetic Monte Carlo

model of surface of step reactions in flowing water in relation to step morphologies and velocities during dissolution was developed and observations of the heteroepitaxial growth of a secondary nano-phase of a manganese carbonate was published.

SANDIA NATIONAL LABORATORY/ALBUQUERQUE

CONTRACT: AL85000

PERSON IN CHARGE: J. Merson

Molecular Simulations of Layered Minerals & Their Interactions with Hazardous Material

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An atomic level understanding of mineral-water interactions is important for the evaluation and prediction of numerous properties for clays and other minerals, especially in the treatment of environmental waste. In particular, the behavior of water at the clay-water interface controls many processes including solvation, sorption, precipitation, and growth. Our ability to understand these complex processes 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, composition, and nano-size of clays it is important to apply theoretical molecular models to obtain a fundamental understanding and interpretation of these phenomena. We have developed a general force field Clayff suitable for the simulation of hydrated mineral systems, including kaolinite and montmorillonite. Interatomic potentials for Clayff were derived from parameterizations incorporating structural and spectroscopic data from a variety of simple hydrated compounds. A flexible water model is used to describe the water and hydroxyl behavior.

The structure and dynamics of various saturating amounts of water within an expanded kaolinite were examined using NVT molecular dynamics and the Clayff force field. No constraints on atomic positions were imposed, thereby allowing relaxation of all atoms at the interface. Kaolinite is characterized by layering of gibbsite and siloxane sheets that ultimately provide two distinctive external basal surfaces with relatively hydrophilic and hydrophobic behavior, respectively. Analysis of the equilibrium trajectories indicates contrasting behaviors in coordination number, hydrogen bonding, and orientational order for the water molecules at these two surfaces. Water molecules exhibit ordering up to 8 or 9 Å from either of the surfaces.

Molecular simulations were also performed to determine the structure and behavior of methane and H₂O in the interlayer of various montmorillonite clays. Molecular dynamics using NPT ensembles and large simulation supercells provide atom trajectories for simulation times up to 200 ps. Some order of methane-hydrate structure is preserved within the interlayer and is related to formation of methane clathrate structures with H₂O and the clay surfaces, and the formation of a hydrogen bonded network in the interlayer. The theoretical results support recent experimental observation of a stable methane hydrate intercalate with Na-montmorillonite.

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. Simultaneous measurements of stress, strain, acoustic emission locations, and permeability allow the interaction between fluid flow, pressure and compaction localization to be studied. A major result to date is that compaction localization produces up to a two-order-of-magnitude decrease in permeability. 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. 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. Experiments designed to detect pore pressure evolution and compaction hardening have been completed on saturated, undrained specimens. In addition to the previous suite of measurements, pore pressures were measured at three points along the length of the cylindrical sample. Large, compaction-induced, increases in pore pressure were observed as the effective stress state evolved into a regime where shearing should dominate compaction. However, the AE measurements showed that the dominant deformation mechanism remained compaction localization. A new theoretical model for localized compaction based on spinodal phase decomposition is being developed that includes initial formation of the compaction bands as well as the propagation and interaction of the bands to complete compaction of the specimen. Hertzian grain contact fracturing is a consistent micromechanism that leads to the phenomenology of the theoretical model.

Micromechanical Processes in Porous Geomaterials

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The primary objective is systematic investigation of the microscale characteristics of earth materials, and how these microscale characteristics control the macroscopic behavior. Our approach integrates experimental rock mechanics tests, quantitative microscopy, and theoretical and numerical analyses. The research focuses on the porous earth materials that are central to geoscience applications, including geologic sequestration of greenhouse gases and hydrocarbon exploration and production.

Highlights:

A state of the art laser scanning confocal microscopy laboratory was set up. The facility allows for 3D imaging of porous media and fluid flow processes and direct visualization of two-phase flows, dissolution, and flow in fractures. A miniaturized combined flow/load cell was designed to enable visualization of flow in fractures.

Hydromechanical tests were performed with a transparent epoxy fracture replica. We found that with increasing normal stress, fracture aperture is reduced. The frequency distribution is bimodal and “squeezed” to lower values with increased normal stress. Deformation under normal load is not uniform, but instead depends upon the geometry of the contact areas. With increased shear stress, the average aperture increases as the fracture becomes dilatant with increased surface mismatch. The aperture

distribution shifts to larger values, but maintains its bimodal shape, and is consistent with the mechanical behavior of rock joints observed during laboratory shear tests, where at low normal stresses the area in contact during shearing is a small percentage of the entire surface. Results are reported in Grasselli & Fredrich, "Direct Imaging of flow in fractures," Proc. 2004 Eurock and 53rd Geomechanics Colloquium, 2004.

We considered eight data sets collected during synchrotron microtomography experiments performed at the GSECARS 13-BM beamline at the Advanced Photon Source. Four data sets were collected for synthetic sandstones, and the other four were collected from Castlegate sandstone. The data were analyzed and applied in massively parallel numerical simulations of single phase flow. The numerical calculations are compared to experimental measurements on core samples, and results offer insight into the significance of the micron-scale roughness of the pore-grain interface, the locally heterogeneous nature of pore-scale flow, and representative length scales and volumes necessary to predict bulk macroscopic fluid flow behavior.

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 and dissolution experiments in fractures were performed at New England Research (NER). Sandia provides numerical modeling of the experiments, via the lattice Boltzmann (LB) method, and measurements of dissolution rates for modeling.

Experiments at NER used flat walls of high-density (low porosity) dental plaster; these flat walls were 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 flat-wall experiments produced high (uneroded) areas directly opposite asperities in the textured surfaces, and high areas and long "stringers" in the lees of obstacles. The specific dissolution patterns in the experiments were reproducible. Results were presented as "Evolution of fracture geometry," presented at "Dynamics of Fluids in Fractured Rocks" Symposium at Berkeley (LBL) CA, Feb 11-14, 2004.

The 3D LB models reproduced the experimental patterns of dissolution, including the development of the long stringers in the lees of obstacles. The new capabilities of the code were benchmarked, and a robust precipitation model added. The 3D models have a broad application, and have also been applied to the formation of clots in arteries and the growth of artificial bone. The latter results are published in the Journal of Biomechanics [2004, in press].

Three Dimensional 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.

Two-Phase Immiscible Fluid Flow

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The objective of this research is to develop quantitative understanding of the critical processes controlling two-phase flow and transport in rock fractures, with potential applications in radioactive waste isolation, CO₂ sequestration and petroleum engineering. Our previous research identified the importance of phase structure in controlling system behavior. We have developed experimental systems to create and measure a wide range of phase structures, and flow and transport through them. Current efforts focus on models of phase structure, parametric relationships for flow, transport and inter-phase transfer, and behavior in fracture-matrix networks.

Our previous experimental studies have demonstrated two important classes of phase structures in variable aperture fractures: satiated structures, wherein the invading phase fully entraps the defending phase, and fingered structures resulting from gravity destabilization. Both classes are accurately modeled using modified invasion percolation (MIP) algorithms that account for the influence of gravity, in-plane curvature and simultaneous invasion-reinvasion of two phases.

The MIP algorithm with simultaneous invasion-reinvasion of two fluids was shown to reproduce the dynamics of gravity-driven wetting fingers in variable-aperture fractures. Fragmentation behind the fingertip, pulsating flow and the stop-and-go dynamic of fingers were simulated, closely following experimental observations. Average finger widths are within 20% of experimental measurements. (Water Resources Research 39 (13) doi:10.1029/2002WR001542, 2003)

Parametric studies of the influence of fracture properties on satiated phase structure, and associated flow

and transport properties are ongoing. The areal saturation (S_f) of the flowing phase at saturation is shown to depend on the ratio of two dimensionless parameters related to the fracture properties (C/δ , where the curvature number C , representing the mean influence of in-plane curvature, is the ratio of the mean aperture to the correlation length, and δ is the coefficient of variation of the aperture field). As C/δ goes to zero, behavior is as in standard invasion percolation within a correlated field, and $S_f \sim 0.37$. As C/δ increases above ~ 0.1 , S_f increases, approaching 1 for large $C/\delta \sim 10$. (Physical Review E 68, 061110, 2003)

We have also investigated infiltration in meso-scale laboratory fracture-matrix networks, demonstrating the occurrence of dynamic preferential pathways. (Water Resources Research, 38(12), 1281, doi:10.1029/2001WR001002, 2002).

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. The goal of this research is to enhance fundamental understanding of upscaling processes through systematic physical and numerical experimentation. To challenge our understanding, laboratory experiments involving the collection of over 200,000 permeability values (with a gas mini-permeameter) from six different heterogeneous blocks of rock using six different scales of measurement were conducted.

Over the last year numerical experiments have been performed to explore the coupled effects of media heterogeneity/anisotropy and non-uniform flow (i.e., instrument characteristics) on permeability upscaling. Tests are designed to mimic the laboratory upscaling experiments; that is, the numerical experiments simulate flow from a mini-permeameter through media with heterogeneous characteristics similar to that of the sampled rocks. Simulations assume fully three-dimensional steady state, single-phase flow under isothermal, Darcian flow conditions. A stripped-down finite difference flow code developed at New Mexico Tech is being used. These simulations are performed on three-dimensional, single- and multi-scale Gaussian random fields with statistical properties taken from the sampled rocks. These heterogeneous permeability fields are being generated with the GSLIB family of geostatistical tools.

To date, efforts have largely focused on developing and verifying the computational framework to be used for the simulations. Numerous simulations have been performed to refine the resolution of the computational grid and the size of the sample domain, while striking a balance between model accuracy and computational burden. We have achieved numerical results within 0.3% of the analytical solution (mass flow and pressure) on grids of approximately 7M nodes. Using this grid, numerical experiments reproducing upscaling data acquired from various sandstone rock samples are being conducted.

These experiments will help develop confidence in the modeling by comparing the results of the numerical upscaling studies with that physically measured. Once confidence is gained we will turn our

attention to other instruments like linear core tests and radial flow pump/slug tests. Effort to code and test these other flow geometries is currently underway.

Transport Visualization for Studying Mass Transfer and Solute Transport in Permeable 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].

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

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This project is collaborative with M. Ingber of the University of New Mexico and A. Graham of Los Alamos National Laboratory.

The purpose of this program is to combine experiments, computations, and theory to make fundamental advances in our ability to predict transport phenomena in concentrated, multiphase, disperse systems, particularly when flowing through geologic media.

Processes for the sequestration of carbon dioxide in porous reservoirs involve several components of multiphase flows. If hydraulic fracturing is used to develop zones of high permeability, the flow and resulting distribution of the proppant can have a large impact on the subsequent sequestration process. Furthermore, the creation of precipitates can drastically alter the characteristics of the porous formation itself. Also, emulsions can form and fingering can take place at the supercritical CO₂/brine interface.

New tools were developed to study meso-, and macro-scale interactions in multiphase flows. The suspension continuum models originally developed by Phillips et al. and Nott and Brady were extended to account for normal stress contributions in general three-dimensional flows. These suspension constitutive models were implemented in sophisticated Navier-Stokes finite element code, GOMA. GOMA features abilities to model multispecies transport and flow through saturated and partially saturated porous media (Int. J. Multiphase Flow 28, 137-166 [2002]). A new free-surface tracking model was also implemented into GOMA. This has been used to predict the behavior of bubbles of fluid rising through another fluid. Other tests of GOMA continued, including modeling of flow instabilities, gravity and temperature effects and non-Newtonian fluid effects (important in modeling hydrofracturing fluids used to increase the capacity of CO₂ sequestration zones). Experimental measurements based on nuclear magnetic resonance (NMR) imaging were taken to validate the suspension models (Int. J. Numerical Methods in Fluids 39, 465-483 [2002]). A new NMR method was developed to allow imaging of three component systems (JMR 161, 198-203 [2003]). Experiments, as well as boundary element method calculations, were also used to improve our understanding of the boundary effects the case of precipitates flowing through narrow channels as occur in geologic porous media.

PART II: OFF-SITE

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Grant: DE-FG02-02ER15361

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 are writing up measurements of the association of the ions in the following salts: sulfuric acid, hydrochloric acid, sodium sulfate, sodium hydrogen sulfate, lithium sulfate, and potassium sulfate. Methods for predicting second, cross, virial, coefficients for interactions involving water have been published. 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. We have shown that our new method can predict hydration free energies of ions at high temperatures with good accuracy and used the method to predict sodium and chloride ions at many high temperature state points. 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.

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Grant: DE-FG03-94ER14414

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.

We studied the reaction products of an experiment that held coal, clay minerals, and water for 6 months at 300°C, 100 MPa. The coal released a large amount of isotopically light B to the water during thermal alteration. This leaves the B remaining in the coal product (graphite) relatively heavy (-3‰). In turn the coexisting clay mineral incorporated the isotopically light B from the water. The reacted coal had a very large influence on the boron isotopic chemistry of the water, and suggests that simple organic matter maturation could account for the observed ¹⁰B enrichment with depth in formation waters of the Gulf Coast Sedimentary Basin.

Our most recent microscale isotopic ratio measurements on organic matter (coal, kerogen) by SIMS have demonstrated that: 1) Organic matter (kerogen and coal) is very heterogeneous in isotopic composition ($\delta^{11}\text{B}$ from -1 to -70‰). This heterogeneity may be important to interpreting processes of mass transfer (i.e. hydrocarbon generation) and may be overlooked by bulk isotope ratio analyses. 2) The range of N, S and B isotope ratio measurements in our hydrothermal experiments and in the naturally heated coal is comparable to the ranges we observe in coals that were diagenetically altered (vitrinite reflectance values of 0.3 to 1.4%). 3) The N, S and B compounds in coal all show a gradual change in isotope ratio with increasing thermal maturity. There does not appear to be a specific temperature at which each element shows a dramatic change in content or isotope composition. 4) The range of isotope variations for B (~70‰) is 3 times greater than the range of N and S (~20‰) and is therefore a very useful indicator of thermally altered organic matter, and tracer of the generated hydrocarbons.

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

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Critical energy facilities face a variety of hazards and risks from tectonic instabilities in the complex earth system, including primarily earthquakes, but also including volcanic eruptions and landslides. Understanding these hazards and forecasting these risks has been the motivating rationale for our work under this project. We have pioneered a large array of modeling and numerical simulation techniques to develop a deep understanding of the basic physical processes associated with strong space-time simulations during the last three years. Our work has been a joint effort of model development, theoretical understanding and testing with observed data. We have now successfully formulated and tested a class of forecast algorithms that are 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. Of the last 8 earthquakes larger than magnitude 5.0 that have occurred in southern-central California since the forecast period began, 7 fell within 1 standard deviation (± 11 km) of a forecasted location. We are also developing new applications of topologically realistic earthquake fault system models of the space-time dynamics for use in forecasting. Data to which we apply our methods include GPS and Synthetic Aperture Radar Interferometry data, which give us new information about crustal deformation. In our work we have also determined that 1) statistical field theory techniques based on supersymmetric considerations indicate that the evolution of earthquake seismicity can be described by a linear theory over short times, since the nonlinear clusters in the patterns have very small amplitude; 2) there are at least 4 distinct classes of earthquakes, each with a distinct set of scaling exponents; 3) the non-equilibrium driven, mean-field earthquake fault system in southern California has many characteristics of equilibrium systems; and 4) new models with threshold weakening can be shown to generate aftershocks and foreshocks. The scaling properties of the Gutenberg-Richter relation are strongly affected by the time scale of the threshold weakening, indicating the appearance of a new scaling field.

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Grant: DE-FG02-85ER13445

Infrared Spectroscopy and Stable Isotope Geochemistry of Hydrous Silicate Glasses

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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.

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 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 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 published 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 145: 391-405.*

Part 3: We prepared large rhyolitic samples with homogeneous water contents and diffusion couples, before working with more difficult basalts. We are preparing samples containing varying water contents but the same, homogeneous hydrogen isotopic compositions.

We are preparing a related paper that was presented at last fall's AGU meeting (*KA Kelley, T Plank, S Newman, E Stolper, TL Grove, S Parman, and E Hauri (2003) Mantle melting as a function of water content in arcs, Eos. Trans. AGU, 84(46), Fall Meet. Suppl., Abstract V41D-06.*

Part 4: Our bi-daily analyses since 1998 continue. Looking at seasonal trends compared with clean-air data for the same latitude, we have found that the local contribution to the CO₂ in the atmosphere, unlike the total CO₂ analyzed, has a seasonal cycle, being larger and lighter during the summer and autumn than during the winter and spring. Diurnal variations give different information than do daily measurements at the same time of day.

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

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Three major projects were carried forward: 1) A study of Ca isotopes in calcite grown from solution. The shift in Ca isotopes ($\Delta(^{44}\text{Ca}/^{40}\text{Ca})$) in calcite crystals relative to that of the parent solutions were determined by TIMS. Alkalinity, pH and concentrations of CO_3^{2-} , HCO_3^- , and CO_2 in solution were determined. Solutions with different Ca concentrations were used. In all cases, the condition $[\text{Ca}] \gg [\text{CO}_3^{2-}]$, obtained. A wide range in $\Delta(^{44}\text{Ca}/^{40}\text{Ca})$ was found for the crystals, extending from 0 to -1.5 per mil. The results show that $\Delta(^{44}\text{Ca}/^{40}\text{Ca})$ is a linear function of the saturation index (Ω). “Rate-controlled calcium isotope fractionation in synthetic calcite” D. Lemarchand, G. J. Wasserburg, D. A. Papanastassiou (2004) GCA, in press. 2) A study of the sources of Sr in ground water in a carbonate aquifer. Major element concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured in groundwaters and bedrock from the Madison aquifer in western South Dakota in order to investigate controls on the downgradient evolution of dissolved Sr in a carbonate groundwater system. It was confirmed that the major element chemistry of groundwaters evolves according to dolomite dissolution, anhydrite dissolution, calcite precipitation, and ion-exchange with clay minerals. “Anhydrite and the Sr isotope evolution of ground water in a carbonate aquifer.” A. D. Jacobson and G. J. Wasserburg, (2004) Chemical Geology, submitted. 3) A theoretical investigation of the evolution of metals in galaxies was carried out. A proposed model appears to explain the observations on damped Lyman-alpha systems with red shifts from $z = 0.5$ to 4.5 . The model considers the onset and cessation of infall from the intergalactic medium and appears to explain the abundances found in halo stars while providing a plausible mechanism for making globular clusters. “Chemical evolution of galaxies and enrichment of the intergalactic medium” Y.-Z. Qian and G. J. Wasserburg (2004) Astrophysical Journal, in press.

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Grant: DE-FG03-01ER15163

Precipitation at the Microbe-Mineral Interface

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Microbial biomineralization can dramatically modify the distribution of metals in the environment. Our goal is to investigate how microbial activity affects the nature and distribution of nanoparticulate metal sulfide biomineralization products. The first stage of research focuses on how thermodynamics control the rate of microbial sulfate reduction, and the consequences for the characteristics of nanoparticulate products. Using *Desulfovibrio desulfuricans* as an example, we found that the energy available from sulfate reduction exerts significant control on the respiration rate. As a result of thermodynamic control, significant amounts of sulfate remain at the end of experiment, where sulfate reduction ceases. Although the residual amount of sulfate, or threshold sulfate concentration, varies with initial lactate and sulfate concentrations, the free energy from lactate oxidation and sulfate reduction remains same, about -85 kJ mol^{-1} lactate, at the end of experiments. We are currently extending our experiments to the complete pathways of acetate oxidation and sulfate reduction by *Desulfobacter postgatei*. We are setting up anaerobic flow-through sand columns to use thermodynamic control to study how microbial metabolism affects the form of metal sulfide nanoparticles and their aggregates, as well as their transport through porous media. We will compare how transport of biogenic and inorganic-synthesized nanoparticles differ. The results of this work will improve understanding of the ways in which microorganisms influence the physical and chemical nature of their surroundings.

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

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

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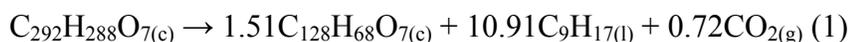
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Diffusion/Dispersion Transport of Chemically Reacting Species

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It has been demonstrated (see Program Summary Book, 2002) that incongruent melting at 150°C and 830 bars of an immature type-II reactant kerogen represented by $C_{292}H_{288}O_{7(c)}$ to produce a mature (oxidized) kerogen corresponding to $C_{128}H_{68}O_{7(c)}$, crude oil with an average composition of $C_9H_{17(l)}$, and CO_2 gas can be described by writing



in which oxygen and hydrogen are conserved. Consideration of the stoichiometries of incongruent melting reactions analogous to Reaction (1) for reactant kerogens with different atomic hydrogen to carbon ratios ((H/C)s) and/or (O/C)s permits calculation of the volume of oil (mole of reactant organic carbon (ROC))⁻¹ that can be generated in, as well as the minimum volume of oil (mol ROC)⁻¹ that must be expelled from hydrocarbon source rocks as a function of the H/C and O/C of the reactant kerogen. It can be deduced from Reaction (1) that nearly 11 moles of crude oil are produced from one mole of the reactant kerogen, which increases to 39.5 moles with increasing C and H/C in the reactant kerogen to $C_{415}H_{698}O_{22(c)}$. The secondary porosities created in source rocks by Reaction (1) and others like it are of the order of 75-80 volume percent of the oil generated, which requires expulsion of the remainder. This minimal volume of expelled crude oil is comparable to, or exceeds the oil produced and in proven reserves in major oil fields such as the North Sea, the Paris and Los Angeles Basins, and those in Kuwait, Saudi Arabia, and elsewhere in the Middle East. For example, taking account of the average weight percent organic carbon in the immature kerogen (~1.68) with an average H/C of ~ 1.16 in the Early Cretaceous source rocks in Kuwait, which have an average aggregate thickness of ~210 meters, it can be shown that all of the oil produced and in proven reserves in Kuwait (121×10^9 bbls or 6.8×10^6 bbls km⁻²) can be accounted for by minimal expulsion from the source rocks of oil generated at 150°C and 830 bars solely by the incongruent melting process.

UNIVERSITY OF CALIFORNIA, DAVIS

NEAT ORU

4440 Chemistry Annex

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Grant: DE-FG02-97ER14749

Thermodynamics of Minerals Stable Near the Earth's Surface

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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 – alunite 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.

UNIVERSITY OF CALIFORNIA, DAVIS

Department of Chemistry, Department of Geology
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Tailored Crystal Growth and Impurity Control Using Nanocluster Adsorbates

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The morphologies and growth rates 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 preparation, corrosion, single-crystal production, and mineralization in geochemical and biological environments. We are studying this problem both theoretically, through quantum calculations and dynamic simulations, and experimentally, by conducting atomic-force microscopy (AFM) experiments on KDP (potassium dihydrogen phosphate) crystals in the presence of adsorbate complexes of differing properties that affect growth.

From the calculations, we acquire estimates of the step energies and terrace morphologies on the growing KDP surfaces, as well as the detachment energies of purported growth units. We find, for example, that growth morphology of the {100} hillock on KDP qualitatively correlates with the detachment energy of KH_2PO_4 monomers. The rate of growth of the {001}-facing step could be limited because of the increased lability of growth units that do not contain hydrogen bonds to the step edge.

Experimentally, we also find that the hydrogen-bonding structure of the adsorbates, including nanometer-sized cluster adsorbates, determines whether it will pin growth steps. Pinning means that the adsorbate stops motion of elementary steps, causing step bunching and the formation of supersteps that can consist of hundreds of elementary steps. In the experiments, we employ a series of Co(III)-amminophosphate, Co(III)-amminopyrophosphate, Rh(III)-aquophosphate and Rh(III)-acetate complexes that vary in size up to a nanometer. We find that the step pinning depends only on whether the step-pinning molecule is able to both accept and donate hydrogen bonds in order to pin elementary steps, which matches well with our interpretation of the calculated detachment energies. Large clusters and adsorbates which can donate, but not accept, hydrogen bonds in the bond-chain directions do not affect growth rates.

UNIVERSITY OF CALIFORNIA, DAVIS

Department of Physics and Geology, and Center for Computational Science and Engineering
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Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes Using Numerical Simulations of Complex Nonlinear Earth Systems

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Critical energy facilities face a variety of hazards and risks from tectonic instabilities in the complex earth system, including primarily earthquakes, but also including volcanic eruptions and landslides. Understanding these hazards and forecasting these risks has been the motivating rationale for our work under this project. We have pioneered a large array of modeling and numerical simulation techniques to develop a deep understanding of the basic physical processes associated with strong space-time correlations during the last three years. Our work has been a joint effort of model development, theoretical understanding, and testing with observed data. We have now successfully formulated and tested a class of forecast algorithms that are 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. Of the last 8 earthquakes larger than magnitude 5.0 that have occurred in southern-central California since the forecast period began, 7 fell within 1 standard deviation (± 11 km) of a forecasted location. We are also developing new applications of topologically realistic earthquake fault system models of the space time dynamics for use in forecasting. Data to which we apply our methods include GPS and Synthetic Aperture Radar Interferometry data, which are other new types of crustal deformation data. In our work, we also have determined that 1) statistical field theory techniques based on supersymmetric considerations indicate that the evolution of earthquake seismicity patterns can be described with a linear theory over short times, since the nonlinear clusters in the patterns have very small amplitude; 2) there are at least 4 distinct classes of earthquakes, each with a distinct set of scaling exponents; 3) the non-equilibrium, driven, meanfield earthquake fault system in southern California has many characteristics of equilibrium systems; and 4) new models with threshold weakening can be shown to generate aftershocks and foreshocks. The scaling properties of the Gutenberg-Richter relation are strongly affected by the time scale of the threshold weakening, indicating the appearance of a new scaling field.

UNIVERSITY OF CALIFORNIA, DAVIS

Department of Geology

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Grant: DE-FG02-01ER15145

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

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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, and disordered metal carbonates. Electrochemical determinations of Gibbs energies of formation for Brady protodolomite, Westrich high magnesian calcites, the hematite-to-dolomite conversion, the La, Lu, Y, Tb, Nd and Pr(III) carbonates, and magnesite, hydromagnesite and artinite have been completed.

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 M_2O_3 metal oxides 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.

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. The method does not involve adjustable parameters. We are presently extending our lattice-energy calculations to metal carbonates with the aragonite structure, which constitutes a much 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 to determine the charge on the metal ion. We plan to publish the experimental and theoretical results together in each case.

UNIVERSITY OF CALIFORNIA, LOS ANGELES

Department of Earth and Space Sciences
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Grant: DE-FG02-89ER14049

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

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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.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

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

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

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

Project Description: We have mostly targeted active faults and young petroleum fields in southern California for study, such as the Refugio-Carneros Fault in the Transverse Ranges near Santa Barbara, and the offshore South Ellwood fault in the Santa Barbara Channel. Subsurface data and published structural-seismic sections are being analyzed 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 and the geochemical mixing of fluids.

Results: Our 2003 studies have shown that the Refugio-Carneros Fault is relatively unique amongst the numerous faults in the region in being a conduit of high temperature fluid and hydrocarbon migration. We have recently documented evidence for isotopic disequilibrium, in the form of co-varying carbon and oxygen isotopes during rapid carbonate crystallization resulting from rapid CO₂ degassing in oil field tubing. Our goal is to develop a quantitative understanding of this phenomenon in order to interpret isotopic signatures found in fault zone cements. A study in an offshore Santa Barbara oil field has calculated fault permeability from the rate of sea water influx into an underpressured reservoir. The permeability is about 20 md, which is similar in magnitude to the overall reservoir permeability. On the hydrogeologic modeling front, new papers characterize fault-valve behavior and earthquake recurrence in a generic transpressional profile. New simulations have been developed to model site-specific fluid and stress transients immediately following large earthquakes in convergent continental margins that can be constrained with seismic deformation data from the recent Antofagasta, Chile earthquake. In addition, a reactive flow 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 complementary basis for ongoing studies of fault mineralization and reactive flow.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA
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Grant: DE-FG02-00ER15114

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

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The vorticity interaction mechanisms governing miscible displacements in three-dimensional heterogeneous porous media are investigated by means of detailed simulations in the regimes of viscous fingering, channeling, and resonant amplification. The computational results for spatially periodic and random permeability distributions are analyzed in detail with respect to the characteristic wavenumbers and norms associated with the individual vorticity components. This enables the identification of the mechanisms dominating specific parameter regimes. Nominally axisymmetric displacements such as the present quarter five-spot configuration are particularly interesting in this respect, since some of the characteristic length scales grow in time as the front expands radially. This leads to displacement flows that can undergo resonant amplification during certain phases, while being dominated by fingering or channeling at other times. The computational results also provide insight into the effects of density-driven gravity override on the interactions among these length scales. While this effect is known to play a dominant role in homogeneous flows, it is suppressed to some extent in heterogeneous displacements, even for relatively small values of the heterogeneity variance. This is a result of the coupling between the viscous and permeability vorticity fields in the viscous fingering and resonant amplification regimes. In the channeling regime, gravity override is somewhat more effective because the coupling between the viscous and permeability vorticity fields is less pronounced, so that the large scale structures become more responsive to buoyancy effects.

UNIVERSITY OF CALIFORNIA, SANTA CRUZ

Institute of Geophysics and Planetary Physics
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Grant: DE-FG02-01ER15144

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

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Objective: Develop high-resolution/high-fidelity multi-domain seismic imaging techniques and apply these techniques to local parameter estimation for subsurface structures and properties.

Project Description: The project is a collaborative effort between LANL and UCSC. The research at UCSC is implemented at the Modeling and Imaging Laboratory, Center for Study of Imaging and Dynamics of the Earth, Institute of Geophysics and Planetary Physics. The purpose of this project is to develop new theories/methods for multi-domain one-way wave propagation. This efficient wave equation based method can be widely used in seismic modeling, imaging, illumination and parameter estimation.

Results: We developed the method for processing the local angle domain information using wave equation based propagators. With this method, the wavefield is extrapolated using wide-angle multi-domain one-way propagator. A local plane wave decomposition technique is used to extract the angle domain information from the wavefield. The angle domain information can then be used in illumination, velocity updating and imaging processing.

A three-dimensional multicomponent prestack depth migration method is developed. An elastic screen propagator based on one-way wave propagation with a wide-angle correction is used to extrapolate both source and receiver wavefields. The elastic screen propagator neglects backscattered waves, but can handle forward multiple-scattering effects, such as focusing/defocusing, diffraction, interference, and conversions between P- and S-waves. Vector imaging conditions are used to generate a P-P image and a P-S converted wave image. The application of the multicomponent elastic propagator and vector imaging condition preserve more information carried by the elastic waves. It also solves the polarization problem of converted wave imaging. Partial images from different sources with correct polarizations can be stacked to generate a final image.

We also developed a wave-equation based illumination analysis method. The approach uses the one-way screen propagator to provide fast and accurate wavefield extrapolation. The method can avoid the singularity problem usually linked to the high frequency asymptotic method. It provides a practical tool for three-dimensional full-volume illumination analysis in complicated structures.

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Contract: DE-FG02-02ER15311

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.

UNIVERSITY OF CHICAGO

Center for Advanced Radiation Sources

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Grant: DE-FG02-94ER14466

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

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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 FY1999, more than 500 beam time proposals were received, 350 outside users (25% students) have conducted experiments, and 180 publications have been produced. New results include (1) structure determination of the hydrated α -Al₂O₃ (0001) surface (Eng et al. 2000); (2) observation of partial Fe occupancy on the hydrated α -Fe₂O₃ (0001) surface explaining the large reactivity difference between α -Al₂O₃ (0001) and α -Fe₂O₃ (0001) (Trainor et al. 2002); (3) Pb speciation at the biofilm-metal oxide interface (Templeton et al. 2003); (4) observed oxidation of Mn(II) during surface reaction of rhodonite, suggesting Mn mobility retardation via precipitation and/or hydrolysis (Farquhar et al. 2002); (5) identification of chloride complexes as the Cu species in hydrothermal fluid inclusions from an ore-forming region in Australia (Mavrogenes et al. 2002); (6) confirmation of strong arsenic sequestration by iron hydroxide plaques on plant roots from a Superfund site (Keon et al. 2002); (7) observation of sharply terminated Cr diffusion fronts in soil aggregates caused by locally rapid Cr(VI) reduction by microbial activity (Tokunaga et al. 2003), (8) observation of heterogeneous incorporation of Sr into coral aragonite (Allison et al. 2001; Finch et al. 2003) and (9) evidence of dynamic effects on fluid distribution in porous media (Wildenschild et al. 2002).

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

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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. Two examples are given here. Spectroscopic and diffraction studies of arsenic-bearing tailings, soils and sediments from the Yellowknife area (Canada) were pursued to identify the mineralogical form of the arsenic and assess its stability in various geochemical environments (with S. Walker and H. Jamieson, Queen's Univ., Ontario Canada). MicroXANES results indicated that fresh flotation tailings contain only sulfide-bound arsenic (As^{-1}). Roaster-generated hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) in all ages of tailings (fresh to 50 years old) contain arsenic in mixed oxidation state (As^{+5} and As^{+3}). This contrasts with iron oxyhydroxides formed by weathering of pyrite (FeS_2) and arsenopyrite (FeAsS) which contain only As^{+5} . MicroXRD analyses allowed definitive identification of hematite and maghemite, minerals that are difficult to distinguish petrographically in these materials. Factors such as charge and ionic size of the impurity introduced and the crystallographic orientation of the calcite surface sites play a major role in site selectivity in trace element incorporation. E. Elzinga and R. Reeder (Stony Brook University) demonstrated that divalent Cu and Zn, which have ionic radii smaller than Ca, are preferentially incorporated into the $\langle 4\bar{4}1 \rangle^+$ steps that define one pair of symmetrically equivalent vicinal faces on polygonized growth spirals. In contrast, other divalent metals with six-fold ionic radii smaller than Ca (Co, Cd, Mn, Mg) have been shown to be preferentially incorporated into $\langle 4\bar{4}1 \rangle^-$ growth steps, which define the second pair of vicinal faces on the growth spirals. Studies by V. Alexandratos and R. Reeder (Stony Brook University) similarly demonstrated that AsO_4^{-3} anions prefer the $-$ vicinal faces as well implying that bulk partition coefficients for As(V) depend on the availability of different calcite surface sites.

UNIVERSITY OF CHICAGO

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Grant: DE-FG02-01ER15254

Kinetic Isotope Fractionation by Diffusion in Liquids

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The overall objective of our research 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. Very significant isotope fractionations were found and the results have been published in *Geochimica Cosmochimica Acta*. Chemical and isotopic fractionation of dissolved species by diffusion in water was also studied using small spherical chambers filled with salt solutions (KCl, LiCl, MgCl₂) 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 MgCl₂ we found no measurable isotopic fractionation of Mg (<0.5 per mil for ²⁶Mg/²⁴Mg) 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 silicates, 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 ⁷Li/⁶Li 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 also found a small but measurable fractionation of Cl isotopes. We interpret the much-diminished isotopic fractionation associated with diffusion in water relative to that in molten silicate liquids as being due to the hydration of the dissolved ions. We have recently developed a new capability for high precision Fe isotope measurements using a multi collector plasma source mass spectrometer, and will use this to determine the degree to which diffusion can fractionate Fe isotopes.

CLARK UNIVERSITY

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Grant: DE-FG02-02ER15367

Physics of Channelization: Theory, Experiment, and Observation

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Our project seeks to better characterize the physical processes that erode landscapes, with emphasis on the formation of drainage channels and channel networks. Our approach consists of tightly coupled theoretical and experimental studies augmented by field observations. The work is performed in collaboration with Prof. Daniel Rothman of MIT. The group at Clark is primarily responsible for experiments while the group at MIT is primarily responsible for theory.

Fluvial erosion in natural systems can be induced by either surficial, overland flows or subsurface, seepage flows. The latter process constitutes the present focus of our project. Using modern laser-aided data-acquisition and digital imaging techniques, we obtain detailed time-dependent two-dimensional topographic data. Our objective is to understand the evolution of the topography as fully as possible.

We have thus far focused three problems. First, we have shown that our experiment yields a characteristic channel spacing that depends on slope and pressure gradient, and have proposed theoretical explanations for this choice of length scale. Second, we have defined, both theoretically and experimentally, the particular values of control parameters that determine the qualitative quasi-stationary features exhibited in our experiment. The third focus of our work has been on the dynamics of channel evolution. We have discovered that the problem may be usefully portrayed as a trajectory in a two-dimensional phase space. Commonalities in all such trajectories indicate surprisingly that the growth of individual channels is at least to some extent independent of other channels in the channel network, in a manner that is determined by the geometry of the subsurface water flow.

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

Center for Wave Phenomena

Green Center

Golden CO 80401

Grant: DE-FG02-98ER14908

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: 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 applied to evaluation of the position, orientation, spatial density and connectivity of fractures and other reservoir heterogeneities.

Project description: CSM investigators are working on inversion and processing of wide-azimuth PP and PS (mode-converted) reflection data for azimuthally anisotropic media. Anisotropic velocity analysis followed by multicomponent depth imaging produces an accurate heterogeneous model of the reservoir. Interpretation of the anisotropic parameters in terms of the physical properties of natural fractures is the main focus of our collaborative research with LLNL and Stanford University.

Project results:

Generation of SS-wave reflection data from PP- and PS-waves. By designing a special convolution of PP- and PS-wave seismograms, we developed a model-independent algorithm that computes full-waveform SS data well-suited for both moveout inversion and AVO (amplitude variation with offset) analysis.

Velocity analysis of multicomponent data in the Gulf of Mexico. The convolutional method of generating SS data described above and joint moveout inversion of PP- and SS-waves were successfully applied to multicomponent data acquired by ocean bottom cable in the Gulf of Mexico.

3-D analysis of nonhyperbolic reflection moveout. To model and invert long-spread reflection traveltimes over fractured reservoirs, we developed an efficient formulation for computing multioffset, multiazimuth nonhyperbolic moveout in anisotropic, heterogeneous media by tracing a single (zero-offset) ray.

Inversion of multicomponent VSP data. An algorithm for estimating the stiffness coefficients of arbitrarily anisotropic media by inverting multicomponent VSP (vertical seismic profiling) data was devised and applied to a multiazimuth survey from a fractured reservoir at Vacuum field, New Mexico.

Seismic characterization of multiple fracture sets. Using the linear-slip theory, we proposed a method for establishing the maximum number of vertical or dipping fracture sets whose orientations and compliances can be resolved from the effective stiffness matrix (i.e., from seismic data).

COLORADO SCHOOL OF MINES

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Grant: DE-FG02-03ER15390

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

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We have developed a fiber-optic strainmeter to estimate moduli and seismic wave attenuation at low frequencies (10-3000 Hz) in a stress-strain experiment. The system follows a Mach-Zehnder interferometer setup from which phase lags (attenuation) and deformations (moduli) are estimated from the fringe pattern. By using interferometry high sensitivity to deformations (picometers) and phase lags (microradians) is achieved. Stress-strain measurements using strain gages or ultrasonic wave propagation sample only part of the core sample, the fiber-optic strainmeter would analyze the rock sample response to an applied stress as a whole.

UNIVERSITY OF COLORADO

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

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We are exploring a new technology that is based on using low-frequency strain wave attenuation data to monitor changes in fluid saturation conditions in two-fluid phase porous materials. The attenuation mechanism is related to the loss of energy due to the hysteresis of resistance to meniscus deformation (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. We are conducting a feasibility field study at the Maricopa Agricultural Center near Maricopa, AZ. The field site is operated by the University of Arizona and has facilities for controlled water irrigation and a comprehensive array of instruments used for measuring water saturation and flow. Three strategically placed pairs of tiltmeters and seismometers are used to record solid Earth tides and microseisms respectively. The aim is to detect changes in the recorded signals that reflect changes in the physical properties of the site in response to irrigation with a biosurfactant. We compare measured tidal tilts with theoretical, site specific tidal tilts and then look at temporal changes between the stations at the irrigation site. Similarly, for the seismic signals, we look for temporal changes in the differences of the responses of the three instruments. We are also examining changes in amplitude ratios between horizontal and vertical components of the seismic signals. To date we have observed clear differences in the signals from the three stations, with the differences being larger, the closer the stations are to the irrigation site. These observations are correlated with periods of high temperature and may be due to thermal excursions caused by the cover over the 50 m by 50 m site. Starting in October, 2004 we will irrigate for a six week period with a fluid containing biosurfactant at a concentration of 50 ppm. The surfactant reduces the surface tension of water from a nominal value of 70 mN/m to 30 mN/m.

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

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The objective of this research is to develop quantitative understanding of the critical processes controlling two-phase flow and transport in rock fractures, with potential applications in radioactive waste isolation, CO₂ sequestration and petroleum engineering. Our previous research identified the importance of phase structure in controlling system behavior. We have developed experimental systems to create and measure a wide range of phase structures, and flow and transport through them. Current efforts focus on models of phase structure, parametric relationships for flow, transport and inter-phase transfer, and behavior in fracture-matrix networks.

Our previous experimental studies have demonstrated two important classes of phase structures in variable aperture fractures: satiated structures, wherein the invading phase fully entraps the defending phase, and fingered structures resulting from gravity destabilization. Both classes are accurately modeled using modified invasion percolation (MIP) algorithms that account for the influence of gravity, in-plane curvature and simultaneous invasion-reinvasion of two phases.

The MIP algorithm with simultaneous invasion-reinvasion of two fluids was shown to reproduce the dynamics of gravity-driven wetting fingers in variable-aperture fractures. Fragmentation behind the fingertip, pulsating flow and the stop-and-go dynamic of fingers were simulated, closely following experimental observations. Average finger widths are within 20% of experimental measurements. (Water Resources Research 39(3) doi:10.1029/2002WR001542, 2003)

Parametric studies of the influence of fracture properties on satiated phase structure, and associated flow and transport properties are ongoing. The areal saturation (S_f) of the flowing phase at satiation is shown to depend on the ratio of two dimensionless parameters related to the fracture properties (C/δ , where the curvature number C , representing the mean influence of in-plane curvature, is the ratio of the mean aperture to the correlation length, and δ is the coefficient of variation of the aperture field). As C/δ goes to zero, behavior is as in standard invasion percolation within a correlated field, and $S_f \sim 0.37$. As C/δ increases above ~ 0.1 , S_f increases, approaching 1 for very large $C/\delta \sim 10$. (Physical Review E 68, 061110, 2003)

We have also investigated infiltration in meso-scale laboratory fracture-matrix networks, demonstrating the occurrence of dynamic preferential pathways. (Water Resources Research, 38(12), 1281, doi:10.1029/2001WR001002, 2002).

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

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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.

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Grant: DE-FG02-89ER14080

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 are writing up measurements of the association of the ions in the following salts: sulfuric acid, hydrochloric acid, sodium sulfate, sodium hydrogen sulfate, lithium sulfate, and potassium sulfate. Methods for predicting second, cross, virial, coefficients for interactions involving water have been published. 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. We have shown that our new method can predict hydration free energies of ions at high temperatures with good accuracy and used the method to predict sodium and chloride ions at many high temperature state points. 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.

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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 is 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. Recently we have discovered a way of incorporating linear surface kinetics very efficiently. In essence a tracer particle encountering the surface is absorbed or reflected with a probability that is related to the kinetic rate constant. We have used this idea to simulate the erosion of laboratory scale samples; we observe similar dissolution patterns to those found experimentally.

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.

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

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Direction-specific behavior is a fundamental property of anisotropic materials. Extensive studies have documented this unique property for various materials. Despite these efforts, a fundamental question remains to be answered regarding the direction-dependence of solubility. Thermodynamics dictates that chemical potential necessary to maintain crystal growth differs amongst faces with different surface energies. This leads to the conclusion that multiple solubilities exist for crystals that have faces unrelated by symmetry operations. Yet, little is found in the literature to experimentally verify the face specific solubility for any crystal systems. This study investigates the crystallographic direction-specific behavior of the {10-14} cleavage faces of calcite, a well known anisotropic mineral, at near equilibrium conditions and explores the possible solubility difference between the $\langle -441 \rangle_+$ (obtuse) and the $\langle -441 \rangle_-$ (acute) steps. Experimental results reveal no dissolution in either direction when the ionic activity product (IAP) of Ca^{2+} and CO_3^{2-} in the solution is greater than $10^{-8.41}$, whereas retreat is observed in both steps when IAP is smaller than $10^{-8.51}$. Furthermore, when $10^{-8.26} > \text{IAP} > 10^{-8.45}$, dissolution is seen in the obtuse steps, but not in the acute steps: while the acute steps continue to advance at a rate of 0.06 nm/s, obtuse steps become serrated and start to retreat with an average rate 0.03 nm/s at $\text{IAP} = 10^{-8.45}$. Additionally, growth in the acute steps remains measurable until IAP was reduced to $10^{-8.47}$. Further decrease in IAP to $10^{-8.51}$ finally led to dissolution at all steps.

The above AFM observations suggest the obtuse and acute steps have different thermodynamic stabilities. Putting the observed simultaneous growth and dissolution into the classic thermodynamic framework, we show that these results may indicate the two steps have different solubility constants. Experimental measurements demonstrate that the obtuse steps are 5% more soluble than the acute steps. This may have provided the first crystallographic direction dependent solubility constant for any crystals. These results further suggest that the current thermodynamic database may need significant addition to reflect the anisotropy of crystalline materials.

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

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The proposed work tests a hypothesis that chemical remnant magnetization (CRM) is concordant with the timing of potassic diagenetic processes in argillaceous rocks caused by thrust sheet, progressive burial, and/or migration of heat and fluids due to contact metamorphism. This hypothesis is tested by comparing the timing of chemical remnant magnetization (CRM) recorded by authigenic magnetic minerals to the measured K-Ar dates of diagenetic illite at specific settings (Disturbed Belt, Montana; the timing of CRM in relation to progressive burial and maturation of organic matter in the Mississippian Desert Limestone, and magnetization associated with heat and fluids accompanying through marls adjacent to Tertiary intrusions in the Isle of Skye). The results describing the work on the Isle of Skye are detailed below.

Previous results on the study of the clay mineralogy of the Jurassic sedimentary rocks of Skye, Scotland showed a hypothetical connection between the smectite-to-illite conversion and magnetite authigenesis/remagnetization. A presence-absence test and the timing of acquisition of a dual polarity early Tertiary (50-60 Ma) CRM suggests that magnetite authigenesis is related to the smectite-to-illite conversion. A modified version of Illite Age Analysis is used to derive the age of diagenetic illite in these marls that contain both detrital and diagenetic illite. The measured K-Ar dates of illite and percentage of 2M1 illite both decrease with clay size fraction from 160-213 Ma (1-2 micron) to 101-105 Ma (< 0.25 micron) from three marls. The age of diagenetic illite is derived by a non-linear extrapolation of measured K-Ar dates to 0% 2M1 illite and these extrapolated ages (40- 67 Ma) are concordant or slightly younger than the age of remagnetization and Tertiary intrusions.

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

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Dissolution Mechanisms of the Carbonate Minerals

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Oxide and carbonate minerals are central in regulating the chemical composition of environmental aqueous systems. Dissolution and precipitation of iron and manganese oxides, calcite, and other carbonates control pH, alkalinity and contaminant mobility. Thus, a detailed, mechanistic understanding of these reactions is essential for reliable quantitative modeling. Our approach examines the relationship between macroscopic and microscopic observations of mineral dissolution and precipitation. Collectively we find that macroscopic phenomenon (such as aqueous iron or manganese and associated heavy metal pollutants such as chromium, arsenic, or lead) released per square meter per second can be linked to microscopic processes of surface complexation, step retreat, and film precipitation. Study of carbonate group mineral dissolution kinetics using scanning probe microscopy and bulk solution flow reactors revealed a complex association between microscopic and macroscopic behavior. Geometric models employing microscopic step retreat velocities measured on CaCO_3 and MnCO_3 proved to be accurate predictors of the absolute macroscopic dissolution over a wide range of pH values. The same is true for FeCO_3 and MgCO_3 only at $\text{pH} < 4$. In other cases, microscopic and macroscopic carbonate dissolution rates differed by an order of magnitude.

Applied in conjunction with our experimental observations, we showed that molecular modeling was an especially valuable tool for understanding the mechanisms of surface reactions. In particular, calculated bulk and surface energies were useful in predicting microscopic and macroscopic rates for carbonates. A log-linear relationship between calculated lattice energies and measured macroscopic dissolution rates was established. The rigid ion model was further applied to simulate the microscopic processes active in dissolution. For larger pits, we showed that ion pair translation energies predict experimentally observed step velocities.

Scaling microscopic phenomenon to macroscopic observations is integral to the construction of quantitative and predictive models, which can be further linked from macroscopic to field scale dimensions. When accomplished, this combined model can be employed to provide rational and effective solutions to problems of environmental contamination and remediation.

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

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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.

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

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

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

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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 *in situ* studies of mineral-water interfaces arises from X-ray scattering effects. This set of techniques is practical only at high-intensity synchrotron radiation sources. We have performed such experiments at the APS since 1997. These experiments demonstrated the first uses of low-angle X-ray reflectivity, thin-film diffraction, X-ray standing waves, crystal truncation rod measurements, and resonant anomalous X-ray reflectivity 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 variety of mineral-water systems (carbonates, silicates, and oxides).

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Grant: DE-FG02-02ER15364

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

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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.

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Grant: DE-FG02-00ER15032

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

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Isotopically labile organic hydrogen in fossil fuels 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 oil and maturing kerogens in source rocks to evaluate paleoenvironmental and diagenetic influences.

In 2003 we concluded a study of D/H in terrestrial petroleum systems (Schimmelmann et al., in press, *Organic Geochemistry*). D/H ratios of terrestrially-sourced whole oils and their respective saturated, aromatic, and polar fractions, individual *n*-alkanes, formation waters and non-exchangeable hydrogen in kerogen were measured from source rocks from seven Australian petroleum basins. Data for 75 oils and condensates, their sub-fractions, and 52 kerogens indicate that oil sub-fractions have δD values comparable to δD_{oil} , with a $\Delta\delta D$ offset ($\delta D_{kerogen} - \delta D_{oil}$) averaging ca. 23‰. The weighted-average δD of individual *n*-alkanes is usually identical to δD_{oil} and $\delta D_{saturated}$. A trend of increasing δD with *n*-alkane chain length in most oils causes individual *n*-alkanes from an oil to vary in δD by 30‰ or more. A modest correlation between δD for aromatic sub-fractions and formation waters indicates that about 50% of aromatic C-bound H has exchanged with water. In contrast, δD_{oil} and $\delta D_{saturated}$ show no evidence for H-exchange with formation water under reservoir conditions at temperatures up to 150°C. Acyclic isoprenoids and *n*-alkanes show essentially indistinguishable δD , indicating that primary isotopic differences from biosynthesis have been erased. Overall, extensive exchange of C-bound H in petroleum with other hydrogen is apparent, but seems to have affected most hydrocarbons only during their chemical genesis from precursor molecules. Our isotopic findings from terrestrial-sourced oils should be qualitatively relevant for marine oils as well.

Kerogens prepared from a suite of samples from the New Albany Shale with vitrinite reflectance (R_o) from 0.29 to 1.4% were characterized by ^{13}C -NMR, FTIR, and hydrogen stable isotope mass-spectrometry. With increasing thermal maturity, preferential generation of isotopically lighter and more saturated hydrocarbons results in residual kerogen that is characterized by decreasing H/C ratios and increases in (1) the δD values of non-exchangeable hydrogen, (2) the abundance of aromatic hydrogen, and (3) H-isotopic exchangeability.

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Grant: DE-FG02-91ER14175

Self-Organized Mega-Structures in Sedimentary Basins

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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 significantly 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.

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Grant: DE-FG02-96ER14619

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

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

Project Description: We have mostly targeted active faults and young petroleum fields in southern California for study, such as the Refugio-Carneros Fault in the Transverse Ranges near Santa Barbara. Subsurface data and published structural-seismic sections are being analyzed 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 and the geochemical mixing of fluids.

Results: Our 2003 studies have shown that the Refugio-Carneros Fault is relatively unique amongst the numerous faults in the region in being a conduit of high temperature fluid and hydrocarbon migration. We have recently documented evidence for isotopic disequilibrium during rapid calcite crystallization resulting from rapid CO₂ degassing, in the form of co-varying carbon and oxygen isotopes. Our goal is to develop a quantitative understanding of this phenomenon in order to interpret isotopic signatures found in fault zone cements. A study in an offshore Santa Barbara oil field has calculated fault permeability from the rate of sea water influx into an underpressured reservoir. The permeability is about 20 md, which is similar in magnitude to the overall reservoir permeability. On the hydrogeologic modeling front, new papers characterize fault-valve behavior and earthquake recurrence in a generic transpressional profile. New simulations have been developed to model site-specific fluid and stress transients immediately following large earthquakes in convergent continental margins that can be constrained with seismic deformation data from the recent Antofagasta, Chile earthquake. In addition, a reactive flow 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 complementary basis for ongoing studies of fault mineralization and reactive flow.

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

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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.

JOHNS HOPKINS UNIVERSITY

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Grant: DE-FG02-96ER14616

Predictive Single-Site Protonation and Cation Adsorption Modeling

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Research efforts this year have focused on finalizing a quantitative characterization of the development of proton surface charge on the surfaces of minerals. This is necessary for a fundamental understanding of reactions between solids and aqueous electrolyte solutions. Despite many experimental studies of charge development, few attempts have been made to integrate the results with a theoretical framework that permits prediction. In the present study, 53 sets of proton surface charge data referring to wide ranges of ionic strengths, types of electrolyte and oxide were analyzed with the aid of the triple-layer model of surface complexation. The application of crystal chemical, electrostatic and thermodynamic theory to the results enables prediction of all the surface complexation parameters needed to calculate proton surface charge for any oxide in 1:1 electrolyte solutions. Assymmetric binding of electrolyte ions is built into these predictions. Predicted trends of electrolyte cation binding and surface charge for high dielectric constant solids (e.g. rutile) are opposite to those on low dielectric constant solids (e.g. amorphous silica). The results are described in Sverjensky, D.A. (2004, *Geochimica et Cosmochimica Acta*, in press) "Prediction of surface charge on oxides in salt solutions: revisions for 1:1 (M+L-) electrolytes". 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.

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

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

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

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

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

UNIVERSITY OF MARYLAND

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Grant: DE-FG02-94ER14467

Theoretical Studies on Heavy Metal Species in Solution

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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. In Fiscal Year 2003 we have extended our studies on the UV-vis spectra of species in solution to As and Sb oxidation state III and V sulfides and to polysulfides S_n^{-2} , $n=2-6$, the bisulfide anion, SH^- , hydrogen sulfide, H_2S and the sulfanes, S_nH_2 , $n=2-5$. We correctly reproduce the general trends observed experimentally, with absorption energies increasing from polysulfides to As, Sb sulfides to SH^- to H_2S . As and Sb (V) species, both monomers and dimers, also absorb at characteristically higher energies than do analog As and Sb (III) species. There is also a small reduction in absorption energy from monomeric to dimeric species, for both As and Sb III and V. Our results indicate that for the As and Sb sulfides, the oxidation state, degree of protonation and degree of oligomerization can all be determined from the visible-UV absorption spectrum. We have also calculated the aqueous phase energetics for the reaction of S_8 with SH^- to produce the polysulfides, S_nH^{-1} , $n = 2-6$. Our results are in excellent agreement with available experimental data, and support the existence of a S_6 species. Recently the removal of gas-phase elemental Hg has been observed by several research groups after polar sunrise in the boundary layer in Arctic regions. At the same time Hg compounds are observed to accumulate in the polar snowpack. Several different oxidation reactions involving gas-phase Br and BrO have been hypothesized to explain this process. Molecular quantum mechanical methods are here applied to evaluate the energetics for such reactions, in both the gas-phase and aqueous solution. The formation of HgO from the reaction of Hg_0 and BrO in the gas phase is found to be unfavorable energetically but HgBr and HgBr₂ can form exothermically through the oxidation of Hg_0 by either Br atom radicals or Br₂.

UNIVERSITY OF MARYLAND

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Grant: DE-FG02-02ER15327

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

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In this second phase of research, which is a collaboration between the Ohio State University (Dr. Steven Lower) and Virginia Tech (Dr. Michael Hochella, Jr.), we used force microscopy to measure inter- and intra-molecular forces between inorganic solids (e.g., silica and goethite) and two different Gram-negative microorganisms (*Escherichia coli* and *Shewanella oneidensis*). The measured forces were compared to theoretical models that describe van der Waals, electrostatic, and steric forces between a bacterium and mineral. Different force classes were found to dominate each of the two bacterium-goethite pairs. Overall, *S. oneidensis* exhibited a preferential affinity towards goethite relative to *E. coli*. We hypothesized that this preferential affinity was due to the production of outer membrane proteins by *S. oneidensis*. Therefore, we measured forces between a mineral and a bacterium that had been genetically modified to produce a fluorescently tagged protein. Simultaneous force microscopy and confocal laser scanning microscopy measurements suggested that outer membrane proteins can indeed form a bond between a Gram negative microorganism and an inorganic surface.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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Collaborative Research: Evolution of Pore Structure and Permeability of Rocks under Hydrothermal Conditions

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Both temporal and spatial variations of permeability are common in the Earth; such variations are driven by a diverse and complex set of processes including fracturing, diagenesis, cementation, brittle pore collapse, compaction owing to pressure solution or plastic flow, crack healing, crack sealing. Each mechanism will respond to a particular set of driving forces, including local non-hydrostatic stresses; reduction of interfacial energy; dissolution into under saturated liquids, precipitation from oversaturated fluids, or reactions between phases. To identify the dominant process, kinetics laws need to be developed for each mechanism. Some processes are more efficient in changing permeability than others. In particular, neo-mineralization and dilatant micro fracturing are capable of producing large changes in permeability with relatively small changes in total porosity, but compaction during creep is less efficient, provided that capillary forces are capable of maintaining steady-state interfacial angles. Two examples of experiments to determine rates follow: 1.) When samples of Sioux quartzite were inserted into a hydrothermal pressure vessel and heat-treated at temperatures of 300-500°C confining pressures of between 300 MPa and 125 MPa and fluid pressures from 125 MPa to 250 MPa, permeability was reduced by as much as three orders of magnitude. Reductions occur fastest at higher temperatures and higher effective pressures. 2.) During deformation 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, Solnhofen limestone failed by dilatancy and localized deformation. 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.

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Physics of Channelization: Theory, Experiment, and Observation

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Our project seeks to better characterize the physical processes that erode landscapes, with emphasis on the formation of drainage channels and channel networks. Our approach consists of tightly coupled theoretical and experimental studies augmented by field observations. The work is performed in collaboration with Prof. Arshad Kudrolli of Clark University. The group at Clark is primarily responsible for experiments while the group at MIT is primarily responsible for theory.

Fluvial erosion in natural systems can be induced by either surficial, overland flows or subsurface, seepage flows. The latter process constitutes the present focus of our project. Using modern laser-aided data-acquisition and digital imaging techniques, we obtain detailed time-dependent two-dimensional topographic data. Our objective is to understand the evolution of the topography as fully as possible.

We have thus far focused three problems. First, we have shown that our experiment yields a characteristic channel spacing that depends on slope and pressure gradient, and have proposed theoretical explanations for this choice of length scale. Second, we have defined, both theoretically and experimentally, the particular values of control parameters that determine the qualitative quasi-stationary features exhibited in our experiment. The third focus of our work has been on the dynamics of channel evolution. We have discovered that the problem may be usefully portrayed as a trajectory in a two-dimensional phase space. Commonalities in all such trajectories indicate surprisingly that the growth of individual channels is at least to some extent independent of other channels in the channel network, in a manner that is determined by the geometry of the subsurface water flow.

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.

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

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The project was for the support of three Mineralogical Society of America and Geochemical Society short courses and companion Reviews volumes in 2003:

[1] Zircon: experiments, isotopes and trace element investigations. April 3 and 4, 2003, Freiburg, Germany. Convenors: John M. Hanchar and Paul W. O. Hoskin. Registrations were taken by the Mineralogical Society of America and the course had 60 participants (20 students and 40 professionals). Reviews in Mineralogy and Geochemistry volume 53: Zircon: experiments, isotopes and trace element investigations (500 pp.) ISBN 093995065-0 (\$36 non-members, \$27 MSA, GS, and CMS members) - 2500 copies printed on 12/04/2003.

[2] Uranium Series Geochemistry April 3-4, 2003 on Convenors: Bernard Bourdon, S. P. Turner, Gideon M. Henderson, and Craig C. Lundstrom. Registrations were taken by The Geochemical Society and the course had 90 participants (68 students and 22 professionals). Reviews in Mineralogy and Geochemistry volume 52: Uranium Series Geochemistry (656 pp.) ISBN 093995064-2 (\$40 non-members, \$30 MSA, GS, and CMS members) - 2500 copies printed on 03/06/2003.

[3] Biomineralization. December 6-7, 2003, Napa, California. Convenors Patricia Dove, J. J. DeYoreo and S. Weiner. Registrations were taken by the Mineralogical Society of America and the course had 101 participants (48 students and 53 professionals). Reviews in Mineralogy and Geochemistry volume 54: Biomineralization (381 pp.) ISBN 093995066-9 (\$36 non-members, \$27 MSA, GS, and CMS members) - 2500 copies printed on 11/21/2003.

NEW ENGLAND RESEARCH

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Grant: DE-FG02-98ER14906

Evolution of Fracture Permeability

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Pore fluid flow within fractured rocks is a subject of primary importance to various fields of study 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 content 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.

We find that when experimental parameters (e.g. initial surface topography, flow rate history, and total experiment time) are duplicated, the topography developed on the plaster sample is reproducible. The flow channel networks, as observed visually and through numerical simulations, evolves from a homogeneous system to one more (self) organized and complex. The permeability initially drops as the experiment begins and the surfaces settle into place, then gradually rises with several further smaller decreases as some supporting asperities are destroyed.

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

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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.

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK

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Fluid and Particulate Transport in Self-Affine Fractures

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We studied the motion of a passive tracer in fluid flow in geological fractures with self-affine fractally rough walls by numerical simulation using the lattice-Boltzmann method. The focus of the calculations was to further investigate the experimental observation that the tracer front, in the limit of high-Peclet number and low Reynolds number, itself developed a self-affinely rough boundary. The self-affine surface was generated using a Fourier synthesis method and the fracture pore space is the region between one such surface and a suitably shifted replica. An initially flat front advected by the flow progressively distorts into a self-affine front with Hurst exponent equal to that of the fracture walls. The lower cutoff of the self-affine regime depends only on the aperture, while the upper cutoff grows with the lateral shift and linearly with the width of the front. In particular, the range of length scales over which self-affinity is observed is much greater than the characteristic length scales of the fracture itself, the aperture and correlation length. This work shows how a fractal geometry can impose itself on a flexible object convecting through it. In addition, we observe significant anisotropy in dispersion, in that the fluid and tracer motion is much more strongly altered when the mean flow is orthogonal to the lateral shift than the case when the two are parallel. We are currently attempting to develop a quantitative understanding of the relation between flow and geometrical anisotropies. Other active topics in this project are the evolution of self-affine fracture surfaces due to deposition and erosion of particulates, and the enhanced dispersion effects resulting from non-Newtonian fluid transport in fractures.

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK

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Stress-Dependent Acoustic Propagation and Dissipation in Granular Materials

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This project is a joint collaboration between City College of New York (CCNY) and Schlumberger-Doll Research (SDR). The goal of the project is to combine experiments, theory and simulations to develop an understanding of the elastic and viscoelastic properties of granular materials. We focus our studies on the following projects:

(i) Nonlinear elasticity and acoustics of granular materials. We attempt to understand the elastic response of a granular assembly under loading. Our experiments reveals that elasticity theory fails to describe the elastic properties of granular assemblies. The understanding of this failure has been a longstanding question in the field. We show that a correct treatment should include the collective relaxation mechanisms related to structural disorder and nonaffine motion of grains. Next, we perform a theoretical investigation that allows for grain relaxation in collaboration with Cornell University. The incorporation of additional degrees of freedom results in predictions which are in far better agreement than previously.

We also investigate the Green (response) function of random packings of grains in order to discriminate between the different theories of stress transmission. We show that elasticity theory, while approximating qualitatively the stress profiles, breaks down by not taking into account the dynamics of grain relaxation, in analogy with our studies on the elastic moduli.

(ii) Compaction and stress relaxation. The relaxation and dissipative properties of cohesionless granular assemblies under compression are being studied both experimentally and numerically. We investigate the system's exploration of the static configurations through a novel compaction procedure at varying confining pressures. Once the system is fully compactified we study the slow relaxation dynamics under an applied strain. Computer simulations reveal that the origin of the long stress-relaxation dynamics is the collective nature of the motion of the particles.

(iii) Dissipation in granular matter. An important goal of this project is to elucidate the origin of the dissipation mechanisms in granular materials. To this end we have initiated a series of experiments, simulations and theory to calculate the effective mass of a rigid cavity filled with loose granular particles. This work is ongoing.

STATE UNIVERSITY OF NEW YORK, STONY BROOK

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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).

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Microscale Processes and Macroscopic Behavior of Porous Geomaterials

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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.

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Grant: DE-FG02-92ER14261

Pore Scale Geometric and Fluid Distribution Analysis

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We have focused on three dimensional (3D) pore scale medium characterization, permeability computations for throat structures, and residual fluid distribution in Berea (water wet) and polyethylene (oil wet) cores.

X-ray computed microtomography combined with X-ray attenuating dopants is used to obtain 3D images of the pore network and to resolve two phase distributions at residual fluid conditions in the pore space. Employing numerical image processing algorithms based upon computational geometry to identify individual pores, throats, and fluid "blobs", we characterize the pore space geometry and extract water and oil distributions at the level of individual pores in both imbibition and drainage displacements. Preliminary results on fluid distribution have also been obtained for constant fractional flow conditions (i.e. injection of fixed wetting:non-wetting fluid volume ratio) in polyethylene cores.

We have results on pore characterization, including distributions for pore volume, pore surface area, throat surface area, and principal direction diameters for pores and throats. Single phase lattice Boltzmann computations are used to predict permeabilities for all individual throats reconstructed from the images. These computations use actual (digitized) geometries with no shape assumptions. These permeabilities will be used in network flow model simulations for prediction of bulk permeability.

We have results on oil and water distribution in the pore space at residual oil and water conditions. We also consider the effects on residual fluid distribution due to the injection and gelation of a water-based gel. In extensive studies of Berea cores it has been observed that introducing water-based gels in the displacement process (for example, in water shut-off treatment of production wells) reduces permeability to water more than to oil. A number of micro-scale mechanisms have been proposed for this disproportional permeability reduction. Our results provide supporting evidence for the involvement of gel compaction (dehydration) and oil trapping, while discounting gel blockage in throats, as mechanisms contributing to this effect.

NORTHWESTERN UNIVERSITY

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Interactions of Propagating Compaction Fronts and Pore Fluids in Porous Rock

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Evidence from laboratory experiments and field observations on porous rocks (and other materials) has indicated that compaction does not necessarily occur homogeneously, but, instead, is localized in narrow planar zones that are perpendicular to the maximum compressive stress. Because the permeability of these zones is reduced by several orders of magnitude, they present barriers to fluid flow across them. Consequently, their formation in reservoirs or aquifers can adversely affect attempts to inject or withdraw fluids, such as 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 an alternative solution corresponding to localization in a planar band. 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 versus strain curve and in a limited range of lateral confining stress. Predictions of localization are, however, sensitive to the evolution of the yield surface with inelastic strain. A new model of an elliptic yield surface with axes that evolve differently with inelastic shear strain and inelastic volume strain more accurately models behavior in experiments and allows for localization under less restrictive conditions.

Conditions governing the extension of compaction to tens of meters in length, as observed in the field, have been addressed by analyzing the stress in front of a compaction band, modeled as a flat ellipsoidal inclusion with elastic properties different from those of the surroundings and subject to an inelastic compactive strain. Inelastic compaction in the band increases the compressive stress, but the full stress state is three-dimensional and the stress path depends on the mismatch of elastic properties. A second calculation identifies the energy released in steady state propagation of a band in a plane layer as approximately equal to the remote compressive stress times the inelastic compaction, with a correction for the elastic mismatch.

UNIVERSITY OF NOTRE DAME

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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.

THE UNIVERSITY OF OKLAHOMA

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

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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, and migration of basinal fluids. Results from Jurassic rocks on Skye, Scotland and preliminary data from Mesozoic rocks in the disturbed belt, Montana, are consistent with a hypothesized relationship between remagnetization and the smectite to illite conversion. We are testing the hypothesized connection by conducting K-Ar dating of illites as an alternative method for constraining the ages of magnetic mineral phases in our field areas in collaboration with Crawford Elliott (Georgia State). 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. Results from the Mississippian age Deseret Limestone (Utah) suggest that kerogen maturation is an alternative pathway for magnetite authigenesis and acquisition of a CRM. We are currently testing this mechanism by investigating Madison Group carbonates in the Sawtooth Mountains, Montana. 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, Great Glen Fault) that, based on petrographic, isotopic and fluid inclusion analyses, appear to be related to the migration of basinal-type fluids. The timing of these events, which range from the Devonian to the early Tertiary, has been established based on comparison of the pole positions to the Apparent Polar Wander Path.

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

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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. We have completed development and testing of modules for two and three-dimensional EM modeling, data functionals for MT and active source applications, and sensitivity calculations. Initial inversion of magnetotelluric data (a multiple frequency problem) using a data space OCCAM approach are underway; more novel inversion schemes will be tested in the coming year, along with tests on cross-hole EM (a multiple source problem).

PENNSYLVANIA STATE UNIVERSITY

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Nanoscale Characterization of Corrosion at the Microorganism-Glass Interface

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Experiments to investigate the characteristics of microbial corrosion of silicate and apatite glass and crystal compared with abiotic dissolution have been carried out. The effects of polymerization on dissolution of aluminosilicate glass under abiotic conditions have also been investigated to lay the groundwork for understanding controls on dissolution. Corrosion of surfaces has been investigated in the presence of several microbes: a common soil bacterium (*Bacillus* sp.), a nitrogen-fixing bacterium (*Azotobacter vinelandii*), a dissimilatory iron-reducing bacterium (DIRB, *Shewanella putrefaciens/oneidensis*), a cyanobacterium (*Anabaena*), a methanogen (*Methanothermobacter thermoautotrophicus*), and an iron-oxidizing bacterium (*Thiobacillus ferrooxidans*). 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. thermoautotrophicus*, as well as its cell-free supernatant, incubated with Ni-containing silicate glass increases the rate of nickel release to solution as compared to abiotic dissolution. The enhanced nickel release in the presence of *M. thermoautotrophicus* appears to be achieved by changes in solution pH. Extraction of Mo from a silicate mineral analogue is accelerated by a high-affinity ligand (a possible “molybdophore”) secreted by a nitrogen-fixing soil bacterium when Mo-limited. 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 soluble P released 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. Anaerobic incubation of the Fe oxide mineral goethite with iron-reducing *Shewanella putrefaciens* results in isotopically light Fe(II) remaining in solution relative to the goethite. Fe(II) sorbed onto goethite is isotopically heavy relative to the mineral, demonstrating the importance of adsorption in fractionation processes. The iron-oxidizer *Thiobacillus ferrooxidans* was shown to influence copper isotopic fractionation during the dissolution of the copper-sulfide mineral chalcocite. Although many bioessential elements are found in low concentrations in rocks, soils, and seawater, microbially enhanced extraction of these trace elements remains poorly understood.

PENNSYLVANIA STATE UNIVERSITY

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

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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. This stress- and chemistry-mediated evolution in fracture porosity, and related permeability, is followed by lumped parameter models representing mineral dissolution, transport, and re-precipitation in hydraulically open and closed systems.

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.

PRINCETON UNIVERSITY

Department of Geosciences

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

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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.

In our functional group analysis of naturally occurring organic molecules, we found a significant fraction of organohalogens associated with humic substances and in the senescent and decaying plant material. In the last year we focused our investigation on identifying the biogeochemical processes involved in the formation of organohalogens in decaying plant material. Using the haloperoxidase enzymes common in soils we could convert Cl^- present in plant leaves to organochlorines, and these reactions depended on the enzyme concentration, temperature, and pH. We are exploring whether similar reactions occur in nature at rapid rates. Further we are trying to conduct detailed speciation of organohalogens associated with decaying plant material using electrospray ionization Fourier-transform ion cyclotron resonance mass spectrometry. Preliminary studies indicate that the aromatic organochlorines, which we identified using X-ray absorption spectroscopy, are present in the form of polychlorinated flavonoids. We are also finding significant concentrations of long chain aliphatic chlorinated compounds. A field station is built in Pine Barrens and in Princeton University campus (under construction) to evaluate the rates of formation and the stability of natural organohalogens in the environment.

Like organochlorines, we are also finding organobromines at high concentrations in soils, estuarine and marine sediments, and suspended particulate matter in ocean waters. The concentration of organobromines correlates directly with organic carbon in sediments. Although such a correlation was found earlier from bulk Br measurements, the speciation of Br was not conducted before. These data sets suggest that halogenation of organic molecules may play an important role in the preservation of carbon in soils and sediments.

PURDUE UNIVERSITY

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

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The objective of this research is to investigate the effects of time-varying length-scales on seismic wave propagation through fractured rock. The principal focus will be on experimentally linking the frequency-dependent seismic properties of fractures with their intrinsic hydraulic scale, with the ultimate goal of predicting hydraulic behavior based on seismic characterization and scaling this relationship from the laboratory scale towards the field scale.

An acoustic imaging system outfitted with acoustic lenses was developed to study the effect of fracture heterogeneity on the spatial distribution of seismic energy, velocity anisotropy and energy partitioning on local and global scales. After five generations of acoustic lens design, we have developed a set of acoustic lens that enable us to change the size of region sampled by a factor of four. The system has been designed and developed to perform scaling measurements as well as to perform Fourier Imaging of single fracture. This system will enable the investigation of the effect of measurement-scale on seismic determination of fracture properties.

Work was also performed to develop photolithographic techniques to construct synthetic fractures with a known fracture geometry that is controlled over several orders of magnitude in length scale. These samples will be used in conjunction with the acoustic imaging system to examine the role of length scales involved in fracture geometry on seismic interpretation. The samples are made from acrylic with a thin layer of photoresist (which contains the fracture void geometry) to enable direct visualization of alteration of fracture void geometry and fluid phase distribution within the void geometry. The work involved in sample development included the adaptation of the photolithographic method from the micro-model scale previously used (600 microns) to the current sample size of 150 mm. A transparent sample confinement cell was also designed and fabricated that is used to change the normal stress on the fracture. The confinement cell is transparent to enable the acquisition of digital images of the fracture plane.

Future work will be performed with the new samples and acoustic imaging system to make measurements of the local and global hydraulic and seismic parameters for fracture samples.

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Transport Properties of Fluid-Bearing Rocks

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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) and can be broadly categorized into three related efforts: (1) the effect on permeability when pores are surrounded by faceted crystal faces; (2) constraining the transport rates and morphology of carbon along grain boundaries; (3) measuring the 3-D geometry of individual pores by atomic force microscopy (AFM).

Many naturally occurring materials exhibit pores bounded by rational faces (facets) instead of the curved surfaces predicted in theoretical treatments and exhibited in rocks like quartzite. Recent analyses of materials exhibiting variable degrees of faceting, from moderately faceted quartzite to highly faceted amphibolite, show that permeability is significantly affected only when pore walls are highly faceted. Highly faceted pores remain disconnected at low fluid fractions, much like pores with high dihedral angles.

The transport and morphology of elemental carbon along grain boundaries may significantly affect electrical conductivity of Earth materials. All experiments indicate that diffusion of carbon along grain boundaries is sluggish; movement may be accelerated only when grains coarsen (e.g. through diffusion of silica). The results suggest that films may only exist provided that the carbon is produced as a film from another C-bearing phase, and that the grain boundaries are stable. Grain boundary migration causes isolation of discrete grains of carbon that are connected only at high volume fractions.

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

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

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

Results: In saturated sand, the resistance at all electrodes was similar and low. 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, after the sand had drained, it produced a large resistance decrease at the nearby electrodes within two minutes. In all studies, the quadrature voltages were not proportional to the real voltages, so capacitive effects were observed which provided more information than resistance alone. Furthermore, the sand bed exhibited hysteresis, and did not behave in the same way when being saturated as when being drained. We have extended an interpretation originally proposed by Knight et al. who studied sandstone, to model these hysteresis data at the scale of pores among sand grains.

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

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An experimental investigation of miscible displacements at constant volume flow-rate under the coupled effects of mobility contrast and gravity over-ride has been performed in a Hele-Shaw cell. The main variable was the Gravity number, G , a measure of the relative importance of gravitational to viscous forces. Properties such as interfacial length and injected area as functions of time and G were recorded. Viscous fingering was enhanced by the distortion generated by the effect of gravity. Independently of the Gravity number, and Peclet number (Pe) the area grew linearly in time. The calculated thickness of the injected fluid was found to be almost constant at a value of 0.5~0.58 with only a weak dependence on Peclet number (Pe). The displacement efficiency and breakthrough time decreased with increase of G , while the longitudinal finger growth rate increased with increasing G . To further simulate the effect of a porous medium tests have been performed in a single layer of regularly packed spheres between parallel plates. Porosity and hydraulic conductivity (permeability) of the porous medium were measured. Properties such as interfacial length and injected area as functions of time, Peclet number, mobility number (M) and Gravity number were recorded. The evolution of the interfacial length, transversely averaged finger length, the displacement efficiency, breakthrough time and the longitudinal finger growth rate had similar characteristics as those of the Hele Shaw cases. The fraction volume of the displacing fluid m (or FD , the ratio of the displacing fluid volume to the pore space) was again used as a diagnostic tool. In this case too the area grew linearly in time so that m was constant in any one experiment. However it was found that this fraction m was not almost constant as it was for the Hele Shaw cell but dependent on G , M and Pe , ranging in value from 0.15 to 0.78 depending on the parameter combinations considered.

STANFORD UNIVERSITY

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

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

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

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Geochemical Controls on Nuclear Magnetic Resonance Measurements

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Proton nuclear magnetic resonance (NMR) has the potential to provide a wealth of information about the physical, chemical, and biological properties of geological materials. The goal of our research is to advance the fundamental understanding of the link between the NMR response and the geochemical properties of geological materials. While it is well established that the presence of iron is a dominant factor in determining the NMR response of rocks and soils, we lack an understanding of the effects of the specific mineralogic form of the iron and the distribution of the iron on NMR relaxation mechanisms. In addition the current models of NMR relaxation times in porous materials greatly oversimplify both the geometry of the pore system and the related interaction between the water protons and the paramagnetic iron.

We are conducting a three-year laboratory-based study of NMR relaxation time measurements in water-saturated porous materials where sample composition, pore structure and geochemical conditions are carefully controlled or determined. NMR samples are prepared by coating pure quartz sand with minerals containing both Fe(III) and Fe(II). The surface area and porosity of each sample is determined, and the distribution of the iron-bearing mineral examined using scanning electron microscopy. We measure the NMR time constants T1 and T2 of samples at chemical equilibrium and as the chemistry of the system changes due to changing redox conditions and ongoing biological activity. We are working initially with systems that can be described as spatially homogeneous and will then investigate the role of pore-scale variability in geochemical properties in determining NMR relaxation times.

Central to this research is the recent completion of a new Environmental Geophysics Laboratory in Earth Sciences at Stanford University and the acquisition of a Maran Ultra NMR core analyzer. The Maran allows us to acquire low frequency measurements of NMR relaxation times, and to modify the internal magnetic field. With these new laboratory facilities, we can undertake an extensive experimental and theoretical study of the fundamental geochemical controls on the NMR response of geological materials.

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Porous Reservoir Rocks with Fluid: Seismic and Transport Properties

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The goals of our research are to model rock physical properties in general and properties of sediments with gas hydrates and high pore pressure specifically.

1. Modeling rock properties: We discovered that the relative permeability of the non-wetting phase increases with pore pressure gradient. This increase strongly depends on the details of pore geometry. The relative permeability also exhibits a non-linear dependence on pressure gradient, surface tension and wettability. Because numerical flow simulations for two-phase fluid flow are very time consuming even with modern parallel computing power we have implemented several new optimization schemes customized for the Lattice-Boltzmann algorithm. Implementing these schemes, we were able to achieve a X12 speedup of with 14 processors, while non-optimized code gave only a factor of 4. Parallel implementations allow us to perform both single-phase and two-phase flow simulations with much greater efficiency.
2. Gas hydrates: Effective elastic medium models were developed which place the hydrate in the sediment as a pore fluid component, a load bearing sediment frame component or as an elastic cement at grain contacts. The models were used to analyze data from hydrate bearing onshore sands in the NW Canada Eileen region and hydrate-bearing ocean bottom sediments from offshore of the southeastern United States (ODP 995). The results show methane hydrate does not act as a grain contact cement at NW Eileen. In contrast for ODP 995 the modeling results show that methane hydrate acts as contact cement. The results also suggest that a large volume of methane gas may be trapped in the sediments beneath the gas hydrate-containing interval at site 995.
3. Over pressure prediction: We measured compressional and shear wave velocities and porosity of sediments at low pressures. We found the velocities to vary with the fourth root of the effective pressure and that water saturated wave velocities and V_p/V_s ratio show large porosity dependence. A power law fit was used to describe the normalized porosity reduction that is roughly proportional to the effective pressure to the two-thirds.

STANFORD UNIVERSITY

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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 due to structural heterogeneities in sandstone aquifers and reservoirs. The integrated research plan includes mapping, characterization, and numerical modeling of structural heterogeneities (sheared, compactive and dilatant deformation bands, joints, sheared joints, and fault zones) in the Aztec sandstone, at the Valley of Fire, Nevada, to understand their effects on groundwater and hydrocarbon flow in this analog aquifer/reservoir. The project is divided into three subprojects.

(1) Paleo-hydrologic and geochemical fieldwork have revealed two alteration and paleo-fluid flow events: the earlier (with hematite the dominant product) is correlated with the emplacement of Cretaceous Sevier thrusts; the later (with goethite the dominant product) is largely synchronous with Tertiary strike-slip faulting. It is inferred that the earlier event resulted from expulsion of reducing basinal fluids, whereas the later event is associated with the migration of meteoric fluids.

(2) Upscaling based on field data and fluid flow modeling show that fault rock permeability is 1 to 3 orders of magnitude less, and breakthrough pressures are 1 to 2 orders greater than the median host rock permeability and capillary pressure. Calculated maximum sealable hydrocarbon column heights, using standard fluid properties, range between 10 to 69 m of gas, and 17 to 120 m of oil. We conclude that faults formed by shearing of joints in high permeability sandstone systems can act as barriers to flow during reservoir production and might be capable of sealing moderate hydrocarbon columns on an exploration time scale.

(3) Mapping compaction bands at the kilometer scale and detailed microscopic examination are underway to characterize their patterns and to investigate their impact on fluid flow. Numerical models of systematic arrays of compaction bands demonstrate that these structures reduce permeability by 1 to 2 orders of magnitude at scales relevant to reservoir production, while inducing similar magnitudes of permeability anisotropy. To understand how these structures initiate and propagate preliminary laboratory experiments were completed in collaboration with scientists at Sandia National Laboratories, the University of Wisconsin, and the U.S. Geological Survey.

STANFORD UNIVERSITY

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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 especially 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.

TEMPLE UNIVERSITY

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Grant: DE-FG02-96ER14644

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).

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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 Kr-85 standards, (3) measure Kr-85 in samples from a hydrogeologically simple aquifer, and (4) apply Kr-85 to measure recharge to 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 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. This technique will permit Kr-81 or Kr-85 measurements from 10 or 2 liter water samples.

Results: During FY2003, work focused on steps 1, 2, 3, 5 and 6.

Sample collection (step 1) was completed from the Memphis Sand aquifer from both confined and unconfined regions for Kr-85 analysis. Water was also collected from very deep (500 to 900 meters) boreholes at a proposed French hazardous waste disposal site for Kr-81.

The degassing system (step 2) was rebuilt to repair leaks due to stress corrosion, and operation was modified to prevent a recurrence. Many test samples and 8 groundwater samples were processed

A CO₂ trap was added to the Kr separation system (step 3). Kr recovery for steps 1-3 is greater than 95%, while the blank is below 0.1%.

The Second Enrichment System's (step 5) heated (operating at 325 C) quadrupole filter assembly eliminated memory effects. An RF amplifier is being installed to enable operation at higher frequencies to improve transmission, thereby reducing sample loss due to implantation into the poles.

Replacement of the third dye laser in step 6 solved a serious wavelength instability problem that should significantly improve reproducibility and dynamic range.

TEXAS A&M UNIVERSITY

Texas Engineering Experiment Station
College Station TX

Grant: DE-FG02-00ER15033

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

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Sequestration of carbon dioxide in depleted gas reservoirs appears to be a viable option, with a possible economic spin-off from the recovery of significant gas reserves. Little is known regarding the kinetics of calcite dissolution, diffusion of carbon dioxide in natural gas, and displacement of natural gas by carbon dioxide under conditions to be encountered in these reservoirs. This project is conducting research to better understand these phenomena through experimental determination of the reaction kinetics for calcite dissolution, coefficient of dispersion, and displacement mechanisms in respect to supercritical carbon dioxide at temperatures and pressures typically found in reservoirs. The requisite data will be used to develop a model for mass transport and reaction kinetics for the injection and storage of carbon dioxide in carbonate or carbonate-bearing depleted gas reservoirs. Calcite dissolution rates at 1 atm under high pCO₂ have been obtained in various synthetic brines containing geologically relevant concentrations of calcium and magnesium. Rates exhibit near first-order kinetics and are largely independent of brine concentration ($n = 1.4 \pm 0.2$, $k = 0.05 \pm 0.007$ moles/m²/hr). The interpreted fitting parameters were found to be highly sensitive to errors in calculated saturation state. Current models do not adequately predict the equilibrium calcium and carbonate ion activities under these conditions. Discrepancies between the predicted and observed values were strongly correlated with increasing calcium activity. An empirical correction factor to the carbonate ion activity coefficient was derived to correct for this error. A series of gas displacement experiments (20°C to 80°C and 500 psig to 3000 psig) yielded CO₂ dispersion coefficients from 0.01 to 0.3 cm²/min. Methane recovery at carbon dioxide breakthrough is 73 % to 87 % of initial volume. 3D simulation models of one eighth of a 5-spot pattern were constructed to evaluate injection of supercritical CO₂ under typical field conditions. Results indicate a large amount of CO₂ is sequestered: about 1.2 million tons in 29 years (40-acre pattern), and 4.8 million tons in 56 years (80-acre pattern). Also, a significant amount of natural gas is produced: about 1.3 BSCF or 74% OGIP (40-acre pattern), and 4.9 BSCF or 68% OGIP (80-acre pattern).

TEXAS A&M UNIVERSITY

Texas Engineering Experiment Station
College Station TX

Grant: DE-FG02-00ER15034

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

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The goal of this project is to assess the feasibility of time-lapse seismic monitoring of CO₂ sequestration using coupled fluid flow and seismic modeling in fractured reservoirs. Concurrently we want to develop a formalism for the assimilation of static and dynamic data sources in the reservoir and quantification of uncertainty in performance predictions of CO₂ sequestration, particularly for fractured hydrocarbon reservoirs. During the first year, we focused on the development of a set of numerical modeling codes that allow us to simulate both fluid flow (CO₂) and seismic wave propagation in fractured reservoirs. Our goal is to couple the codes to quantify the changes in seismic reflections that might be observed in realistic applications of CO₂ sequestration in fractured reservoirs. For rapid simulation of CO₂ injection into fractured reservoirs, we generalized the streamline-based flow simulation methods to naturally fractured reservoirs using a dual-media approach. Using streamline time of flight as a spatial variable, we developed a general dual porosity dual permeability system of equations for saturation calculations in naturally fractured reservoirs. An examination of the scaling behavior of the computation time indicates that the streamline approach can be up to two orders of magnitude faster for large-scale field applications. We have also continued our investigation of published theoretical solutions for the effective elastic properties of fractured media, both isotropic and anisotropic. In particular, we have looked at the variation in attenuation of seismic waves with phase velocity direction for several fracture-filling fluids. The results for CO₂ apply to the bulk modulus and density of two different phases of CO₂ (liquid and supercritical) that could be encountered in the subsurface. There is clearly a suggestion that different attenuation may result from different phases of CO₂. The development of processing techniques to accurately measure attenuation could help identify movements of CO₂ as well as to characterize its *in situ* properties. These theoretical results will provide important inputs for viscoelastic finite difference modeling using codes recently installed by a visiting scientist supported by DOE on this project.

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Grant: DE-FG02-03ER15430

Predicting Fracture Porosity Evolution in Sandstone

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The goal of this research is to develop an understanding of how fracture growth and diagenetic alteration interact to systematically create and destroy fracture porosity. Our initial objective will be to study a key link between mechanical and chemical processes in opening fractures. Specifically, a new theory of quartz cementation postulates that the rate-limiting step for quartz cementation is precipitation, with supply and transport being of secondary importance. We are testing the hypotheses that this cementation process governs evolution of (1) fracture porosity and (2) fracture growth velocity (the subcritical crack index), which, in turn, controls many aspects of fracture pattern development. Despite the important influence of fracture systems on fluid flow, our understanding of the properties of these systems and how they evolve in sedimentary basins is exceedingly meager, owing in part to formidable challenges in collecting meaningful samples of fracture patterns. A practical benefit of our fundamental research is that it will lead to predictions of linked structural and diagenetic attributes, therefore potentially increasing the range of samples that provide meaningful fracture information. High temperatures and reactive fluids in sedimentary basins dictate that interplay and feedback between mechanical and geochemical processes could significantly influence evolving rock and fracture properties. We are studying mechanical and diagenetic feedback loops using new models of cementation, improved measurement methods of key mechanical properties, advanced fracture-mechanics-based fracture growth modeling, and high-resolution cement and microstructure quantification. This cross-disciplinary research will result in a fundamental advance in our understanding of how the diversity of natural fracture patterns evolves and better predictions of fracture pattern attributes in the subsurface where sparse sampling is the rule.

UNIVERSITY OF TEXAS AT DALLAS

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Grant: DE-FG02-01ER15166

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

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The sandstones of the Frontier Formation in the Powder River basin have been variably interpreted as being deposited as offshore bars, storm deposited prodelta sand sheets, and wave-dominated deltas. Regionally, these sandstones show a mixture of different upward coarsening facies successions associated with distinctly different overlapping sandstone bodies separated by mudstones. These are interpreted as different delta lobes. Paralic and non-marine facies are absent, reflecting high degrees of top-truncation, likely caused by the generally low-accommodation and basin-distal setting.

Several scales of facies variability within these sandstones are relevant to subsurface production issues. Variability of different sand bodies with length scales of several kilometers to tens of kilometers represents large-scale reservoir compartments. These compartments show varying internal reservoir heterogeneity, depending on the proportion of river-, tide- and wave-influence within lobes.

The Wall Creek member of the Frontier Formation, is the focus of an intense 3D reservoir characterization study at the Raptor Ridge locality. Here, two 2D and two 3D GPR surveys were acquired. 10 cores were drilled within the surveys, and analyzed for porosity and permeability (mini perm, routine plug, and pulse decay). The outcrops and GPR volumes show shallow, sub-tidal fluviially-derived channelized units alternating with mud-draped tidally-reworked bar deposits within an overall upward-coarsening unit that exhibits larger-scale, southward dipping clinofolds. This suggests both river and tide influence in a prograding delta lobe. The sandstone has been mapped as lobate-shaped and passes into more bioturbated and wave-dominated facies to the northeast. There is distinct along-strike facies variability, which relates to longshore drift orientation and the position and spacing of rivers.

Much of our focus has been on 3D characterization of calcite cements. These cements form as distinct and partly interconnected nodular layers that result in up to 15% volume reduction of net porous sandstone. Petrographic and geochemical data suggest that the nodules are long-lived with the major growth phase occurring between 400 to 800 m burial depths.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Department of Geosciences

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Contract: DE-FG02-00ER15112

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

Department of Geosciences
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Contract: DE-FG02-02ER15326

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

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In this second phase of research, which is a collaboration between the Ohio State University (Dr. Steven Lower) and Virginia Tech (Dr. Michael Hochella, Jr.), we used force microscopy to measure inter- and intra-molecular forces between inorganic solids (e.g., silica and goethite) and two different Gram-negative microorganisms (*Escherichia coli* and *Shewanella oneidensis*). The measured forces were compared to theoretical models that describe van der Waals, electrostatic, and steric forces between a bacterium and mineral. Different force classes were found to dominate each of the two bacterium-goethite pairs. Overall, *S. oneidensis* exhibited a preferential affinity towards goethite relative to *E. coli*. We hypothesized that this preferential affinity was due to the production of outer membrane proteins by *S. oneidensis*. Therefore, we measured forces between a mineral and a bacterium that had been genetically modified to produce a fluorescently tagged protein. Simultaneous force microscopy and confocal laser scanning microscopy measurements suggested that outer membrane proteins can indeed form a bond between a Gram negative microorganism and an inorganic surface.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

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Contract: DE-FG02-03ER15389

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

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Oxygen, silicon, and aluminum are the most abundant elements in the earth's crust. Of the bonds that oxygen forms, ~85% involve either Si or Al. The objective of this project is to understand, at the atomic level, the reactivity of a wide range of reagents with the SiOSi and SiOAl bonded interactions that comprise the building blocks of silicate minerals. We will undertake ab initio periodic and molecular orbital calculations to generate electron density distributions for the reagents and silicate structures. The Laplacian of the electron density distribution, provides a unique opportunity to establish an electron density model of reactivity. By evaluating the critical point properties of the Laplacian of the electron density distribution, a spatial mapping of sites of potential electrophilic and nucleophilic attack at the surfaces and in the bulk of important silicate minerals will be identified for the first time, providing mechanistic insight into how Lewis acids mount electrophilic attacks and how Lewis bases mount nucleophilic attacks on specific SiOSi and SiOAl bonds. These results will be tested using high-resolution rate measurements, an approach that has proven to be highly successful in organic and inorganic chemistry. This research will investigate the reactivity of Lewis acids (electrophilic reagents) like H_3O^+ , H_3O_2^+ and NH_4^+ and Lewis bases (nucleophilic reagents) like OH^- , F^- , AlO_4^- , H_3SiO_4^- , $\bullet\text{OH}^-$, and OCH_3^- with SiOSi and SiOAl bonded interactions. In addition, we will consider the reactivity of substances that can act as both Lewis acids and bases simultaneously (e.g. H_2O , H_2O_2 , HF , HF_2^- , and CH_3OH). Our results will explain why some of these reagents react vigorously while others will not react at all, based on detailed analyses of the properties of the electron density distributions at mineral surfaces. This project not only aims to develop a general understanding of which reagents will react with bonded interactions in silicates but also to establish mechanisms for how the reactions might proceed. With this information we will attempt to formulate a theory of chemical reactivity based on the properties of the electron density distributions of both molecular reagents and surfaces of silicate crystals.

UNIVERSITY OF WISCONSIN

Department of Geology and Geophysics
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Grant: DE-FG02-93ER14389

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 we have contoured $\delta^{18}\text{O}$ 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 2 Ma. 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 or zircon) of 0.1 to 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. The first Cameca 1280 ion probe has been ordered and will be delivered to the University of Wisconsin in December 2004. It will be dedicated to stable isotope chemistry. Drs. Noriko Kita and Bin Fu have been hired to work with this instrument, which will be used in future studies of isotopic zonation in minerals such as zircon, carbonates, and quartz.

UNIVERSITY OF WISCONSIN

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Grant: DE-FG02-03ER14995

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

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This research is emphasizing the use of recently developed 3D time domain forward and inverse modeling algorithms to analyze the grounded-electric-source transient electromagnetic (GESTEM) method for subsurface imaging. This method offers a benefit over other surface EM methods in that it produces vertical currents in the subsurface which makes it more sensitive to resistors such as oil reservoirs and injected CO₂. To better understand the fundamental physics of the GESTEM method we started with a homogenous earth model, and plotted the current distribution versus time for both grounded electric and inductive loop sources. Decomposing and plotting the diffusing wavefield in terms of horizontal and vertical components indicates that the total-current maximum a) exists directly below the source at all times, b) is composed of currents that are entirely horizontal, and c) diffuses downward more slowly than that produced by a loop source. The fact that the maximum is near to the surface at all times causes ‘static shifts’ in GESTEM data which make simple interpretation difficult. However, while the maximum horizontal component is forced to exist near the surface, the maximum of the vertical component migrates downward at 45 degrees to the surface, thus allowing it to reach greater depths at earlier times than the horizontal components produced both by the grounded electric and inductive loop source.

We next complicated the model somewhat to include conductive and resistive layers in an otherwise homogenous $\frac{1}{2}$ space. The work has shown that measuring either the magnetic field or its time derivative will detect a conductive layer at depth, but is fairly insensitive to a resistive layer. The lack of resolution of resistive layers is due to the fact that a vertical current source within the earth does not produce magnetic fields at the surface. However, the horizontal electric field at the surface is sensitive to both resistors and conductors due to charge build up at the layer interface. Thus magnetic field measurements at the surface will only be sensitive to perturbations in the horizontal currents, while the electric fields will respond to both variations in both the horizontal and vertical currents.

UNIVERSITY OF WISCONSIN

Department of Civil and Environmental Engineering
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Grant: DE-FG02-98ER14850

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

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During 2003 we concentrated our borehole breakout research on two high porosity (26-28%) sandstones (Mansfield and Tablerock). Tablerock sandstone is composed of 55% quartz and 37% weaker feldspar grains. Grain cementation is substantial through microcrystalline quartz. Critical far-field stresses induced failure around boreholes in the form of V-shaped (dog-eared) breakouts, the result of dilatant intra-and trans-granular microcracking subparallel to both the maximum horizontal far-field stress and to the borehole wall. On the other hand, boreholes in Mansfield sandstone, which contains mainly quartz grains (90%) held together primarily by spot-sutured contacts, failed by developing fracture-like breakouts. These are long and very narrow (several grain diameters) tabular failure zones perpendicular to the maximum stress. Evidence provided mainly by SEM observations suggests a failure process initiated by localized grain-bond loosening along the least horizontal far-field stress springline, the packing of these grains into a lower porosity compaction band resembling those discovered in Navajo and Aztec sandstones, and the emptying of the loosened grains by the circulating drilling fluid starting from the borehole wall. Although the immediate several grain layers at the breakout tip often contain some cracked or even crushed grains, the failure mechanism enabled by the formation of the compaction band is largely non-dilatant, a major departure from the dilatant mechanism observed in Tablerock sandstone. The experimental results suggest that unlike our previous assertion, the strength of grain bonding and the mineral composition, rather than the porosity, are major factors in the formation of compaction bands and the ensuing fracture-like breakouts. Some breakout dimensions in both rocks are correlatable to the far-field principal stresses, and can potentially be used (in conjunction with other information) as indicators of their magnitudes.

WOODS HOLE OCEANOGRAPHIC INSTITUTION

Department of Geology and Geophysics
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Grant: DE-FG02-00ER15058

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

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A fundamental understanding of the effect of stress on permeability is of importance in many fault mechanics and reservoir engineering problems. Recent laboratory measurements demonstrate that in the cataclastic flow regime, the stress-induced anisotropic permeability reduction in porous rocks can be separated into 3 different stages. The onset of shear-enhanced compaction marks the transition from stage I to stage II. Before the shear-enhanced compaction, permeability and porosity reduction in stage I are solely controlled by the effective mean stress, with negligible permeability anisotropy. Stage II starts at the onset of shear-enhanced compaction, when a critical yield stress is attained. In stage II, the deviatoric stress exerts primary control over permeability and porosity evolution. The increase in deviatoric stress results in drastic permeability and porosity reduction and considerable permeability anisotropy. A transition from stage II to stage III takes place progressively during the development of pervasive cataclastic flow. In stage III permeability and porosity reduction becomes gradual again, and permeability anisotropy diminishes. Microstructural observation on deformed samples using laser confocal microscopy reveals that stress-induced microcracking and pore collapse are the primary forms of damage during cataclastic flow. Motivated by these observations, we formulate a cumulative damage model to characterize the effect of stress on permeability and its anisotropic behavior. In our model, the effects of effective mean stress and differential stress on permeability evolution are decoupled. By introducing stress sensitivity coefficients in our model, we propose a first-order description of the dependence of permeability evolution on different loading paths. This unified model provides a quantitative measure on stress induced permeability anisotropy, and thus helps us gain new insights into the coupling of stress and permeability.

WOODS HOLE OCEANOGRAPHIC INSTITUTION

Department of Marine Chemistry and Geochemistry

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Grant: DE-FG02-97ER14746

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

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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 INSTITUTION

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Grant: DE-FG02-86ER13466

Organic Geochemistry of Continental Margin and Deep Ocean Sediments

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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 particular long term interest has been to better understand the role of migrating gas in these reservoirs. Past research, in collaboration with scientists at Cornell, Louisiana State University and Texas A&M, has shown that the oil gas system throughout a 200 mile north to south transect across the northern Gulf of Mexico continental shelf and slope has been very dynamic with as much as 30 volumes of gas having passed through and altered oils to the north of the transect. Modeling together with our previous geochemical data shows the source, maturity, and the degree of alteration of these oils and also that the reservoirs have only recently been charged. Furthermore, the Cornell modeling results suggest that earlier oil which entered these reservoirs was probably very efficiently flushed upward and out into the overlying water column. The total volume of gas which has been involved in gas washing decreases in moving southward along our transect so that oils in the southern-most Green Canyon wells show little or no alteration attributable to gas washing. Work this year has been focused on the best way to utilize a new technique, GCxGC, as a powerful visual correlation tool, for showing changes in all the important diagnostic compounds and the processes affecting them in a single oil at one time. Results so far show the close relationship between reservoir and biodegraded seep oils in the Gulf of Mexico Green Canyon area. For the Gulf of Mexico transect oils, the new GCxGC results compare favorably with more labor intensive and less intuitively obvious ion extraction fragmentogram procedures used previously.

WRIGHT STATE UNIVERSITY

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Grant: DE-FG02-03ER15379

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

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This project has focused on experimental investigations on the nanoscale chemistry and dynamics of carbonate mineral surfaces exposed to aqueous solutions. The kinetics of dissolution and growth of magnesite (MgCO₃), calcite (CaCO₃) and dolomite CaMg(CO₃)₂ from elementary step edges have been studied with *in-situ* hydrothermal Atomic Force Microscopy (AFM), revealing atomic level information on the interaction of inorganic and organic ions with specific sites on reacting surfaces. The kinetics of step edge dissolution in magnesite and dolomite were highly non-linear versus solution pH and saturation state; key evidence for large differences between cation and anion dynamics at these mineral-water interfaces. The work provides key kinetic parameters necessary to extend dissolution and growth kinetic data to non-stoichiometric solutions – conditions that are more the rule than the exception in CO₂ sequestration scenarios involving deep aquifers as well in most natural waters. Mineral growth research of carbonates provided further insight into the mineralization process at the nanometer scale through Lateral Force Microscopy (LFM). LFM revealed qualitative differences in the structure and/or composition of surface grown layers on existing dolomite and calcite substrates. The differences are attributed to differences in interfacial free energies between the native substrate-water interface and the grown layer-water interface. The free energy associated with the interface between a carbonate surface and supersaturated aqueous solution is influenced by excess interfacial strain energy that was in turn influenced by solution composition. X-ray Photoelectron Spectroscopy (XPS) investigations led to the conclusion that carbonate mineralization from even moderately oversaturated solutions often leads to highly defective and compositionally heterogeneous solid phases. Subsequent kinetic studies of the dolomite-water interface led to additional conclusions related to low-temperature formation of dolomite. These studies demonstrated that near equilibrium, dolomite growth is both thermodynamically and kinetically favored, but that as solution concentrations rise, formation of more calcium-rich solid phases become kinetically favored even in the presence of dolomite seed crystals. The presence of sedimentary dolomite may therefore be intimately linked to natural water saturation state at the time of mineralization.

UNIVERSITY OF WYOMING

Department of Geology and Geophysics
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Grant: DE-FG02-03ER14623

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

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Our work is progressing on several fronts. The first emphasis area recognizes the potential chemical complexities of simultaneous growth and precipitation of carbonate minerals of different composition. The second emphasis area deals with the dissolution of refractory minerals that could provide cations for precipitation of carbonates in a sequestration context. We have followed earlier work on Sr carbonate precipitation on dissolving calcite with similar work on the precipitation of cobaltcalcite on dissolving calcite. In both cases, precipitates form from solutions of varying Sr/Ca or Co/Ca ratios once supersaturation has been reached. We have observed precipitation in our patented hydrothermal atomic force microscope under elevated temperature conditions, and developed protocols for predicting the composition of the precipitate in mixed solutions. The dissolution rate of calcite decreases as the cobalt concentration increases. Changes in flux can be caused by changes in step velocity or step density, or both. In our case, step velocity is the main reason for change in dissolution flux; step density changes little. The morphology of etch pits changes in response to changes in cobalt concentration, providing hints as to the key reactive sites on the mineral surface. On a second research front, we have investigated the effects of pH-jumps (from near-neutral to 1) on hematite dissolution in the hydrothermal atomic force microscope at 125C. Dissolution does not appear to take place via step retreat, but through a much more complex set of processes. Studies are on-going to confirm the temperature dependence of hematite dissolution rate in order to constrain the amount of step motion that would be expected under these conditions. Even with reasonable, however, the lack of step motion over 11 hours requires that hematite dissolve substantially from parts of the surface other than the steps. This suggests that there are dissolution modes in operation that are not very well known. We have observed that pH oscillation can produce dissolution rates that are 2 or 3 times higher than under fixed pH conditions, a finding that may be of use in accelerating important carbon sequestration reactions.

YALE UNIVERSITY

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

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During the year October 2002 to September 2003 we focused on four 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. This has consisted of experiments at Sheffield University on growing plants under varying O₂/CO₂ ratios by David Beerling (Sheffield) and Dana Royer (Yale) 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.
2. Burning experiments were initiated to test the role of varying O₂ on the intensity and spread of fires. This work was done at the fire labs at Ohio State University by Richard Wildman from Yale. Wildman did thermogravimetric analysis on the ignition of various natural forest fuels (leaves, bark, grass, peat, etc) as a function of O₂ concentration. He also followed 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%). Results 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.
3. Critical parameters were measured on the black shale that we are studying in terms of 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, and sulfur and their changes with depth.
4. Long reviews were written and published on the role of plants in silicate weathering and on Phanerozoic atmospheric oxygen. In addition, two papers dealing with carbon cycle modeling at important species extinction boundaries were published, along with two papers, based on earlier DOE-sponsored research on plants and weathering.

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

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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:

Modeling of kinetically controlled metamorphic reactions in siliceous carbonate rocks in two dimensions elucidates the role of kinetics in the flow and reaction pathways. Trace element modeling indicates significant kinetic effects even for high-temperature metamorphic to igneous sequences. Field-based kinetic studies reveal morphological variations in metamorphic garnets that indicate substantial deviations from chemical equilibrium during mineral nucleation and growth. A review of flow and reaction in the deep crust integrates fundamental concepts including flow laws, porosity, permeability, reaction kinetics, and mass transport mechanisms, with a synthesis of flow regimes from field examples. Field and modeling studies of metamorphosed carbonate rocks, Connecticut, show that crustal fluids mobilize a wide variety of elements, including the rare earths. In these rocks, lithologic contacts and fractures were primary flow conduits, consistent with field-modeling results for the subduction complex on Tinos, Greece. Oxygen and carbon isotopic data from shallow-crustal rocks of the Conasauga Group indicate that fluid flow was largely confined to fractures and stratigraphic boundaries in limestones, but was pervasive in shales, illustrating how the flow regime is critically dependent on rock type. Modeling of weathering and erosion of black shales examines the feedback between atmospheric oxygen levels and oxidation of organic matter and pyrite. *Ab initio* calculations examine oxygen and hydrogen isotope exchange between water and orthosilicic acid.

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

ON-SITE INSTITUTION	FY99	FY00	FY01	FY02	FY03
Argonne National Laboratory	740	438	552	530	445
Brookhaven National Laboratory	595	870			
Los Alamos National Laboratory	1260	1235	1235	1189	1353
Lawrence Berkeley National Laboratory	2160	2332	2367	2570	2045
Lawrence Livermore National Laboratory	1445	1736	1784	1644	1523
Oak Ridge Institute for Science and Education	110	155	30		
Oak Ridge National Laboratory	1235	1145	1293	1340	1190
Pacific Northwest Laboratory	760	815	727	822	875
Sandia National Laboratory	1635	1324	1367	1470	1355
total, on-site published	9940	10050	9624	9565	8786
total, off-site published	12851	10649	10393	10487	10513
total, operating published	22791	20699	20017	20052	19299
total, equipment	1235	1340	1402	1200	1023
Total GEOSCIENCES-published	24026	22039	21419	21252	20322
OFF-SITE INSTITUTION					
American Museum of NY (Mathez)	87				
Arizona, Univ. of (Harpalani)		10			
Arizona State Univ. (Shock)				225	
Arizona State Univ. (Hervig/Williams)	70		102	105	108
Boston Univ. (Klein)	129	116	122	127	132
Caltech (Stolper)	150	135	150	150	156
Caltech (Wasserburg)	400	325	225		225

Calif., Univ. of Berkeley (Banfield)			178		
Calif., Univ. of Berkeley (Helgeson)	197	190	179	182	164
Calif., Univ. of Berkeley (Nishiizumi)	160	144	144		
Calif., Univ. of Berkeley (Sposito)	73	74	74		
Calif., Univ. of Davis (Rock)			161	163	171
Calif., Univ. of Davis (Navrotsky)	169	160	166	166	198
Calif., Univ. of Davis (Casey)	121	108	72	178	109
Calif., Univ. of Davis (Rundle)					141
Calif., Univ. of Los Angeles (Harrison/McKeegan)	124	126	130	132	135
Calif., Univ. of Santa Barbara (Meiburg)		69		68	66
Calif., Univ. of Santa Barbara (Boles)		70	79	71	78
Calif., Univ. of Santa Barbara (Spera)	92	82			
Calif., Univ. of Santa Cruz (Wu)	267	251	299	308	388
Calif., Univ. of San Diego (Weare)				125	125
Chicago, Univ. of (Sutton/Rivers)	440	475	500	525	550
Chicago, Univ. of (Sutton)	299		148	129	
Chicago, Univ. of (Richter)			96		99
Clark Univ. (Kudrolli)				45	45
Colorado School of Mines (Klusman)		159		161	
Colorado School of Mines (Batzle)					140
Colorado School of Mines (Tsvankin)	240	216	230		239
Colorado, Univ. of (Rajaram)	60	54	54	106	70
Colorado, Univ. of (Rundle)	136	122	130	136	
Colorado, Univ. of (Spetzler)	168		185	153	143
Colorado, Univ. of (Ge)	120	101	94		
Colorado, Univ. of (Nagy)	99	128	62		
Columbia University (Broecker)	130				

Connecticut, Univ. of (Torgersen)	188			27	35
Delaware, Univ. of (Wood)	236		141		138
Florida, Univ. of (Ladd)	70	63	83	111	89
George Washington Univ. (Teng)				143	
Georgia State Univ. (Elliott)				26	21
Georgia Tech (Dove)	145				
Gordon Res. Conf. (Kronenberg, Jessell)				10	
GSY-Inc. (Mackie)			46		
Harvard Univ. (Martin)					85
Hawaii, Univ. of (Martel)		117	108		
Idaho, Univ. of (Nicholl)			36	54	
Idaho, Univ. of (Wood)					10
Illinois, Univ. of (Kirkpatrick)		395		209	233
Illinois, Univ. of (Bethke)				117	214
Illinois, Univ. of Chicago (Sturchio)					59
Illinois, Univ. of Chicago (Nagy)				150	
Indiana, Univ. of (Ortoleva)	124	112	117	120	124
Indiana, Univ. of (Schimmelman)			78	84	119
Institute for Scientific Information (Zamojcin)				10	
Johns Hopkins Univ. (Garven)		77	78	75	89
Johns Hopkins Univ. (Veblen)	110	99	150	155	160
Johns Hopkins Univ. (Sverjensky)	110	100	90	140	140
Kent State Univ. (Maurice)	69				
Lehigh Univ. (Ilton)	115	104	115	115	
Louisiana State Univ. (White)			41		40
Louisiana State Univ. (Dutrow)					9
Maryland, Univ. of (Lower)				20	67

Maryland, Univ. of (Tossell)	48	63	59	63	79
Mass. Inst. Tech. (Harvey)		35	37	38	
Mass. Inst. Tech. (Toksoz)		240	240	240	
Mass. Inst. Tech. (Toksoz)	160	144			
Mass. Inst. Tech. (Evans)	198	185	194	205	209
Mass. Inst. Tech. (Rothman)	134	135	133	152	158
Michigan Tech Univ. (Turpening)			165	11	114
Mineralogical Society of America (Speer)			62	40	30
Minnesota, Univ. of (Yuen)	100	90	90	90	
NAS/NRC (Schiffries/DeSouza)	100	90	90	90	
NAS (Wessner)				114	
Nevada, Univ. of (EPSCOR - McCall)			8	9	6
Nevada, Univ. of (Long)	106	96			
New England Res. (Brown)	372			204	199
New Mexico Inst. Min. Tech. (Wilson)	72	65	65	94	101
New Mexico, Univ. of (Ingber)	80	71	71	71	
NY, City Univ. of CC (Koplik)	99	89	90	95	98
NY, City Univ. of CC (Makse)					85
NY, State Univ. of Stony Brook (Schoonen)	65	60	60	102	65
NY, State Univ. of Stony Brook (Wong)	106	95	95		120
NY, State Univ. of Stony Brook (Lindquist)	95		67	64	64
NY, State Univ. of Stony Brook (Hanson)	164	155			
Northwestern Univ. (Rudnicki)	91	89	88	91	120
Notre Dame, Univ. of (Maurice)		70	70	121	174
Oklahoma, Univ. of (Elmore)	131	127	124	102	103
Oklahoma State Univ. (Nicholl)	40	36			
Oregon State Univ. (Haggerty)		76	68	75	

Oregon State Univ. (Egbert)				80	89
Penn State Univ. (Elsworth)		109		99	98
Penn State Univ. (Brantley)	142	110	147	160	145
Princeton Univ. (Myneni)		102	102	102	
Purdue Univ. (Pyrak-Nolte)	180		85	102	105
Purdue Univ. (Johnson)	238				
Rensselaer Polytech. Inst. (Newell)				44	45
Rensselaer Polytech. Inst. (Watson)	179	161	198	199	199
Rice University (Mango)	213				
San Diego State Univ. (Jiracek)				5	
Smithsonian Institution (Sorensen)		88			
Southern California, Univ. of (Maxworthy)		85		82	84
Stanford Univ. (Brown)	268				
Stanford Univ. (Mavko)	115	104	104	151	149
Stanford Univ. (Borja)					99
Stanford Univ (Knight)					143
Stanford Univ. (Nur)	219	200	200	200	200
Stanford Univ. (Nur)	150	135			
Stanford Univ. (Orr)	136				
Stanford Univ. (Pollard/Aydin)	199	179	260	257	267
Stanford Univ. (Segall)	93	97	100		
Temple Univ. (Strongin)	60	60	60	83	87
Tennessee, Univ. of (Thonnard)			122	129	146
Texas A&M Univ. (Kronenberg)	350			65	
Texas A&M Univ. (Morse)		259		128	130
Texas A&M Univ. (Datta-Gupta)		304		111	130
Texas, Univ. of (Banner)	152				

Texas, Univ. of (Laubach)					196
Texas, Univ. of (Sharp)	59				
Texas, Univ. of Dallas (McMechan/Bhattacharya)	137	124	262		95
Texas Tech Univ. (Graham)	100	90	90	90	9
Utah, Univ. of (Forster)		25	50	50	
Utah, Univ. of (Tripp)	80	73	77		
Utah State Univ. (Hestir)	84				
Utah State Univ. (Evans)	147	85	85	85	
Virginia Tech (Rimstidt)					114
Virginia Tech (Dove)		202		121	126
Virginia Tech (Hochella)	161	159	66	88	
Virginia Tech (Bodnar)	118	108			
Washington, Univ. of (Unsworth/Booker)	205		95		
Washington Univ., St. Louis (Shock)	201		196		
Wisconsin, Univ. of (Alumbaugh)	52	50	52		101
Wisconsin, Univ. of (Alumbaugh)		10			
Wisconsin, Univ. of (Haimson)	127	115	107	110	106
Wisconsin, Univ. of (Valley)	147	336		168	
Wisconsin, Univ. of (Banfield)	114	103			
Wisconsin, Univ. of (Wang)	95				
Woods Hole OI (Whelan)	377		180	197	206
Woods Hole OI (Zhu)		41	43	44	46
Woods Hole OI (Seewald)	134	120	120		
Wright State Univ. (Higgins)					70
Wyoming, Univ. of (Eggleston)		95	85	85	52
Yale Univ. (Lasaga/Rye/Bolton/Ague)	247	222	300	326	327
Yale Univ. (Berner)	197		109	110	110

Other	316	505	559	124	
OFF-SITE TOTALS	12851	10649	10393	10487	10513