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Summary of FY 1998 Geosciences Research

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FOREWORD

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. The Division of Engineering and Geosciences, part of the Office of Basic Energy Sciences of the Office of Energy Research, supports the Geosciences Research Program. The participants in this program include Department of Energy laboratories, academic institutions, and other governmental agencies. These activities are formalized by a contract or grant between the Department of Energy and the organization performing the work, providing funds for salaries, equipment, research materials, and overhead. The summaries in this document, prepared by the investigators, describe the scope of the individual projects. The Geosciences Research Program includes research in the broad areas of geophysics, geochemistry, resource evaluation, hydrogeology and solar-terrestrial interactions, and their subdivisions, including earth dynamics, properties of earth materials, rock mechanics, underground imaging, rock-fluid interactions, continental scientific drilling, geochemical transport, solar/atmospheric physics, and modeling, with emphasis on the interdisciplinary areas. All such research is related either directly or indirectly to the Department of Energy's long-range technological needs. Further information on the Geosciences Research Program, including recent program activities and highlights, may be found on the World Wide Web 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 Energy Research (OER) through its Office of Basic Energy Sciences (OBES). 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 nations 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 emphasizes research leading to fundamental knowledge of the processes that transport, modify, concentrate, and emplace (1) the energy and mineral resources of the earth and (2) the energy byproducts of man. The Geosciences Research Program is divided into five broad categories:

1. Geophysics and Earth Dynamics.
2. Geochemistry.
3. Energy Resource Recognition, Evaluation, and Utilization.
4. Hydrogeology.
5. Solar-Terrestrial Interactions.

The following outline of current research in these categories is intended to be illustrative. The program evolves with time and progress in these and related fields. Individual research projects supported by this program at DOE laboratories, 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.

1. GEOPHYSICS AND EARTH DYNAMICS

A. Large-Scale Earth Dynamics. Research on the physics of lithospheric dynamics such as plate motion, mountain building, basin development, and regional scale uplift/subsidence and its concomitant effects.

B. Evolution of Geologic Structures. Research on the physical controls and physical effects of the dynamic evolution of geologic structures (e.g., folds, faults, basins, volcanoes) on a local or regional scale.

C. Properties of Earth Materials. Research on physical properties of rocks and minerals determined in the laboratory or in the field (in situ), by direct or indirect techniques, and applicable on the spatial and temporal scales of geologic processes.

D. Rock Mechanics, Fracture, and Fluid Flow. Research on the response of rock and rock units to induced stress and the role of fluid flow as a cause and/or effect.

E. Underground Imaging. Research to characterize the layering, mineralogy, lithology, geometry, fracture density, porosity, fluid content, and composition of the lithosphere using geophysical methods.

2. GEOCHEMISTRY

A. Thermochemical Properties of Geologic Materials. Research on the thermodynamic and chemical properties of geologic materials and their kinetic/dynamic interactions.

B. Rock-Fluid Interactions. Research on the chemical and mechanical consequences of rock-fluid interactions and the mass and energy transport controls of such interactions.

C. Organic Geochemistry. Research on naturally occurring carbonaceous and biologically derived substances of geologic and energy importance.

D. Geochemical Transport. Research (both experimental and theoretical) on the geochemical separation, transport, and concentration of materials in the earths crust induced by the spatial and temporal dynamics of lithospheric processes leading to a predictive capability.

3. ENERGY RESOURCE RECOGNITION, EVALUATION, AND UTILIZATION

A. Resource Definition and Utilization. Research to develop new and advanced bases for the physicochemical dynamics needed for improved energy and energy-related resource exploration, definition, and use.

B. Reservoir Dynamics and Modeling. Research on the physiochemical dynamics of geothermal and hydrocarbon reservoirs in their natural and perturbed (by production, injection, or reinjection) states.

C. Properties and Dynamics of Magma. Research on the origin, migration, emplacement, and crystallization of natural silicate liquids and their heat energy.

D. Continental Scientific Drilling. Research on the scientific objectives of the OBES Geosciences Research Program using advanced technologies in shallow, intermediate, and deep drilling for earth observation facilities. Scientific research and advanced drilling technologies development are coordinated by an Interagency Coordinating Group (DOE, the U.S. Geological Survey, and the National Science Foundation) under the aegis of the Interagency Accord on Continental Scientific Drilling.

4. HYDROGEOLOGY

A. Fluid Transport Dynamics and Modeling. Research on the chemical transport and energy/mechanical consequences of fluid interactions and transport, leading to a predictive capability.

B. Thermochemical Properties of Energy Materials. Research on the thermodynamic and chemical properties of materials and their kinetic/dynamic interactions in fluidrock systems.

C. Perturbations of Fluid Flow. Research on the physicochemical dynamics and chemical transport of fluidrock systems in response to mechanical and energy perturbations, leading to a predictive capability.

5. SOLAR-TERRESTRIAL INTERACTIONS

A. Magnetospheric Physics. Research on the fundamental interactions of the solar wind with the terrestrial magnetic field and the earths magnetosphere as a model magnetohydrodynamic generator and associated plasma physics research.

B. Upper Atmosphere Chemistry and Physics. Research on thermal, compositional, and electrical phenomena in the upper atmosphere and the interactions induced by solar radiation.

C. Solar Radiation and Solar Physics. Research on the structure and dynamics of the sun and the characteristic interactions of solar radiation with the earth, including the effects of solar radiation on the climate.

PART I: ON-SITE

CONTRACTOR: ARGONNE NATIONAL LABORATORY

Argonne, Illinois 60439

CONTRACT: W-31-109-Eng-38

CATEGORY: Geochemistry

PERSON IN CHARGE: N. C. Sturchio

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

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

Project Description: The principal 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. These techniques provide high-resolution atomic-scale structural information that cannot be acquired by any other means. Experiments are being performed on common rock- and soil-forming minerals under conditions representative of geochemical environments near the earth's surface. Types of reactions being investigated include dissolution-precipitation, adsorption-desorption, and oxidation-reduction.

Results: Progress during the past year included further successful demonstrations of the ability to perform *in situ* X-ray reflectivity, diffraction, and standing wave studies of reacting mineral surfaces under chemically controlled conditions. During the past year, experiments were conducted to characterize the atomic structure of the calcite (104) cleavage plane in contact with aqueous solutions, and to observe changes in this structure as a function of solution composition and time, using X-ray reflectivity measurements. We are focusing on the relaxations of near-surface oxygen atoms on calcite and the structure of adsorbed water. A study of the structure of adsorbed fatty acids on calcite was performed. X-ray standing waves and surface X-ray absorption spectroscopy were combined to determine the structure and amount of divalent Zn, Co, and Ni adsorbed onto calcite. It was found that these ions exchange for calcium ions of calcite, and occupy a position that is relaxed inward relative to (104) plane by about 0.12 (104) lattice units; their metal-oxygen bond lengths are close to those in the respective metal carbonates. A structural study of trace tetravalent U in natural calcite was performed using extended x-ray absorption fine structure spectroscopy. Experimental studies of clay mineral growth kinetics using powder X-ray diffraction techniques were continued, in collaboration with K. L. Nagy (Sandia National Laboratories).

CONTRACTOR: Brookhaven National Laboratory

Associated Universities, Inc.
Upton, Long Island, New York 11973

CATEGORY: Geology, Geophysics, and Earth Dynamics

CONTRACT: DE-AC02-98CH10886

PERSON IN CHARGE: K. W. Jones

Study of the Microgeometry of Geological Materials Using Synchrotron Computed Microtomography

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Objectives: The objective of this project is to gain improved knowledge of the properties and behavior of geological materials on a grain-size scale. Measurements are made to determine: 1) the microgeometry of typical rock types, 2) changes in the microgeometry of the rocks as a function of applied pressure, and 3) fluid-flow paths through the rocks.

Project Description: Experimental data are obtained using the technique of synchrotroncomputed microtomography. Intense x-ray beams from the Brookhaven National Synchrotron Light Source pass through the sample and strike an area scintillation detector. Light from the scintillator is detected with a charge-coupled device and stored for later analysis. The tomographic volume is found by analyzing a series of the two-dimensional views obtained as the sample is rotated around an axis normal to the x-ray beam. The maximum number of voxels in the final volume is about 10^{10}. The minimum voxel size is about 3 µm on an edge.

Results: Data obtained from the study of vesiculated basaltic lavas during FY 1997 were analyzed using a 3D image geometry analysis package to measure vesicularity, specific surface area, and interconnectivity of the vesicles. The results showed that the bubbles have roughly spheroidal forms of different sizes with vesicularities ranging from 45 to 80% with 90% of the vesicles being interconnected. Specific surface areas were found by counting voxel faces and by use of 2-point correlation functions. Investigation of the geometry of sandstones and limestones was continued using several samples from the Vosges region of France. When analyses are complete, a comparison will be made with the results from earlier investigations of Berea and other sandstones. Investigations of the microstructures of other materials including type-I deep-sea spherules and artificial dunites were begun. Work on the meteorites demonstrated the feasibility of detecting small nuggets of platinum group elements and the three-dimensional structure of cavities that are features of these materials. A preliminary investigation of the feasibility of detecting surface changes in a glass exposed to an acid environment was performed. The usefulness of the method requires that the surface layer be greater than the instrumental spatial resolution of about 0.003 mm. There should be applications of this approach with respect to fluid flow in petroleum reservoirs, subterranean storage of carbon dioxide, and transport of contaminants in ground water.

CATEGORY: Geochemistry

CONTRACT: DE-AC02-76CH00016

PERSON IN CHARGE: A. Vairavamurthy

Geochemistry of Organic Sulfur in Marine Sediments

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Objectives: The overall objective is to gain a fuller understanding of the geochemical role of the sulfur system in transforming sedimentary organic matter from organized structures typical of biopolymers (*e.g.*, proteins and carbohydrates) to heterogeneous sedimentary geopolymers, such as humic substances and kerogen. A major emphasis is placed on understanding the abiotic mechanisms of sulfur incorporation into organic matter and its influence in the preservation of organic matter in marine sediments.

Program Description: Sulfur is believed to be involved in preserving organic matter in sediments, in converting this organic matter to petroleum and in controlling the timing of petroleum generation from a source rock. A fundamental geochemical issue is the mechanism of incorporation of sulfur into sedimentary organic matter. Although it is accepted that H_2S and its partial oxidation products (such as polysulfide ions) are involved, there is controversy about its molecular mechanism, and the active species involved. This project, which is aimed at understanding the formation and transformation of sedimentary organic sulfur during early diagenesis, has four major components: (1) studies of sulfur speciation in sediments, (2) mechanistic studies of organic sulfur formation, (3) mechanistic studies of the pathways of transformation of organic sulfur compounds in sediments, and (4) development of analytical methods. The suite of complementary spectroscopic and chromatographic techniques used (particularly synchrotron-radiation-based XANES spectroscopy for sulfur speciation and liquid chromatography combined with mass spectrometry, LC-MS) give detailed structural information on sulfur and its associated organic moieties.

Results: In earlier studies, we established that sulfonates constitute an important fraction of organic sulfur in marine sediments. However, the structures of the organic moieties associated with this functionality are not well understood. A major problem in studying sulfonates is that these hydrophilic molecules are not amenable to separation and detection by common chromatographic techniques. Electrospray ionization combined with mass spectrometry (ESI-MS) is becoming popular for analyzing polar- and hydrophilic- organic compounds because electrospray transforms the non-volatile aqueous analytes into gas-phase ions under mild ambient conditions that then can be detected sensitively by mass spectometry. We applied this technique to analyze hydrophilic organic molecules, especially the organic constituents isolated in natural waters. Because most natural waters contain several major inorganic ions, including magnesium and sodium among cations and chloride among anions, the organic matter isolated from the waters may contain variable amounts of inorganic ions, mainly depending on the isolation method used. Our preliminary studies with several low-molecular-weight compounds suggested that the presence of magnesium ion complicates the mass spectra of organic molecules by forming adduct with the latter. Consequently, we undertook detailed studies to understand the effect of magnesium in the ESI-MS analysis of low-molecular-weight organic molecules. Our results clearly showed that magnesium ion forms various gas-phase complexes with functionalized organic molecules, including low-molecular-weight carboxylic acids, thiols, and amino acids, so that the numerous peaks appearing in the ESI-MS spectrum do not directly reflect the composition of analytes in the sample. Mono-functionalized coumpounds, such as propionic acid, mainly formed dinuclear complexes, whereas poly-functionalized compounds, such as glutathione, generated significant amounts of mononuclear and other types of polynuclear complexes, in addition to dinuclear complexes. An equimolar mixture of five carboxylic acids (propionic-heptanoic) gave numerous peaks distributed in the 300 to 100 m/z range in five Gaussian-shaped groups, each representing gas-phase ions with a particular molecular formula. Using a statistical approach, we showed that, for a particular molecular formula, such a Gaussian distribution of peaks can arise from a series of samples containing magnesium ion and should be interpreted with caution. Ideally, magnesium ion and other cations that can form complexes should be removed before analyzing organic samples by ESI-MS. We showed that using on-line liquid chromatographic separation before introducing the sample into the mass spectrometer conveniently resolves this problem.

CONTRACTOR: Lawrence Berkeley National Laboratory

University of California
Berkeley, CA

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CATEGORY: Geophysics and Earth Dynamics

Person in Charge: S. Benson

High-Resolution Imaging of Electrical Conductivity Using Low-Frequency Electromagnetic Fields

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Objectives: The objective is to develop numerical and field techniques for high-resolution imaging of electrical conductivity using magnetotelluric (MT) and controlled-source electromagnetic (CSEM) methods. Applications of high-resolution conductivity imaging include the mapping of groundwater, resource exploration and reservoir characterization, subsurface processes monitoring, and general geological mapping of the crust of the earth.

Project description: Many fundamental questions relating to resolution, depth of exploration, required bandwidth in frequency and spatial sampling rate remain to be answered. To resolve some of these questions four main tasks have been selected in this project; 1) improvement of the q-domain imaging method using the wavefield transform and tomographic inversion, 2) development of an approximate analysis and imaging method using Born inversion, 3) development of a rapid and practical 3-D inversion scheme, and 4) development of a borehole time-domain EM system. Some of these tasks are driven by the pressing need to interpret an increasing amount of field data available to us. The data may be in the frequency domain, but can only be interpreted properly if and when tasks 2 and 3 become successful. Also, the evident success of the q-domain tomographic imaging process strongly argues for the development of a suitable wideband borehole system (task 4).

Results: Over the past few years, laboratory measurements using scale models successfully demonstrated the proof of concept of the wavefield transform (Becker *et al.*, 1997; Das, 1998), and provided specifications for a full-scale field system. Following the guidelines a prototype field-scale transmitter was designed, constructed and field-tested using a 100 m deep well at the Richmond Field Station operated by the University of California at Berkeley. The tests were principally designated to assess transmitter performance and were performed in a borehole-to-surface configuration with a commercially available receiver (Geonics EM47). Because of the short transmitter-receiver separations and the relatively low formation conductivity, the recorded data lacked the bandwidth needed for its transformation to the wavefield domain. Consequently, transmitter performance was evaluated by comparing the observations with theoretical data.

A new integral equation formulation has been derived using the magnetic field (MFIE). In obtaining numerical solutions, the MFIE method appears to be potentially more efficient since magnetic fields vary smoothly in an anomalous body. To begin, the new approach has been successfully tested in obtaining approximate solutions (Lee *et al.*, 1998). Development of the non-linear Born approximation

(Habashy *et al.*, 1993) has been continued. Modification has been made to ensure continuity of the current, instead of the electric field, to handle the current channeling more efficiently.

Center for Computational Seismology (CCS)

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Objectives: The objectives of this project are to (1) provide state-of-the-art computing resources for seismological and other geophysical activities that support a wide range of DOE scientific programs, from field investigations to innovative supercomputing methods for the geosciences, (2) facilitate the development of new methods for integrated, multi-parameter imaging and visualization of subsurface properties and processes, (3) deliver and support the resulting computational tools for ongoing applications as needed in DOE scientific programs, and (4) maintain a training environment in modern computational methods for staff scientists, students and visitors.

Project Description: CCS is the core computing resource within Earth Sciences at LBNL that supports a wide range of geophysical research needs, including activities from theoretical studies in wave propagation, seismic imaging and inverse theory through a rich spectrum of projects to substantial efforts in supplying special software and hardware for data acquisition and analysis required in the numerous and varied field investigations underway. CCS resources have been upgraded during the past year to a 4-cpu Sun Ultra enterprise 4000 system with 1 GByte memory, 100 GBytes of disk space, 24- and 36-inch color plotters and several different tape drives. The local CCS network served by this system includes Silicon Graphics and Sun workstations, color X-terminals and PC/Macintosh computers that support more than 30 regular users and as many different research projects. A number of commercial and in-house data processing packages are available for handling large seismic data sets acquired in geophysical surveys or earthquake monitoring projects.

Research focuses on subsurface imaging for geophysical and hydrological properties, in three dimensions, at scales from meters to the entire earth, with addition of the fourth dimension (time) in monitoring applications. Fluid disposal or contaminant sites, geothermal and hydrocarbon reservoirs, gas fields, active fault zones, as well as Earth's mantle and core have all been targets in one project or another.

Results: Currently the CCS research topics may be grouped loosely into three general categories - the first one primarily involves computation in solving forward problems in geophysics, the other address the inverse problems that are fundamental to applications:

1. Wave propagation studies, including non-linear phenomena, scattering, effects of extreme heterogeneity, composite media theory, guided waves in fractures or fault zones, anisotropy, and the role of fluids;
2. Imaging techniques, such as travel-time and attenuation tomography, single-well, cross-well and VSP data reduction, joint seismic/radar surveys, analysis of coupled geophysical/hydrological effects, and time-varying image construction for monitoring subsurface processes;
3. Seismic source parameter estimation for explosions, earthquakes and fractures, accomplished largely through inversion for source moment tensor components and rates of moment release in dynamic systems at various scales.

Field applications at this time range widely and include geophysical and hydrological studies at Yucca Mountain, environmental remediation projects at LLNL, LBNL, and Dover AFB, reservoir definition work in hydrocarbon and geothermal fields, and high-resolution monitoring of microearthquakes in studies of reservoir dynamics as well as major seismogenic fault zones.

Seismic Resonance Characterization of Fractured Geologic Structures

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Objectives: The principal objectives of this research are to develop a basic understanding of the resonance characteristics of fractured rock and to develop the associated theory required to determine the mechanical properties and geometries of fractures in rock from resonance measurements.

Project Description: Research will begin with laboratory resonance tests on rocks samples with material anisotropy and attenuation. Subsequent resonance measurements will focus primarily on the effects of fracture properties and geometries on the resonance frequencies and mode shapes. Techniques for selective excitation and detection of modes will be developed and used to estimate the normal and shear stiffnesses of dry and fluid-saturated fractures with heterogeneity and anisotropy in fracture stiffness. Numerical codes will be developed in parallel to assist in the understanding and interpretation of the laboratory resonance measurements.

Results: The effects of (1) rock anisotropy and (2) single and multiple fractures on the shifts in resonance frequencies and resonance peak broadening (*i.e.*, attenuation) of simple one-dimensional rock bars were investigated. The anisotropy work focused primarily on transversely isotropic rocks in which the anisotropy is caused by either bedding structure (sandstone) or preferentially oriented microcracks (granite). Resonance measurements were performed on cube-shaped samples under free-vibration conditions. A numerical inversion technique was developed and used to determine the five elastic constants of the rocks by matching the observed and computed resonance frequencies of the samples. Elastic moduli derived from the resonance measurements were in general smaller than those determined from ultrasonic transmission tests and larger than those measured by static stress-strain tests. This result may be attributed to frequency-dependent wave velocities resulting from scattering off microcracks and grain contacts.

The frequency spectra computed using the elastic properties from the inversion showed excellent agreement with the measured spectra. Good agreement was also observed between the computed mode shapes and those measured experimentally with a scanned laser vibrometer. The effects of fractures and fracture viscoelasticity on the resonance of rocks were investigated using a one-dimensional propagator code and laboratory experiments on rock bars. The introduction of fractures altered the resonance frequencies and mode shapes of the rock. The magnitude of these effects was observed to be largest for modes with nodes located on or near the fractures. Introduction of water into the fractures resulted in viscoelastic attenuation. All these effects can be accurately modeled with a propagator code in with the fractures are modeled as a displacement-discontinuity boundary condition with a complex fracture stiffness. These results demonstrate that fractures in rock have distinct resonance signatures that can potentially be used for fracture location and stiffness determination using mode-dependent frequency shifts, and for fracture rheology determination using peak broadening.

Deformation and Fracture of Poorly Consolidated Media

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Objectives: The objective of this research is to investigate the process of hydraulic fracturing and of borehole breakout formation in poorly consolidated granular rock. Specifically we are interested in studying the mechanisms leading to these two types of borehole failure, and establishing whether either or both could be used as *in situ* stress indicators in high porosity weak rocks.

Project description: For borehole breakout studies we employ a specially fabricated biaxial loading cell mounted inside a compression loading machine, which allow us to carry out drilling of axial boreholes (diameters of 14-40 mm) in rock blocks (150x150x230 mm) already subjected to a state of true triaxial *in situ* stress. Berea sandstone of 24-26% porosity, other sandstones, and artificial granular material of similarly high porosity are tested. For hydraulic fracturing experiments we use cylindrical rock specimens (100x150 mm) mounted in a triaxial vessel through which we apply lateral and axial loads, as well as pore pressure and borehole fluid pressure.

Results: In this initial year of the project we first designed, fabricated, and calibrated a new biaxial loading cell. This cell enables the application of two independent mutually perpendicular stresses (each up to 110 MPa) to rectangular rock blocks.

We also performed a series of physical and mechanical properties tests on the high porosity Berea sandstone obtained from an Ohio quarry. Based on our tests, the rock can be classified as weak, highly porous and permeable, with a definite non-linear triaxial strength criterion. We have completed ten experiments of breakout-inducing drilling under a pre-existing triaxial state of stress simulating *in situ* conditions. Borehole failures are demonstrably unlike any observed in rocks such as granite and limestone. In the latter rocks breakouts are the result of dilatant inter- and intra-granular cracking parallel to the largest horizontal stress, leading to the well known 'dog ear' or 'V'-shaped breakout cross sections. In the presently tested sandstone, breakouts appear to be the culmination of a non-dilatant debonding of the grains at the points of highest stress concentration due to the reduced cementing matrix material (as inferred from the very high porosity). This failure mechanism leads to fracture-like or slot-like breakouts orthogonal to maximum compression, an orientation that is counter-intuitive, but reasonable if one realizes the non-dilatant nature of the failure. These breakout fractures extend for large distances from the borehole wall and could be a major source of 'sand production' in petroleum-producing wells.

The breakout fractures in the present tests are noticeably varying in length depending on the state of applied far-field stress, but their width is consistently limited to 5-7 grain diameters.

Effects of Micro- and Macro-Scale Interfaces on Seismic Wave Propagation in Rock and Soil

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Objectives: The objective of this proposal is to determine the effects of multi-scale heterogeneity on seismic wave propagation through soils and rocks. Specifically, we will address (1) heterogeneity within a fracture; (2) heterogeneity from multiple fractures and fracture networks; and (3) discontinuities in unconsolidated and poorly consolidated media.

Project Description: Soils and rocks are open, multiphase, biogeochemical systems that play an important role in the production of oil and gas, the maintenance of environmental quality, and the geotechnical stability of a site. They consist of solid, liquid, and gaseous phases that produce heterogeneity on multiple length scales that may vary temporally because of participation in the hydrogeologic and tectonic cycles. Because the physical heterogeneities can change in time, active monitoring techniques need to be developed for quantifying the changes in soils and rocks. Some sources of heterogeneity in soils and rocks arise from the physical structure of these media, such as pore and grain distributions, grain contacts, cracks, fractures, stratification, and laminae, as well as heterogeneity from the distribution of fluids within the structural components of these media. Achievement of the proposed research objective depends on the determination of the effect of micro-scale phenomena on macro-scale measurements through the combination of laboratory experiments and numerical analyses

Results: Experimentally measured compressional wave anisotropy caused by the presence of a single fracture and multiple parallel fractures was compared to theoretical predictions based on the displacement discontinuity theory. The comparison between the theoretically predicted transmission coefficients and the experimentally determined values enabled the inverstigation of the robustness of the displacement discontinuity theory for obliquely incident compressional waves on a single fracture and on multiple parallel fractures. The following behavior was observed which is predicted by the analytical solution for plane-wave propagation across a displacement discontinuity: (1) at high frequencies the group time delay is not as sensitive to changes in stiffness as transmitted amplitudes; (2) the transmission coefficient decreases in magnitude with increasing frequency; (3) the transmission coefficient decreases for glancing angles of incidence to the fracture; and (4) that a discontinuity in the value of the transmission coefficient should occur at the orientation when the trajectory of a wave crosses additional fractures. However, the experimental data did not match the predictions of the theory; single values of normal and tangential fracture specific stiffness could not be used to fit the transmission data for all angles of incidence for all frequencies. Further effort is needed to explore the frequency dependent fracture stiffness. If the frequency dependence gives an indication of the distribution of asperities or contact regions in a fracture, this information could be used to predict the hydraulic properties of fractures.

CATEGORY: Geochemistry

Person in Charge: S. M. Benson

Integrated Isotopic Studies of Geochemical Processes

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Objectives: Combine high-precision measurements of isotopic ratios in natural materials with mathematical models to understand the spatial and time scales of geochemical processes of interest for energy management.

Project Description: Current effort is concentrated on Sr, Ca, O, C, He, Ne, Ar, Xe, Pb, and Nd isotopic ratios, and on problems of mass transport in fluid-rock systems, interpretation of past global climatic change, crustal magmatic and tectonic processes, and Quaternary geochronological methods. A mathematical basis for the application of isotopic measurements of fluids and rocks to the field-scale parameterization of hydrological systems is a major effort of the Center. Modeling is accompanied by systematic measurements of relatively simple natural systems, and by improved sampling and measuring techniques. Emphasis in development is on microsampling of geological materials, on high-precision measurement of the small amounts of recovered material, and on rapid, automated low-blank chemical separation of trace elements. Other efforts of the Center are aimed at geochemical techniques for dating and correlation of sedimentary and volcanic rocks, and for understanding the timescales and mechanisms of crustal processes such as extensional faulting, mountain building, and volcanism. All efforts are aimed at improved characterization of natural rock and fluid systems.

Results: (1) The chemical and isotopic compositions of lichens growing on recent basalt flows (<30 years old) in Hawaii were analyzed to assess the relative importance of different biogeochemical factors for establishing living organisms on rocks. The metal contents of three lichen samples collected from Kilauea volcano were analyzed using the X-ray microprobe (beam line 10.3.1) at the Advanced Light Source at LBNL. These lichens (*Stereocaulon volcanii*) were found to contain significant concentrations of copper and zinc. These results represent one of the first studies demonstrating accumulation of metals from rocks containing background concentrations of metals.

(2) Acquisition and installation of new Micromass Isoprime mass spectrometer designed for continuous-flow analyses of stable isotopes was completed. The system was modified to enable continuous-flow analyses of stable chlorine isotopes using the GC-combustion system with the Isoprime. Early testing of this capability was very promising.

(3) It is predicted that during formation of gas hydrates from water and gas, noble gases incorporated in the hydrate phase will be fractionated relative to their composition in the water phase. Noble gas concentrations and fractionation factors [F(^{4}He), F(^{22}Ne), F(^{84}Kr) and F(^{132}Xe) as well as helium isotopic compositions] were determined for 8 gas hydrate plus pore water specimens collected from the Blake Ridge hydrate field in order to evaluate this theoretical prediction. The simplest explanation for the observed noble gas distribution is that samples contain mixtures of air (probably a contaminate acquired during sampling and processing) and two end-member gases. One of the end member gases is depleted in Ne but significantly enriched in Kr and Xe relative to noble gases dissolved in seawater. This end member composition is anticipated if the source of this gas is the hydrate phase in equilibrium with seawater. Noble gas analyses may play an important role in understanding the dynamics of gas hydrate reservoirs but significantly more work is needed.

(4) Noble gases, carbon dioxide, nitrogen and ^{14}C are being monitored in gas discharging from Mammoth Mountain. The helium and carbon isotopic compositions and the ^{3}He/CO$_2$ ratio are indicative of a magmatic source. Since 1990, several regions of coniferous forest, totaling 50-60 ha, have died off due to anomalous CO$_2$ discharge from soil gas. In these tree-kill zones, soil gas CO$_2$ varies from 30-90% with gas flow rates up to 320 l/hr-m^2. Variations in noble gas abundances, ^{3}He/CO$_2$, and excess N$_2$ indicate that the anomalous gas discharge is derived from a combination of magmatic degassing and thermal metamorphism of carbonates. The persistently high ^{3}He/^{4}He ratio combined with the magnitude and duration of gas emission at the surface and estimates of the size of the emplaced dike requires continued degassing from a deeper magma system. A more rapid increase in CO$_2$/^{3}He relative to CO$_2$/^{4}He combined with a gradual decrease in the helium isotopic composition suggests that the influence of the crustal gas source is increasing. We have also found that the high CO$_2$ flux in the soil

gas fractionates the air gases (N_2, noble gases) in the soil. The degree of fractionation is much larger than predicted by simple Fickian diffusion and is more consistent with Dusty Gas Models for gaseous diffusion in porous materials.

(5)Noble gas isotopic compositions were measured in basalts from the Basin and Range Province of the western United States that were erupted over the last 15Ma. The helium R/Ra values of these lavas vary between 3 and 7 Ra and generally correlate well with variations in Sr and Nd isotopes. The earliest-erupted basalts from these fields possess low He, Nd, and Sr isotopic compositions suggesting that a lithospheric end-member dominates the isotopic composition. Isotopic compositions of later-erupted basalts appear to be dominated by increasing proportions of asthenospheric mantle. Some samples deviate from the simple two end-member trend (having much lower helium isotopic ratios) suggesting contamination by incompletely-degassed crust or a lithospheric source with much higher He/Nd and He/Sr ratios. We have also measured noble gases in a group of basalts from southwestern Utah, where little crustal extension has taken place. In contrast to the strong correlation between Sr and Nd seen in the above basalts, variations in Sr and Nd in these rocks do not correlate well. We suggest this may reflect heterogeneities within the lithosphere beneath the Colorado Plateau or progressive melt infiltration from the convecting mantle.

(6) Measurements of $^{234}U/^{238}U$ ratios are being used to understand effective reaction rates in fluid-rock systems. The approach follows on from work done using Sr isotopes. The U isotope system has complementary properties; ^{234}U both decays radioactively and at the same time is injected into pore fluids by leakage from the solid phase. Leakage from the solid phase drives the pore fluid $^{234}U/^{238}U$ up, whereas, dissolution-precipitation reactions drive the pore fluid toward the equilibrium activity ratio of 1. Measurements were made of pore fluids from deep sea sediments, where solute transport in the fluid is by diffusion, and hence can be modeled well. The preliminary results show that the reaction rates estimated from U isotopes are essentially the same as those estimated from Sr isotopes, indicating the approach is giving accurate solution-precipitation rates, and that the rates are very low (10^{-7} grams reacted per gram solid per year).

Isotopic and Chemical Composition of Fault Zone Fluids

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Objectives: The San Andreas Fault (SAF) is weak in an absolute sense and relative to adjacent plate interiors. Near lithostatic fault zone fluid pressures are thought to play a critical role in fault weakening and the discriminating factor between fluid-pressure based models of fault weakening is the origin of the fault zone fluids. The isotopic and chemical composition of fluids associated with the SAF system are being measured to identify fluid source and flow rates through the fault system.

Project Description: Explanations for SAF weakness invoke either low friction fault zone materials or super-hydrostatic fluid pressures within the fault zone. However, heat flow and stress orientation data have not been reconciled with laboratory friction coefficient measurements on fault gouge materials, so that elevated fluid pressures are the preferred explanation. Models invoking high fluid pressures are similar but rely on different fluid sources. During the earthquake cycle fault zone fluid pressure increases to near lithostatic values and induces rupture. Dilation accompanies rupture, locally lowering the fault zone fluid pressures and the cycle begins again. Crustal fluids, connate or meteoric, may be drawn into the fault zone in response to fault rupture and become trapped by mineral reactions; the high fluid pressures required to weaken the fault are reestablished by compaction of the sealed fault-zone materials. In this model, the base of the seismogenic zone, defined by the brittle-ductile transition, is treated as an impermeable boundary. In an alternative model, fault-weakening fluid pressures are generated by a high flux of deep crustal or mantle fluids that are continually supplied to the seismogenic zone from the ductile lower crust at super-hydrostatic pressure. To investigate fluid source and influence on SAF dynamics, we conducted a chemical and helium isotopic study of groundwater associated with the SAF and companion faults. We found that the groundwater contained elevated $^3He/^4He$ ratios, thus providing evidence for a geopressured mantle fluid source (Kennedy *et al.*, 1997, Science, 278, 1278-1281).

It is likely that mantle helium is associated with other more abundant mantle volatiles, certainly CO_2 and perhaps water. However, using estimated mantle $CO_2/^3He$ ratios, the vertical CO_2 flux inferred from the helium isotopic data is low and appears inadequate, by at least an order of magnitude, to re-establish fault-weakening fluid pressures on the relevant time scale. Apparently, an additional source of fluid (water, CO_2, etc.) is required. Also, it is not clear if the springs and wells sampled in this study tapped fluids directly from a fault zone or from the adjacent crust. If the fluids are directly from the fault zone, then the observation that mantle helium is mixed with fluids from the adjacent crust, as indicated by dissolved solids and water isotopes, implies that elements of both models are important. Since weakness is generated by high fluid pressures in the fault zone relative to surrounding crust, infiltration of crustal fluids into the fault zone requires episodic reversals of the fluid pressure gradient.

To address these two issues, we initiated a program to sample and analyze rocks and minerals associated with the fault zones and surrounding country rocks. These samples will be analyzed for noble gases and the isotopes of Sr, Nd, Pb, C, and O.

Results: We have identified appropriate sampling sites, sample collection, and initiating the analysis phase. The minimal vertical relief along the main strike of the SAF complicated selection of appropriate sampling sites. Never-the-less, 250 samples from deformation zones (gouges, breccias, fault veins, slickensides, cataclasites), vein fillings, and hosts from over 20 localities along the San Andreas and adjacent faults from South San Francisco to East Los Angeles were collected. Samples from the exhumed San Gabriel Fault, a deeper equivalent of the SAF, were also collected, as well as samples from the Santa Ynez Fault, another former strand of the SAF embedded in Miocene limestones. All the major lithologies (granites, gneisses, sandstones, limestones, marbles and serpentinites) were sampled. Preliminary analyses of noble gases extracted from fluid inclusions hosted in faulted rocks gave the same helium isotope signature as previously observed in the groundwater.

Thermodynamics of High Temperature Brines

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Objectives: This project covers theoretical and experimental studies concerning the thermodynamic properties of aqueous electrolytes and other systems at high temperatures. The components important in natural waters and other geochemical fluids are emphasized. The resulting data are important in understanding various geological processes, in exploiting geothermal and other natural resources, and in fission-product waste disposal. Moreover, this information has a wide range of applicability, since similar fluids arise in many industrial processes and in high-pressure steam power plants.

Project Description: The project includes both experimental and theoretical programs. The experimental program involves measuring heats of mixing or dilution of solutions at temperatures extending above 300°C and pressures to 1 kbar. The new calorimeter was tested, measurements were made first for the mixing of NaCl(aq) with $CaCl_2$(aq), and recently for NaCl(aq) with $MgCl_2$(aq) and for the dilution of $MgCl_2$(aq).

Results: The heat of mixing and of dilution results for $CaCl_2$-NaCl-H_2O and for $MgCl_2$-NaCl-H_2O are being incorporated in general equations of state for those systems. Recent theoretical results include an equation of state for $CaCl_2$-H_2O for temperatures above 250°C. This equation represents phase equilibria and volumetric properties. Its structure involves theoretically calculated properties of quadrupole-dipole mixtures with moments appropriate for $CaCl_2$ and H_2O, respectively, together with a few empirical terms fitted to all available experimental data. The development of this earlier equation received support also from the Chemical Sciences Division of BES, DOE.

Clay Mineral Surface Geochemistry

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Objectives: The objectives of this project are to determine the mobility and surface speciation of Cs^+ counterions, as well as interlayer water structure, for 12.4 Å Cs-smectite hydrates using Monte Carlo and molecular dynamics simulations.

Project Description: Smectites are clay minerals with expandable interlayers and substantial cation exchange capacities. Molecular modeling techniques can provide an understanding of the hydrated Cs-smectite interlayer necessary to predicting the permeability of clay liners to radiocesium cations at nuclear waste containment facilities.

Monte Carlo (MC) simulations were used to determine the configuration of Cs^+ and water molecules present in stable Cs-smectites with 12.4 Å layer spacings. The program MONTE, written by Neal Skipper and Keith Refson and compiled on Cray J90s at the National Energy Research Scientific Computing Center (NERSC), was used. The smectites examined include octahedrally charged hectorite, tetrahedrally charged beidellite, and montmorillonite, which has both tetrahedral and octahedral charge sites. Molecular dynamics (MD) simulations based on MC-equilibrated Cs-smectites revealed the diffusion of Cs^+ and water molecules over 800 ps. The code MOLDY, written by Keith Refson and compiled on the Cray T3E at NERSC, was used. Coordinate data from MD runs have been animated using RM SceneGraph in order to visualize molecular interactions. Further information may be found at http://esd.lbl.gov/sposito/.

Results: Monte Carlo calculations provided radial distribution function and coordination number data that revealed both the ability of Cs^+ to organize water into a partial hydration shell, as well as the highly distorted nature of interlayer water structure as compared to bulk water.

Comparison of MD trajectories revealed the effect of clay charge site on Cs^+ mobility. The recessed charges of hectorite held Cs^+ in fixed locations at the midplane of the interlayer, whereas the near-surface tetrahedral charges within beidellite drew cations to fixed positions closer to the clay layers. When both charge sites were present, as in montmorillonite, the Cs^+ became somewhat more mobile. All Cs^+ were in inner-sphere surface complexes and moved through jump diffusion, except in Cs-montmorillonite with 2/3 water monolayer. This system featured four cations tightly bound to two tetrahedral charge sites, while two remaining Cs^+ exhibited diffusional motion. Water molecules diffused at rates a fraction of those in bulk water.

The results confirmed the findings of experiments, which predict low mobility of Cs^+ in smectites. Such agreement indicates the potential functions used may be reasonably accurate, and provides further evidence supporting the use of smectite clay liners within nuclear waste containment facilities in order to retard the movement of radiocesium.

CATEGORY: Hydrogeology

Person in Charge: S. Benson

Investigation of Groundwater Flow Paths in Fractured Aquifers through Combined Inversion of Strontium Isotope Ratios and Hydraulic Head Data

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Objectives: Identify zones of preferential groundwater flow using innovative geochemical techniques emphasizing isotope ratio measurements and hydrologic inverse methods employing fractal geometry concepts.

Project Description: The $^{87}Sr/^{86}Sr$ isotope ratio in groundwater often evolves in response to water-rock interaction, and gives an indication of water-rock contact time that should be less complicated than one based on chemical concentrations. Preferential flow zones or "fast paths" in which residence times are much shorter than other areas may thus be observed as zones of unusual $^{87}Sr/^{86}Sr$; exploitation of this effect is a major goal of this study. Additional geochemical data may be used to separate reaction effects from the effects of mixing between contrasting water masses, and also to complement the $^{87}Sr/^{86}Sr$ analysis. A second component of the study concentrates on the physical hydrology. A state-of-the-art technique that processes fields of hydraulic head data to identify zones of unusually high or low permeability is being used. This inverse method incorporates fractal geometry, which facilitates a search for both the complex structure and parameters of heterogeneous permeability distributions, using only a few unknown parameters.

Identifying groundwater flow directions and the locations of any preferential flow zones that might serve as conduits for rapid transport of contaminants is a critical task in preserving the quality of groundwater resources.

Results: A suite of approximately 90 groundwater samples collected in and near the Idaho National Engineering and Environmental Laboratory (INEEL) were analyzed for Sr stable isotope ratio ($^{87}Sr/^{86}Sr$) and dissolved element concentration data. Subsamples of many of these were provided to researchers at Los Alamos National Laboratory (LANL), who measured $^{234}U/^{238}U$ ratios as part of an EMSP program project. Clear patterns in the spatial distribution of $^{87}Sr/^{86}Sr$ and $^{234}U/^{238}U$ ratios strongly suggest relatively fast groundwater flow in an elongate zone passing through the center of the southern INEEL boundary, and slower flow on both sides of this zone. Concentrations of 14 dissolved elements provided additional information on regional flow patterns and helped to highlight the unique properties of the isotope ratios as groundwater tracers.

The second focus of the project used computer models to analyze the $^{87}Sr/^{86}Sr$ and hydraulic head data quantitatively. SUTRA, an established groundwater flow/solute transport/reaction code was embedded in IFSINV, an inverse model based on Iterated Function Systems, yielding a code that can use observed Sr isotope data and hydraulic head data to infer the existence and locations of fast flow paths. A traditional zone-based inverse method was also developed, in which the location of a potential fast flow path was specified a priori. The models confirmed the hypothesis suggested by the $^{87}Sr/^{86}Sr$ data - that the observed pattern can be produced by the existence of a relatively fast flow zone passing through the southern boundary of the INEEL flanked by slower flow zones. Furthermore, it demonstrated that the lack of a similar pattern in the head data did not obviate the fast path hypothesis. The head patterns expected near a fast flow zone are more complicated and not as readily apparent as the $^{87}Sr/^{86}Sr$ patterns. The contributions of the modeling part of the study are in demonstrating methods for simultaneous, quantitative interpretation of head and water chemistry data and illustrating the complementary nature of the two data types. The modeling results suggest that geochemical data can be more easily interpreted as indicators of preferential flow zones than hydraulic head data.

Geochemical and Isotopic Constraints on Processes in Oil Hydrogeology.

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Objectives: This research project evaluates the processes which produce, dissolve and distribute noble gases and noble gas isotopes among liquid hydrocarbon, gaseous hydrocarbon and aqueous phases. This project also uses the abundances and isotopic composition of noble gases in hydrocarbon systems to evaluate hydrocarbon sources and characteristics, groundwater end-members, and migration processes, mechanisms, and time scales.

Project Description: The mechanisms, processes and time scales of fluid flow in sedimentary basins represents a fundamental question in the Earth Sciences with direct application to exploration and exploitation strategies for energy and mineral resources. This project investigates the noble gas composition of hydrocarbon samples on a basin and field scale where adequate commercial production and ancillary information are available, to provide a test of the use and applicability of noble gases to delineate end members, migration mechanism and migration paths for hydrocarbons. Samples are analyzed for the five stable noble gases (He, Ne, Ar, Kr, Xe) and their isotopes.

Results: Negotiations with various oil companies for the provision of samples in the North Sea and the Gulf of Mexico are progressing. Talks and plans have been significantly slowed by the low price of oil and oil company mergers. Torgersen will use his sabbatical leave to secure the samples.

The analysis of the Elk Hills oil field gases was completed and submitted for publication. The investigation of noble gas data from that field shows strong enrichment in the ratio of Xe,Kr relative to ^{36}Ar that is derived from the source rock. Xe,Kr enrichments in shales and other carbon-rich rocks have been noted by previous workers but have not been distinctly noted in hydrocarbons. This initially enriched Xe,Kr signal from the source rock appears to be diluted by interaction with groundwater. The large volume of water seen by the migrating oil and the higher solubility of noble gases in the hydrocarbon relative to groundwater results in a transfer of noble gases from groundwater to the hydrocarbon phases which dilutes the enriched Xe, Kr signal. The results suggest that noble gases are a useful tool for tracing hydrocarbon migration.

Current investigations are evaluating ^{3}He with respect to the involvement of mantle heat in the maturation of hydrocarbon sources. ^{4}He and ^{40}Ar/^{36}Ar ratios are being evaluated with regard to the temporal constraints radiogenic ^{4}He and ^{40}Ar provide with regard to model 'ages' of the source area and groundwater with which the hydrocarbon interacts during migration and reservoir storage. Neon isotopes will be evaluated with respect to groundwater equilibration temperatures, air contamination and nucleogenic neon isotopes produced in the source regions. Non-radiogenic ^{36}Ar will be evaluated as a measure of the total volume of groundwater that interacted with the hydrocarbons in the time between primary migration and commercial production. Kr and Xe isotopes will be evaluated as an indicator of the enrichment of the source area seen in many sedimentary rocks.

Reactive Chemical Transport in Structured Porous Media: X-ray Microprobe and Micro-XANES Studies

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

Project Description: Predicting transport of trace elements between various environmental compartments is currently often unsuccessful, partly due to lack of relevant information at compartment boundaries. Batch studies can yield insights into kinetics and equilibrium in well-mixed systems, but much of the subsurface is very poorly mixed. Without in-situ, spatially- and temporally-resolved chemical information, transport between compartments can only be described with system-specific, nonmechanistic, mass transfer models. In this project, the synchrotron x-ray microprobe and micro-XANES techniques are used to obtain such measurements in a variety of critical microenvironments. Past efforts in this project focused on selenium transport and reduction in two types of microenvironments, that found at surface water-sediment boundaries, and that found within soil aggregates. In FY 1998, the project emphasis shifted to consider reactive transport of another environmentally important contaminant, chromium.

Results: Initial studies on reactive transport of Cr included flow-through experiments in columns of aggregated soils, including spatially-resolved, real-time tracking of initial contamination processes within soil aggregates, and later characterization of Cr redistribution upon long-term drying. The aggregate microcosms were prepared and incubated in the laboratory, with microprobe and micro-XANES analyses conducted at the National Synchrotron Light Source and the Advanced Photon Source. The flow-through experiments were conducted under unsaturated conditions characteristic of contamination at a flux rate lower than the saturated permeability of the soil profile. Columns were infused with Cr(VI) solutions (concentrations up to 5200 ppm) under steady unsaturated flow. Film flow of the contaminant solution through continuous macropore networks was visually observed. X-ray microprobe mapping of total Cr distributions showed active macropore transport paths and transport into individual soil aggregates. Micro-XANES analysis showed persistence of Cr in the Cr(VI) form along preferential transport pathways, and some reduction to Cr(III) within aggregates. X-ray microprobe and micro-XANES mapping of the aggregated soil columns following 2 months of slow drying (representing post-contamination conditions in a semi-arid environment) revealed reoxidation of Cr(III) to Cr(VI), and localized precipitation of Cr(VI). Localized zones of Cr(VI) precipitation were smaller than 0.1 mm, space about 0.5 mm apart, and strongly correlated with Ca.

Unsaturated Fast Flow in Fractured Rock: Testing Film Flow and Aperture Influences

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Objectives: The nature of unsaturated fast-flow in fractured rocks needs to be understood in order to obtain reasonable constraints on vadose zone transport. Water films along unsaturated fractures have recently been shown to be capable of supporting fast flow and transport, and revealed limitations of existing aperture-based models. In this project, theoretical considerations and experiments are combined to improve our understanding of unsaturated flow in fractured rocks.

Project Description: Recently, the concept of film flow was introduced as a possible process by which preferential flow could occur along truly unsaturated fractured rock. Our work concerns water films on fracture surfaces under near-zero (negative) matric potentials, and examines the possibility of fast, unsaturated flow under "tension". "Films" in this context are a complex network of thick pendular regions that form within topographic depressions and thin films on topographic ridges. Thus, the thickness and connectivity of pendular film regions is expected to be important in controlling film flow on individual fracture surfaces. We showed that at matric potentials greater than that needed to saturate the rock matrix, transmissive water films can develop on fracture surfaces. The matric potential dependence of the average film thickness and film transmissivity of a Bishop Tuff fracture surface were measured using equilibrium and steady-state methods, respectively. The water “films” investigated in the previous study as well as the present one develop on rough surfaces, range in average thickness from about 1 to 50 μm, and flow in the laminar regime. In the FY 1998 work, additional concepts and experimental tests of film flow were pursued. These developments include introduction of the film hydraulic diffusivity and transient film flow equation, and new methods for measuring relations between average film thickness, matric potential, and film hydraulic diffusivity.

Results: By considering films on fracture surfaces as analogues to water in partially saturated porous media, the film hydraulic diffusivity and equation for transient film flow are obtained from their porous medium counterparts, the hydraulic diffusivity and the Richards equation. Several different measurement techniques, based upon previously developed soil physics methods, were developed for application to studies of film flow. The experiments performed in the present study were done on surfaces of roughened glass (9 μm root mean square roughness). Equilibrium and transient measurements of film thickness, matric potential, and film hydraulic diffusivity were measured through x-ray fluorescence of a solute tracer. The Se(VI) tracer provided a signal proportional to film thickness, and was monitored using a synchrotron x-ray fluorescence microprobe (National Synchrotron Light Source, beamline X26A). Fast film flow, defined here as flow with average velocities greater than 10 m y^{-1} under unit gradient conditions, was observed for average film thicknesses greater than 2.5 μm and matric potentials greater than -1 kPa on the roughened glass surface. The measurements showed the average film thickness dependence on matric potential is approximated as a power function. It was also shown that within the range of parameters tested, the film hydraulic diffusivity increases with increased film thickness (and with increased matric potential). Such a trend is indicative of flow through directly interconnected surface channels, and has been termed "hypodiffuse" by P. G. de Gennes. The possibility for the opposite, "hyperdiffuse", trend was suggested by de Gennes for porous media at low water contents.

Colloid Transport in Unsaturated Porous Media and Rock Fractures

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Objectives: The objective of this project is to improve the mechanistic understanding on colloid transport in unsaturated porous media. Since the classic filtration theory for predicting colloid transport cannot be directly used for transport in unsaturated media, this research is designed to develop a comprehensive understanding and model for colloid transport through vadose environments.

Project Description: In the vadose zone, sorption of colloid-associated contaminants at air-water interfaces can influence contaminant fate and transport. For solutions containing surface-active molecules, measurement of changes in surface tension with changes in solute concentration permits calculation of their surface excess through the Gibbs adsorption equation. However, for suspensions of particles, surface tension changes are often not detectable. Much effort has been devoted to characterizing surface accumulations of particles and associated species. Previously developed methods include surface microlayer sampling using stainless-steel mesh, skimmer devices, slides, and jet drop collection. Because of the large uncertainties in thicknesses and interfacial areas sampled using these methods, results are often reported as the enrichment factors for a given estimated thickness. In this study, a simple dynamic method was developed to quantify colloid surface excesses at air-water interfaces without requiring assumptions concerning the thickness of interfacial regions.

Results: We developed and tested the first quantitative method for measuring colloid partitioning at the gas-water interface, a simple bubble column method. This method permits quantification of surface excesses of a wide range of inorganic, organic, and microbial colloids, as well as molecular species complexed onto colloids. We define colloid particle surface excesses in a manner similar to that used for dissolved molecules. This quantity is the excess number of particles per unit interfacial area relative to that obtained by assuming that the bulk suspension concentration extends unchanged up to the air-water interface. In dilute suspensions, this colloid surface excess is linearly related to the bulk suspension concentration through a partition coefficient, *K*. Using this method, we measured the partition coefficients (K) of many common types of subsurface colloids under environmentally relevant conditions. Montmorillonite is essentially non-surface active (with respect to air-water interfaces) at any given pH and ionic strength. Illite was slightly surface-active, with increased K values at lower pH and higher ionic strength (K= 0 to 40 μm). Kaolinite particles are very highly surface-active at pH below 7 (K values are up to 240 μm). Humic acid is slightly to moderately surface-active. Goethite is extremely surface-active at pH below 9 (K values are up to 320 μm). Through these measured K values, we are now able to predict what types of colloids are surface active, to what degree, and under what conditions. An article describing this method was published on Environmental Science and Technology (Wan and Tokunaga, ES&T, 1998), and another manuscript presenting the results using this method is to be submitted to the Journal of Colloid and Interface Science.

CATEGORY: Energy Resource Recognition, Evaluation and Utilization

PERSON IN CHARGE: S. M. Benson

International Hydrogeology Research Cooperation

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Objectives: To establish research cooperation with hydrogeologists in Russia, Japan and European countries, to carry out research jointly in hydrogeology with emphasis on contaminant flow and transport in heterogeneous geological systems, and to benefit from each others' discussions and experiences.

Project Description: The project was originally initiated to establish research cooperation in hydrogeology and geochemistry of radioactive contamination with Russian scientists during the major changes in Russia over the last few years. Under the project we have established close scientific understanding and research cooperation with Moscow State University, Russian Academy of Sciences institutes, and institutes of the Russian Ministry of Atomic Energy. Every year, two to five Russian scientists spend 1-3 months at LBNL to have in-depth discussions with U.S. scientists, to carry out joint research work and to prepare scientific papers to be published in U.S. journals. An international conference on Scientific and Engineering Aspects of Deep Injection Disposal was co-sponsored under this project, and subsequently, selected authors prepared chapters for a state-of-the-art book on the subject that was published by the Academic Press in 1996. Under this project, the first joint U.S.-Russian field test at Chelyabinsk Mayak site was carried out to study the hydrochemical and geophysical condition of the site, which is the most radioactively contaminated site in the world. The results were published in the Journal of Environmental Geology in March 1997. This fiscal year, the successful cooperative research effort was expanded from Russian effort to cooperation with European and Japanese colleagues.

Results: Activities included not only joint research with Russian colleagues, but also with colleagues from Sweden and Japan. With Russian colleagues, we continued our active cooperation. With Japanese colleagues, we have started research in new site characterization techniques for evaluating heterogeneous geologic formations. With Swedish colleagues, we are cooperating in research into coupled thermo-hydro-mechanical (THM) processes. This is based on our earlier research in coupled THM modeling and code development. Cooperation with the Swedes has already borne fruit.

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CATEGORY: Geophysics and Earth Dynamics

PERSON IN CHARGE: F. J. Ryerson

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

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Objectives: The objective of this research is to provide new fundamental understanding of the coupling of rock deformation and fracture at the grain scale to macroscopic properties and to and fluid flow.

Project Description: This project is concerned with simulation of rock deformation and fracture at grain and larger scales. During the initial phase of the project a 2-dimensional field-theory model for rock fracture was developed and then used to determine how heterogeneity in different microscale parameters affects behavior in the simulated compression tests, and how macroscopic stress strain behavior is related to the formation of cracks. More recently, we have extended our work to include simulation of rock deformation in 3-dimensions. This work uses high-resolution 3-dimensional tomographs of the rock microstructure as input, and is focused on studying the fundamental physics of coupled rock deformation and fluid flow. This includes evaluation of the effects of local heterogeneity on the permeability field, as well as extending our work on crack nucleation and propagation.

Results: During the past year we developed and tested a highly efficient finite-element model, custom designed to use high-resolution X-ray tomographs of rock microstructure as input. These tomographs can resolve features as small as a few microns in size, but to fully resolve all the details of the tomographic image requires 10^7-10^8 elements, or in extreme cases 10^9 elements. This is far beyond the capacity of most finite-element codes, even using parallel computers. Fortunately, as all the elements in the tomograph are cubic, the stiffness matrix for a typical element can be calculated in advance, which results in a much-simplified code. Furthermore, we derived a new stiffness matrix from a lattice-spring model, as opposed to the usual strain-energy methods; it is a sparse matrix and requires only one tenth as many arithmetic operations to compute the nodal forces as a conventional finite element. This streamlined model can simulate systems as large as 10^7 elements on a single processor.

We also implemented a grain scale failure criterion based on local strain rather than stress. Using this criterion the finite element model predicted brittle fracture behavior very similar to that observed in a bone sample that was imaged under compressive load.

Velocity Analysis, Parameter Estimation, and Constraints on Lithology for Transversely Isotropic Sediments

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Objectives: Our major objective is to obtain constraints on lithology using the anisotropy parameters recovered from seismic data, in order to improve analysis of seismic rflection data collected in areas where the geology is complicated by anisotropy and heterogeneity.

Project Description: The influence of anisotropy leads to significant distortions in seismic reflection data processing and errors in interpretation that can result in drilling in the wrong place or to the wrong depth, and errors in data analysis that may turn a play into a non-play or vice versa. Theoretical constraints on the elastic stiffnesses in a transversely isotropic medium and algorithms newly-developed at the Colorado School of Mines for processing seismic reflection data exhibiting transverse isotropy are being combined with rock physics analysis to determine how constraints on anisotropy translate into constraints on lithology and improved interpretation of seismic reflection data. Expected benefits of this project are improved processing and interpretation of seismic reflection data in the oil exploration industry and increased understanding of the connections between seismic properties and other physical properties of rocks and sediments exhibiting anisotropy.

Results: Investigators from the Colorado School of Mines have developed new algorithms and codes for processing 2-D and 3-D seismic reflection data in vertically inhomogeneous transversely isotropic media and orthorhombic media. These results have been published in Geophysics and in The Leading Edge and were presented at the 1997 annual meeting of the Society of Exploration Geophysicists (SEG) and the Eighth International Workshop on Seismic Anisotropy in 1998. These results have also been submitted to Geophysical Prospecting and to the Geophysical Journal International. Results from research at Stanford include the development of a set of mathematical tools for constructing the elastic properties of anisotropic rocks and for deconstructing elastic moduli into rock properties. These results were presented at the 1997 Stanford Rock and Borehole Geophysics Project Annual Meeting for Stanford's oil industry consortium. LLNL researchers have investigated the range of values and algebraic sign of two key anisotropy parameters in layered transversely isotropic media and how these values are related to fluid content. These results were presented at the 1997 annual meeting of the SEG and were submitted to Geophysical Prospecting. LLNL researchers collaborating with Schlumberger researchers have also developed models to describe stress-induced anisotropy in granular media. These results have been published in the ASME Journal of Applied Mechanics and a proceedings volume for a conference sponsored by the Institute for Mathematics and its Applications.

Visco-, Thermo-, and Poroelasticity of Rocks and Rock/Fluid Mixtures

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Objectives: Our main objective is to understand factors affecting physical properties of rocks in order to improve our ability to predict rock behavior from knowledge of rock components. One new tool developed to accomplish this objective is the recent discovery of exact results in poroelasticity and thermoelasticity for two component composite rocks and the application of these ideas to effective medium theories for poroelastic composites. This project exploits these as well as other new results, with the expectation that new insight into the poro-, thermo-, and viscoelasticity of rocks will result. Such insight should prove important for understanding partial melt in both the upper and lower mantle, for clarifying earthquake source mechanisms, for interpreting seismic reflection survey data for oil and gas exploration, for oil field engineering practices related to drilling and pumping, and for related issues in environmental cleanup of DOE sites. This type of information is important for interpretation of both seismic and electrical geophysical field data.

Project Description: Four major approaches are being considered in this project: (1) development and application of viscoelastic property bounds to rock/fluid mixtures, (2) volume averaging methods for rock/fluid mixtures, (3) double-porosity/dual-permeability methods for fractured reservoirs, and (4) development and use of a new generalization of Eshelby's formula from elasticity theory for poroelastic and thermoelastic composite inclusions analysis problems. These types of results are all of interest in the oil and gas industry. The same basic framework can also be employed to treat reservoir characterization problems, especially regarding the effects of changing stress on matrix and fracture permeability in double-porosity models used for reservoir pumpdown studies. In addition to single-fluid reservoir analysis, related ideas have been applied to partial saturation problems, in which both gas and oil, or gas and water may be present and distributed thoroughout the reservoir volume in a complicated, inhomogeneous manner. Related ideas (Gassmann's fluid-substitution formulas) can play a very significant role in interpretation of seismic AVO (amplitude versus offset) data used as direct hydrocarbon indicators.

Results: A new theory of the elastic behavior of granular materials and/or cracked materials under uniaxial stress has been developed and its implications continue to be explored. This work was done in collaboration with industry (Schlumberger-Doll) and a major paper on the topic was published in ASME Journal of Applied Mechanics. In collaboration with Stanford researchers, we developed some new approximate formulas that can be used to describe the elastic behavior of cemented sandstones. Agreement with laboratory data was shown to be quite acceptable. These results were published in the journal Mechanics of Materials. In collaboration with Professor Graeme Milton of the University of Utah and Dr. Leonid Gibiansky of Princeton University, we developed a method for obtaining rigorous bounds in both 2D and 3D on the shear modulus of viscoelastic composites such as rocks that contain mixtures of two viscoelastic constituents, for example, quartz and a viscous fluid, or quartz and clay. This work extends and completes the previous work of the Gibiansky and Milton on the bounds for the bulk modulus of viscoelastic composites, and furthermore shows how well various realizable theoretical models (*i.e.*, effective medium theories such as the self-consistent method) produce results consistent with the bounds. Two papers describing this work have now been published in Proceedings of the Royal Society of London. In collaboration with researchers at the University of Wisconsin, we had previously developed methods to determine and in some cases drastically reduce the number of elastic coefficients required to describe the behavior of a double-porosity system in the presence of changing pore pressure for applications to reservoir pumpdown. This work was published in the Journal of Geophysical Research. Subsequent work in this area has been done on elastic wave propagation through such media, leading to equations that permit the parameters that determine wave speed and attenuation to be decoupled in a significant new way. This work is scheduled to appear in International Journal of Rock Mechanics, and extensions of the work continue through studies of methods to estimate coefficients in these equations that can be computed from knowledge of the constituents and their physical properties. Related work on volume averaging to establish a firm theoretical foundation for poroelasticity and its extensions has been published in International Journal of Solids and Structures and in Journal of the Mechanics and Physics of Solids in collaboration with Professor Steven Pride from France.

Reactive Solute Transport and Processes of Dissolution and Deposition in Single Fractures in Rock

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Objectives: The objective of this research is to measure local rates of dissolution and precipitation on the walls of individual fractures and correlate differences in reaction rates to changes local fracture aperture. Much use will be made of high-resolution physical topography measurement and numerical simulation of reactive flow.

Project Description: The experiments and simulations will be done on rock samples containing a single laboratory-made or natural fracture. Detailed imaging of the fracture aperture before and after alteration will be 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 will work with simple but relevant systems in order to maximize our understanding and impact: samples will be monomineralic rocks with low porosity and low bulk permeability (such as quartzites and marbles), under fully saturated, single-phase flow conditions. We will attempt measurements in undersaturated, dual-porosity, and more chemically complex settings as success dictates.

Results: We have performed a series of dissolution experiments on a laboratory-made fresh fracture in Carrara marble configured with the two sides of the fracture slightly out of register, and have made careful topographic measurements of the fracture surfaces after each dissolution step in order to follow the progress of dissolution visually. Approximately 0.5 g of material was dissolved from the fracture in each test. If distributed uniformly, this amounts to the removal layer approximately 30 microns thick. This is near the resolution limit of the digital imaging system, and in fact, we saw no obvious changes in the digital images of the surfaces following the first dissolution step. Analysis of the image data taken after the second and third dissolution steps is in progress, as is numerical simulation of fluid flow in the fracture. We have also measured the topography of a second Carrara core in preparation for follow-on experiments, whose conditions will depend on image analysis and flow modeling results of the first core.

The Role of Carbon and Temperature in Determining Electrical Conductivity of Basins, Crust, and Mantle.

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Objectives: The intent of this work is to comprehend the electrical conduction mechanisms in carbon-bearing rocks and in mantle minerals so electrical conductivity measured in the field can be related to formation conditions and existing state of crustal rocks and to temperatures in the mantle.

Project Description: Electrical conductivity depends strongly on temperature T and on the presence of other phases such carbon, fluids, or ore minerals at the lower temperatures of the crust and basins. Thus, one research approach is to measure the electrical conductivity of mantle minerals as a function of temperature, orientation, oxygen fugacity fO_2, and iron content. These data supply the best models for "electrogeotherms" yet available. Another approach is to document textures of carbon in crustal rocks from basins and metamorphic zones and relate them to rock conductivity. In this case texture of carbon distribution is mapped with electron microscopy in the same samples used for conductivity measurement. The approach this year was to look at the effect of pressure on electrical properties of olivine. We report new measurements of electrical conductivity of olivine that were made in a multi-anvil press using solid buffers (Mo-MoO_2) to stabilize oxygen partial pressure. The temperature range was 1000-1400°C and the pressure range was 4-10 GPa. When pressure effects are interpreted as activation volumes in the Arrhenius equation, they yield values of order 0.6 ± 0.6 cm^3/mole. Values of the pre-exponential factor are of the order of hundreds of S/m, and the zero-pressure activation energy is about 1.5 eV, in agreement with laboratory measurements at lower pressure conditions. In addition, we analyzed older literature data, which produced a similar result but with larger variation. The common practice of assuming that the pressure effect on electrical conductivity of olivine in Earth's upper mantle depends weakly on pressure has rested on uncertain grounds.

Results: At depths of 30-400 km in Earth's mantle, these new observations suggest that neglecting pressure effects on olivine conductivity is justified. A weak pressure effect also supports the small polaron (Fe^{3+}) model as the dominant conduction mechanism, although the mainly positive activation volumes argue for a component of lattice deformation. When applied to the depth range 200-400 km in the Earth, the laboratory data yield conductivities of order 10^{-2} S/m, slightly lower than the range of geophysical conductivity profiles but well within this range after allowing for probable effects of oxygen activity and temperature uncertainty.

The results apply to our understanding of mantle dynamics, plate tectonics, and the distribution of heat sources beneath the crust.

Water distribution in partially saturated porous materials

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Objectives: To determine the distribution of water in partially saturated porous materials by measuring the complex electrical properties and to investigate the relationships between electrical transport and other transport properties in materials with well-characterized microstructures.

Project Description: The purpose of this project is to measure the unsaturated electrical properties of fused glass bead samples ranging in porosity from 1 to 43 percent. Measurements include dielectric constant and electrical resistivity as functions of saturation. The complex impedance from 10^{-3} to 10^{6} Hz is measured because impedance spectra provide information regarding the number and arrangement of conduction mechanisms and the distribution of the liquid phase. The fluids used to saturate the samples have a range of ionic composition, and hence, electrical conductivity. This permits the comparison of impedance spectra of samples at similar saturations to better understand the relationship between fluid distribution and the corresponding conduction mechanisms. These measurements are of particular importance because field electrical measurements in unsaturated regions (including electrical resistance tomography, electromagnetic depth sounding, and induced polarization) depend on reliable laboratory measurements for accurate interpretation. The degree of difficulty of remediation problems in the vadose zone may depend on reliable information regarding the interconnectedness and distribution of the fluid phase.

The results will be analyzed in terms of mechanism of conduction and compared to existing measurements and models. These comparisons include permeability, cation exchange capacity, and ultrasonic velocity. All of these transport properties depend to some degree on microstructural properties as well as saturation level. Detailed microstructural characterization of the material will be performed and relationships between the microstructure and interconnectedness of fluid as a function of saturation will be explored.

Results: Laboratory impedance measurements on fused glass bead samples continued on samples ranging in porosity from 5 to 30%. Variable salinity NaCl solutions are being used as saturating solutions in an attempt to isolate individual conduction mechanisms as functions of frequency and saturation. Distinct conduction mechanisms are observed and are under investigation. Data have been analyzed in an attempt to establish links between electrical and other transport properties. This work was presented at the Fall 1997 AGU and a summary paper was written and submitted to Water Resources Research. Samples of natural sandstone are being prepared for experimental measurements. Samples were selected to have similar porosities and microstructural properties as the glass bead samples, with the additional complications of clay, weathering products, and surface conduction.

Collaborations with field EM modelers and theoreticians were initiated. The goal is to better interpret field data in terms of water content and physical properties. Thus far, the collaborations are promising, resulting in a publication with LBL investigators and a patent disclosure with LLNL researchers. The work with Hubbard is particularly noteworthy as multi-frequency lab measurements were required on materials over a wide range of conditions (saturation, temperature). A neural network has been implemented to predict electrical properties over a wider range of conditions and initial results using borehole tomographic radar have been successful. Work in this area will continue.

CATEGORY: Geochemistry

PERSON IN CHARGE: F. J. Ryerson

An Experimental Investigation of Mechanisms Controlling Glass Dissolution

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Objectives: The objective of this project is to identify the underlying molecular mechanisms responsible for dissolution of glass and to utilize this understanding in the development of quantitative models for predicting glass dissolution rates in nature.

Project Description: This project uses a combination of conventional glass dissolution experiments and NMR to characterize the solution interface to determine the mechanisms controlling glass dissolution. The dissolution behavior of simple SiO_2 glass was used to develop a mechanistic model based on three principal observations: (1) the pH dependence of dissolution rates (2) the saturation effect and (3) the effect of absorbed alkali cations on dissolution rates. The results are relevant to a number of problems including the stability of radioactive waste glasses, weathering of volcanic glasses, and obsidian hydration age dating, among others.

Results: Based on our initial multinuclear nuclear magnetic resonance (NMR) spectroscopic observations of the change in silanol (>SiOH) and outer-sphere alkali sorption at pH 4 and 10, we have expanded our study to provide a complete determination of silica surface chemistry as a function of pH. The ^{29}Si cross-polarization NMR results show that silanol surface complexes decrease with increasing pH. The pH dependence of the alkali surface complexes is opposite to that of the silanol complexes (>SiOH). The ^{23}Na and ^{133}Cs NMR results show that the alkali cations form outersphere surface complexes and that the concentration of these complexes increases with increasing pH. With this data we use surface complexation modeling to re-evaluate amorphous silica reactivity as a function of solution pH and reaction affinity in NaCl and CsCl solutions. The resulting thermodyanmic parameters will then be applied to pH-dependence of silica glass dissolution as a function of alkali sorption and pH.

Mineral Dissolution and Precipitation Kinetics: A Combined Atomic-Scale and Macro-Scale Investigation

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Objectives: Our objectives are to build and test an atomic force microscope (AFM) capable of operation at up to 150°C and 10 atm pressure, to apply this AFM to direct, in-situ, and real-time observation of step dynamics during dissolution and growth of oxide and silicate minerals at elevated temperature and pressure, and to use rate and stoichiometric data from parallel macroscopic dissolution and growth experiments to interpret mineral rates using a combined microscopic Burton-Cabrera-Frank and macroscopic surface-complexation model.

Project Description: This project combines atomic-scale and macro-scale approaches to the study of mineral-fluid interaction in order to significantly improve our understanding of, and ability to predict the course of, mineral dissolution and precipitation processes. We have successfully built a high temperature-pressure flow-through AFM that allows atomic-scale kinetic experiments under geologically relevant conditions for important oxide and aluminosilicate minerals. This is a unique capability. Identical conditions are being investigated using macroscopic wet-chemical rate experiments, including conditions both near and far from equilibrium. We are measuring rates of dissolution and precipitation, determining activation energies, measuring rates of step motion across surfaces (including anisotropy), and investigating step-step interactions that affect rate. With this capability we can address many still-open questions concerning the exact forms for rate laws near and far from equilibrium, the microscopic interpretation of these rate laws in terms of dissolution and precipitation mechanisms operating under various conditions, and the question of what exactly the "active area of interaction" and "active sites" are on mineral surfaces.

Results: During this fiscal year we completed construction, testing and calibration of our unique Hydrothermal AFM (HAFM) up to a temperature of 150°C and 10 atm pressure. All design objectives were successfully accomplished. We produced the first real-time images of barite dissolution under hydrothermal conditions both near and far from equilibrium. We also made the first real-time images of dissolution of several other minerals under hydrothermal conditions: calcite, hematite, and anorthite. Results documenting our observations were published in several papers published in Langmuir and Mineral. Mag.. Talks were given at several international and national scientific meetings including the Goldschmidt Conference, the Geological Society of America, etc. A joint patent application was filed by LLNL and the University of Wyoming. We established a research collaboration with Dr. Guntram Jordan (Ruhr Univ. Bochum, Germany), who spent a sabbatical leave with Dr. Eggleston at U. Wyo.

Collaborative Research: Studies for Surface Exposure Dating in Geomorphology

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Objectives: The objective of this research is an experimental and theoretical program to fully develop the systematics of *in situ* produced cosmogenic nuclides in terrestrial surface samples and their application to the dating of surface features and processes. This work includes determination of precise production rates and production depth profiles, studies of altitude and latitude effects, intercalibration with other methods, isolation of *in situ* produced nuclides from other lithologies an development of *in situ* produced ^{14}C. This research is a collaborative endeavor between LLNL (Caffee, Finkel, AMS), UC Berkeley (Dietrich, geomorphology; Nishiizumi, geochemistry) and LANL (Reedy, cosmogenic nuclide modeling; Poths, noble gas mass spectrometry).

Project Description: In the past year work at LLNL, has attacked two components of the overall project objectives: *In situ* ^{14}C and spallogenic ^{36}Cl. ^{14}C has a half-life that is significantly shorter than the other commonly measured *in situ* cosmogenic nuclides. This makes it ideal for determining recent erosion rates and for burial dating of recent formations. Blank problems and difficulties in quantitatively extracting ^{14}C from rocks have limited the applicability of this nuclide. Work is nearly completed on constructing and calibrating an extraction line for determining ^{14}C in quartz samples.

Many geologic problems, *e.g.*, studies involving basalts, require dating of formations that do not contain quartz. ^{36}Cl is an alternative nuclide to use in these cases. The use of ^{36}Cl is made more complex by the existence of two modes of production: spallation from K and Ca and thermal neutron capture form Cl. The thermal neutron capture production has a very different depth profile and much greater dependence on rock composition and moisture than does spallation. We have begun chemical studies to develop methods for determining pure spallation ^{36}Cl.

Results: We have constructed a gas line for extracting ^{14}C from quartz. The high melting temperature of quartz has proven an obstacle, which we have now surmounted by using a high-temperature tube furnace rather than a radio-frequency generator. We have also found a source of ^{14}C-free carrier gas to use as an isotope spike. Tests performed on this spike indicate that 0.5 mg has no ^{14}C beyond that normally added during graphitization of the C. Blank tests performed on samples spiked with dead carbon have shown that we can now melt 20 g of quartz and extract carbon with a blank of approximately 2-3 x 10^6 atoms of ^{14}C. The next phase was the separation of the meteoric ^{14}C from the *in-situ* ^{14}C. Tests performed to date suggest the meteoric ^{14}C is released at lower temperatures without the use of an oxidizing atmosphere. The *in-situ* ^{14}C is released quantitatively at higher temperatures under oxidizing conditions. The procedure we are presently employing is one in which the meteoric 14C is released at ~ 600-800 C in nitrogen gas. The temperature is then raised to ~ 1400 C and the ^{14}C is released into the carrier/spike gas. This flow gas is essentially atmospheric in composition so it effectively oxidized the released C to CO_2.

Dating depositional surfaces: Applications of *in situ* Cosmic-ray Exposure Dating

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Objectives: Cosmogenic isotope abundance patterns will be determined for different types of aggradational surfaces of known to assess the applicability of this method for deposits of this type. Such data are required if the climate and other information held in these surfaces is to be fully exploited.

Project Description: Landscape evolution depends strongly on climate and tectonics, and landscape history may in principle be inverted to obtain information regarding these two forcing factors. A major group of landscape features is those involving the emplacement and modification of depositional surfaces. Providing a temporal framework based upon cosmic-ray exposure dating for the interpretation of such features is challenging, as they may be modified subsequent to deposition, and may possess a pre-depositional exposure history. In our work, we propose to develop and validate sampling and analytical methods for three different depositional settings in the western US: debris flow fans, lacustrine shorelines, and fluvial deposits using a combination of ^{10}Be, ^{26}Al, ^{21}Ne and *in situ* ^{14}C at LLNL's Center for Accelerator Mass Spectrometry Sampling strategies will exploit the depth dependence of cosmogenic nuclide production to constrain inheritance and post-depositional disturbance. The measurements will provide a basis for future investigations requiring the dating of such surfaces, and provide additional constraints on Quaternary climate and tectonics in the western US.

Results: This is a new project

Thermodynamic and Transport Properties of Aqueous Geochemical Systems

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Objectives: The objectives are to (1) measure precise and accurate osmotic/activity coefficients, solubilities, densities, and mutual (Fick's law) diffusion coefficients for aqueous brine salts and their mixtures and osmotic/activity coefficients for acidic sulfate mixtures; (2) develop reliable methods to estimate such properties for multicomponent solutions from binary solution properties; and (3) calculate generalized transport coefficients.

Project Description: The general techniques of classical thermodynamics and of linear irreversible thermodynamics are used to understand and model equilibrium and transport processes in brines and other aqueous electrolyte mixtures relevant to energy programs. Properties being measured are osmotic/activity coefficients and solubilities by the isopiestic method, densities by pycnometry and vibrating densimetry, and diffusion coefficients by Rayleigh and Gouy interferometry.

One major goal is to measure highly accurate data for systems involving geochemical brines and chemical pollutants. A second goal is to develop estimation methods for accurate predictions of these properties for aqueous electrolyte mixtures of arbitrary complexity, using the accurate new data as test systems. Osmotic/activity coefficients are being analyzed using extended forms of Pitzer's equations, and transport data are being analyzed as Onsager transport coefficients.

Results: Diffusion experiments were performed at four different solute ratios of mixtures of NaCl and Na_2SO_4 at 25°C and at a total molarity of 1.5 mol/dm^3, along with the limiting binary solutions NaCl and Na_2SO_4 using Rayleigh interferometry. These experiments extend our previous measurements at 0.5 and 1.0 mol/dm^3 at 25°C, and were made using the Gosting diffusiometer with computer-controlled data collection in real time. These diffusion experiments were performed in collaboration with Professor John G. Albright and a graduate student at Texas Christian University. At 1.5 mol/dm^3 both the NaCl main-term and cross-term coefficients each have a maximum as a function of solute composition fraction, whereas the Na_2SO_4 cross-term coefficient has a minimum. In addition, the cross-term coefficients are opposite in sign.

Isopiestic vapor-pressure experiments were completed for aqueous H_2SO_4 + $MgSO_4$ mixtures at 25 °C, at six molality fractions z of H_2SO_4 of z • 6/7, 5/7, 4/7, 3/7, 2/7, and 1/7, and now extend from low to supersaturated molalities at all composition fractions. A total of 284 data points were measured. The results are being modeled with extended versions of Pitzer's equations, and will include terms for the interaction of Mg^{2+} with HSO_4^-.

The building in which our laboratory had been located for many years was closed this year, our experimental isopiestic measurements were shut down in May, 1998, and our equipment was put into storage while a new laboratory was being remodeled. We began moving into this new laboratory in November 1998 and reassembled the isopiestic apparatus and its constant temperature water bath. The diffusion measurements were not affected by this move since they are being performed off site.

During this period four journal articles were published, along with a note in Applied Radiation and Isotopes. One of these papers reports our diffusion results for aqueous NaCl + Na_2SO_4 mixtures at 1.0 mol/dm^3. Another report (in collaboration with Dr. Donald G. Archer of the National Institute of Standards and Technology) gave a extended Pitzer ion-interaction equation of state for aqueous $MgSO_4$ valid from freezing temperatures to 440 K, which was based on our critically-assessed thermodynamic data base for this system. Joseph A. Rard is serving as the guest editor of the Kenneth S. Pitzer Memorial Tribute to be published by the Journal of Solution Chemistry.

CONTRACTOR: Los Alamos National Laboratory

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Contract: W-7405-ENG-36

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CATEGORY: Geophysics and Earth Dynamics

Fast 3D Seismic Modeling and Prestack Depth Migration Using Generalized Screen Methods

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Objectives: The intent of this work is to develop and explore seismic modeling and imaging for regions of complex geology that greatly improves on the results of conventional implementation of Kirchhoff migration.

Project Description: Modeling and migration of seismic data are among the most important ways we can learn about the structure of the earth. The demand for processing large seismic datasets to obtain high-quality images has thus become of critical importance. The finite difference method is the most popular method for modeling wave propagation through complex structures. Finite difference can also be used for migration; however, it requires enormous computational resources and is not feasible on even the largest computers. The approach taken by this project for doing efficient and reliable modeling and migration is to develop and explore use of dual-domain (space-wavenumber) methods for seismic modeling and imaging.

Results: We have been developing a suite of methods for doing efficient and reliable seismic wave modeling and migration. The methods use generalized screen propagators for one-way wave equations. Results using the methods developed for simple 2D models and for the Marmousi dataset (an industry-standard dataset) show good agreement with finite-difference and integral-equation approaches. This project continues our screen propagator studies, and applies our tools using more complex 2D/3D earth models, leading to capabilities for obtaining more reliable images of the earth's subsurface as well as for better understanding how seismic waves interact with the complex structure of the earth's lithosphere

The Role of Carbon and Temperature in Determining Electrical Conductivity of Basins, Crust, and Mantle.

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Objectives: The intent of this work is to comprehend the electrical conduction mechanisms in carbon-bearing rocks and in mantle minerals for relating electrical conductivity measured in the field to formation conditions and existing state of crustal rocks and to temperatures in the mantle.

Project Description: Electrical conductivity depends strongly on temperature T and on the presence of other phases such carbon, fluids, or ore minerals at the lower temperatures of the crust and basins. Thus, one research approach is to measure conductivity of mantle minerals as functions of temperature, orientation, oxygen fugacity fO_2, and iron content. These data supply the best models for "electrogeotherms" yet available. Another approach is to document textures of carbon in crustal rocks from basins and metamorphic zones and relate them to rock conductivity. In this case texture of carbon distribution is mapped with electron microscopy in the same samples used for conductivity measurement. The approach this year was to look at the effect of pressure on electrical properties of olivine. We report new measurements of electrical conductivity of olivine that were made in a multi-anvil press using solid buffers (Mo-MoO_2) to stabilize oxygen partial pressure. The temperature range was 1000-1400°C and the pressure range was 4-10 GPa. When pressure effects are interpreted as activation volumes in the Arrhenius equation, they yield values of order 0.6 ± 0.6 cm^3/mole. Values of the pre-exponential factor are of the order of hundreds of S/m, and the zero-pressure activation energy is about 1.5 eV, in agreement with laboratory measurements at lower pressure conditions. In addition, we analyzed older literature data, which produced a similar result but with larger variation. The common practice of assuming that the pressure effect on electrical conductivity of olivine in Earth's upper mantle depends weakly on pressure has rested on uncertain grounds.

Results: At depths of 40-400 km in Earth's mantle, these new observations suggest that neglecting pressure effects on olivine conductivity is justified. A weak pressure effect also supports the small polaron (Fe^{3+}) model as the dominant conduction mechanism, although the mainly positive activation volumes argue for a component of lattice deformation. When applied to the depth range 200-400 km in the Earth, the laboratory data yield conductivities of order 10^{-2} S/m, slightly lower than the range of geophysical conductivity profiles but well within this range after allowing for probable effects of oxygen activity and temperature uncertainty.

The results apply to our understanding of mantle dynamics, plate tectonics, and the distribution of heat sources beneath the crust.

Nonlinear Elasticity in Earth Materials

P. A. Johnson, (505-667-8936; Fax: 505-667-8487; paj@lanl.gov), J. A. TenCate, T. J. Shankland, E. Smith, and R. A. Guyer)

Objectives: Research objectives are to investigate the physical manifestations of nonlinear elasticity in rock, including those indicating reservoir/repository characteristics and those affecting seismic observations, and to characterize nonlinear properties of rocks. Of primary importance is developing and applying a holistic model describing the nonlinear response of rock over broad stress-strain-frequency ranges so that practical applications can proceed.

Project Description: Increasingly rapid progress is being made in the field of dynamic nonlinear elasticity of earth materials. Roughly ten years ago three groups of scientists (at Los Alamos, at the Institute of Applied Physics, and the Institute of Physics of the Earth in Russia) independently initiated this research field. Early and continued OBES support has been instrumental in making it possible for this research field to flourish. Today the field of dynamic nonlinear elasticity of earth materials has recognized importance in the domains of geomaterials, materials science, and strong ground motion, and there are an ever-increasing number of researchers working within it.

Rocks display unique elastic behavior. They are extremely nonlinear, being hysteretic, possessing discrete memory, and having slow dynamics [a long term memory of strain]. Although similar nonlinearities may exist in, for example, powdered metals, it is rocks that exhibit these characteristics "in spades" (to quote one of our colleagues). Thus, our study of nonlinearity in earth materials affords us opportunities to apply our knowledge to other materials as well. Nonlinear behavior plays a central role in developing new methods with which to characterize rock properties, for instance, interrogating the entire elastic microstructure of rock. Our work involves developing a comprehensive theoretical and experimental framework that (1) employs static and dynamic laboratory investigation of rocks to provide a macroscopic and microscopic description of the elastic state, and (2) provides for turning the microscopic description into a prescription for rock properties that can be used to predict change in stress state, both static and dynamic.

Results: Several new measurements reveal more about the nature of slow dynamics. When a moderate ac strain is applied to a sample, the sample softens (it becomes a weaker "spring"). After the ac strain is removed, the sample gradually stiffens (*i.e.,* it "recovers") until it returns to its original state. The process has been found repeatable over hundreds of cycles and experiments and over a period of more than a year. Moreover, the recovery process turns out to be logarithmic in time. Remarkably, this log(time) recovery is true for a wide variety of samples we have studied, from concretes, to sandstones, to limestone. log(time) recovery is found in many physical systems. Many can be found in systems that exhibit creep. Current work is focused on learning more about how slow dynamics may relate to creep.

CATEGORY: Geochemistry

Uranium-Series Concordance Studies

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Objectives: The goal of this project is to provide unique information on the behavior of U-series members in the environment using improved capabilities for Quaternary dating.

Project Description: Uranium-series disequilibria techniques are well-established and valuable tools for geochronology and geochemistry. Such measurements have typically been made by decay counting; however, there are considerable advantages in using mass spectrometric techniques. We have previously used BES funding to develop such techniques. The goal of this current proposal is to apply these new mass spectrometric methods to answer basic questions in Quaternary dating and geochemistry. Emphasis will be placed on: 1) modeling magma chamber processes using U-series disequilibria in young volcanic systems at Hawaii and Mid-Ocean Ridges and 2) evaluating ^{235}U-^{231}Pa and ^{230}Th-^{226}Ra-Ba disequilibria as a geochronometer for young volcanics using mineral isochrons and in carbonate systems using a multi-element concordia approach. This work will provide information on the recent evolution of magmatic systems and has application to natural hazard risk assessment, paleoclimate studies, and the carbon cycle.

Results: *Resolving Magma Chamber Residence Times Using U-Series Disequilibria* (with K. Cooper and M. Reid): We are measuring Ra-Th disequilibria in minerals separated from samples of lava from

Kilauea and Hualalai Volcanoes in Hawaii in order to delimit the residence time of Hawaiian magmas at different stages of volcano evolution and in different settings in the same volcano (*i.e.*, summit *vs.* flank eruptions). To date, we have measured Ra-Th disequilibria in minerals separated from a xenolith brought to the surface in the 1800-1801 eruption of Hualalai Volcano, and these results yield an age for the xenolith of less than 800 y before present.

Possible Contamination of MORB Glasses By Sedimentary Material (with B. Bourdon, D. Bourlès, and C. Langmuir): It has often been suggested that U series disequilibria measured in mid-ocean ridge basalts (MORB) can be perturbed by contamination with sedimentary or hydrothermal material found near the ridge axis where the basalts are erupted. Here, we provide an independent way of estimating the maximum degree of contamination by sediment using constraints from ^{10}Be. While all of the samples have large U-series daughter excesses typical of MORB, there is no ^{10}Be detected in any of the picked and leached glasses, indicating that the U-series disequilibria in carefully picked and cleaned MORB samples are magmatic in origin.

Evidence for Radium-Barium Fractionation in Plagioclase from a Zero-Age Mid-Ocean Ridge Basalt: The occurrence and subsequent sampling of an eruption event at the Northern Gorda Ridge in 1996 has allowed us to evaluate Th, Ra, and Pa systematics for both plagioclase and whole rock fractions of a truly "zero-age" sample. The plagioclase results permit us to evaluate ^{226}Ra/Ba/^{230}Th internal isochrons for dating basalts. These results suggest that Ra-Ba fractionation may have occurred during plagioclase crystallization, in agreement with theoretical models. The whole rock data allow us to more accurately determine ages for axial and off-axis lavas based on external isochrons and characterize the recent episodicity of axial volcanism at this site.

Rates of Geomorphic Processes using Cosmogenic He and Ne

J. Poths (505-665-2636; Fax: 505-665-6637; jpoths@lanl.gov)

Objectives: To quantify rates of surficial processes and expand the utility of cosmogenic noble gases as chronometers for dating young (<0.5Ma) surfaces.

Project Description: Our primary objective is to expand our knowledge of the timescales associated with geomorphic processes by applying cosmogenic He and Ne to specific geomorphic problems. One focus is on soil formation. We are investigating the relationship between various indices of soil formation and the time since onset of soil formation in arid and semi-arid settings. In addition, we are testing a method for dating of stream terraces and the soils formed in them on the Pajarito Plateau. These soil processes are strongly influenced by paleoclimatic effects. Another unifying theme of the work is understanding the nucleogenic background component that interferes with surface exposure dating. Understanding this component is important in our work on dating of the Missoula Floods, determining the formation mechanism for the turtlebacks in Death Valley, and investigating the paleoaltitude of the Rocky Mountains.

Results: We have continued to work with data from stream terrace deposits and their associated soils in several locations on the Pajarito Plateau, New Mexico. Detailed depth profiles allow the effects of pre-exposure of source material, bioturbation and time since deposition to be independently quantified. This study also provides confirmation of the semi-quantitative method of dating soils through correlation functions. Work is continuing to determine if differences in dates from cosmogenic ^{21}Ne (much older) and cosmogenic ^{10}Be for one of the Turtlebacks in Death Valley reflects a complicated burial and exhumation history or a nucleogenic interference in ^{21}Ne. Flood-scoured surfaces from along the Columbia River show a wide range in age (>10 ka), suggesting that the Missoula floods were a repetitive phenomenon. Initial work with the Fish Canyon Tuff (27.5Ma) has demonstrated proof of principle for using cosmogenic ^{21}Ne as a paleoaltimeter. Surface samples, later buried by the Carpenter Ridge Tuff, contain much more ^{21}Ne* than shielded samples. This work also implies that relative dating of stream terraces (*e.g.,* above) can be extended into the past for paleoclimate studies.

Surface Exposure Dating in Geomorphology

R. Reedy (505-667-5446; Fax: 505-665-4414; rreedy@lanl.gov), with K. Nishiizumi (U.C. Berkeley; 510-643-9361; kuni@ssl.berkeley.edu), W. E. Dietrich (U.C. Berkeley) R. C. Finkel (LLNL]), and M. W. Caffee (LLNL)

Objectives: The production of cosmogenic nuclides in terrestrial surface samples and the use of these nuclides to date and characterize young (<1 Ma) surfaces are studied.

Project Description: Geological samples start accumulating cosmogenic stable and radioactive nuclides such as 0.7-Ma ^{26}Al once they are formed very near the surface or brought to the surface from depths of many meters. These nuclides are often the only way to characterize the recent-surface record of such samples, such as dating when they were exposed on the Earth's surface or inferring erosion rates. To interpret the measurements of the concentrations of these nuclides in surface samples requires good rates for their production. This project uses measurements of cosmogenic nuclides in well-characterized samples plus numerical simulations using computer codes developed at Los Alamos to get better production systematics for many in-situ-produced cosmogenic nuclides as a function of target composition, elevation, and geomagnetic latitude.

Results: Recently measured cross sections for the production of these nuclides continue to be compiled and evaluated. Work was done with Dr. J. Sisterson on measuring needed neutron cross-sections at the Los Alamos Neutron Scattering Center and other sources of energetic neutrons.

Contacts have been maintained with groups exposing artificial samples on the Earth's surface. Contacts are being continued with others on the work being done on studying production rates with natural samples. These and other measurements will be modeled using MCNPX in testing the ability of the code to model the production of in-situ-produced cosmogenic nuclides.

Microbial Dissolution of Iron Oxides

L. Hersman (505-667-2779; Fax: 505-665-6894; hersman@lanl.gov) with P. Maurice (Kent State University) and G. Sposito (U.C., Berkeley)

Objectives: Our overall objective is to determine the mechanisms of iron release during microbially enhanced iron oxide dissolution by an aerobic microorganism. During this first year, work at Los Alamos National Laboratory has been focussed on four aspects of the proposed research:

Using high performance liquid chromotography (HPLC), purify a siderophore (produced by a *Pseudomonas* sp.) for use in dissolution experiments at UC Berkeley,

During dissolution, determine if reductants are being produced by the *Pseudomonas* sp., Conduct a series of growth experiments on various Fe oxides, and provide those same Fe oxides for atomic force microscopy (AFM) analysis at Kent State University.

Project Description: The purpose of this research is to investigate the mechanisms used by aerobic microorganisms to obtain Fe for growth. Currently little is known about Fe oxide dissolution processes in oxic environments. 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. Los Alamos National Laboratory is investigating the growth characteristics of a *Pseudomonas* sp. whose only source of Fe is either hematite or geothite. Additionally, we supply siderophore for siderophore-mediated investigations at UC Berkeley and provide microbially reacted, Fe oxide surfaces for AFM analysis at Kent State University.

Results: We have examined the relationship between siderophore production and the source of Fe in the growth medium. Siderophore appears to have been produced in excess, in that there was more siderophore produced than would be required to dissolve enough Fe for growth. In fact, it appears that these bacteria produced enough siderophore to dissolve about 5 times as much Fe as needed. This is supported by our earlier finding that when grown on Fe(III)(hydr)oxides, *P. mendocina* over dissolves Fe. These two findings are enormously important with respect to the desorption/dissolution of both Pu and U, in that microorganisms may produce an excess of siderophore in natural environments, relative to their immediate Fe nutritional needs.

CATEGORY: Solar-Terrestrial Physics

Energy Transport in Space Plasma

S. P. Gary (505-667-3807; Fax: 505-665-7395; pgary@lanl.gov)

Objectives: The long-term goal of this research is to understand the flow of plasma energy in the near-Earth space environment from a small-scale point of view. The objective of this research is to use plasma theory, simulations, and data analysis to express the consequences of plasma microinstabilities as concise relationships that may be used in large-scale models of space plasmas that describe the solar-terrestrial interaction.

Project Description: Particle velocity distributions and parameters observed by Los Alamos plasma instruments on scientific spacecraft as well as computer simulationsare 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.

Results: Our most important accomplishment in 1998 was the demonstration that the electron heat flux in the solar wind is bounded by a constraint that is similar to the predicted condition for the onset of the whistler heat flux instability. We have concluded that this bound is imposed by enhanced fluctuations from the whistler instability and may be used in fluid models of the solar wind.

The Solar Wind-Magnetospheric Interaction

J. Birn (505-667-9232; Fax: 505-665-3332; jbirn@lanl.gov)

Objectives: The goal of this research is to further the understanding of the structure and dynamics of the Earth's magnetosphere, coupled to the fast-flowing solar wind plasma on the one hand and to the ionosphere on the other.

Project Description: The focus of this research is the investigation of the large-scale structure and evolution of the Earth's magnetosphere, using theory, numerical modeling, and correlative studies of data from multiple sites within and near the magnetosphere (including the Earth itself as well as scientific satellites).

Results: Our most significant accomplishment in 1998 was the identification of the coupling mechanism between magnetospheric substorm activity and ionospheric consequences. Through computer simulations, we were able to demonstrate the important role of plasma flows, resulting from magnetic reconnection in the Earth's magnetic tail. The braking and diversion of these flows distort the magnetic field and thereby build up the electric currents that flow into and through the ionosphere and perturb the ground magnetic field. This study also revealed the important role of plasma pressure gradients in the diversion of electric currents.

Energetic Particle Acceleration and Transport

G. D. Reeves (505-665-3877; Fax: 505-665-7395; reeves@lanl.gov)

Objectives: The overall goals of this project are (1) to better understand the acceleration and transport of energetic particles during magnetic storms, substorms, relativistic electron enhancements, solar energetic particle events, and other magnetospheric processes, (2) to develop empirical models of the structure and dynamics of the Earth's radiation belts and other energetic particle regions, and (3) to develop a better understanding of the space environment as a system and to better understand the effects of the space environment on spacecraft and their operations.

Project Description: This effort concerns the analysis of energetic particle data from a variety of US programmatic and NASA scientific satellites. Those include the series of geosynchronous spacecraft that carry Los Alamos energetic particle detectors, the GPS satellites, which also carry Los Alamos energetic particle detectors, NASA's POLAR satellite, and others. The energies of the particles of interest range from keV to hundreds of MeV. The lower end of this range lies somewhat above the thermal plasma energies and is therefore sensitive to local acceleration processes such as magnetospheric substorms. The higher end of the energy range is well suited to the study of energetic particles in the earth's radiation belts and those that can penetrate the Earth's magnetic field, such as galactic cosmic rays and particles produced in solar flares. We also investigate the effects of those particles on spacecraft systems and instrumentation.

Results: Our most important accomplishments in 1998 centered on the study of the Earth's relativistic electron belts (part of the Van Allen Radiation Belts). Relativistic electrons can have a serious impact on spacecraft hardware and operations through the bulk charging and uncontrolled discharge of insulators. We used new observations to put together data from up to 11 simultaneously operating satellites to produce unprecedented spatial and temporal resolution. We found that relativistic electron fluxes change on time scales ranging from minutes to the 11-year solar cycle. An important new result was the discovery that the “characteristic” 2-3 day delay in the peak fluxes seen by geosynchronous satellites is typical only of that region of space. Deeper in the radiation belts where the GPS satellites operate the time to peak is typically only 12 hours. This has caused serious re-thinking of the entire relativistic electron acceleration and transport theories.

CONTRACTOR: Oak Ridge National Laboratory

Lockheed Martin Energy Research Corporation
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CONTRACT: DE-AC05-96OR22464

CATEGORY: Geochemistry

PERSON IN CHARGE: David. R. Cole

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

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

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

Results: Work was completed this year on a paper describing our experiments to determine the activity/composition (a/X) relations of H_2O-N_2 and H_2O-CO_2 fluids at 500°C, 500 bars It describes experiments which tightly constrain a/X relations for both solution series, and provides two-parameter Margules models, derived using a graphical linear programming approach, which accurately represent the data. This is the first available data for the H_2O-N_2 system, and results for H_2O-CO_2 fluids indicate that there are significant errors in published thermodynamic models. For both systems, the experiments show that there are continuously positive deviations from ideal behavior over the entire join. For H_2O-CO_2, these are significantly larger than suggested by previous models of this system. Error analysis was performed to evaluate uncertainties in the experimental data and in the reference values for pure water in equilibrium with the Ni-NiO buffers. The combined uncertainties in the calculated activities are less than ~ 5 percent.

Work was begun to determine a/X and phase relations for the system H_2O-CO_2-NaCl at 500°C, 500 bars. Experiments were performed with two types of samples: those prepared to locate an isoactivity curve across the ternary, and those prepared to constrain the position of the halite-saturation surface. In the first, a Ni-NiO oxygen buffer was added to the reactants. During the experiment the activity of water is fixed by the oxygen buffer and hydrogen in the pressure medium, and water will either be formed or break down in a given capsule, shifting the mole fraction towards equilibrium.

To constrain the halite saturation curve, an inner capsule is used which contains excess NaCl. Initially, the capsule contains no water, and the amount of NiO added is limited to constrain the maximum amount of water that can form. During the experiment, the water dissolves NaCl from the inner capsule, and the bulk composition of the fluid moves along the halite saturation surface. By measuring the amount of water formed and the amount of NaCl left in the inner capsule, a point on the halite saturation curve can be determined. Experiments on H_2O-CO_2-NaCl fluids were performed at 500°C, 500 bars. H_2O-CO_2-NaCl samples were reacted at $a(H_2O) = 0.350$, 0.425, 0.437, 0.448, 0.560, 0.606, 0.678, 0.798, and 0.841. Results indicate that fluids with these activities lie in the vapor-NaCl two-phase region, and that a fluid with $a(H_2O) = 0.841$ has a composition close to the three-phase (vapor + brine + halite) field. Data from these experiments and NaCl solubility runs also suggest that the vapor corner of the three-phase field lies near $X(H_2O) = 0.760$, $X(NaCl) = 0.065$.

Fundamental Research in the Geochemistry of Geothermal Systems

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Objectives: The objective of this project is to provide fundamental information on geochemical reactions that play pivotal roles in a wide range of geological processes, but that specifically impact reservoir dynamics, corrosion, and heat extraction in active geothermal systems. The speciation of elements in aqueous solutions, mineral solubilities, kinetic and equilibrium partitioning of stable C-O-H isotopes, and other fluid-solid interactions are primary subject areas for this research.

Project Description: At Oak Ridge National Laboratory, a long-term basic research program in experimental hydrothermal geochemistry, stable isotope geochemistry, and igneous petrology has led to the development of unique methodologies for extracting rigorous and unambiguous information on a wide range of geochemical processes. This capability permits the efficient and definitive examination of specific problems hampering the ability to quantitatively model fluid-rock interaction processes related to the discovery and exploitation of geothermal resources. Research topics in this project are selected in close cooperation with geothermal industry representatives and are frequently augmented by parallel research on more applied aspects of the same problems funded by the U.S. Department of Energy's Geothermal and Wind Technologies Program.

Results: Current topics include: a) the aqueous geochemistry of aluminum, which affects permeability development and scaling in geothermal systems, and b) the effect of pressure and dissolved salts on the partitioning of the stable isotopes of oxygen and hydrogen between geothermal brines and other phases, which is central to the use of stable isotopes in elucidating fluid sources and fluxes and reservoir temperatures and dynamics.

The solubility of boehmite, AlOOH, has been precisely determined across the pH range of 2-10 in 0.03 to 5.0 molal NaCl solutions, at temperatures of 100 to 290°C. This study utilized our unique, high-temperature pH measurement capabilities, which permitted continuous and highly accurate determination of pH over the entire solubility profile. The results demonstrate considerably lower minimum solubilities than several recent literature studies, but are in fairly good agreement with these earlier results in strongly acidic and basic solutions at low salinity. We are able to model our results to extract the stepwise equilibrium constants for the formation of the aqueous species of aluminum, $Al(OH)_y^{3-y}$, where y varies from 0 to 4. These are the only results available on the properties of these species in highly saline brines.

Using the ORNL high-temperature hydrogen-electrode cell, studies of the dissolution and precipitation rates of boehmite were initiated in neutral to basic solutions at 100-290°C at 0.1-molal ionic strength. The equilibrium solubilities obtained after each addition of acid or base were in excellent agreement with our previous solubility measurements performed at the same conditions. The rates of both dissolution and precipitation reactions are extremely fast at high pH, so that only the runs performed at 100°C are now being analyzed in detail to extract the kinetics of these processes.

The effect of dissolved salts and pressure on the equilibrium partitioning of oxygen and hydrogen isotopes (isotope salt and pressure effects) has been investigated in the systems liquid-vapor water and mineral-water at elevated temperatures. First, the effect of 0-5 molal NaCl solutions on D/H fractionation between brucite [$Mg(OH)_2$] and water were investigated at 200-500°C. Dissolved NaCl slightly (up to 7 per mil), but systematically increased the brucite-water D/H fractionation at the all temperatures studied. These results obtained from brucite-water experiments agree well with those from our NaCl liquid-vapor equilibration experiments at 200°C, but are slightly lower above 300°C. In the liquid-vapor experiments, the vapor phase becomes increasingly non-ideal with increasing temperature.

The results obtained from brucite-pure water D/H fractionation experiments at 200-500°C and at 21-800 bars are slightly (2-5 per mil), but consistently lower than the literature data obtained at the same temperatures, but at higher pressures (1000 bars). These discrepancies could be due to the difference in pressure (isotope pressure effect). In order to investigate possible pressure isotope effects, we have determined D/H partitioning between brucite and water at 380°C, and at 500 and 2000 bars. The temperature was chosen where largest pressure effects were suggested on D/H partitioning in the literature. The results obtained, -25.7 and -24.8 per mil at 500 and 2000 bars, are virtually indistinguishable within analytical errors (about 1 per mil). Our results suggest that pressure effect on D/H partitioning is much smaller than calculations in the literature.

Ion Microprobe Studies of Fluid-Rock Interaction

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

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

Results: A sulfur isotope study continues on sulfides from the Scapa Field (Western North Sea), as well as samples from other North Sea fields. The presence of complex, large zonations in sulfur isotope values in individual sulfides is widespread, with a general temporal trend starting with relatively heavy (+10 to +20 per mil) values, shifting to lighter (to -20 per mil) values before gong to extremely heavy values (up to +70 per mil). In addition, the bulk of the sulfur isotope values are heavier than original seawater sulfate, suggesting that there is a significant mass balance problem in the reservoir sandstones. The results suggest that the original sulfides were formed from sulfate that was transported into the sandstones, and that had already undergone extensive bacterial sulfate reduction. This was followed by an influx of relatively pristine sulfate that was subsequently almost completely reduced by bacterial action at 60-80°C, with the waning stages in a system that was closed to additional sulfate input. These observations suggest that sulfide formation was triggered by cross-formational fluid flow associated with significant mass transfer.

An investigattion was conducted on sulfate reduction during the earliest stages of diagenesis, as pyrite infillings of foram tests recovered from very shallow (0-15cm) sediment burial depths in Monterey Bay, California. Sulfur isotope values range from -40 to -4 per mil, which indicates that the sulfate was reduced by biologic processes in a system that was mostly closed to input of additional sulfate. Correlation between isotope ratios and textures of sulfides in the tests suggest that mapping of sulfur isotope values may provide a means of tracking the temporal progression of bacterial colonization within the sediments.

SIMS has been used to precisely determine hydrogen concentration depth profiles in obsidian glass artifacts. Contrary to conventional beliefs, the concentration depth profile indicates that diffusion rates are compositionally dependent. Preliminary results suggest that the hydration depths may be time correlative, and that this method may provide a method of accurately dating the ages of obsidian artifacts if accurate hydrogen transport models can be developed. This work also has significant implications for the modeling of waste glass sequestration and durability.

The sulfur isotope ratios in sulfides were measured in the Martian meteorite sample ALH84001. The results suggest that the sulfides were probably not formed by bacterial sulfate reduction. Investigation of other meteorites indicates that processes active on Mars are capable of significant sulfur cycling and fractionation. The range in values can be explained by inorganic processes, suggests significant interplay between atmospheric and crustal sulfur reservoirs, and may support the presence of hydrothermal circulation cells at some time during Martian crustal evolution.

A new method was developed to experimentally determine mineral-fluid hydrogen isotope fractionation factors, using the capability of the ion probe to precisely measure D/H ratios in very shallow (<2 microns deep) sputter craters. The rims of a single crystal are reacted with a fluid that is either isotopically heavier or lighter than the expected equilibrium fluid. The narrow rim of the reacted crystal approaches equilibrium with the fluid, and by measuring the isotope ratio of the outermost portion of the rim, a value of the solid that is very close to equilibrium can be determined. By using fluids that are both heavier and lighter than the equilibrium value, we can bracket the true fractionation factor. Experiments on epidote indicate that the method can bracket the equilibrium value to within a few per mil, and that experiments can be run to relatively low temperatures (300°C).

Experimental Studies of Fundamental Stable Isotope Exchange Reactions

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Objectives: The objective of this project is to obtain reliable information on the partitioning of the stable isotopes of oxygen, carbon, and hydrogen among minerals and fluids of critical importance in defining fluid-rock interaction parameters, such as fluid sources and fluxes, temperatures, and duration of fluid-rock interaction, in a variety of settings including oil, gas, and geothermal reservoirs, sedimentary basins, and waste repositories.

Project Description: This project is currently focussed on: a) the oxygen isotope partitioning between aqueous fluids and the mineral hematite and magnetite in the 25-800°C range; and b) the exchange rates and equilibrium fractionation of hydrogen and carbon isotopes among gaseous species in the system H_2O-CO_2-CH_4-H_2. Multiple novel experimental methods are used to promote recrystallization and/or synthesis of the iron oxides minerals. Synthetic catalysts and natural minerals, including magnetite and hematite, are investigated for isotopic exchange among the C-O-H gases.

Results: Thermophilic bacteria (45-75°C) that reduce amorphous Fe(III)-oxyhydroxide to magnetic iron oxides have been discovered in deep subsurface samplings of two geologically and hydrologically isolated sedimentary basins; one of Cretaceous age in Colorado and the other of Triassic age in Virginia. Molecular analysis based on 16S rRNA gene sequences revealed that some of these bacteria represent an unrecognized phylogenetic group of dissimilatory Fe(III)-reducing bacteria. The precipitation of magnetite (Fe_3O_4) and siderite ($FeCO_3$) mediated by iron-reducing bacteria *in vitro* provide an opportunity to study isotope fractionation between these mineral phases and coexisting fluid. Oxygen isotope compositions were determined for siderite and magnetite-rich (65-88%) iron oxides formed experimentally between 45 and 75°C by thermophilic bacteria obtained from deep subsurface environments. Bacteria were cultured using glucose, acetate or hydrogen, as electron donor and amorphous Fe(III)-oxyhydroxide as an electron acceptor. Well-crystallized siderite and magnetite were formed after two to five days of incubation, and were aged three to five weeks before isotopic analysis. Siderite-water oxygen isotope fractionations were essentially constant regardless of temperature (25.8 per mil between 45 and 65°C). Magnetite-water oxygen isotope fractionations exhibited a temperature dependence, with values ranging from -0.09 per mil at 50°C to -1.08 per mil at 70°C.

The equilibrium carbon isotope fractionation factors between CO_2 and CH_4 were experimentally determined in the presence of a Ni-catalyst at temperatures from 300-500°C. The measured values are slightly (0.7-1.0 per mil), but systematically larger than theoretical calculations reported in the literature.

Our previous results of experiments of the hydrothermal reduction of dissolved CO_2 in NaCl solutions to carbon precipitates to CH_4 at 200°C and 500 bars, and at 300°C and 500 bars were analyzed on the basis of a first-order reaction model. Our model analyses showed that the rate of CO_2 reduction slowed down with time, suggesting that the catalytic activity of a Ni-Fe alloy was suppressed, due probably to carbon deposition, during the course of the reactions. Carbon isotope fractionations were also calculated from the model, assuming no reverse reactions. The calculated values were typically more negative than those of equilibrium processes, strongly suggesting a kinetic isotope effect.

Potentiometric Studies of Geochemical Processes

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Objectives: The objective of this project is to utilize ORNL's unique, high temperature, hydrogen-electrode, pH-measurement cells and other potentiometric approaches to study aqueous reactions and water/mineral interactions relevant to DOE's geoscience mission areas.

Project Description: The pH is considered the master variable in aqueous systems, controlling the nature of dissolved species, the rates of homogeneous and heterogeneous reactions, the solubility and absorbtivity of rock minerals, the transport and deposition of contaminants and ore components, the volatility of mineral acids and the thermal stability of organic acids. In this program we develop and use unique experimental facilities to directly measure the pH of aqueous solutions and the activities of important dissolved ions over broad ranges of temperature, salinity and pH, and use these measurements to quantify the dissociation constants of inorganic and organic acids and bases, the hydrolysis and complexation of metal ions in solution and the solubilities and surface properties of minerals.

Results: The solubility of zincite (ZnO) was investigated in 0.03 molal sodium trifluoromethanesulfonate (NaTr, a "non-complexing", 1:1 electrolyte) solutions from 25 to 250°C, employing *in situ* pH measurement in the hydrogen-electrode concentration cells (HECC's). Two titrant pumps facilitated forward and reverse titrations along the solubility curve, approaching equilibrium from either under- or super-saturation. This permitted demonstration of thermodynamic reversibility and extraction of the stability constants for Zn^{2+}, $Zn(OH)^+$, $Zn(OH)_2^\circ$ and $Zn(OH)_3^-$ over the entire temperature range, resolving a long-standing controversy in the literature regarding the relative stabilities of the intermediate hydrolysis products of Zn^{2+}. A similar approach was used to investigate the solubility of magnetite (Fe_3O_4) in 0.1 molal NaTr solutions from 100 to 250°C. Under strongly reducing conditions and high pH's, the solubilities determined closely match the most recent experimental results in the literature, but are lower by orders of magnitude than calculations using the SUPCRT database, which is widely used by geoscientists. Under mildly acidic conditions, the results of this study clearly demonstrate reversible metastable equilibrium between magnetite and hematite (Fe_2O_3), despite the strongly reducing conditions of the HECC experiments. This indicates that Fe^{2+} can be reversibly leached from the magnetite surface, while tetrahedrally coordinated Fe(III) remains unreactive. This has important implications for redox-controlled reactions and biogeochemistry in subsurface aquifers.

Studies of mineral surface chemistry at elevated temperatures continued during this period with determination of the sorption of Ca^{2+} and Nd^{3+} (analogs for toxic divalent metals and trivalent actinides) on rutile (TiO_2) surfaces in dilute NaCl solutions from 25 to 250°C. These studies demonstrate that, for a distance in pH units above the point of zero charge of the mineral surface, the sorption of multivalent cations increases markedly with increasing temperature, indicating that migration of toxic metals will be hindered by surface sorption reactions at elevated temperatures, such as encountered in geothermal systems and high level radwaste near-field environments.

The complexation of Al^{3+} by SO_4^{2-} (the principal source of acidity in acid rain and acid mine drainage) was studied by both homogeneous pH titrations from 50 to 125°C and by gibbsite ($Al(OH)_3$) solubility measurements at 50°C. The complexation of Nd^{3+} by acetate (the most abundant organic acid anion found in natural waters) was also determined in dilute NaCl solutions from 25 to 225°C.

Mechanisms and Rates of Isotope Exchange in Mineral-Fluid Systems

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Objectives: The major objective of this research is to measure the rates of isotopic exchange between mineral and fluids controlled by one of two general mechanisms: surface reactions leading to recrystallization and volume diffusion.

Project Description: Equilibrium isotope fractionation factors and rates of isotopic exchange (via diffusion or mineral transformation mechanisms) form the cornerstones for interpretation of stable isotope data from natural systems. Microscale studies (high precision of small sample sizes or *in situ* spot analysis) of mineral-fluid interaction in natural systems indicate that: (a) isotopic heterogeneity and disequilibrium may be more widespread than previously realized, (b) isotopic disequilibrium can occur at high as well as low temperatures, (c) different minerals exhibit varying susceptibilities to retrograde fractionation and re-equilibration, and (d) the mechanisms of isotopic exchange are varied depending on the prevailing geochemical conditions (*e.g.*, temperature, pressure, fluid chemistry, fluid/solid ratio, etc.). Because of the recent advances in analytical techniques, the need for accurate, reliable fractionation factors and rate constants has never been greater. Realizing this need, we have focused our BES research on the experimental determination of rates and equilibrium fractionations for a variety of geologically relevant mineral-fluid (gas) systems for which data are either lacking, limited, or in some cases, controversial.

Results: An oxygen and carbon isotope exchange study has been completed on the system: calcite-H_2O-NaCl-CO_2 at temperatures between 500 and 700°C, pressures between 0.5 and 2 kbar, NaCl concentrations of 0, 1, 3, 5 molal, and XCO_2 of 0.1 and 0.2. Isotopic rates increase markedly with increasing salinity and pressure. An increase in NaCl from 0 to 1 molal leads to an increase in oxygen isotope exchange rate of nearly two orders of magnitude, whereas the rate increases by only a factor of about 7 with an increase from 1 to 3 molal. A linear increase in rate of about 0.4 log units (moles of O $m^2 s^{-1}$) per kbar change in pressure is observed regardless of the salinity. When CO_2 is present, the isotopic exchange rates tend to be more sluggish and the pressure effect is somewhat less pronounced.

Hydrogen isotope fractionation factors between epidote and water were measured at high temperatures (300-600°C) and pressures (2 kbar) using large single crystals reacted with waters that isotopically bracket the composition of the starting material. The outer 0.5 – 2 microns of the isotopically exchanged crystals were analyzed by the ion microprobe, which provided somewhat less precise analytical data than can be obtained with conventional methods. However, the advantage of the present technique is that it allows fractionations to be determined in experiments in which isotopic exchange demonstrably occurs through a diffusion process and not by recrystallization. This, in turn, permits unambiguously reversed experimental data on equilibrium fractionation factors. Despite initial epidote-water fractionations that were far from equilibrium in some experiments, diffusional exchange rates were sufficiently high in this system to bracket the equilibrium fractionation within analytical error to temperatures as low as 300°C. The measured fractionations vary systematically with temperature, decreasing from -36 per mil at 300°C to -54 per mil at 600°C. The present method should be applicable to other hydrous mineral-water systems and help resolve some of the existing discrepancies with regard to the magnitude and temperature dependence of hydrogen isotope fractionation factors.

Oxygen isotope fractionations in laboratory systems have been determined between chlorite and water at 170-350°C. In one series of experiments, the Northrop-Clayton partial isotope exchange method was used where three (sometimes four) isotopically different waters were reacted with chlorite at 350°C and

250 b. Additional fractionation data have been determined from hydrothermal granite-fluid experiments (170-300°C) where chlorite formed from biotite. The amount of chlorite, quantified through XRD and microscopic analysis, increased with increasing temperature, salinity and time. The chlorite oxygen isotope compositions were calculated from mass balance and compared to the final measured ^{18}O values of the fluid. The equilibrium fractionation factors averaged 0.14, 0.8 and 2.9 per mil for 300°, 250°, and 200°C, respectively. The curve that defines our data (170-350°C) is in good agreement with results reported for semi-empirical and empirical calculations. These results can be used in studies of fluid-rock interaction to estimate either paleo-temperatures or the isotopic compositions of fluids in equilibrium with the rock.

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Local Reactions on Carbonate Surfaces: Structure, Reactivity, and Solution

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Objectives: The purpose of this program is to develop a fundamental, microscopic under-standing of the structure and chemistry of carbonate surfaces, including the interactions between adsorbates and mineral surfaces.

Project Description: This project involves an interdisciplinary theoretical and experimental effort designed to gain a fundamental, molecular level understanding of carbonate mineral surface structure and chemistry. Carbonate minerals are particularly important in the global carbon dioxide cycle and in subsurface contaminant migration processes. The availability of large single-crystals allows fundamental measurements to be made on well-defined surfaces. By linking experimental studies of geochemical reactions on single-crystal surfaces with first-principles quantum-mechanical model calculations to describe the surface and interfacial structure and chemistry, a systematic study of the factors controlling the surface chemistry of carbonate minerals can be made. In particular, the effects of substitutional impurities and other point chemical defects on the structure and geochemical reactivity of carbonate mineral surfaces and interfaces can be isolated and quantified. Moreover, this improved microscopic under-standing will eventually provide insights into the behavior of these materials in natural systems.

The approach to meeting program goals, involves three interdependent areas of effort: development of *ab initio* models for the structure and chemistry of the calcite cleavage surfaces; vacuum studies of the structure and chemistry of the cleavage surface; and comparison of surfaces in vacuum with those in model geochemical environments.

Results: Recent work has focused on experimental and theoretical studies of the effects of solution chemistry on the dissolution of calcite. The overall results suggest that the types of binding energy differences used to explain dissolution rates in relatively pure solutions far from equilibrium are supported by observation made at equilibrium. Experimental measurements have included observations of pit structure at equilibrium and the effects of Mn and Sr on the rates of pit growth while dissolution is occurs. Theoretical work includes the addition of back reactions to our Kinetic Monte Carlo model of dissolution and initial molecular level calculations of solution flow surface topography effects on dissolution.

The shape of pits formed at in water at equilibrium with calcite provides information about the energies of steps on the surfaces exposed. Previous work has demonstrated that for nearly pure water, steps on the cleavage surface with slightly different geometry's dissolve at different rates. Both terrace ledge kink (TLK) and kinetic Monte Carlo (KMC) models can reproduce the results by assuming different binding energies, which depend upon the detailed geometry of different binding sites. Although the slowest dissolving site was assumed to have a larger binding energy, steric or entropic effects may have caused these differences in dissolution rates. New observations of pits at equilibrium confirm the different binding energy assumption and provide an indication of the relative energies of the two types of surface steps. Since surface energies per unit energy are equivalent at equilibrium, steps on the side of an equilibrium pit with the most -shallow slope have the highest energy. The differences in step reactivity are highly solution dependent. Far from equilibrium, the fastest dissolving side produces pits with a slope shallower than that observed for the steps that dissolve most slowly. However, at equilibrium the relative slopes of the fast and slow direction reverse.

Various divalent cations are well known to influence the dissolution and growth of calcite. Earlier results have shown that Mn significantly slows the dissolution rates of calcite and that the rapidly dissolving steps were the most effected. Additional work demonstrates that this effect depends upon ion size. Although Mn influenced the fast and slowly dissolving directions to different degrees, Sr (as might be expected due to it's larger size) primarily influences the larger sites of the normally fast dissolving direction. For both metals, the fastest dissolving steps were the most influenced, but the smaller ion also decreased the dissolution of the steps with the more closed geometry.

A kinetic Monte Carlo (KMC) model has been used within a solid on solid model of surfaces to determine the reaction or dissolution rates of five different surface sites. A back reaction step has been added to the KMC model to allow study of dissolution nearer to equilibrium. This model has been used to pit the absolute fates for fast and slow directions at different of bicarbonate in solution. Not only to the dissolution rates change, but the pits change shape. These different effects are readily reproduced by the model.

The examination of solution flow rates as they affect step dissolution rates and the shape of deep pits shows strong effects of flow and solution. We have developed a 2D cellular automata (CA) model to simulate the effects of dissolution, re-adsorption, diffusion, and fluid flow on calcite surface crystallographic step evolution. A unique feature is the ability to treat fluid flow effects on the step kink growth kinetics and morphologies. Our AFM wet cell data in the reaction-controlled regime (fast flow) have been reproduced quantitatively. Initial calculations for slower flows (diffusion controlled) have qualitatively reproduced the observed AFM step velocities and morphologies, and have revealed a dependence on fluid flow direction. Efforts are currently focused on eliminating a computational bottleneck caused by large differences in time constants for the fluid versus the solid and on developing methods to determine the back-reaction rate constants from the fluid flow dependencies. Future work will focus on extensions to 3D using the lattice gas automata (LGA) approach, which will permit simulation of calcite pit growth for reactive boundary layers in the flowing fluid.

Structure and Reactivity of Iron Oxide and Oxyhydroxide Surfaces and Interfaces

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Objectives: The objectives of this program are to (1) develop molecular models of hydroxylated ferric and ferrous oxide and oxyhydroxide surfaces (2) use these models to better understand the relationship between structure and reactivity for this class of minerals, and (3) use this knowledge to improve thermodynamic calculations using surface complexation models.

Project Description: Ferric oxides have high specific surface areas, high affinities for oxyanions and heavy metals, and actively respond to changes in redox conditions in natural environments. These minerals are therefore important in a variety of low-temperature geochemical processes, particularly those in which adsorption and dissolution couple with fluctuations in redox potential. In this project, the effects of crystal chemistry on adsorption are evaluated using computational molecular modeling techniques. These results are then used to produce a more robust thermodynamic description of adsorption at the mineral-water interface.

Results: *Hydroxylation of Hematite (012):* A parameterized classical potential model for the interaction of water and hydroxide with iron oxide was used to calculate the optimal proton arrangement and proton binding energies on the (012) surface of hematite. Energy minimization calculations indicate that approximately 75% of adsorbed water molecules are dissociated on this surface, in agreement with recent TPD and HREELS measurements. Surface protonation/deprotonation energies were calculated from the predicted optimal arrangement of protons on the neutral (012) surface. The calculated surface protonation energies were then used to model the experimentally observed surface-charging curve of hematite in aqueous solution. Excellent agreement was found between the calculated and measured surface charge for ionic strengths ranging from 0.001 to 0.1M. Our calculations favor the value of 8.5 for the pH of zero charge of hematite over the more recent result of 6.7.

The Structure of Magnetite (001): Using a polarizable ionic model, we have studied the structural features of hydroxylated iron oxide surfaces. Recently, we have extended this approach to study magnetite (Fe_30_4) (001). Molecular dynamics calculations identified a novel mode of reconstruction taking place on this surface. In the proposed reconstruction, the twofold coordinated iron ion in the top monolayer rotates downward to occupy a vacant half-octahedral site in the plane of the second-layer iron ions. At the same time, half of the tetrahedral iron ions in the third iron layer are pushed upward to occupy an adjacent octahedral vacancy at the level of the second-layer iron ions. The other half of the thirdlayer iron ions remains roughly in the original positions. The driving force for the reconstruction can be easily understood using arguments based on Pauling bond order.

Hydrolysis of Trivalent Metals: The factors influencing the reactivity of trivalent metal ions toward hydroxide ions, as revealed by the first hydrolysis constant for proton loss from the hexaaquo complex, have proven elusive to define. Density functional electronic structure (DFT) calculations were performed on a series of hexaaquo and hydroxo penta-aquo complexes involving trivalent metal ions Al^{3+}, Cr^{3+}, Fe^{3+}, Sc^{3+}, Mn^{3+}, Ti^{3+}, V^{3+}, Y^{3+}, Ga^{3+}. The relative energies of deprotonation were used to define a linear free energy relationship, which gives an excellent correlation of the relative values of the first hydrolysis constants of this series of trivalent metal ions. The DFT method thus provides a sound basis for understanding the reactivities of these ions, and provides further confidence, motivation and means for developing a more fundamental understaing, through DFT calculations, of the electronic structural effects that promote or inhibit hydrolysis.

Protonation Constants of Tetrahedral Oxyacids: Density functional calculations have been performed on several protonation states of the oxyacids of Si, P, V, As, Cr, and S. Structures and vibrational frequencies are in good agreement with experimental values where these are available. A reasonably well-defined correlation between the calculated gas-phase acidities and the measured pK_a in aqueous solution has been found. The pK_a/gas-phase acidity slopes are consistent with those derived from previous molecular mechanics calculations on ferric hydrolysis and the first two acidity constants for orthosilicic acid. The successive deprotonation of other H_nTO_4 species, for a given tetrahedral anion T are roughly consistent with this slope, but not to the extent that there is a universal correlation among all species.

Deprotonation of Al, Fe, Cr Polynuclears: Density functional calculations are performed on $M_3(OH)_7(H_2O)_6^{2+}$ and $M_3O(OH)_6(H_2O)_6^{+}$ clusters for M=Al, Cr(III), and Fe(III), allowing determination of the relative acidities of the -hydroxo and aquo functional groups. Contrary to previous predictions and rationalizations, $=Fe_3OH$ and $=Al_3OH$ groups have nearly the same intrinsic acidity, while $=Cr_3OH$ groups are significantly more acidic. The gas-phase acidity of the Fe_3OH site is in good agreement with the value predicted by the molecular mechanics model previously used to estimate the relative acidities of surface sites on iron oxides. Acidities of aquo functional groups were also computed for Al and Cr. The $=AlOH_2$ site is more acidic than the $=Al_3OH$ site, whereas the $=Cr_3OH$ site is more acidic than the $=CrOH_2$ site.

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

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Objectives: The project objectives are to 1) develop an improved understanding of the interfacial mechanisms of electron transfer between dissimilatory Fe(III)-reducing bacteria and Fe(III) oxides; and 2) define the mineral structural, thermodynamic, and kinetic factors that control the rate and extent of bacterial Fe(III) oxide reduction as a basis for predicting microbiologically driven reduction rates and transformations in subsurface environments.

Project Description: Bacterial iron (III) reduction is a key process in sediments and subsurface environments that controls the aqueous and solid phase speciation of Fe and other polyvalent metals, radionuclides, and contaminants (*e.g.*, Co, U, Cr, Tc, etc). In spite of its widespread importance, the mechanisms of bacterial electron transduction to Fe(III) oxides and the factors that control it remain unknown. Research in this project is investigating microscopic aspects of bacterial iron (III) oxide reduction using spatially-resolved synchrotron based spectroscopies, high resolution electron and scanning probe microscopies, and transmission and conversion electron Mössbauer spectroscopies. Laboratory experiments using: 1) a well-studied bacterium (*Shewanella putrefaciens*) and abiotic reductants (ascorbate, cysteine, AQDS) and 2) synthetic, epitaxial iron oxide films and crystallites of known face exposure and variable defect densities will investigate fundamental hypotheses related to electron transfer at the oxide-organism interface. Key issues to be determined are the influence of Fe(III) oxide surface structure and energy on microbiologic reduction and the nature/spatial distribution of geochemical products formed; and the architecture of the bacteria-mineral association including the spatial location of the cytochromes and exopolysaccharide (EPS) relative to the oxide surface and areas of reduction.

Results: The project was initiated in late FY 98 so results to date are preliminary. *Selection and characterization of experimental materials*: Our initial focus is on the (0001) surface or basal plane of hematite. The primary sample requirement is for a contiguous, single Fe(III) oxide face that is greater than 10x the length of the microorganisms (*ca.* 1.5 μm). Faces with different degrees of roughness and defects will be used. We have investigated a number of hematite samples to find those suitable for the microbiologic studies. Based on this screening, we have selected three different (0001) faces for research: 1) tabular, specular hematite from Brazil, 2) epitaxially-grown hematite (0001) (Scott Chambers, PNNL), and 3) hydrothermal synthetic hematite grown in our laboratory. The (0001) specular hematite surface is contiguous for distances exceeding 1 mm, and exhibits growth steps with nm size hematite precipitates along their axes. Surfaces between the steps are remarkably flat. Tabular synthetic hematite was reproducibly synthesized with an approximate 20 μm contiguous (0001) face that exhibited various types of growth and surface features. The epitaxial hematite exhibits a characteristic LEED pattern for (0001), but has nm sized growth islands over its surface. Each material will be used for different purposes: 1) the synthetic hematite for surface structure studies and evaluation of reduction front penetration, 2) the specular hematite for colonization studies, and 3) the epitaxial hematite for valence state and biomineralization mapping of the organism footprint and its surroundings. A smaller synthetic tabular hematite [(0001) length of 1 μm] has also been prepared to link our studies with macroscopic crystallites to more frequently reported ones with hematite powders.

Abiotic reduction studies: As a control for the bacterial studies, abiotic experiments using ascorbate, cysteine, and bio-reduced AQDS (anthraquinone disulfonate) as reductants have been initiated using the 20 μm synthetic hematite. The experiments are performed in an anoxic flow through cell where the tabular crystallites are mounted parallel to (0001), and the evolving surface morphology studied *in-situ* with scanning probe microscopy as pH-controlled mM solutions of reductant are pumped through the cell. Chemical measurements will be performed on the reduced hematite surfaces, and lattice fringe images will be collected on crystallite cross sections to determine reductive penetration and surface passivation. These experiments will illustrate surface structural features that promote or retard reductive dissolution by small molecules. Comparative experiments with bacterially colonized surfaces will enable identification of surface modification features produced by microorganisms and the preferred surface structural features for bacterial electron transduction.

Bacterial colonization studies of Fe(III) oxide: An anoxic flow through cell was developed and tested in which epitaxial hematite coupons or tabular hematite crystallites can be mounted and microbial colonization/oxide dissolution studied *in-situ* by laser confocal microscopy and scanning probe microscopy. Microbial colonization of the surface of specular hematite occurred primarily along step features, but the organisms avoided flat step terraces. The integration of microbial, chemical, and surface structural imaging is an important project focus.

XAS measurements of Fe(II) reference solids: XANES spectra were collected under anoxic conditions at APS for the following Fe(II)/Fe(III) containing standards: 1) five mixed Fe(II)/Fe(III) aqueous solutions at acid pH, 2) goethite (FeOOH), 3) hematite (Fe_2O_3), 4) ferrihydrite (Fe_2O_3-nH_2O), 5) siderite ($FeCO_3$), 6) green rust ($[Fe^{II}_{(6-x)}Fe^{III}(OH)_{12}]^{x+}[(A^{2-})_{x/2}$-$yH_2O]^{x-}$), and 7) iron sulfide ($FeS_2$). Other standards that will be run at the next beam-line opportunity include 1) magnetite (Fe_3O_4), 2) vivianite [$Fe_3(PO_4)_2$-$8H_2O$], and 3) hematite and goethite doped with various concentrations of adsorbed Fe(II). From these standards, we will develop complex calibration curves for iron valence state and chemical mapping in and around the organism footprint on iron oxide films of approximately 50 nm thickness.

CONTRACTOR: Sandia National Laboratories

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CONTRACT: DE-AC04-94AL85000

CATEGORY: Geophysics and Earth Dynamics

PERSON IN CHARGE: H. R. Westrich

Shear Strain Localization and Fracture Evolution in Rocks

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Objectives: This research seeks an improved understanding of the mechanism of the formation of faults and fractures in rock and the prediction of their causative stresses, location, orientation, thickness, and spacing. The research examines the applicability of a theory that describes faulting as a constitutive instability leading to a localization of shear deformation from a homogeneous pattern of deformation.

Project Description: An experimental program is undertaken that entails four parts: (1) A systematic evaluation of the Rudnicki-Rice constitutive parameters under axisymmetric and truly multiaxial stress states. Several rock types are used to cover a range of porosities, including low-porosity Tennessee marble, intermediate porosity Gosford sandstone, and higher porosity Castlegate sandstone. (2) Experiments to measure and compare the actual and predicted development of strain localization in axisymmetric and plane-strain compression (3) Multiaxial stress tests on pressurized thin-walled cylinders with superimposed torsion to investigate special phenomena, vertex hardening, leading to strain localization at relatively small deformations. (4) Post test petrographic observations concerning the details of shear banding and the potentially accelerating effects of imperfections in experimental boundary conditions. The foregoing research is integrated with a parallel theoretical study by Rudnicki.

Results: Previous work showed that a vertex forms at the load point on the yield surface for Gosford and Berea sandstones. New results for Castlegate sandstone showed that vertex hardening occurred in this very porous, 25 to 30%, sandstone as well. In axisymmetric compression tests Castlegate sandstone was found to develop inhomogeneous compaction features that may be experimental analogs of naturally occurring compaction bands. The bifurcation approach to strain localization is being applied to attempt to explain these features. Constitutive models were developed for Tennessee marble using triaxial test data and are being used to predict the results of plane strain and torsion tests. Multiaxial constitutive models are needed for predicting localization conditions for comparison with experimental results. Critical constitutive parameters for marble have been measured and a constitutive model developed that captures the hardening, softening and dilatant behavior under conventional triaxial stress states. Using the constitutive model, we modeled the predicted behavior of the marble for more general stress paths. Localization is predicted to occur post-peak for the triaxial stress state, but pre-peak for plane strain tests. This is in accord with the less-clear-cut strain observations that indicated pre-peak localization during plane strain testing of Tennessee marble. One surprising result was that significant plastic strain is predicted to occur in the out-of-plane direction for plane strain deformation.

Inversion of Full Waveform Seismic Data for Shallow Subsurface Properties

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Objective: This research plans to demonstrate the applicability of full waveform seismic inversion methodologies to shallow subsurface environmental characterization or remediation targets.

Project Description: Inversion of full waveform seismic data is a large-scale, nonlinear, geophysical inverse problem. A successful attack on this problem requires robust computational tools for i) calculating realistic simulated seismic data from a prescribed earth model, and ii) inverting these data to recover the earth model properties. The general inversion procedure entails iteratively refining a candidate earth model until an acceptable match is obtained between predicted (*i.e.*, computed) and observed seismic data. Typically, a least squares measure of data misfit is adopted. Imposition of model regularization constraints during each iteration restricts the non-uniqueness associated with the problem, and allows noisy data to be examined. This formal inversion approach for recovering earth model properties may be especially relevant to shallow subsurface targets where the seismic arrivals (reflections, refractions, diffractions, surface waves, *etc.*) are not easily separated via conventional data processing techniques.

Results: Significant effort has been devoted to designing, implementing, and testing a seismic wave propagation algorithm appropriate for three-dimensional, heterogeneous, isotropic, elastic media. The algorithm is based on the velocity-stress equations of elastodynamics, a system of nine, coupled, first-order partial differential equations. Dependent variables include the three components of the particle velocity vector, and the six components of the stress tensor. Earth model parameters (P and S wavespeeds, and mass density) are stored on uniform, but staggered, three-dimensional spatial grids. Temporal and spatial derivatives in the equations are numerically approximated by centered finite-difference operators with 2nd-order and 4th-order accuracy in the gridding intervals, respectively. Arbitrary three-dimensional recording geometries, geophone and/or hydrophone receivers, and a variety of seismic energy sources (force, dipole, couple, explosion, torque) can be accommodated. The veracity and accuracy of computed results has been established by comparing algorithm output to various well-known responses of homogeneous earth models to point seismic sources. Presently, the algorithm is implemented in a single processor computer workstation environment. In order to examine large earth models in reasonable execution times, a parallel version of the code is being contemplated.

Micromechanics of Failure in Brittle Geomaterials

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Objectives: The objective of this project is to provide a fundamental understanding of the effects of grain boundary structure and cementation, damage state, and load path on the deformation and failure mode of brittle porous and nonporous geologic materials by measurement of mechanical behavior under high pressure and deviatoric stress, quantitative microstructural characterization of pristine and deformed samples, and theoretical analysis.

Project Description: Knowledge of the failure behavior of rocks is important for several energy-related applications, including oil and gas exploration and production, underground disposal of nuclear waste, and drilling technology. The experimental investigation will provide a detailed understanding of the micromechanical processes associated with the brittle failure of geomaterials and includes triaxial tests following various load paths which are defined by the ratio K of the change in the radial confining (horizontal) stress to the change in the axial (overburden) stress. Tests are conducted to various stages of failure, and include measurement of strain and acoustic emission. The micromechanical failure process are further elucidated and characterized quantitatively using light microscopy, laser scanning confocal microscopy, and scanning electron microscopy. Work focuses on porous carbonate and siliciclastic rocks, although related experiments are also being performed on low-porosity crystalline rocks in order to study completely the effect of certain parameters. The results of the laboratory tests and microstructural studies are used to guide analyses using fracture mechanics and continuum plasticity theories.

Results: (1) The volumetric imaging technique developed previously can be more fully exploited by extracting quantitative statistical descriptions of the microgeometry from the volumetric image data (for example, for systematic studies of damage evolution with stress, or, for correlation of pore geometry with bulk transport properties such as permeability). In collaboration with another BES-funded researcher, W.B. Lindquist (SUNY), we have been applying the 3dma code originally developed by Lindquist and coworkers to extract quantitative statistical geometric descriptions from synchrotron microtomographic data. Particular emphasis has been placed on investigating detailed aspects of the image processing and binarization, and in verifying the robustness of the extracted microgeometric statistical descriptions. In collaboration with R.M. O'Connor, we have also (with funding under a separate project that leverages the BES-supported work) developed a computational framework to perform pore-scale flow simulations on the binarized image volumes obtained using LSCM.

(2) The new imaging, statistical characterization, and numerical simulation capabilities are being applied to various materials: Berea sandstone, Fontainebleau sandstone with porosities ranging from 5-25%, glass bead packs sintered to varying porosity, and ceramic fibrous insulations used in the US Space Program (in collaboration with Dr. Jochen Marschall, NASA Ames).

(3) Three-dimensional LSCM imaging is being performed to elucidate the micromechanics and statistically characterize the damage structure in deformed samples of dunite to investigate the effect of ductile grain-boundary lining second phases on brittle failure.

Resolution and Accuracy of 3-D Electromagnetic Imaging

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Objectives: The objective of this research is to develop and analyze techniques for quantifying the resolution of, and appraising the accuracy of images produced by 2D and 3D electromagnetic inversion schemes, and to apply these techniques to field data.

Project Description: Non-linear electromagnetic inversion for 2D and 3D subsurface imaging of electromagnetic properties has rapidly evolved over the last decade due to its potential benefit in the areas of contaminant waste site characterization, oil and mineral exploration and delineation, and ground water resource evaluation. However, before we can proceed on inverting field data and interpreting the resulting images with any level of confidence, methods of appraisal and error analysis must be developed. The purpose of this project is to examine established methods for this purpose such as calculating the model covariance and model resolution matrices through direct matrix inversion using

Bakus-Gilbert theory, and examine procedures that estimate these resolution parameters without direct matrix inversion; the latter is required when iterative techniques such as Conjugate Gradients are employed within the inversion scheme.

Results: Linearized methods have been developed for appraising image resolution and parameter accuracy in images generated with two and three-dimensional non-linear electromagnetic inversion schemes. When direct matrix inversion is employed, the model resolution and model covariance matrices are calculated using formulas derived from traditional inverse theory. The columns of the model resolution matrix have been shown to yield estimates of the Backus-Gilbert spread functions. Plotting the width of these spread functions in different directions yields empirical estimates of the horizontal and vertical resolution throughout the imaging region. Two different forms of the model covariance matrix have been examined. The first (the data-model covariance matrix or DMCM) assumes that the only error found in the imaging process is due to data noise. The second covariance matrix (the total model covariance matrix or TMCM) assumes that both the data and the regularization or stabilization terms are associated with stochastic errors. The square root of the diagonal of these matrices yields estimates of parameter sensitivity and uncertainty, respectively. When the conjugate gradient method is employed, an iterative Monte Carlo method can be applied to statistically estimate the model covariance matrices. A method for calculating individual columns of the model resolution matrix using the conjugate gradient method has also been developed. Examples these analysis techniques have been applied to synthetic 2D and 3D cross well EM data sets as well as a 2D data set collected at the Lost Hills Oil Field in California.

Because the inversion and analysis techniques require multiple solutions of forward problem, we have been experimenting with preconditioning techniques to speed up these computations. We are now currently studying decomposing the electric field into curl free and divergence free projections and preconditioning by the projections to reduce solution run times and eliminate spurious modes. Initial tests at low induction numbers have shown an order of magnitude reduction in solution run times. Finally, we have completed the development of a massively parallel 3D magnetotelluric inversion code based on non-linear conjugate gradients and plans call for its use in the resolution study.

CATEGORY: Geochemistry

PERSON IN CHARGE: H. R. Westrich

Cation Diffusion Rates in Selected Minerals

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Objectives: Determine experimental cation diffusion coefficients for enstatite and carbonate minerals at temperatures less than 1000°C for evaluating disequilibrium behavior in geological, nuclear waste, energy, and materials concerns.

Project Description: Evaluation and modeling of geochemical processes related to nuclear waste, energy, and materials problems will require the accurate determination of cation diffusion data in silicate minerals and carbonates. A new technique for the preparation of diffusion couples using thin film technology was developed in an effort to evaluate the relatively slow diffusion of Mg^{2+} and Ca^{2+} in phases such as pyroxene and calcite where diffusion rates are on the order of 10^{-22} to 10^{-16} m^2/s in the temperature range of 700 to 1000°C. Resistive evaporation of enriched stable isotopes onto polished mineral surfaces is used to create a thin film-mineral diffusion couple, which were annealed in a controlled oxygen fugacity furnace for periods up to three months in order to provide a diffusive penetration depth of approximately 0.2 microns. Depth profiles of the tracer isotope are obtained using an ion microprobe and are then fit to appropriate diffusion models to obtain precise and reproducible diffusion coefficients.

Results: The self-diffusion of calcium and the tracer diffusion of magnesium in calcite at one atmosphere total pressure and temperatures from 550 to 800°C have been experimentally measured using isotopic tracers of ^{25}Mg and ^{44}Ca. Diffusion coefficient values were derived from the depth profiles obtained by ion microprobe analysis. The resultant activation energies for magnesium tracer diffusion and calcium self-diffusion are respectively: $E_a(Mg) = 284 \pm 74$ kJ/mol and $E_a(Ca) = 271 \pm 80$ kJ/mol. The results provide a means of interpreting the thermal histories of carbonate minerals, the mechanism of dolomitization, and other diffusion-controlled processes. The experimental work has been complemented by atomistic simulations of calcium self-diffusion in calcite. Lattice energy, defect formation energies, and activation energy for cation migration have been calculated. The electronic polarization of oxygen ions has been explicitly incorporated in a shell. Pair-potentials for Ca^{2+} ions and C and O comprising the carbonate molecular ion were simultaneously fitted to experimental lattice, elastic, dielectric, and vibrational data for calcite, and the structure and elastic properties of aragonite. The resulting potential parameters for the CO_3^{2-} group were then transferred to models for the structures and bulk moduli of the carbonate minerals incorporating Mn, Fe, Mg, Ni, Zn, Co, Cd to obtain a fully consistent set of interaction parameters.

Organic Anion-Mineral Surface Interactions During Diagenesis

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Objectives: Identification of mechanism(s) of organic acid control of dissolution and growth of silicates, and linkage of surface chemistry to global processes.

Project Description: Rates were measured in the laboratory as a function of mineral, temperature, organic acid levels, pH and time, and molecular modeling was done to constrain reaction stoichiometries.

Results: Digital imaging of weathered basalts quantifies the nature and extent of field weathering that will control the release of radionuclides from nuclear waste glasses.

Heterogeneous Nucleation and Growth Kinetics of Clays

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Objectives: Clay nucleation occurs heterogeneously and growth may occur epitaxially on detrital minerals. However, the role of nucleating substrates on the kinetics is unknown. Our goal is to quantify clay growth on various substrates, to assess "reactive" surface area, and to provide kinetic data for accurate modeling of weathering and diagenesis.

Project Description: In collaboration with Kathryn L. Nagy (now at University of Colorado), experiments are performed in which the growth surface (single or powdered crystals) is characterized before and after reaction by various techniques used by the surface physics community to investigate thin films. These include Tapping Mode Atomic Force Microscopy (TMAFM), ion beam analyses, rotating anode, and synchrotron X-ray reflectivity and X-ray diffraction (XRD). Comparison is made with results from standard powder experiments in which rates are quantified from solution chemistry changes. Clay growth occurs under controlled solution composition and temperature conditions that mimic nature. Nucleation site densities and nucleated crystal morphologies are monitored to acquire information on reactive surface areas, a parameter considered typically by bulk measurements such as gas adsorption. Molecular modeling of the bonding interactions between substrate and overgrowth as well as overgrowth morphology provides a fundamental basis for interpreting the experimental results.

Results: New data for gibbsite growth on powdered kaolinite and single crystal muscovite at 80°C in pH 3 solutions were combined with published data for gibbsite growth on gibbsite powders. All rates obey the same linear function of saturation state when reactive surface area is specifically considered. This function is $\text{Rate}_{\text{ppt}} = (2.6 \pm 0.3) \text{ x } 10^{-10}\, g^{\,(0.90 \pm 0.01)}$ mol m^{-2} sec^{-1} where $g \equiv |\Delta G_r|/RT$ for the measured range of saturation states from $\Delta G_r = 0$ to 2.1 kcal mol^{-1}, where $\Delta G_r = RT[\ln(Q/K)]$ for the reaction $Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+$. Identification of the growth phase as gibbsite was confirmed by rotating anode powder X-ray diffraction. Rates on kaolinite were determined using steady-state measured changes between inlet and outlet solutions in single-pass stirred-flow experiments. Rates on muscovite were determined by measuring the volume of precipitated crystals in images obtained by Tapping Mode™ atomic force microscopy. All rates were normalized to substrate surface area. Linearity of growth rates with saturation state suggests that the dominant nucleation and growth mechanisms are two-dimensional. Reactive surface area as defined now for heterogeneous crystal growth in reactive-transport models must be modified to include substrates other than that of the growing mineral and to account for the role of geometric and chemical controls on epitaxial nucleation and growth.

Atomistic Simulations of Clay Minerals and Their Interaction with Hazardous Wastes: Molecular Orbital and Empirical Methods

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Objectives: Examine the interaction of selected metal ions, anions, and organic contaminants on the external and interlayer surfaces of clay minerals using molecular orbital and empirical simulation methods. The computer simulations will improve our understanding of the fundamental mechanisms of adsorption processes and may help to predict and optimize environmental approaches for the mitigation of hazardous waste.

Project Description: Modeling of clay and clay-fluid systems combine energy minimization and molecular dynamics methods using both molecular cluster and periodic system representations of the bulk clay minerals, their external and interlayer surfaces, and the interacting fluids. One set of modeling techniques uses an empirically derived forcefield to describe the energy of all atomic interactions. Bulk structures, relaxed surface structures, and intercalation processes are evaluated and compared to experimental and spectroscopic findings for validation. More sophisticated calculations incorporate state-of-the-art molecular orbital methods that complement the empirical models. *Ab initio* approaches based on density functional theory (DFT) are used to examine the electronic structure of various clay minerals. Massively parallel computers provide the capability to obtain fully optimized periodic structures for large unit cell structures typical for clay minerals. Electron density distributions, deformation maps, HOMO/LUMO extents, and electrostatic potentials are used to evaluate the crystallographic control and mechanisms for contaminant sorption. This project is being performed in collaboration with Kathryn L. Nagy (University of Colorado) and Cynthia J. Hartzell (Northern Arizona University).

Results: Molecular modeling of the large tributylphosphate (TBP) complex of europium (Eu^{3+}) provides a test of the sensitivity of empirical force field calculations to organic molecules within the interlayer of a trioctahedral smectite clay (hectorite). A non-bonded version of the consistent-valence force field was utilized. Parameterization is based on the structures of simple clays and oxides. The simulations were carried out with complete translational freedom for all atoms. Energy minimization of the hectorite supercell containing, within the interlayer, the $Eu \cdot 3TBP$ complex as the tri-nitrate, 8 sodium cations, and 48 waters of hydration resulted in a d-spacing of 18.66 Å. Molecular dynamics simulations at 298 K resulted in a d-spacing of 17.40 ± 0.15 Å. The experimental d-spacing for hectorite absorbed with the TBP solvate of $Eu(NO_3)_3$ is 17.18 ± 0.04 Å. The swelling behavior of the hectorite was accurately simulated based on the molecular dynamics equilibration of the clay with interlayer Na^+ and a range of water content. A comparison of several different structural substitutions (Li^+ in octahedral site, Al^{3+} in tetrahedral site, and non-substituted hectorite) was made based on periodic DFT calculations. Electrostatic potential maps help to evaluate the influence of the charge substitution on the interlayer structure.

CATEGORY: Hydrology

PERSON IN CHARGE: H. R. Westrich

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

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Objectives: Develop a quantitative understanding of the critical processes controlling two-phase flow and transport in fractures based on detailed physical experiments and high-resolution numerical simulations. This understanding may subsequently be abstracted for use in conceptual models applied at large-scale to applied problems in petroleum extraction and the isolation of hazardous or radioactive waste.

Project Description: Under two-phase, immiscible fluid-flow conditions, phase-geometry within the fracture (*i.e.*, geometry saturated with each phase) ultimately controls: the permeability to each phase, fluid pressure/saturation relations, and solute dispersion within each phase. Phase geometry is a function of both the aperture field and the two-phase flow processes themselves. Phase “fingering”, separate from the single-phase concept of flow channelization, occurs where capillary fingering, gravity-driven fingering, or viscous fingering is dominant, emphasizing the importance of understanding the two-phase displacement processes. Systematic physical experimentation is coupled with concurrent numerical simulation to explore the interplay between capillary, gravitational, and viscous forces in the control of phase structure, and thus flow and transport in rough walled fractures. Understanding of capillary, viscous, and gravity fingering is explored in order to identify mechanisms that may be used to damp or enhance fingered flow. In addition, a conceptual understanding is developed for the phase invasion processes controlling replacement of a fully entrapped, immobile phase as it dissolves into the flowing phase.

Results: High resolution (time, space, concentration, aperture) full-field light transmission techniques to make such measurements in transparent fractures constructed out of analog materials have been developed and evaluated. Aperture and solute concentration fields are being used to test and develop capabilities for large scale modeling of single phase flow, solute transport (diffusive to advective dominated) and phase dissolution in fractures containing entrapped phase structures. We incorporated a conceptual model for calculating interface curvature into a Modified Invasion Percolation (MIP) solver. A dimensionless parameter that weighs the relative importance of aperture induced curvature (between the two fracture surfaces perpendicular to the plane of the fracture) and in-plane curvature (interfacial curvature in the plane of the fracture) arises and adds rich structural behavior to the phase invasion process. We have compared simulation results to all data available from past experiments in our lab and find MIP to simulate our experiments very well. Experiments were designed that fully test the model under conditions of small capillary number (ratio of viscous forces to capillary forces) systematically varying the bond numbers (ratio of gravity to capillary forces). We explored the idea of upscaling MIP to fracture networks for evaluating deep and rapid movement of water and contaminants in fractured rock formations, and find MIP to predict gravity-driven flow features within fracture networks.

Laboratory Investigation of Constitutive Property Upscaling

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Objectives: Our objectives are: (1) physically investigate permeability upscaling for a variety of geologic materials, (2) interpret the measured permeability upscaling in light of the physical characteristics of the porous medium and measurement characteristics of the sampling instrument, and (3) use the acquired information to test conceptual and theoretical models of permeability upscaling.

Project Description: Physical investigation of permeability upscaling is conducted with a specially adapted air-minipermeameter, termed the multi-support permeameter (MSP). The MSP allows rapid, precise, non-destructive measurement of permeability over a range of discrete sample supports (*i.e.*, sample volumes). By varying the size of the minipermeameter tip seal, measurements spanning five orders of magnitude on a per-volume basis are made subject to consistent boundary conditions and flow geometry. Thousands of measurements on multiple faces of meter-scale blocks of rock are collected with each of five different tip seals (0.31 - 5.08 cm ID) plus a single large tip seal (15.24 cm ID) designed to integrate over the entire sampling domain. This process is repeated on multiple rock samples, each of which exhibits different textural and structural characteristics. To quantify permeability upscaling, key summary statistics are calculated from the acquired data sets and analyzed with reference to their corresponding sample support.

Results: Over 150,000 permeability measurements, associated with six different sample supports, have been collected from four rock samples: a planar bedded sandstone, a sandstone exhibiting nested scales of cross-stratification, a densely-welded tuff, and poorly-welded tuff. For each rock sample and each summary statistic investigated (*e.g.*, mean, semivariogram), distinct and consistent upscaling trends were measured. Rocks of similar genetic origin (*e.g.*, tuffs) were found to exhibit similar statistical and upscaling characteristics, while rocks of differing origin (*e.g.*, tuffs vs. sandstones) exhibited distinct differences. The noted differences can largely be attributed to variations in the physical attributes (*i.e.*, spatial patterns, correlation length scales) characterizing the individual rock samples. Quantitative interpretations were pursued through comparisons drawn with theoretical upscaling models, each differing according to key fundamental assumptions. Results indicate that the non-uniform flow geometry imposed by the minipermeameter coupled with local-scale (*i.e.*, at or below the smallest scale of measurement) heterogeneity are key processes influencing the measured permeability upscaling. As a first step toward modeling upscaling under non-uniform flow conditions, linear filter analysis was employed to characterize the sample support (*i.e.*, effective size of the sample support and the spatial weighting of heterogeneities comprising that support) associated with each MSP measurement.

Multi-component Convection in Porous Media and Fractures

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Objectives: This research seeks to understand the physical and chemical processes controlling multi-component convection in porous and fractured media and to develop quantitative relationships between system parameters (solute concentrations, permeability and system geometry), system stability, flow field structure, and convective transport.

Project Description: We apply high resolution, full field light transmission techniques to study the onset and development of convection in simulated porous media (Hele-Shaw cells) and fractures. The light transmission technique allows quantitative measurement of the solute concentration fields in time thus allowing direct measurements of the mass flux of components. Experiments are first designed to test theoretical stability relations as a function of the solute concentrations, solute diffusivities and the medium's permeability. Structural evolution and convective transport as a function of dimensionless control parameters is then determined across the full range of parameter space. We also consider the application of lattice gas automata techniques to numerically model the onset and development of convection.

Results: The dimensionless buoyancy ratio (R_p), given by the ratio of fluid density contributions by the two components, is one of three dimensionless parameters required to define system behavior. Laboratory experiments were designed using the salt-sucrose, two-component system where the initial buoyancy ratio was varied systematically so that the range of parameter space spanned conditions that were nearly stable ($R_p = 2.8$) to those that were highly unstable ($R_p = 1.4$). Results of the experiments show that the evolving unstable flow field is more complicated than has been described by other investigators. The initial mm-scale perturbations evolve into cm-scale fingers that travel vertically. An

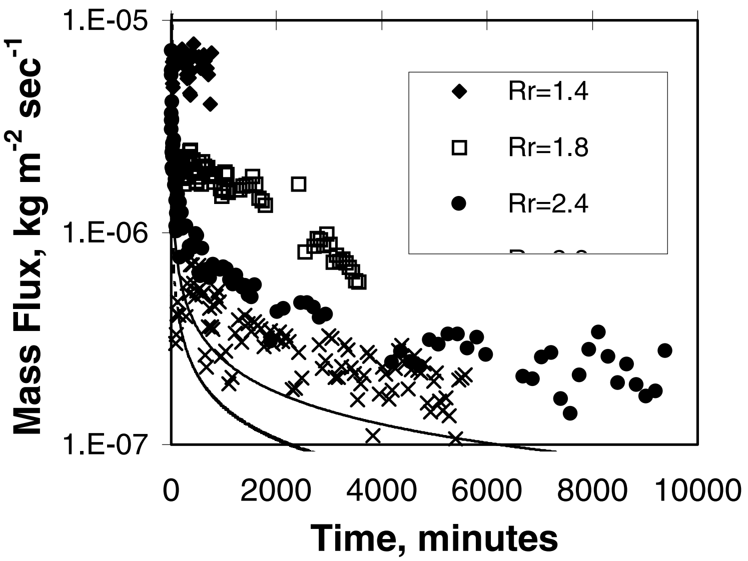

Figure. Mass flux as a function of time for four different buoyancy ratios compared with Fickian fluxes.

individual finger grows to several cm, slows/stalls, and often becomes a conduit for later-developing fingers to travel. These 'follower' fingers travel through the original stalled finger, causing it to lengthen, and then stall again. The process is repeated until fingers reach the horizontal cell boundaries. An individual finger viewed late in time is actually the result of many interactions of previous fingers. Results also show that the rate of concentration growth is linear for the most unstable systems and approaches square root of time for the more stable systems. These concentration field growth rates cause the vertical transport of mass to be much greater than would be expected in similar, stable systems. The figure above shows mass flux for four experiments of varying buoyancy ratio, compared with the mass flux determined from Fick's law for a system of the same concentration, but assumed stable. For the most unstable system (R_p =1.4), the mass flux is approximately one order-of-magnitude greater than the Fickian-derived flux.

Lattice-Boltzmann (LB) simulations were also performed for a single experiment and compared to data. Both 2D and 3D LB models were considered. The 3D model captures the Taylor-Aris dispersion across the Hele-Shaw cell gap width while the 2D model does not. Both models exhibit many features of the experiment, however, the simulated finger growth rates are ~2 to 4 times slower than in the experiments; this discrepancy may reflect the difficulty in matching the initial conditions in the lab experiments where a strip separating the fluids was pulled out at the start.

Continuum- and Particle-Level Modeling of Concentrated Suspension Flows

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Objectives: 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.

Project Description: The proposed research will elucidate the underlying physical principles that govern concentrated multiphase systems in areas essential to continued progress in geosciences. In order to be of use in real world applications, significant enhancements to currently available continuum-level suspension flow models will be required. We will use both experimentation and high performance computing to obtain microstructural information that is necessary to the development and refinement of the continuum models. For example, we expect to use this microstructural information to gain insight into the physics of particle bridge formation and collapse and particle sedimentation, which are particularly important in sand control issues found in petroleum production. Further, we expect that continuum-level modeling could eventually be directly implemented in codes currently used to predict hydraulic fracturing operations in the petroleum industry. However, the understanding gained about the physics of multiphase flows will have much broader application in geosciences.

Results: The continuum model originally developed by Phillips *et al.* (1992) has been extended to simulate non-neutrally buoyant particles and non-Newtonian suspending fluids. The extension entails the modification of the momentum and continuity equations to allow the fluid to have a spatially varying density and an additional gravity-driven diffusion term in the particle flux equation. The model predicts the settling of particles by density-driven instabilities as well as uniform hindered settling. Generalized Newtonian equations are included in the term for viscosity, which varies locally with the concentration of particles and the shear rate. Results from the new model, which has been implemented into a general-purpose finite element computer code, are being compared with experimental measurements based on nuclear magnetic resonance (NRM) imaging. Concurrently, two other continuum-level models are being adapted for use in the same finite element computer code. In addition, a multipole-accelerated boundary element method (BEM) is being developed to simulate several thousand individual interacting particles. These simulations lead to detailed information on individual particle and fluid motion that is unobtainable through experiments, and they will aid in determining accurate continuum approximations such as the gravity-driven diffusion terms.

PART II: OFF-SITE

GRANTEE: American Museum Of Natural History

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GRANT: DE-FG02-92ER14265

Influence of carbon on the electrical properties of crustal rocks

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Objectives: Understand the adsorption of carbon on silicate surfaces in the presence of carbonaceous gases; determine the nature and origin of carbon in deep crustal rocks; and seek applications to a section of the San Andreas Fault system currently the object of seismic research.

Project Description: The adsorption study will be conducted by fracturing rocks and single crystals of synthetic forsterite, natural olivine, quartz, and amphibole under identical conditions in the presence of CO-CO_2 gas mixtures, using experimental and analytical techniques developed in our previous studies. The composition and distribution of carbon in a suite of deep crustal rocks will be determined using time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and electron probe techniques. To learn if carbon deposition plays a role in active fault systems, we shall also determine the nature and distribution of carbon in rocks and outcrops at Parkfield, CA. This is a joint project with A.G. Duba (LLNL) and T. J. Shankland (LANL).

Results: TOF-SIMS yields mass spectra of the upper several monolayers of an analytical surface. The applicability of TOF-SIMS to the characterization of carbon compounds on crack surfaces in rocks is demonstrated. A pyroxene grain from the interior of a gabbro xenolith from the 1801 flow of Haulalai volcano, Hawaii, was chosen for this initial study because well-developed carbonaceous films are known to exist on crack surfaces in these rocks. In addition to the anticipated major elements (Si, Al, Fe, Mg, Ca), several minor and trace elements (B, Li, Na, Ti, Mn, Co, Ni, Cu) were identified in the positive ion mass spectra. The unsputtered surface is covered with a hydrocarbon-rich layer, as indicated by the presence of numerous light C_xH_y fragments and a group at several hundred m/z. This layer is much better developed than the ubiquitous atmosphere-derived hydrocarbon layer observed on nominally clean, unsputtered surfaces and therefore must be indigenous. High concentrations of Ni and Cu are associated with the carbon-rich layer and may exist as organo-metallic compounds. Several C-N fragments, possibly indicative of biogenic compounds, were also identified in negative ion spectra. Imaging reveals the presence of localized islands enriched in oxides of Si, Al, Na and Ca beneath the carbonaceous layer. This study demonstrates that TOF-SIMS can be used to provide unique and geochemically useful information on crack surfaces in rocks.

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GRANT: DE-FG03-95ER14533

Reaction Mechanisms of Clay Minerals and Organic Diagenesis: An HRTEM/AEM Study

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Objectives: The objectives of this study were to gain an improved understanding of the microstructures and reaction mechanisms for diagenetic reactions in selected layered silicate minerals and organic materials found in surficial environments.

Project Description: We studied clay and detrital minerals as well as organic matter in sequences of Upper Cretaceous and Lower Tertiary clastic rocks from the southern Rocky Mountains using a range of analytical and structural techniques. We were especially interested in: (1) the berthierine-to-chamosite reaction, (2) smectite illitization, (3) organic diagenesis, and (4) XRD versus TEM size distributions of clay minerals. This research was designed to lead to an improved understanding of the states of illite (I) and smectite (S), berthierine and chamosite, organic matter, and detrital minerals in diagenetic environments. The results provided information for determinations of reaction mechanisms and establishment of kinetic models that permit one to predict the extent to which the formation of certain clay minerals occurs at various depths, temperatures, and times. Size distributions of clay minerals are important indicators of reaction progress, but there are questions regarding the differences between sizes determined using different experimental techniques. We compared XRD to TEM measurements and found significant differences.

Results: Phyllosilicates generally have large surface areas and exhibit a broad range of crystallite sizes. It is widely accepted that crystallite size distributions are approximate indicators of grade of diagenesis and metamorphism. Most size measurements have been made using X-ray diffraction (XRD), with some made using transmission electron microscopy (TEM). We found that mean thicknesses of illite-muscovite in ion-milled rock samples are up to four times larger than those in separates. Cleaved crystals of illite-muscovite dominate in separates of all samples, indicating breakage along cleavage planes during sample preparation. These relations suggest that XRD profile analysis can be a poor quantitative measure of true crystallite sizes in rock samples. Sample preparation for XRD analysis can significantly alter the original size distributions; the poor approximations to lognormal distributions improve (perhaps misleadingly) during physical separation. Interpretation of growth conditions from size distributions of separates is therefore not without risk. Only size distributions of unseparated samples, or separates where the effects of the separation process are known, should be used as indicators of crystal-growth conditions. Our data also imply that the conventionally measured illite crystallinity values and associated data (mean crystallite size, lattice strain, crystallite size distribution) determined from the $< 2\mu m$ (micrometers) grain-size fraction samples may be representative of the given separate used for crystallinity studies, but are not directly characteristic of the whole rock. We conclude that although XRD measurements are far simpler and faster, sample preparation may seriously skew the results; for best results, measurements need to be done or at least correlated with TEM analyses.

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Grant: DE-FG03-94ER14414

Chemical Dynamics of Hydrocarbon Reservoirs Investigated by Secondary Ion Mass Spectrometry

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Objectives: Microanalyses of oxygen and boron isotopes in authigenic silicates are being obtained to determine their variation in hydrocarbon-producing sedimentary basins. These analyses can be used to constrain mass transport processes occurring during diagenesis and hydrocarbon migration.

Project Description: Current research examines the isotopic heterogeneity of authigenic silicates (quartz, feldspar, clay minerals) in the Gulf Coast Sedimentary Basin in order to interpret the chemical environment of precipitation during burial diagenesis. *In situ* analyses of O-isotopes help determine the timing of reservoir cementation and the volumes and chemistry of the paleofluids responsible. Concurrent changes in B-isotopes were investigated as an aid to interpretation of the sources of fluids. Organic matter is a potential source of B in clastic sedimentary basins undergoing burial and thermal maturation. Understanding sources of B is required to interpret mass transport processes and develop better models to explain fluid flow and hydrocarbon migration.

Results: In 1998 research focused on 1) Developing techniques for extraction of B from organic matter and testing the B-content and isotopic variation in organic matter and clay minerals. 2) Developing a protocol for measurement of B-isotopes in clay minerals by SIMS. 3) Design and implementation of hydrothermal experiments for examining B-isotopic changes as a function of temperature during the reaction of smectite to illite.

Extraction of B from kerogen and oil was tested using a Parr Bomb technique with mannitol in the aqueous solution to collect B. Gases released from the Parr Bomb can potentially contain BCl_3, therefore the gases were bubbled through mannitol to collect any gas phase B. Results found ppb levels of B in the 7 oil samples collected from different reservoirs, but 140 ppm B was found in the kerogen. This indicates that kerogen is a significant B source in thermally maturing sediments, but that the B does not go into oils, but into waters associated with hydrocarbons. Results were compared to SIMS analyses of kerogen in thin section and were found to agree within error.

The most important discovery for analysis of B-isotopes in clay minerals was the essential removal of adsorbed-B from the surfaces of clay minerals, either extracted from a sample or in thin section. The surface adsorbed-B can represent up to 20% of the total-B and often reflects contamination from drilling fluids or thin sectioning and polishing fluids. The B that is fixed in tetrahedral sites of authigenic illite is what reveals the fluid chemistry during diagenesis. To remove adsorbed-B clay separates or thin sections must be soaked in a mannitol solution (B-complexing agent) before analysis.

A hydrothermal reaction vessel was designed for reacting smectite to illite under conditions of constant T, P, and fluid:mineral ratio. A Teflon Bridgeman seal allowed rapid sampling on a daily basis. Multiple gold capsules (14) were sealed with reactants and loaded in the vessel, which contained an internal and external thermocouple to monitor the T within 5°C and P within 50 psi. Three experiments were setup using NBS 951 boric acid solution in a 1:1 fluid/mineral ratio, with K-saturated smectite as a starting material. The reaction to illite was conducted with high and low concentrations of B, and at 300° and 350°C. Samples are to be collected at intervals during the reaction progress. Examination of changes in the B and O-isotopes and mineralogical changes will be monitored during reaction progress. Illitization will take approximately 4-5 months for each experiment and equilibrium conditions will be determined by monitoring changes in O-isotopes of the fluid and illite. The difference between the fixed-B $\delta^{11}B$ in the authigenic illite/smectite and the fluid will be used to determine a B-isotope fractionation factors as a function of temperature.

GRANTEE: Boston University

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GRANT: DE-FG02-95ER14498

Nonlinear Systems Approach to Understanding the Origin of Geodetic Crustal Strains (Collaborative Research)

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Objectives: To develop a physical understanding of the origins of geodetic crustal strains in nonlinear geomechanical systems, to examine the space-time patterns and correlations that occur in these systems, and to use these patterns to forecast the future activity that may produce disasters affecting a wide variety of critical energy facilities.

Project Description: A variety of nonlinear dynamical processes operate within the complex earth system. Signatures of these processes include the appearance of scaling (fractal distributions), global and local self-organization, intermittancy, chaos, and the emergence of coherent space-time correlations, patterns, and structures. The geodynamical effects observed in earthquake systems, particularly crustal straining, dynamical segmentation, and intermittant seismicity, are being modeled in massively parallel simulations in an effort to clarify the origins of these phenomena. Simulations and theoretical investigations are particularly aimed at quantifying the limits of predictability for catastrophes (disasters) that occur within the earth system. We are currently developing both the simulation methods for earthquake models, and the statistical mechanical analysis techniques needed to understand and interpret the results. From these simulations, we will then predict geodetic and other deformation associated with impending earthquakes to be tested against Global Positioning System, Synthetic Aperature Radar, seismicity, and other field data.

Results: We made important progress in several fundamental problem areas during this past year. These include: 1) *Why earthquakes stop.* According to the classical theory of tensile Griffith fracture, as applied to shear fracturing in earthquakes, an earthquake cannot self-arrest until the boundaries of the fault are reached. We found that spectral properties, as defined by the Hausdorff dimension H of the shear stress field roughness determine whether earthquakes grow or arrest. The critical value for arrest, H = 0.5, corresponds to a Brownian Walk through the stress-deficit field. 2*) Space-time correlations and patterns in earthquake activity*. We developed a new technique that allows patterns to be understood as eigenstates of a suitably constructed space-time correlation operator. We found that these methods can be used to forecast the progression of patterns through pattern-state space. 3*) Observational tests of earthquake models with implications for the physics of earthquakes.* Our work has indicated that under shear loading, faults reside in a metastable state near a classical spinodal that governs the nucleation and growth of slip events. To test and validate these models, we have calculated a number of physical quantities to observational data. Preliminary tests indicate excellent agreement between predictions and observations.

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GRANT: DE-FG02-90ER14144

Diffusional Transport and Fluid Connectivity in Mineral Aggregates

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Objectives: The primary objective of this research is to experimentally determine diffusional transport kinetics (rate and mechanism) of oxygen and selected geologically and environmentally important chemical species in natural and hot-pressed single and polyphase aggregates of common mineralogies over a range of temperatures, pressures, and coexisting fluid compositions. A vital component of this research is to establish the distribution (connectivity) of coexisting fluids of common geological compositions in these aggregates and to correlate the fluid distribution to the diffusional transport kinetics. The results provide much needed data on the nature of grain boundaries in rocks and the rates of transport of chemical components through rocks. Applications of these data include evaluating the retentiveness of different geological medium for the isolation and confinement of nuclear and chemical waste, modeling the migration of hydrocarbons through different rock types to refine exploration and development strategies for more efficient oil and natural gas recovery, and determining patterns of circulation of hydrothermal meteoric water and associated ore-body deposition and geothermal energy systems. In addition, these data place valuable constraints on the strength of earthen materials and the importance of different deformation mechanisms accommodated by diffusional mass transport.

Project Description: Bulk diffusional transport rates are determined in natural and hot-pressed aggregates of common mineralogies either 'as-is' or after textural equilibration with fluids common to natural environments ($H_2O \pm CO_2 \pm NaCl$ fluids). The transport rates are determined from profiles of chemical or isotopic tracers measured using an ion microprobe (SIMS). The bulk diffusivities are correlated with the physical nature of the grain boundaries and sample textures (fluid distribution), which are characterized using transmission (TEM) and scanning (SEM) electron microscopy.

Results: Most of the research activities in the past year focused on experimental determinations of Si bulk diffusion in natural and hot-pressed aggregates of the common minerals quartz, feldspars, and forsterite. The results for each are summarized below.

Silicon bulk diffusion rates were determined in a fine-grained (1.2 μm diameter) natural quartz aggregate from Hot Springs, AR. The diffusion experiments were done at 600° to 800°C and 150 MPa confining pressure (hydrothermal), and at 800° to 1100°C and 1 atm (in a stream of dry N_2). The temperature dependence is described by the Arrhenius parameters: $D_{0,\,bulk} = 3.7 \times 10^{-10}$ m^2/sec and Q = 137 ±18 kJ/mol, and $D_{0,\,bulk} = 6.2 \times 10^{-9}$ m^2/sec and Q = 178 ±38 kJ/mol for the hydrothermal and dry experiments, respectively. The results of this study provide valuable constraints on the role of diffusion-accommodated deformation in quartz-rich rocks.

Grain boundary diffusion rates of ^{30}Si in aggregates of albite, orthoclase and anorthite compositions have been experimentally determined at either 0.1 MPa in dry N_2 (<1 ppm H_2O) and from 800-1100°C or hydrothermally at 100 to 150 MPa and from 600-800°C. ^{30}Si and ^{18}O concentration profiles were measured using SIMS and depth profiling or step scanning. The ^{18}O profiles were longer than the ^{30}Si profiles consistent with published oxygen grain boundary diffusion rates. For silicon diffusion the activation energies in the 0.1 MPa series are 210±71 kJ/mole for Ab, 194±71 kJ/mole for Or, and 176±61 kJ/mole for An. Although the values for all three compositions at the dry conditions of the 0.1 MPa anneals are similar, diffusion in the An aggregate is measurably slower. For the hydrothermal Or anneals at 150 MPa the activation energy is 147±27 kJ/mole. At 150 MPa water pressure the diffusion rate is faster than in the dry anneals at 0.1 MPa by about a factor of 100. For Ab aggregates, the Si diffusion rate at 900°C and 0.1 MPa is about 100 times slower than that for oxygen at 900°C and 100 MPa hydrothermal. Dry oxygen diffusion in the 0.1 MPa series is faster than Si diffusion as indicated by longer ^{18}O profiles. Thus, Si is the rate limiting grain boundary diffusion species in feldspars at the experimental conditions studied.

Silicon diffusion rates were determined in fine-grained (~4.5 μm) hot-pressed forsterite aggregates at 900° to 1200°C and 0.1 MPa using a ^{30}Si-tracer and standard SIMS analysis. There is no measurable difference in diffusion rates between samples buffered by excess MgO or SiO_2, nor samples run in dry N_2 or H_2/CO_2. The results yield the Arrhenius parameters $D_{0,\,bulk} = 5.4 \times 10^{-9}$ m^2/sec and Q = 203±36 kJ/mol. At 1200°C, the ^{30}Si grain boundary diffusion rate is ~10^9 greater than the Si volume diffusion rate and indicates that diffusional transport of Si in forsterite aggregates is dominated by grain boundaries.

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GRANT: DE-FG03-85ER13445

Infrared Spectroscopy and Hydrogen Isotope Geochemistry of Hydrous Silicate Glasses

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Objectives: The focus of the proposed project is the combined application of experimental petrology and geochemistry with stable isotope geochemistry to problems in petrology and geochemistry, with particular emphasis on the behavior of the volatile components, H_2O and CO_2, in geological systems ranging from high to low temperatures.

Project Description: This project integrates (1) laboratory studies directed toward the development of analytical techniques and a solid understanding of the physical chemistry of geological systems through carefully controlled experiments, and (2) syntheses and field studies in which these techniques and chemical principles are applied to specific petrological and geochemical problems. A key feature of this project is the combination of methodologies from stable isotope geochemistry with those from other fields (*e.g.*, experimental petrology, mineralogy, and atmospheric science). Results of this work will continue to be applied to developing quantitative constraints on geological processes involving H_2O and CO_2. Our results also contribute to a deeper understanding of the chemical and physical properties of volatile-bearing systems and have applications to both earth and materials science.

Results: (1) An extensive study of C and H isotopic compositions of natural apatites was completed. Apatites are ubiquitous and unusual in that they have significant quantities of C, O, and H, and thus they have considerable promise as tracers of petrogenesis. (2) Studies of the temperature and water content dependence of the speciation of hydrous components between water molecules and hydroxyl groups in rhyolitic glasses and melts was completed. This work is of practical value in that it can be used as a cooling rate indicator and geothermometer for hydrous volcanic glasses. (3) A new technique based on the pressure-dependence of the solubility of minerals in silicate melts was developed to determine the partial molar volumes of components in melts at high pressures. These are the only measurements that determine partial molar volumes directly at elevated pressure. (4) Elevated H_2O, B, and Cl contents and Cl/H_2O ratios in host glass and glass inclusions in samples from Loihi, Hawaii, were used to document extensive interaction between the magma and a sea-water-derived component, suggesting that interactions between magmas and their hydrothermally altered envelopes is a significant process. (5) The ion microprobe was used to measure $\delta^{18}O$ values of +10 per mil in glass inclusions in mantle-derived olivines. These glasses represent the most extreme oxygen isotope ratios reported in mantle-derived material and provide direct evidence of the recycling of crustal material that interacted with water at low temperature into the mantle at subduction zones. (6) A program of sampling air in Pasadena and determination of the concentrations and isotopic ratios of CO_2 and H_2O was begun. The focus has been to explore the potential of these measurements for elucidating sources and amounts of pollution and for complementing other measurements of urban atmospheres being routinely made to monitor air quality. (7) D/H ratios of unexchangeable hydrogen in dated wood in lake sediments was used to study the climatic record over the past 10,000 years in the vicinity of Lake Emma, in the San Juan Mountains of southwestern Colorado.

GRANTEE: California Institute Of Technology

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GRANT: DE-FG03-88ER13851

Isotope Tracer Studies of Diffusion in Silicates and of Geological Transport Process in Aqueous Systems Using Actinide Elements

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Objectives: The research program was directed to three principal objectives: 1) The determination of the concentration and isotopic composition of Os in rivers, estuaries and the oceans; 2) The nature of U transport on colloids and particles in natural waters.

Project Description: We are carrying out studies of the transport of actinide and platinum group elements in rivers, bogs, estuarine environments and the oceans. This involves development of advanced laboratory analytical procedures and improved field filtering techniques. The distribution of U and Th on colloids and in solution was studied. These techniques have been applied to both oxic and anoxic environments and establish clear relationships for element transport in natural conditions.

Results: 1) The isotopic composition of Os in sea water and in some rivers was directly determined for the first time. 2) The concentration of Os was first estimated in both seawater and some major rivers. The problem of tracer sample equilibration was identified but not fully solved. Recent works by Levasseur *et al.* (1998) and Sharma *et al.* (1998, *Trans. Amer. Geophys. U., Eos Supplement* 79:519) have shown a possible means of obtaining equilibration. 3) The technical developments outlined in item #2 permitted determination of Os isotopic composition and concentration in the Ganges, Brahmaputra and Indus (Sharma *et al.* 1998). The results have direct application to the erosion of the Himalayas and the supply of Os to the oceans and to the transport of Os into the Columbia River Estuary (Porcelli *et al.* 1998, *Min. Mag.* 62A, 1202-1203). 4) A major effort was directed toward the transport of the U, Th series nuclides in the Kalix River watershed through organic rich mires in Sweden and into the estuary. Studies of the transport of these nuclides on detrital particles, Fe oxyhydroxide flow, colloids, and in solution have been completed. The results are published in Andersson *et al.* (1998, *Geochim. Cosmochim. Acta* 62, 385-392) and in manuscripts in preparation for publication (Porcelli e*t al.,* 1999 and Andersson *et al*., 1999, *Min. Mag.* 62A, 57-58). 5) A serious effort was directed at developing a model of transport of the U, Th series nuclides in aquifers. This theoretical treatment covers weathering, nuclear recoil, and chemical exchange with a substratum in the aquifer, and the basic hydrologic properties of an aquifer. This model appears to give a reasonable description of ^{234}U and several other nuclides but cannot explain the high Rn emanation commonly observed. A summary report of these results has been submitted for publication by Tricca *et al.* (in press). 6) A detailed study of ^{238}U-^{230}Th dating of a speleothem (the Soreq cave) in Israel was carried out collaboratively. The results established a precise chronology for the detailed ^{18}0 and ^{13}C stratigraphy covering the last 80,000 years. These results demonstrated a clear relationship with climate change, rainfall and transport of weathering products from soils. These results have been published (Kaufman *et al*., 1998, *Earth Planet. Sci. Lett.,* 156, 141-155) and are widely cited and demonstrate a means of studying climate change on the continents. 7) The Os-Re fractionation between silicate and sulfide melts was determined in MORB basalts and glasses and the isotopic composition of Os measured in the small sulfide samples with high concentrations. This approach permits determination of ^{107}Os/^{108}Os in basalts without the effects of seawater contamination.

The correlation of basalt alteration uses boron isotopes as a monitor of seawater exchange and alteration (Roy-Barman *et al*. 1998, *Earth Planet. Sci. Lett.,* 139, 351-363).

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GRANT: DE-FG03-85ER13419

Advective-Diffusive/Dispersive Transport of Chemically Reacting Species in Hydrothermal Systems

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Objectives: The overall research objective of this project is to quantify the reaction process responsible for the generation of petroleum in sedimentary basins using thermodynamic calculations and compositional information to characterize metastable equilibrium states (Shock, 1988; Helgeson *et al.*, 1993; Seewald, 1994) and the causes and consequences of irreversible reactions in hydrocarbon source rocks and reservoirs.

Project Description: The formation and evolution of petroleum in sedimentary basins is generally attributed to the thermal catagenesis of kerogen; *i.e.*, kinetically controlled irreversible generation of high molecular weight liquid hydrocarbons in bitumen from kerogen and their progressive conversion to the lighter species that predominate in petroleum as a result of increasing temperature and time with increasing depth of burial. This widely accepted time/temperature paradigm is based largely on extrapolation of the results of laboratory pyrolysis experiments to the natural process of petroleum generation by correlating the products of the experiments with observed changes in kerogen composition with depth in sedimentary basins. However, high-temperature pyrolysis experiments are by design irreversible, and the extent to which the results of these experiments represent, or can even be reliably extrapolated to account for petroleum generation in nature has never been adequately documented.

Although the phenomenological association of petroleum generation and maturation with increasing temperature and time during burial is self-evident, the causal implications of this association are highly questionable. In fact, it has been shown that in closed systems, source rocks with hydrogen-rich organic matter may retain their petroleum generating potential at temperatures far greater than those normally associated with the formation of crude oils. It can be demonstrated that degradation of organic matter with increasing depth is an oxidation/reduction process that requires the presence of H_2O.

Theoretical considerations and thermodynamic calculations have led to the hypothesis that hydrolytic disproportionation of hydrocarbons plays a crucial role in the diagenetic deoxygenation of immature kerogen, as well as the generation and maturation of crude oil in hydrocarbon source rocks. Recent field and laboratory evidence supporting this hypothesis indicates that hydrolytic disproportionation of organic matter is not only a dominant process in petroleum source rocks and reservoir systems, but that it plays a widespread and important role in ore deposition and high-temperature metasomatism of sedimentary, granitic, and mantle-derived rocks.

Results: Research carried out in the current budget period has been primarily concerned with generating a chemical and thermodynamic speciation model for kerogen in hydrocarbon source rocks which matches as closely as possible geologic reality. These efforts have led to a preliminary kerogen model, which is currently being tested. Thermodynamic calculations using this kerogen speciation model support the hypothesis that high molecular weight *n*-alkanes, isoprenoids, naphthenes, diterpanes, steranes, hopanes and aromatic compounds in kerogen are in metastable equilibrium with bitumen and hydrocarbons in source rocks and crude oil with carbon numbers > ~ 6 – 15. Although the model needs refining, the calculations clearly indicate that these metastable equilibrium states buffer the oxidation state of the system at fugacities of oxygen, which are within a few tenths of a log unit of those in hydrocarbon reservoirs. Furthermore, the model is consistent with progressive oxidation of kerogen and reduction of crude oil with increasing depth of burial, which matches observed changes in hydrocarbon source rocks. It thus appears that irreversible hydrolytic disproportionation of the light hydrocarbons to form successively lighter species and ultimately methane provides the Gibbs free energy drive for the chemical evolution (maturation) of both kerogen and oil in hydrocarbon source rocks. These findings run counter to conventional wisdom. Consequently, they may have profound implications with respect to future exploration and development of hydrocarbon energy resources in sedimentary basins.

GRANTEE: University Of California, Berkeley

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GRANT: DE-FG03-96ER14676

Collaborative Research: Studies for Surface Exposure Dating in Geomorphology

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

Project Description: Surface exposure dating utilizing cosmogenic nuclides is now acknowledged as a successful means with which to date many terrestrial surfaces. It is also recognized that there are many new applications for these techniques. Although the method rests on a firm physical and geochemical foundation, there are examples of conflicting results. This project includes determination of precise production rates and production depth profiles, studies of altitude and latitude effects, intercalibration with other methods, isolation of *in situ* produced nuclides from other lithologies. The effort will focus on chemical isolation of cosmogenic nuclides of geologic and artificially exposed samples, on implementation of surface exposure dating methods using new radionuclides such as *in situ* ^{14}C and pure spallation ^{36}Cl, measurements of proton and neutron cross sections and development of theoretical production rate calculation.

Results: Although quartz is the most advantageous mineral for studies of cosmogenic nuclide surface exposure dating, many geological settings are very poor or totally lacking in quartz. We have therefore begun to investigate olivine as an alternative to quartz in more mafic lithologies. Although a few groups have attempted to isolate *in situ* produced ^{10}Be and ^{26}Al from olivine, only in one case has the attempt succeeded. There are two obstacles to surface exposure dating with olivine. First, meteoric ^{10}Be must be completely removed. Secondly, olivine must be isolated in very pure form so that it contains a minimum amount of natural Al. In order to attack these problems, we have collected many olivines, especially from Hawaii, for our chemical leaching tests. While we haven't yet been completely successful in solving the first problem, the separation of meteoric ^{10}Be from olivine, we have made considerable progress in removing the second obstacle. We have been able, through selective leaching, to reduce the Al impurities in olivines by more than a factor 10. We will continue experiments designed to develop reliable methods for using olivines in surface exposure dating.

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GRANT: DE-FG03-96ER14667

Microbial Dissolution of Iron Oxides

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Objectives: Our overall goal is to determine the mechanisms of iron release during microbially enhanced iron oxide dissolution by an aerobic microorganism. Research objectives include: (1) to examine the reactivity of a microbial siderophore in the presence of Fe(III)(hydr) oxides and (2) to image mineral surfaces upon reaction with an aerobic Pseudomonas bacteria in order to determine microbial attachment mechanisms and dissolution features. Objective (1) is of principal interest at Berkeley.

Project Description: Research at Berkeley has focused on siderophore-promoted dissolution experiments. The siderophore used was N-[2, 3-dihydroxy-4-(methylamido) benzoyl] desferrioxamine B (DFOMTA), which differs from desferrioxamine B, previously investigated in our research, by having the aromatic moiety given in brackets in place of H on the amino group. This siderophore was developed as a metal-chelating agent for remediation of radioactive waste. Batch sorption experiments were conducted with DFOMTA and goethite, and with DFOMTA and goethite bearing adsorbed Pb(II). Lead was used as a chemical surrogate for actinide metals of importance to waste-remediation scenarios at DOE facilities.

Results: By contrast with DFO-B, DFOMTA exhibited strong adsorption to goethite at $pH < 8$, with a prominent maximum occuring at pH 5. The maximum adsorbed concentration of DFOMTA was an order of magnitude greater than that of DFO-B (which occurred at $pH > 8$). The presence of DFOMTA also had a large impact on the adsorption behavior of Pb(II), which, instead of increasing monotonically for $pH > 4$ as it does in the absence of siderophore, followed the pattern shown by DFOMTA adsorption: increasing from $pH < 4$ to a maximum at pH 5, then decreasing at higher pH. These data suggest that a Pb-DFOMTA complex is the adsorbing species. By sharp contrast, DFO-B only desorbed Pb(II) at $pH > 6$.

GRANTEE: University Of California, Davis

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GRANT: DE-FG03-96ER14629

The Energetics of Reactions at Mineral Surfaces and Their Coupling to Disequilibria

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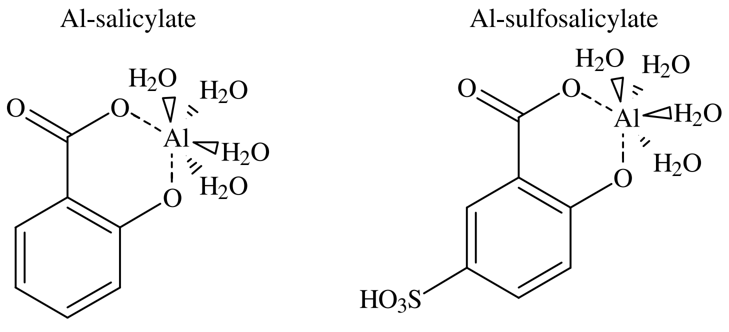
Objectives: We determine rates of bond dissociations in aqueous solutions at a very fundamental level in order to help establish a general reactivity scale.

Project Description: At a molecular scale, most reactions of aqueous geochemical importance involve a bonded atom or molecule that is replaced with another. We employ NMR-spectroscopic methods to characterize the rates of these ligand-exchange reactions in a set of model aqueous aluminum complexes. These data are used to establish a reactivity trend for predicting rates in experimentally difficult settings, such as the removal of a water molecule from a monomolecular step at a mineral surface.

Results: Our experiments have produced a set of rate parameters for a wide range of aluminum complexes, including monodentate isoelectronic complexes like AlF^{2+} and $AlOH^{2+}$, as well as carboxylate complexes of varying structure and denticity. The data determined up to 1999 are compiled in Table 1. Attempts to model the activated equilibria are reported in Phillips *et al.,* (in press) and the relation to surface chemistry is covered in Brown *et al.*, (1999, *Chem. Rev*. 99, 77-174). These measurements are at the most fundamental level of elementary reactions; that is, they proceed as written on the molecular scale.

The data include several surprises, including the fact that the rates of exchange of a hydration water from around the $AlOH^{2+}$(aq) complex is 30,000 times more rapid than around the fully hydrated molecule: Al^{3+}(aq). This extent of labilization by a single bonded hydroxyl is among the largest values measured. In addition, solvent exchanges in simple molecules like those shown in Figure 1differ measurably and, when combined with other data in Table 1, indicate that the extent of labilization does not reflect the size of the chelating ring, but reflects the Lewis basicity of the ligand, which can potentially be estimated by computation. This work is underway.


Al-salicylate

Al-sulfosalicylate

Figure

Specie	(±ln(σ) (s^{-1})	ΔH‡ ($kJ \cdot mol^{-1}$)	ΔS‡ ($J \cdot K^{-1} \cdot mol^{-1}$)	Source
Al^{3+}	1-3	70-85	0-42	1,5
$Al(ssal)^{+}$	3000(±0.08)	37(±3)	-54(±9)	2
$Al(sal)^{+}$	4900(±0.07)	35(±3)	-57(±11)	2
$Al(mMal)^{+}$	660(±.18)	66(±1)	31(±2)	3
$Al(mMal)_2^{-}$	6900(±.02)	55(±3)	13(±11)	3
$Al(ox)^{+}$	109(±.13)	68.9(±2)	25.3(±6.7)	4
AlF^{2+}	111(±0.14)	79(±3)	60(±8)	5
AlF_2^{+}	19600(±.05)	69(±5)	70(±17)	5
$AlOH^{2+}$	31000(±.25)	36.4(±5)	-36.4(±15)	6

[1] Hugi-Cleary *et al*., (1985, Helv. Chim. Acta 68, 545-554)
[2] Sullivan *et al*., (1999, Geochim. Cosmochim. Acta 63, 1471-1480)
[3] Casey *et al*. (1998, Geochim. Cosmochim. Acta 62, 2789-2797)
[4] Phillips *et al*., (1997, Geochim. Cosmochim. Acta 61, 4965-4973)
[5] Phillips *et al*. (1997, Geochim. Cosmochim. Acta, 15, 3041-3049)
[6] Nordin *et al*. (1998, org. Chem. 37, 4760-4763)

Table 1: Rate coefficients for exchange of water molecules from the inner-coordination sphere of Al(III) complexes to the bulk solution, as determined from ^{17}O-NMR spectra. The abbreviations are: ox=oxalate; ssal=sulfosalicylate; sal=salicylate; and mMal=methylmalonate. The estimated uncertainties for are reported as logarithms.

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GRANT: DE-FG03-97ER14749

Thermodynamics of Minerals Stable Near the Earth's Surface

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Objectives: The goals of the project are to increase both the database and the fundamental understanding of the thermodynamics of volatile-bearing mineral phases (amphiboles, micas, clays, zeolites, carbonates) important to surficial, sedimentary, and shallow crustal processes.

Project Description: Using high temperature solution calorimetry, this research determines the enthalpies of formation of hydrous silicates and carbonates. Systematics in energetics of ionic substitutions are sought in order to predict the thermodynamics of complex multicomponent minerals. Mixing properties of mica, amphibole, clay, zeolite, and carbonate solid solutions are also studied.

Results: *Carbonates:* Studies of ordered natural (Fe, Mg)$Ca(CO_3)_2$ samples and synthetic disordered $MgCa(CO_3)_2$, together with our previous work on synthetic (and less ordered) (Fe, Mg)$Ca(CO_3)_2$ solid solutions from a coherent picture of the energetics of disordering in the dolomite-ankerite series. The enthalpy of complete disordering of $MgCa(CO_3)_2$ is 33 ± 6 kJ/mol, about twice as large as that inferred from earlier work on partially ordered materials quenched from high pressure and temperature.

Epidotes: A calorimetric and X-ray powder diffraction study of Fe^{3+} - Al^{3+} substitution in epidotes has been completed. The data suggest a significant role for order-disorder as a function of aluminum content.

Clays: Work on natural kaolinites is completed. It implies little dependence of enthalpy on crystallinity and stacking disorder. Kaolinite is energetically more stable than dickite and is probably the thermodynamically stable polymorph in all natural environments. Work on a set of natural illite-smectites is in progress.

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GRANT: DE-FG03-92ER14307

Electrochemical Measurements of Thermodynamics Properties of Minerals and the Processes of Reconstruction at Mineral Surfaces

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Objectives: We are: (1) measuring thermodynamic properties for carbonate solid-solution minerals that are important in soils and aquifers; (2) devising new theoretical approaches to the calculation of the energetics of calcite-structure metal carbonates in pure and binary phases; (3) and, using AFM to explore the processes of reconstruction at mineral surfaces.

Project Description: We have developed a new method that utilizes electrochemical double cells without liquid junction to determine thermodynamic properties of carbonate and oxide minerals. Such a cell for calcium cadmium-carbonate minerals is (Rock *et al.,* 1994, *Geochim. Cosmochim. Acta* 58, 4281-4291):

$$\mathrm{Cd(Hg,2\text{-}phase)|CdCO_3(s),\ CaCO_3(s)|CaC1_2(aq)|Hg_2C1_2(s)|Hg(1)}\text{—}$$
$$\text{—}\mathrm{Hg(1)|Hg_2C1_2(s)|CaC1_2(aq),CdC1_2(aq)|Ca_xCd_{1-x}CO_3(ss),\ CdCO_3(s)|Cd\ (Hg,2\text{-}phase)}$$

yielding a net cell reaction of:

$$\mathrm{CaCO_3(s)+(1\text{-}x)\ CdC1_2(aq) \rightleftharpoons Ca_xCd_{1\text{-}x}CO_3(ss)+(1\text{-}x)CaC1_2(aq).}$$

Values of for the solid solution relative to the endmembers are obtained from the cell voltage and known activities of the electrolytes. With these values, we estimate excess Gibbs energies of mixing (ΔG^{ex}) and the partitioning of metals into the solid solutions at equilibrium. The ΔG^{ex} values are compared with enthalpies of mixing (ΔH^{mix}) determined via high-temperature, drop-solution calorimetry in Professor Alexandra Navrotsky's laboratories.

Results: Electrochemical measurements of mixing in the $CaCO_3$–$CdCO_3$, $CaCO_3$-$SrCO_3$ $CaCO_3$-$MnCO_3$, and $CaCO_3$-$MgCO_3$ binary system are complete and the results prove the method suitability (McBeath, *et. al., Geochim. Cosmochim. Acta* 62, 2799-2808).

Novel electrochemical cells were also constructed for studies of hydroxycarbonate minerals. For example, the cells:

$$\mathrm{Pb(Hg,\ 2\ phase|Pb(OH)_2\cdot(PbCO_3)_2(s)|KOH(aq,m_1),K_2CO_3(aq,m_2)|HgO(s)|Hg()}$$

and

Zn(Hg, 2-phase, saturated)|$(Zn(OH)_2)_3 \cdot ZnCO_3$(s)|-
K_2CO_3(aq,m_2,KOHaq,m_1)|$Pb(OH)_2 \cdot (PbCO_3)_2$|Pb(Hg, 2-phase)

were used to determine values for hydrocerrussite and hydrozincite (Mercy, *et. al*, *American Mineralogist* 83, 739-745, 1998). These new hydroxycarbonate electrodes can now be used as reference electrodes to study the thermodynamics of wide range of hydroxycarbonate minerals.

We have continued our development of a new theoretical method for calculating lattice energies of calcite-structure metal carbonates. By separating the lattice energy (ΔU) into polarization, electrostatic, and replusive components, the calculation of ΔU is done in a step-wise fashion, whereby each of the three components of ΔU is first found as a function of the partial charge on oxygen (Q_{oxy}) in each of the solid metal carbonates under investigation. The polarization component of ΔU is found through a two-step process. First, the oxygen polarizabilities in the solid metal carbonates are computed via the Lorentz Local Field Method, which requires crystal refractive indices as input. Next, a self-consistent approach is employed to determine the dipole moment on oxygen while it resides in the carbonate mineral. With this information at hand, the polarization contribution to ΔU can be found as a function of Q_{oxy}.

The determination of the electrostatic component of ΔU is done by means of a coulombic point charge approach that takes into account the change in the carbonate ion charge distribution as it transfers to the crystal phase from the gas phase. The charge distribution of CO_3^{2-}(g) is found via molecular-orbital calculations with Gaussian ‘94.

Evaluation of the repulsive segment of ΔU is accomplished by means of the Slater repulsive potential, which is also known as the Inverse Power Law. By imposing an equilibrium condition on ΔU with respect to interionic separation distance, the value of the repulsive energy in each metal carbonate is obtained as a function of Q_{oxy}.

With ΔU calculated as a function of Q_{oxy}, Gaussian ‘94 is used for the determination of Q_{oxy} in each carbonate mineral in order to assign a numerical value to ΔU. After calculating ΔU for a variety of calcite-structure metal carbonates (see G. Mandell and P.A. Rock, J. Phys Chem. Solids 59, 695-702 and 703-712 (1998)). The approach is extended to solid solutions of the same crystal structure type. Excess Gibbs energy values are then predicted for several solid solutions by coupling the lattice energy calculation method of this work to subregular solution model.

We have in progress an AFM study of the processes of dissolution and reconstruction of calcite and dolomite surfaces. We are studying the effects of Mg^{2+}, SO_4^{2-}, $C_2O_4^{2-}$, and $EDTA^{4-}$ on the rates of recession and expansion of surface steps, with the objective of quantifying the rates of these processes as a function of solution-ion concentration composition and the nature of the etch pit on the calcite surface. We have a manuscript in preparation that will be submitted to *Aquatic Geochemistry*.

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GRANT: DE-FG-03-89ER14049

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

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Objectives: The objective of this research is to assess the utility of ^{40}Ar/^{39}Ar K-feldspar thermochronometry and micro-scale *in situ* stable isotope techniques in deriving both fluid evolution and thermal history results for crustal environments that bear upon energy exploration and reservoir assessment.

Project Description: The project focuses on coupling K-feldspar thermochronometry with the capability to perform *in situ* isotope measurements using the ion microprobe to: 1) assess the thermal evolution and cementation history of sandstone petroleum reservoirs, 2) understand the thermal energy potential of active magmatic-hydrothermal systems, and 3) experimentally constrain noble gas solubilities in a spectrum of hydrothermal fluid compositions at elevated pressures and temperatures.

Results: 1) *Thermal and diagenetic histories of sedimentary basins.* Carbonate cements are an important feature of hydrocarbon reservoirs throughout the world because they control fluid flow thereby influencing hydrocarbon accumulation. *In situ* stable isotopic and chemical analyses of carbonate phases indicate that modern day fluids are currently precipitating calcite and Fe-dolomite cements within the Stevens sands at South Coles Levee (SCL) oil field, San Joaquin basin. An early dolomite cement, which is being altered to Fe-dolomite, was also identified. The relative timing of carbonate precipitation within the Stevens sands at SCL was estimated using an independently-derived thermal and burial history of the San Joaquin basin, *in situ* oxygen isotope data, and cementation temperatures derived from equilibrium oxygen isotope fractionation factors for calcite-water, dolomite-water, and dolomite-calcite. The isotopic analysis of the finely intergrown early dolomite and Fe-dolomite phases (ca. 10-25 μm), made possible by use of the ion microprobe, have allowed us to improve the fluid flow model for the petroleum reservoirs within the southern San Joaquin basin. Precipitation of dolomite cements began soon after sediment deposition (~7 Ma) at a temperature of 10±5°C near the water-sediment interface. Paragenetically late and apparently coeval Fe-dolomite and calcite appear to have precipitated within the last 35 years at temperatures near 110°C and from pore fluids with δ^{18}O=+6±1‰, similar to the present day. The isotopic composition of the early dolomite (δ^{13}C=+2.8‰ to +9.0‰) cements suggests that the carbon was likely derived from a zone of methanogenesis. Conversely, the very light carbon isotopic composition of the calcite cements (-19.5‰ to -12.5‰) suggests that the carbon was likely derived from a maturing kerogen source. The identification of a recent cementation event, which is affecting the porosity and permeability of the Stevens sands, suggests that deeper horizons that are presently within the oil generation window could potentially result in new oil fields.

2) *Thermal energy potential of active magmatic-hydrothermal systems*. We have completed a pilot $^{40}Ar/^{39}Ar$ study in the Eldjurta granite, Greater Caucasus Mountains of Russia, investigating the use of basement K-feldspars for recovering thermal histories of magmatic-hydrothermal systems. Using recently developed methods, particularly the multi-diffusion domain model and a technique for correcting for fluid inclusion-hosted Cl-correlated $^{40}Ar_E$, a robust and accurate (±50 ka, ±20°C) thermal history was established. We have begun to apply techniques developed in this study to understand the emplacement age and subsequent thermal evolution of the Geysers geothermal field, Sonoma County, California. Preliminary ion microprobe U-Pb measurements on zircons recovered from borehole cuttings indicate the feasibility of using this method to establish emplacement ages for granitoids as young as ca. 1 Ma. K-feldspar $^{40}Ar/^{39}Ar$ data indicates that post-emplacement cooling was interrupted by transitory re-heating at about 0.5 Ma.

3) *Solubility of noble gases in crustal fluids*. We have completed a pilot study to determine noble gas solubilities as a function of fluid compositions at elevated pressures and temperatures. Solubility experiments were undertaken in fluids of varying salinity (0.0-0.3 mole fraction NaCl) at 2000 bar confining pressure and 350°C and indicate saturation levels of argon up to $\sim 10^{-3}$. This value is essentially identically to that inferred from Ar/Cl ratios from a large (n>100) database of analyzed natural K-feldspars from a variety of crustal environments. These results are inconsistent with existing thermodynamic models for the behavior of inert species in aqueous solutions.

GRANTEE: University Of California, Santa Barbara

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GRANT: DE-FG03-96ER14620

The Hydrodynamics of Geochemical Mass Transport and Clastic Diagenesis: San Joaquin Basin, California

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Objectives: Deep groundwater migration plays an important role in many geologic processes, including diagenesis in sedimentary basins that directly affect other processes, such as overpressuring, oil migration and sediment-hosted ore mineralization during burial because of the control on permeability and porosity. The principal objective is to quantify the hydrogeologic regimes for clastic diagenesis, using the San Joaquin basin of California to establish geologic constraints for numerical modeling at the basin and formation scale.

Project Description: Few hydrogeologic models have been developed or applied to field data sets, rigorously couple geochemical processes, or test conceptual models for diagenesis beyond abstract formation-scale numerical simulations or core-scale laboratory studies. The approach used here is to develop coupled hydrodynamic-geochemical models with computer simulations constrained by geochemical and hydrologic observations for the San Joaquin basin of California. This project has involved the compilation and general mapping of geologic, pore pressure, salinity, and temperature data for the main aquifers in the basin to build a clearer picture of flow patterns, as they exist today at the regional scale. The principal task for us has been to quantify the paleohydrology and thermal history of the San Joaquin basin with a new finite-element code for simulating fluid migration and pressure changes during sedimentation, uplift, and erosion. After the hydrogeologic history has been explored in a hydrodynamic sense, we will conduct reactive-flow simulations to assess mechanisms for diagenesis and chemical mass transport in the clastic wedge. Different diagenetic fluid-flow hypotheses such as compaction dewatering, episodic pulses, meteoric invasion, and cross-formational flow are tested with the coupled hydrogeologic models through a sensitivity analysis. A large data set from cores and pore water chemistry is being generated and complied to use as a constraint on the modeling. This is a collaborative project between Prof. Jim Boles and Grant Garven, and the PIs attend bi-annual meetings in Baltimore and Santa Barbara. They also co-supervise one 4-th year Ph.D. graduate student at Johns Hopkins, Alicia M. Wilson, who resided at UC-Santa Barbara in 1998.

Results: Initial geochemical and hydrologic data sets have been assembled. A new finite-element based code for modeling two-dimensional fluid flow and heat transport has been developed and verified mathematically against published codes. See co-PI Garven for modeling results. The results from this phase of the basin modeling define the hydrogeologic framework for new calculations planned for FY99 that will explicitly model chemical reactions and diagenetic paragenesis.

We are continuing to investigate cement patterns within individual sandstone units to answer the question of how beds become completely cemented. Results thus far show that the cement patterns are very complicated and that beds don't become cemented by simple addition of material from the sides. Apparently, the feedback from cement causes complex changes in permeability on a bed scale. We are compiling a comprehensive data set of water analyses from hydrocarbon reservoirs within the basin, including a number of new unpublished data sets from our own work. Many of these analyses were obtained in conjunction with a joint study with ARCO on the nature of organic acids within the formation waters of the basin. Many of the formation waters in the basin have abundant organic acids. The carboxyl groups of the acids have highly variable and surprisingly positive carbon isotopic signatures. Unknown reactions involving these acids may have caused the relatively positive carbon isotopic signatures in the carbonate cements forming. Results are described at the 1997 AAPG Pacific Section, Bakersfield, California and the 1997 AAPG National Mtg. in Dallas (Franks *et al.,* 1997)

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GRANT: DE-FG03-91ER14211

Magma Rheology, Mixing of Rheological Fluids Molecular Dynamics Simulation, and Lithospheric Dynamics

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Objectives:

- Laboratory measurements of magma rheological properties on magma
- Determination of the structure and properties of multicomponent silicate melts and glasses at elevated temperature and pressure.
- Numerical modeling of porous media thermohaline convection
- Geochemical material balance modeling of assimilation and fractional crystallization subject to energy constraints.

Project Description: This collaborative project with D. A. Yuen at the University of Minnesota will improve our understanding of the thermal, chemical, dynamical and mechanical state of the continental crust and subcrustal lithosphere with particular focus on the interactions between the various subsystems. The work-plan includes: (1) rheological laboratory measurements on melts and magmatic suspensions (2) Determination of the thermodynamical and transport properties of molten silicates by MD simulations (3) Mixing processes of rheological fluids in convection and visualization of complex processes (4) Coupling between mantle convection with temperature-dependent and non-Newtonian rheology and mantle diapirs on the thermal regime and subsidence curves of rift-related basins (5) The dynamical influences of lithospheric phase transitions on the thermal-mechanical evolution of sedimentary basins (6) The development of stress fields and criteria for faulting in the crust (7) Modeling of heat and mass transport driven by thermal and compositional heterogeneities in porous media and finally (8) Open system geochemical modeling of magmatic systems.

Results: Results cited below are for the UCSB part of this project. Additional results are given in the summary of activities by the University of Minnesota team lead by D. A. Yuen. Molecular Dynamics (MD) simulations have been carried out on $CaAl_2Si_2O_8$. Changes in the structure of equilibrium liquid as a function of pressure have been studied to better comprehend the known pressure-dependent properties of network and partially networked silicate melts. Simulations indicate that melt structure at 6 GPa is consistent with edge-sharing Si and Al octahedra and not tetrahedral rings as at low pressure. These rings define ‘holes’ and make the low-pressure melts possess high anionic porosity responsible for its decreasing viscosity with *increasing* pressure as well as the maximum in oxygen tracer diffusivity at 5 GPa. This effect disappears at higher pressures because trigonal bipyramids (5-fold Al and Si) and octahedra (6-fold Al and Si) become the dominant short-range units and allow for higher compression as pressure increases. Consistent with NMR spectroscopy, at low pressure the concentration of non-bridging oxygen is about 5 %. Based on these calculations a model of pressure-dependent speciation equilibria has been derived that enables quantitative predictions of the short-range structure of molten anorthite up to 76 GPa at high temperatures

A large volume of the Earth's crust is characterized by porosity less than 1 vol. %. Fluids may be present to depths of 5-15 km. Such fluids may convect through the crust driven by both thermal and chemical buoyancy (*e.g.*, geothermal gradient and salinity gradients, respectively). The dynamics of chaotic thermohaline convection in low-porosity hydrothermal systems has been investigated. A new doubly advective instability has been discovered. This instability naturally leads to chaotic convection in the lower crust when conditions are appropriate. Unsteady behavior has implications for heat transport, ore-genesis, metasomatism and for the diagenetic history of deep subsiding sedimentary basins. This work has been published in a recent issue of *Earth. Planet. Sci. Lett.* (174,1999, p.213-229).

A high-precision concentric cylinder rheometer with capability in the range 10^{-3} to 3 Nm of torque and shear rates in the range 10^{-4} to 1 s^{-1} at 0.1 MPa and temperatures to 1600°C has been used to make measurements of molten $KAlSi_3O_8$ in a temperature range previously uninvestigated these measurements along with ones at higher and lower temperature for the same material indicate Arrhenian behavior over a large temperature range consistent with the small change in isobaric heat capacity between supercooled $KAlSi_3O_8$ and sanidine at the glass transition temperature.

In other work, a review paper has been published in the *Encyclopedia of Volcanoes* (Academic Press, 2000) entitled "Physical Properties of Magma". This paper summarizes many of the DOE- supported rheological measurements made on magmas in the last decade at UCSB. Finally, a short article (Perspectives) was prepared and published in *Science* regarding an analysis of the significance of new measurements of the partial molar volume of dissolved H_2O in molten silicates and its consequences for magma transport in the crust and mantle as well as the structure of hydrous natural magmas.

GRANTEE: University Of California, Santa Cruz

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GRANT: DE-FG03-98ER14845

Fast 3-D Modeling and Prestack Depth Migration Using Generalized Screen Methods

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Objectives: Develop high accuracy and high efficiency numerical methods for seismic modeling/imaging in three-dimensional complex structures. The methods are based on the generalized screen propagator theory that uses the MFSB (Multiple Forward-scattering Single Backscattering) approximation.

Project Description: The project is a collaborative effort of three institutions, LANL, MIT, and UCSC. The research at UCSC is implemented at the Modeling and Imaging Laboratory, Institute of Tectonics. The approach is based on the fast one-way wave propagation methods with dual-domain (space and wavenumber domains) implementation. The method bridges the gap between high-frequency asymptotic methods and full-wave equation methods, and can generate excellent modeling/imaging results with high efficiency.

Results: We have developed a theory that improves the wide-angle accuracy of screen propagators in strong contrast media. The theory circumvented the perturbation theory and derived very accurate propagators for strong contrast media. This is important especially for the subsalt imaging in oil and gas exploration. In collaboraton with Colorado School of Mines, we have developed the theoretical basis of generalized screen method. It is demonstrated that the higher order terms of the "generalized screen expansion" can further improve the accuracy for wide-angle waves. In the area of modeling primary reflections for elastic media, we have improved the accuracy of wide-angle reflections for elastic waves, especially for the converted elastic waves.

We have developed a hybrid pseudo-screen propagator migration method and applied it to the post- and pre-stack depth migrations for the SEG-EAEG salt model and Marmousi model. The migrated images are the bests or among the best known results. In other work, we improved and expanded WSP (windowed screen propagator) migration method, and introduced a P-S wave decomposition method for multicomponent seismic data and obtained the image from the decomposed data. Full-wave FD reverse-time migration and hybrid method for surface topography removal have also been tested.

GRANTEE: Carnegie Institution Of Washington

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GRANT: DE-FG02-96ER14651

High-Pressure Synchrotron Infrared Spectroscopy: An Integrated and Dedicated Facility at the NSLS

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Objectives: The goal of the project has been the construction of a versatile facility for measuring far- to near-infrared spectra of natural and synthetic materials from ambient to ultrahigh pressures at variable temperatures using new synchrotron infrared microspectroscopy techniques. The measurements address a broad range of problems in Earth and planetary science.

Project Description and Results: An integrated synchrotron facility dedicated to high-pressure spectroscopy and microspectroscopy from far-infrared (IR) to visible wavelengths has been constructed at beam line U2A of the National Synchrotron Light Source (NSLS). A high-performance spectrometer was installed, along with new high-pressure (long working-distance) microscopes adapted for diamond-anvil cells, and a commercial, high-magnification infrared microscope for 1-bar and low-pressure experiments. Together with our high-pressure x-ray facilities at the NSLS, the new facility provides the opportunity for users to conduct synchrotron IR, synchrotron x-ray, and other optical experiments on the same samples, representing a unique and unmatched level of integration in high-pressure and synchrotron techniques. The facility is permitting new classes of high-pressure studies of hydrogen and related planetary materials; minerals of the Earth's crust, mantle, and core; geochemical reactions; glasses and melts; surfaces and interfaces; whole-rock samples; and new high-pressure technological materials.

GRANTEE: The University Of Chicago

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GRANT: DE-FG02-97ER14773

Kinetic isotope fractionation

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Objectives: The main objectives of this research effort are to better understand fluid-mineral chemical exchange mechanisms and associated transport mechanisms. The primary motivation is the well known problem that the rates of solution-reprecipitation measured in the laboratory are often many orders of magnitude faster than what we infer for natural settings. This large difference in behavior is an issue that needs to be understood before we can confidently anticipate mineral reactivities in a given natural setting. At near surface temperatures the processes of interest operate on time scales short compared to the diffusion time in the solid phases, thus the principal mechanism of exchange is via solution-reprecipitation. In terms of transport mechanisms in the fluid phase, we need to be able to distinguish between diffusion and advection.

Project Description: The research as originally proposed involved relatively traditional laboratory experiments using stable isotope tracers to monitor the rate of solution-reprecipitation of geologically important minerals such as calcite. Since writing that proposal, I have been increasingly impressed that what is most needed are new methodologies that will allow us to better determine the reactivity of minerals in natural over long periods of time and the associate transport from sites of dissolution to reprecipitation. With this in mind we have redirected the research towards documenting kinetic isotope fractionations that can be used as monitors of the rate of solution-reprecipitation. The central idea is that diffusive transport in fluids, be they magmatic or hydrous, will fractionate isotopes based on the higher mobility of the light isotopes. This effect can be characterized by an exponent β relating the diffusion coefficients D_i and D_j to the mass m_i and m_j of isotopes i,j : $(D_i / D_j) = (m_j / m_i)^{\beta}$. The central theme of the research has become determining the value of β for a variety of isotopes of different element dissolved in a variety of fluids. We began by studying high temperature systems because in this limit the effect of equilibrium fractionations are minimized.

Results: Both molecular dynamics and laboratory experiments have been used to determine the exponent β in high temperature silicate melts. The molecular dynamics calculations suggest that there is no significant mass dependence to the mobility of Si and O isotopes, but in contrast to this, the mobility of Mg isotopes has a value of $\beta \approx 0.1$. Related laboratory experiments have been carried out using Ge in place of Si (to take advantage of the lower melting temperature of GeO_2compared to SiO_2) and Ca in place of Mg (to take advantage of the high precision of double spike isotopic analysis). The first mobility experiments involved isochemical and isothermal diffusion couples. The relative mobility of ^{70}Ge *vs.* ^{76}Ge and ^{40}Ca *vs.* ^{48}Ca results in estimates of $\beta \approx 0$ (or given the experimental uncertainties, $\beta \leq 0.025$) for Ge isotopes and $\beta = 0.075\pm0.02$ for the Ca isotopes. These results are in very good agreement with our earlier molecular dynamics calculations for the mobility of isotopes of similar element. The demonstration of large (relative to present precision) kinetic isotope fractionations of Ca by diffusion in a condensed phase, and similar expectations for Mg, Fe, and other non structural (or dissolved) cations, provides a geochemical fingerprint for diffusive (as opposed to advective) transport in fluid systems (see also *Geochim. Cosmochim. Acta*, Vol. 63, No. 18, pp. 2853-2861, 1999).

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Grant: DE-FG02-94ER14466 (FY98)

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

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Objectives: GeoSoilEnviroCARS is a national consortium of earth scientists whose goal is to design, construct and operate, as a national user facility, two synchrotron radiation beamlines (one sector) at the Advanced Photon Source, Argonne National Laboratory.

Project Description: The GeoSoilEnviroCARS sector will include instrumentation for: (1) absorption spectroscopy and anomalous scattering; (2) fluorescence microprobe analysis and microtomography; (3) powder and microcrystal diffraction; (4) high-pressure research with diamond anvil cells; and (5) high-pressure research with the large-volume press. The availability of these facilities, dedicated to earth science research, will allow extension of current research at synchrotron facilities to much lower concentration levels, low Z elements, low dimensionality materials (surfaces and interfaces), small volume samples, and transient phenomena. Major areas that will benefit include migration and remediation of toxic metals and radioisotopes in contaminated sediments, redox chemistry of transition metals at the root-soil interface and its role in agriculturally-relevant plant diseases, the chemical nature of hydrothermal fluids and evolution of hydrothermal systems, chemical reactions on mineral surfaces, petrogenesis of strategic elements, phase transitions in mantle minerals, and the properties of the Earth's core.

Results: Excellent progress has been made in terms of both station and instrumentation commissioning and conduct of experiments. Three instruments have been installed and are running on the undulator line: microprobe/microXAFS, diamond anvil cell with laser heating and general-purpose "2+2+kappa" diffractometer. Two instruments are running on the bending magnet beamline: 250-ton multi-anvil press and microtomography. Kirkpatrick-Baez microfocusing mirrors have achieved sub-micron spot size with gains of $> 10^5$ in flux/μm^2 compared to that of the direct undulator beam. The focused x-rays produced by this system are being used for experiments with microspectroscopy, fluorescence microprobe, and microcrystal diffraction. First microtomography experiments were run in May 1998, and a resolution of 5 microns was demonstrated for mm-sized objects.

The high-pressure program has made major breakthroughs. Energy dispersive diffraction in the diamond-anvil cell with high-temperature laser heating has reached pressures of 1.4 Mbar (Earth's core) and 2000°C (3000°C was reached at lower pressures). This marks the first time x-ray diffraction has been done above 1 Mbar at such temperatures. The 250-ton multi-anvil press was successfully commissioned and energy-dispersive diffraction data were obtained up to 28 GPa (280 kbars) and up to 2000°C.

Experiments run to date include (1) oxidation states of vanadium and chromium in olivine/glass pairs produced under controlled fO_2 and temperature conditions, (2) zinc speciation in contaminated soils, (3) real time study of crystallization sequence and kinetics in the hydrothermal FeS system, and (4) microtomography of fungi in tree wood and inclusions in diamonds.

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Grant: DE-FG02-92ER14244

Synchrotron X-ray Microprobe and Microspectroscopy: Technical Development for Advanced Photon Source Research and Low Temperature Geochemistry Applications

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Objectives: The objectives are to develop and apply a synchrotron-based x-ray microprobe that can be used to determine the composition, structure, oxidation state, and bonding characteristics of earth materials with trace element sensitivity and micrometer spatial resolution.

Project Description: The project focuses on development and application of the x-ray fluorescence microprobe on beamline X26 at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Geochemical problems that are under investigation include the nature of hydrothermal fluid inclusions; toxic metal and radioisotope speciation in contaminated sediments; determinations of the chemical histories of contaminated sites through microanalytical studies of indigenous organisms; and redox chemistry of Mn at the root-soil interface and its role in agriculturally-relevant plant diseases.

Results: The capabilities of the microprobe were greatly enhanced with the successful installation of microfocusing Kirkpatrick-Baez mirrors providing a gain in flux/μm^2 of about 1000. This higher sensitivity has had a major impact on applications particularly those involving microspectroscopy of elements at low concentration. Examples of research projects include: *Uranium in Calcite* (with N. Sturchio, L. Soderholm - ANL): The microprobe was used to demonstrate that uranium content in calcite is homogeneous at the resolution scale arguing for its incorporation in the calcite lattice as opposed to inclusions. *Diffusion and Reduction of Chromium in Sediments* (with T. Tokunaga - LBNL): The purpose of this set of experiments was to understand Cr transport (diffusion of CrVI) and reduction (to CrIII), in sediments. Chromium was introduced into initially uncontaminated soils and sediments in the soluble CrVI form. The systems were mapped periodically for total Cr spatial distributions and micro-XANES of selected locations was obtained to identify Cr oxidation states. Some transformation of CrVI to CrIII was observed in most of the systems. Nearly complete conversion to CrIII was observed in the most reducing sediment, often in localized zones of higher Cr accumulation. The highly heterogeneous nature of this process makes the microprobe essential. *Chemical State Microanalysis of Iron* (with J. Delaney - Rutgers U.; M. Dyar - Westchester U.) Fe^{3+}/Fe^{2+} in numerous geological minerals and glasses, determined by wet chemical and Mössbauer techniques, correlate linearly with variations in the energy of the Fe K-absorption pre-edge measured by synchrotron microXANES (SmX). Preliminary experiments using glass with coexisting minerals were done to measure the partitioning of Fe^{3+} and Fe^{2+} between the phases. These results allow determination of natural crystal growth systematics with a precision not previously possible.

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GRANT: DE-FG02-93-ER14327

Nonlinear Transport and Collective Processes in Heterogeneous Media

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Objectives: We propose to seek a better understanding of fundamental physical laws that govern several important nonlinear and collective transport processes in heterogeneous media: dispersion, filtration, rapid porous media flow, and granular flow.

Project Description: Four topics are being considered. First, previous work on hydrodynamic dispersion in two-dimensional porous media flows involving multipole distributions of sources and sinks will be extended to three dimensions. Particular attention will be paid to systems with macroscopic disorder, such as fractures. Next, we will consider flow through porous media in the high Reynolds number regime, where non-linear effects become important. We will use numerical simulations and multiple scale expansions to elucidate the origins of the Forchheimer equation, whose relevance has been experimentally established. Third, we will investigate basic aspects of filtration, in particular the plugging of a porous matrix by deposition and trapping of suspended particles. These removed particles gradually plug the porous medium, giving rise to feedback between transport and filtration efficiency. Finally, we propose to investigate some topics in granular flow, including the effects of vibration on granular packings and the dynamics and clustering phenomena in inelastic gases.

Results: This year's progress on the four topics listed above is as follows. (1) The original research on this sub-project was completed in 1997, but an invited review article summarizing the work was prepared for publication. (2) Our previous numerical work had found an unusual transition in the relation between pressure drop and flow rate in a porous medium as the Reynolds number increased, from linear to cubic to quadratic. We verified the robustness of the transitional cubic regime, using further numerical simulations at higher precision, and variants of the initial multiple scale derivations, and the further developments are consistent with the original behavior. This work, including some further scaling arguments relevant to the quadratic (Forchheimer) regime, was submitted and published. (3) We used Stokesian dynamics simulations to compute the motion of suspended particles in a small model porous bed, to determine the motion of finite-sized particles at junctions in the flow paths and to investigate possible trapping mechanisms. The results were on the one hand submitted for publication, and on the other used for the rules of particle motion in a simplified network simulation of filtration in a porous medium. The latter is designed to handle larger scale systems than those accessible with the (high-resolution) Stokesian dynamics method. (4) We have studied subharmonic collective motion of granular particles in a vibrating tube, using molecular dynamics simulations. The qualitative behavior was found to be sensitive to the depth of the system, and the underlying feature appears to be a new characteristic time associated with the recompaction of the grains. A separate study of surface waves in vibrated granular material related the surface motion to the horizontal motion of the grains, and their variation with depth.

GRANTEE: University Of Colorado

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GRANT: DE-FG03-95ER14499

Nonlinear Systems Approach to Understanding the Origin of Geodetic Crustal Strains (Collaborative Research)

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Objectives: To develop a physical understanding of the origins of geodetic crustal strains in nonlinear geomechanical systems, to examine the space-time patterns and correlations that occur in these systems, and to use these patterns to forecast the future activity that may produce disasters affecting a wide variety of critical energy facilities.

Project Description: A variety of nonlinear dynamical processes operate within the complex earth system. Signatures of these processes include the appearance of scaling (fractal distributions), global and local self-organization, intermittancy, chaos, and the emergence of coherent space-time correlations, patterns, and structures. The geodynamical effects observed in earthquake systems, particularly crustal straining, dynamical segmentation, and intermittant seismicity, are being modeled in massively parallel simulations in an effort to clarify the origins of these phenomena. Simulations and theoretical investigations are particularly aimed at quantifying the limits of predictability for catastrophes (disasters) that occur within the earth system. We are currently developing both the simulation methods for earthquake models, and the statistical mechanical analysis techniques needed to understand and interpret the results. From these simulations, we will then predict geodetic and other deformation associated with impending earthquakes to be tested against Global Positioning System, Synthetic Aperature Radar, seismicity, and other field data.

Results: We made important progress in several fundamental problem areas during this past year. These include: 1) *Why earthquakes stop.* According to the classical theory of tensile Griffith fracture, as applied to shear fracturing in earthquakes, an earthquake cannot self-arrest until the boundaries of the fault are reached. We found that spectral properties, as defined by the Hausdorff dimension H of the shear stress field roughness determine whether earthquakes grow or arrest. The critical value for arrest, $H = 0.5$, corresponds to a Brownian Walk through the stress-deficit field. 2*) Space-time correlations and patterns in earthquake activity*. We developed a new technique that allows patterns to be understood as eigenstates of a suitably constructed space-time correlation operator. We found that these methods can be used to forecast the progression of patterns through pattern-state space. 3*) Observational tests of earthquake models with implications for the physics of earthquakes.* Our work has indicated that under shear loading, faults reside in a metastable state near a classical spinodal that governs the nucleation and growth of slip events. We have calculated a number of physical quantities and compated them to observational data. Agreement between predictions and observations is excellent.

GRANTEE: University Of Colorado

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GRANT: DE-FG03-95ER14518

Theoretical and Experimental Studies of Hydrological Properties of Rock Fractures during Active Deformation

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Objectives: To investigate the dependency of fracture permeability on the state of stress, roughness of fractures, porosity, fluid pressure, mineral dissolution, and precipitation.

Project Description: Hydrological studies in the upper part of the Earth's crust greatly depend on our understanding of the hydrologic parameters such as hydraulic permeability. Fractures ranging from microcracks to large-scale faults are dominant features in rock formations. Considerable effort has been expended on the mechanical properties of rock fractures. Understanding of the hydrologic parameters and their role during hydromechanical processes, on the other hand, is still limited. This project uses a combined theoretical and experimental approach investigating the hydraulic properties of rock fractures. The project consists of three components: 1) analytical studies, 2) laboratory experimenties, and 3) numerical modeling. The analytical study provides theoretical guidance for understanding fracture permeability. The laboratory experiments provide firsthand data on flow characteristics in fractures. The numerical modeling, verified by the analytical study and the laboratory experiments, serves as a predictive tool for situations that are beyond the capability of analytical tools and laboratory experiments.

Results: We conducted theoretical, numerical, and experimental studies on fluid transport in rock fractures. Past theoretical treatment of the characteristics of flow in a rough fracture resulted in a new unique definition of fracture apertures. A new governing equation for incompressible laminar flow in rough fractures was derived, incorporating two vectorial variables of fracture geometry: true aperture and tortuosity. The new equation is more general than the well-known Reynolds equation and can be reduced to the latter when the variations in tortuosity and aperture are small. Explicit analytical expressions of fracture permeability were derived for two non-smooth fractures using this new governing equation. The results show that the error in estimating permeability by using the Reynolds equation can be significant. In a sinusoidal surface fracture, the new equation shows a significant improvement over the solution of the Reynolds equation in both fracture permeability and pressure calculations. This theoretical work not only advanced the fracture permeability calculation, but also laid the foundation for further numerical and experimental studies [Ge, 1997, A governing equation for fluid flow in fractures, *Water Resources Research*, 33 (1), 53-61].

Parallel to the theoretical work, we conducted laboratory experiments and numerical simulations. We built a fracture permeameter. Experiments using smooth and parallel glass fractures were conducted to calibrate the apparatus. After good agreement between the experimental results and the theoretical values of fracture permeability was achieved on the parallel glass model, we extended the experiments to a sinusoidal surface fracture between two blocks made of aluminum. A suite of experiments of different aperture and roughness was conducted. The numerical modeling involved developing a lattice gas automata (LGA) model, an emerging powerful numerical method in studying fluid flow dynamics.

The laboratory experiments and LGA modeling have produced interesting results [Waite, M., 1998, Fluid Flow in Discrete Fractures: An Experimental and Lattice Gas Automata Modeling Study, Ph.D. Dissertation, University of Colorado-Boulder; Waite, M., S. Ge, H. Spetzler, and D. Bahr, 1998, The effect of surface geometry on fracture permeability: a case study using a sinusoidal fracture, *Geophysical Research Letters*, 25(6), 813-816]. We compared the permeabilities using 1) the conventional parallel plate theory employing the vertical separation as the aperture, 2) the new governing equation solution that implicitly considers local true aperture and tortuosity, and 3) experimental and numerical simulations using the true geometry. The data show that there is an excellent agreement between the experiment and numerical LGA results; the conventional parallel plate theory significantly overestimates, while the new theory shows a clear improvement. Both experimental and numerical results show a non-linear increase in the flow rate with the increase in vertical separation. Effective permeabilities inferred from experiments and LGA modeling are smaller than theoretical predictions. Furthermore, as the fracture becomes rougher, the difference between experiment or modeling-inferred values and theoretical predictions grows larger. The cause of this discrepancy probably lies in the fact that, fundamentally, the improved theory still assumes the cubic law holds locally. The data we obtained demonstrated that the decreased effective aperture is largely due to the combined effects of a normal aperture variation and the tortuosity of the flow path.

GRANTEE: University Of Colorado

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Grant: DE-FG0396ER14590

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

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Objectives: The objective is to develop a quantitative understanding of critical fundamental processes controlling two-phase flow and transport in fractures, based on detailed physical experiments and high-resolution numerical simulations. This understanding may subsequently be abstracted for use in conceptual models applied to large-scale problems in petroleum extraction, isolation of hazardous or radioactive waste, remediation of contaminated subsurface media and CO_2 sequestration.

Project Description: Under two-phase immiscible flow conditions, the phase geometry associated with each phase controls the fluid flow and solute transport characteristics. The phase geometry is in-turn determined by a combination of the aperture variability, the capillary and viscous effects inherent in the two-phase flow processes themselves and external forces such as gravity. If one of the fluids can slightly dissolve in the other, then transport of the dissolved fluid also influences phase geometry.

In this collaborative project between Sandia National Laboratories, Oklahoma State University and University of Colorado at Boulder, systematic physical experimentation is coupled with concurrent numerical simulation to explore the factors controlling phase structure, flow, transport and inter-phase mass transfer in rough-walled fractures. A high-resolution light-transmission technique has been developed to facilitate acquisition of accurate experimental measurements of aperture, phase geometry and solute concentrations in transparent analog fractures. Use of this technique will lead to data of unprecedented accuracy for evaluating current understanding of invasion, flow and transport processes, and motivate refinement of theoretical concepts.

Results: A Modified Invasion Percolation (MIP) algorithm has been developed and comprehensively tested, to simulate phase invasion processes influenced by capillary and gravity forces. An essential feature of the MIP algorithm in the context of application to rough-walled fractures is the incorporation of an in-plane curvature term. The inclusion of this term is critical to obtaining phase structures that correspond closely with experimentally measured phase structures. The in-plane curvature term is not incorporated in previously proposed approaches such as standard percolation (SP) or traditional invasion percolation (IP, incorporating only an out-of-plane curvature across the aperture).

To allow a meaningful experimental evaluation of current conceptual models of flow, transport, and inter-phase mass transfer, aperture measurement errors were minimized and quantified. Each component of the light transmission system was evaluated with respect to its contribution to measurement error and the individual errors were combined to yield estimates of the total error at any location within the flow field. This effort indicated that minimizing aperture measurement errors requires a trade-off between precision errors resulting largely from signal noise and accuracy errors resulting from the nonlinearity of light absorbance by the dye used for measurements. The optimal measurement process is fracture and system specific and thus must be carefully evaluated for each new fracture or measurement system.

A careful re-evaluation of saturated and unsaturated flow experiments in rough-walled fractures is in progress, to identify the sources of discrepancy between experimental results and numerical simulations employing the Reynolds equation. It is expected that these efforts will lead to unambiguous and comprehensive evaluations of the Reynolds equation.

Several issues related to the numerical implementation of the Reynolds equation and the adequacy of data resolution are also being investigated. A series of experiments on solute transport in partially saturated fractures was carried out. These experimental results highlight the importance of solute diffusion into and out of low velocity regions adjacent to the entrapped non-flowing phase. Because of these low velocity regions, the front edge of a solute plume appears to be more influenced by flow channeling and the tail portion appears to be stretched out. These experimental results will be compared against numerical simulations of solute transport to better understand the importance of the low velocity regions.

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Grant: DE-FG03-94ER14419

Seismic Absorption and Modulus Measurements in Single Cracks and Porous Rocks: Physical and Chemical Effects of Fluids.

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Objectives: We aim to develop a field tool that can be used for monitoring chemically contaminated sites. At this stage, we are experimentally investigating the effects of contaminants on the attenuation of seismic waves in partially saturated porous rocks.

Project Description: Many contaminants have an affinity for surfaces and in very small concentrations can have a large effect on the flow of a fluid. The mobility of the meniscus affects the energy lost when seismic waves pass through a partially saturated porous rock. We have made, and are making, measurements of this absorbed energy and are incorporating the results into an absorption model (Restricted Meniscus Motion Model). Our research is on track and we anticipate making absorption measurements on artificial and real rocks in the coming year. Parallel with our laboratory measurements and our modeling efforts we are beginning the design of a field study.

Results: To complement the quantitative characterization of the meniscus behavior, flow experiments with a Hele-Shaw cell under different contamination conditions were made. On clean glass, the contact line is smooth on the scale of the Hele-Shaw cell (approx. 10 cm). A contact line roughness in the mm-range may develop; this might reflect a residual contamination. On surfaces covered with organic contaminants (*e.g.*, propanol), fingers and enclosed air pockets in the cm-range with characteristic times on the order of 10 seconds are produced.

To quantify the forces on a moving meniscus, flow experiments through inclined glass tubes under different contamination conditions were made. The results indicate that the force exerted by a receding meniscus is restricted to a maximum determined by the surface tension of the liquid; the force is almost independent of the contact line speed. This result allows for the calculation of the force exerted by the advancing meniscus as a function of the contact line speed.

Measurements with partially saturated, cylindrical glass cracks show that the seismic attenuation and the stiffening of the system depend on the wetting characteristics of the saturant across the solid surface. The restricted meniscus motion model of Waite *et al.* (1997) has been further developed. With this model the seismic characteristics of the model cracks for different saturation conditions can be explained quantitatively.

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GRANT: DE-FG02-95ER14572

The Distribution in Space and Time of Wet Events in the Western North American Drylands

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Objectives: The primary objective of this research is to map out spatial and temporal distribution of the chemical composition of rock varnish in the drylands of the western North America.

Project Description: Obtaining continuous records of climate change in desert regions has proven very difficult. In an attempt to improve this situation, we propose to exploit the climate record kept in rock varnish. The chemical composition of this slowly accumulating (microns per millennium) paten has been shown to change markedly with climate. During dry periods it is Mn-poor and during wet periods Mn-rich. A new thin sectioning technique permits layers as thin as a micron or two to be observed in transmitted light. Mn-poor layers are orange/yellow in color and Mn-rich layers black. The time of the onset of varnish accumulation can be obtained from cosmogenic dating of varnished boulders or from independent radiometric dating of the geomorphic feature on which the varnish-bearing cobbles are located. Varnish samples will be collected from over 30 different regions covering the latitudinal gradient of 20°, from the south margin of the Cordillera ice sheet at north to the subtropical areas of the northern Mexico at south. These samples will then be thin-sectioned to uncover the distinct lamination pattern in rock varnish that recorded Heinrich (H2, H1) and Younger Dryas wet events. Calibration of varnish lamination sequences will be made by: (1) sampling a variety of varnished and radiometrically dated landforms, and (2) cosmogenic dating of varnished boulders. Varnish from the latest Pleistocene moraines (*i.e.*, 25,000 to 10,000 years) and fossil shorelines will be studied in detail to test if there is a temporal correlation among glacial advances, lake level fluctuations, and possibly Heinrich events. Altitudinal variation of the impacts of those wet events will also be investigated.

Results: New analyses on varnish samples from western US, western China, and Israel's Dead Sea suggest that, under favorable environments, varnish can grow as fast as 25 μm/ky, with average growth rates of 10 to 15 μm/ky for most of the Holocene varnish. This indicates that fast growing varnish can yield high-resolution (*i.e.*, ~100 years) climate records. Varnish evidence also indicates that the Holocene climates of the above three desert regions are much more variable than previously thought, and they are spatially asynchronous. In western US, due to the unexpected problems with AMS radiocarbon dating of rock varnish, we have to build a new chronology for varnish lamination sequence without using any of the previously obtained AMS radiocarbon dates on subvarnish organics. We recalibrated the lamination sequence by sampling every possible geomorphic feature in the western US that has been radiometrically dated. Our new calibration supports the previous age assignments for the varnish lamination sequence. It also supports the possible temporal correlation between black layers in varnish and the North Atlantic's Heinrich events.

GRANTEE: University Of Connecticut

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GRANT: DE-FG02-95ER14528

Geochemical and Isotopic Constraints on Processes in Oil Hydrogeology

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Objectives: This research project (with LBNL) will evaluate the processes that produce, dissolve and distribute noble gases and noble gas isotopes among the liquid hydrocarbon, gaseous hydrocarbon and aqueous phases. This project will use measures of the noble gases and noble gas isotopes from several hydrocarbon fields to evaluate source characteristics, groundwater endmembers, migration processes and mechanisms

Project Description: The mechanisms, processes, and time scales of fluid flow in sedimentary basins represent a fundamental question in the Earth Sciences with direct application to exploration and exploitation strategies for energy and mineral resources. This project investigate hydrocarbon samples from regions where adequate commercial production and ancillary information are available to provide a test of the use and applicability of noble gases to delineate end members, migration mechanism and migration paths for hydrocarbons. Samples will be analyzed for five noble gases and multiple isotopes.

Results: The analysis of the Elk Hills oil fields gases was completed and submitted for publication. The investigation of noble gas data from that field shows strong enrichment in the ratio of Xe, Kr relative to ^{36}Ar that is derived from the source rock. Xe, Kr enrichments on shales have been noted by previous workers but have not been distinctly noted in hydrocarbons. This initially enriched Xe, Kr signal from the source rock appears to be diluted by interaction with groundwater. The large volume of water seen by the migrating oil and the higher solubility of noble gases in the hydrocarbon over the groundwater results in a transfer of noble gases from the groundwater to the hydrocarbon and a dilution of the initially enriched Xe, Kr signal. The results indicate the distinct possibility for the use of noble gases as a migration-tracing tool.

Current investigations are evaluating ^{3}He with respect to the involvement of mantle heat in the source region maturation. ^{4}He and ^{40}Ar/^{36}Ar are being evaluated with regard to the temporal constraints total ^{4}He and ^{40}Ar/^{36}Ar provides with regard to the ‘age’ of the source area and the ‘age’ of the groundwater with which the hydrocarbon interacts during migration and reservoir storage. Neon isotopes will be evaluated with respect to groundwater equilibration temperatures, air contamination, and nucleogenic neon isotopes produced in the source regions. Total argon will be evaluated as an indicator of the total groundwater volume the hydrocarbon has interacted with between primary migration and commercial production. Kr and Xe isotopes will be evaluated as an indicator of the enrichment of the source area seen in many sedimentary rocks.

GRANTEE: University Of Delaware

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Grant: DE-FG02-89ER14080.A003

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

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Objectives: The objectives of this research are to combine new experimental measurements on heat capacities, volumes, and association constants of key compounds with theoretical equations of state and with first-principles quantum mechanical predictions to generate predictions of thermodynamic data, which in turn allow quantitative models of geochemical processes at high temperatures and pressures.

Project Description: This project is part of ongoing collaboration between Prof. Everett Shock of Washington University and Prof. Robert Wood of the University of Delaware, which involves:

1) experimental measurements on key compounds;
2) making substantial improvements in theoretical equations of state for aqueous nonelectrolytes and electrolytes based largely on these experimental measurements;
3) pursuing novel applications of these equations of state to the study of high temperature/pressure geochemical processes involving aqueous fluids; and
4) developing and using *ab initio* quantum calculations with Molecular Dynamics simulations to predict chemical potentials of aqueous solutes where experimental measurements are impossible or not available.

The experimental work is conducted at the University of Delaware. Geochemical applications of the data are done at Washington University. Efforts to improve the equations of state and develop predictive methods are shared between the two labs, because this task in particular requires close collaboration between the two Principle Investigators.

Results: Using fluctuation solution theory as a basis, we have developed an equation to predict aqueous electrolytes and non-electrolytes and this has now been accepted for publication (Sedlbauer, O'Connell, and Wood *Chemical Geology*). This equation is an improvement over the previously available predictions and will allow more accurate predictions of geochemical equilibria at high temperatures and pressures. A follow up paper in which we use the above equation of state together with a functional group approach and fit the thermodynamic data for as many organic functional groups as possible has been accepted with minor revisions in *Chemical Geology*. This greatly expands the predictions of thermodynamic properties.

We have been developing a molecular dynamic plus quantum chemistry method of predicting (within about 5 kJ) the chemical potential of any solute in water at essentially any temperature and pressure. We have been doing further tests on water at high temperatures and find that the method works even better at high temperatures (about 800°C) where experimental measurements are available for water (*Chem Phys.*, submitted) and the results are encouraging.

GRANTEE: Desert Research Institute

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Grant: DE-FG03-96ER14611

Multi-component Convection in Porous Media and Fractures

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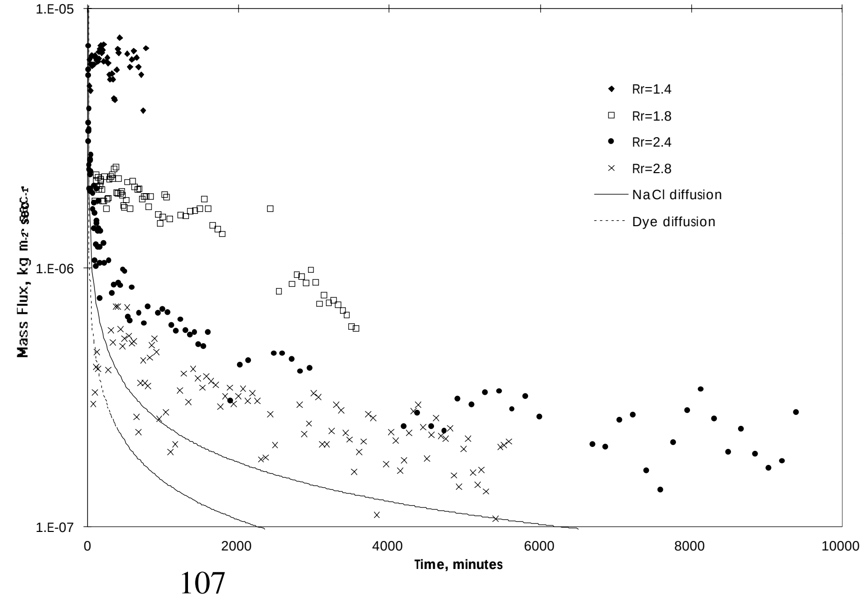
Objectives: This research seeks to understand the physical and chemical processes controlling multi-component convection in porous and fractured media and to develop quantitative relationships between system parameters (solute concentrations, permeability and system geometry), system stability, flow field structure, and convective transport.

Project Description: We apply high resolution, full field light transmission techniques to study the onset and development of convection in simulated porous media (Hele-Shaw cells) and fractures. The light transmission technique allows quantitative measurement of the solute concentration fields in time thus allowing direct measurements of the mass flux of components. Experiments are first designed to test theoretical stability relations as a function of the solute concentrations, solute diffusivities and the medium's permeability.

Structural evolution and convective transport as a function of dimensionless control parameters is then determined across the full range of parameter space. We also consider the application of lattice gas automata techniques to numerically model the onset and development of convection.

Results: The dimensionless buoyancy ratio (R_p), given by the ratio of fluid density contributions by the two components, is one of three dimensionless parameters required to define system behavior. Laboratory experiments were designed using the salt-sucrose, two component system where the initial buoyancy ratio was varied systematically so that the range of parameter space spanned conditions that were nearly stable (R_p =2.8) to those that were highly unstable (R_p=1.4). Results of the experiments show that the evolving unstable flow field is more complicated than has been described by other investigators. The initial mm-scale perturbations evolve into centimeter-scale fingers that travel vertically. An individual



finger grows to several centimeters, slows/stalls, and often becomes a conduit for later-developing fingers to travel. These 'follower' fingers travel through the original stalled finger, causing it to lengthen, and then stall again. The process is repeated until fingers reach the horizontal cell boundaries. An individual finger viewed late in time is actually the result of many interactions of previous fingers. Results also show that the rate of concentration growth is linear for the most unstable systems and approaches square root of time for the more stable systems. These concentration field growth rates cause the vertical transport of mass to be much greater than would be expected in similar, stable systems. The figure above shows mass flux for four experiments of varying buoyancy ratio, compared with the mass flux determined from Fick's law for a system of the same concentration, but assumed to be stable. For the most unstable system (R_p =1.4), the mass flux is approximately one order-of-magnitude greater than the Fickian-derived flux.

GRANTEE: Duke University

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Grant: De-FG02-98ER14883

Calibrating Crack Density and Seismic Velocity Tomogram of Long Valley Caldera: A Piggyback Study Utilizing the August 1998 Long Valley Deep Drilling Plan

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Objectives: To reduce uncertainties of our tomograms of Long Valley and to calibrate our velocity and crack-density models and event locations, we propose to record drill-bit signals from the August 1998 Long Valley drilling effort and to use the drill-bit noise as a source for direct and reflected seismic energy.

Project Description: The objective of the project was to record drill-bit noise and develop signal-processing methods to detect this noise and use it for determining seismic velocities. The steps toward this goal included:

1. Laying out two networks of seismic sensors
2. Recording a pilot signal from the drill bit for use in correlation of the seismic sensors
3. Recording the network signals
4. Signal processing these data into a seismic velocity structure at the drill site.

Our approach was to place both a seismometer and an accelerometer on the head of the drilling string at ground level. These sensors were to be used as pilot signals to correlate data from the two ground networks of seismographs into phase data. These data were then stacked in various ways, including slant stacking, to try to bring out direct and reflected seismic waves that might reveal the local geology and velocity structure.

Results: The data acquisition was carried out between July and August of 1998. The drill rotation was performed with stead speed of about 300 rpm, providing a narrow-band 5Hz signal. The narrow bandwidth made the cross-correlation not particularly successful for both arrays.

For the USGS L22 geophone array, consisting of 60 instruments, some results were achieved after we noticed that the drilling transients produce more broadband energy. A profile obtained by filtering and cross correlating between the array geophones and the rig accelerometer revealed arrivals of two phases. The moveouts of these phases correspond to a slow wave propagating from a close source, suggesting that they could be produced by shallow reflections/mode conversions or by a borehole tube wave scattered by the Earth's surface.

A second array operated in the caldera was recoding data in a sign-bit format using industrial 10 Hz geophones. Unfortunately, the low-frequency cutoff of the geophones was above the expected frequency of the signal, hence the 5 Hz harmonic was severely attenuated. Slant stacking showed that the observed 5 Hz signal comes at shallow angles at a speed of 5000 ft/sec., which corresponds to a velocity of an upper horizon, rather than from the drill bit itself.

GRANTEE: University Of Florida

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GRANT: DE-FG02-98ER14853

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

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Objectives: The overall research objective of this project is to develop micro-mechanical models for the dissolution of porous rocks by a chemically reacting fluid. The aim of the work is an improved understanding of how the coupling between chemical reactions, hydrostatic pressure, and fluid flow produces morphological changes in the sample.

Project Description: Numerical simulation techniques are being developed to model the flow of a chemically reacting fluid through a porous matrix. These simulations will combine a very fast fluid flow code with a stochastic simulation of the transport of chemical reactants and products. The code iterates between fluid-flow simulations and cycles of chemical transport and reaction, to predict the changes in morphology arising from the coupling between chemical reactions at the solid-fluid surfaces and the flow of fluid through the pore spaces. The motivation for this work is to explain the observations of Dr. William Durham (Lawrence Livermore National Laboratory), who found that chemical erosion tends to reduce the small-scale spatial heterogeneity in narrow fractures, while enhancing it on larger scales.

Results: A potentially important variant of the lattice-Boltzmann method has been developed, which directly solves for the steady-state flow in the porous matrix (R. Verberg and A.J.C. Ladd, Simulation of low-Reynolds-number flow via a time-independent lattice-Boltzmann method, *Phys. Rev. E*, 60:3366-3373, 1999). Numerical tests show that the new method is at least an order of magnitude faster than time-dependent solutions of the lattice-Boltzmann equation. In other cases, particularly at higher porosity, the difference in computation time can be 2-3 orders of magnitude. An efficient fluid solver is necessary to permit simulations of the evolving fluid flow in experimentally relevant structures.

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GRANT: DE-FOG5-95ER14517

Biomineralization: Organic-Directed Controls on Carbonate Growth Structures and Kinetics Determined by *In Situ* Atomic Force Microscopy

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Objectives: To determine the kinetics and mechanisms by which selected amino acids interact with calcite surfaces during crystal growth to govern the polymorph and surface structure that forms. The long-term goal is to develop a mechanistic understanding of the physical basis for biomineralization and the larger role of organic compounds in governing carbonate precipitation and growth in natural and engineered Earth systems.

Project Description: Primary biominerals form through biologically mediated activities of marine and freshwater organisms. They result from organic-directed crystal nucleation and growth processes acting in concert to yield chemically and morphologically complex structures. When combined with a macromolecular matrix of proteins, polysaccharides, and lipids, these structures fulfill specific physiological functions such as providing stiffness and strength to mineralized skeletal tissues. An understanding of organic-mineral surface interactions also has application to 1) avoidance strategies for cementation/scaling in oil/gas fields; 2) role of organics in the long-term behavior of carbonates in waste repositories; 3) new biomaterial technologies for synthesis of mineral-based composites.

Previous studies have found that the matrix macromolecules involved in regulating biological crystal growth have an acidic character and often contain aspartic or glutamic acid-rich domains. In vitro studies suggest that these macromolecules possess inhibitory properties that stabilize unusual crystallographic faces by site-specific binding. The mechanistic explanation for this inhibitory effect has focused upon the orientation and interactions of side-chain carboxylates with calcite surfaces and their ability to create extended calcium-interacting domains.

This project combines *in situ* Atomic Force Microscopy (AFM) investigations with kinetic measurements and surface chemical modeling to determine the rates and mechanisms by which amino acids modify the crystallization and dissolution of calcium carbonate minerals.

Results: *1) Surface Site-Specific Interactions of Aspartate with Calcite During Dissolution: Implications for Biomineralization (American Mineralogist, 1997).* Matrix macromolecules involved in regulating the biological growth of calcite in these organisms are known to share a carboxylic-rich character that arises from an abundance of the acidic amino acids, aspartate (Asp) and glutamate (Glu). This study determines the interactions of Asp with calcite {104} faces during dissolution using *in situ* Fluid Cell Atomic Force Microscopy (AFM) and macroscopic ex situ optical methods. In control experiments, etch pit morphologies produced by dissolution in simple undersaturated solutions reflect the inherent symmetry of the {104} faces with a rhombus form. With the introduction of Asp, surface site reactivities are modified to yield isosceles triangular etch pits and hillocks. With continued exposure to Asp-bearing solutions, these triangular pits coalesce and the surface evolves into a network of interconnected tetrahedral etch hillocks. The component tetrahedral 'sides' have Miller-Bravais indices of (0001), (101), and (011). These faces intersect the (104) face in the [010], [] and [] directions to comprise the three edges of the triangular etch pits. Structural and stereochemical constraints suggest that the (101) and (011) faces in the hillock are a combination of corresponding faces from the {102} and {100} crystallographic forms. (Received 1998 MSA Best Paper Award)

2) Thermodynamic Controls on Calcite Mineralization (Science, 1998, in review). The complexity of biomineralized structures suggests the potential of organic constituents for controlling energetic factors during crystal synthesis. Using Atomic Force Microscopy to investigate the thermodynamic controls on carbonate growth, we measured the dependence of step speed on step length and the dependence of critical step length on supersaturation in precisely controlled solutions. These data were used to conduct the first experimental test of the classic Gibbs-Thomson prediction that was proposed in 1948. The data confirmed that a linear relationship exists between critical length and inverse supersaturation and provided estimates of the step edge free energies and free energy barriers to one-dimension nucleation for calcite. The addition of aspartic acid, a common component in biomineralizing systems, dramatically affected growth morphology and altered the magnitude of the surface energy. This finding indicates that aspartate modifies growth through changes in the surface thermodynamics.

3) Reversed Calcite Carbonate Morphologies Induced by Microscopic Kinetics: Insights into Biomineralization (Geochimica Cosmochimica Acta, in review). This investigation of calcite growth quantifies baseline relationships between solution supersaturation and the rates of step advancement. Using in situ Fluid Cell Atomic Force Microscopy, we show that the movement of monomolecular steps comprising growth hillocks on {104} faces during growth of this anisotropic material is specific to crystallographic direction. By quantifying the sensitivity of step growth kinetics to supersaturation, we produce spiral hillocks with unique geometries. These forms are caused by a complex dependence of step migration rates, v_{S+} and v_{S-}, upon small differences in solution chemistry along the conventional 'fast' ($[]_+$ and $[]_+$) and 'slow' ($[]_-$ and $[]_-$) crystallographic directions. As solute activity, a, decreases, v_{S+} and v_{S-} converge and the growth hillock expresses a pseudo-isotropic form. At lower supersaturations where a approaches its equilibrium value, a_e, an inversion in the rates of step advancement produces hillocks with unusual reversed geometries. Comparisons of the kinetic data with classical theoretical models suggest that the observed behavior may be due to minute impurities that impact the kinetics of growth through blocking and incorporation mechanisms. These findings demonstrate the control of crystallographic structure on the local-scale kinetics of growth to stabilize the formation of unusual hillock morphologies that may occur at the near equilibrium conditions found in many natural environments.

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GRANT: DE-FG03-95ER14525 A004

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

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Objectives: The main research objectives are: (a) to determine how faults grow in three dimensions in brittle crystalline rocks (granites and basalts), and (b) to further develop physically based stochastic models for predicting geometric and hydrologic properties of such faults.

Project Description: We are investigating how faults of different scale grow in granite and basalt in three dimensions. We are systematically examining the geometries, structure, and mechanics of faults with trace lengths of a few meters to several kilometers, and using this knowledge to develop physically based stochastic models for predicting the geometry of faults over a wide range of scale and for analyzing their hydraulic behavior. The main efforts this year have been: (a) to finish a physical model for secondary fracturing in three dimensions around a small fault in granite, and (b) to finish a new method for two-dimensional thermo-elastic stress analysis. The secondary fractures dictate how the faults grow. The thermo-elastic method is used to help understand the distribution of joints from which the faults in the granite evolved.

Results: A three-dimensional elastic model can account for the distribution of secondary fractures observed along small subvertical natural faults. The secondary fractures consistently strike about 25 degrees counterclockwise from their host faults and are nearly vertical. They are numerous near the ends of some fault traces but absent along others. They generally are absent along the central portions of the fault traces but in rare cases form echelon arrays. These observations are consistent with secondary fractures having nucleated near the perimeter of a disc-shaped fault, where resistance to slip was high, and propagated normal to the local most tensile stress. The observations and model together have direct implications for how faults grow and conduct fluids. Secondary fractures are likely to be larger at the ends of penny-shaped strike-slip faults rather than at their tops and bottoms. As a result, such faults are more likely to be linked end-to-end rather than top-to-bottom. Hydraulic conductivity should be enhanced at the linkages, so highly conductive regions are more likely to be vertical rather than horizontal. The distribution of joints predicted by the thermo-elastic model is largely consistent with observations, providing further evidence that the joints originated as the granites cooled.

GRANTEE: University Of Illinois At Urbana-Champaign

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Grant: DEFG02- 97ER 14759

Investigation of Groundwater Flow Paths in Fractured Aquifers through Combined Inversion of Strontium Isotope Ratios and Hydraulic Head Data

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Objectives: Identify zones of preferential groundwater flow using innovative geochemical techniques emphasizing isotope ratio measurements and hydrologic inverse methods employing fractal geometry concepts.

Project Description: Preferential flow zones or "fast paths" are expected in many aquifers, especially those that are dominated by fractured rock. These zones may serve as conduits for rapid transport of contaminants; any fast paths must be located and their velocities quantified as part of groundwater protection programs. In the first part of this project, the use of naturally occurring Sr isotopes to indicate groundwater fast paths was developed and applied at the Idaho National Engineering and Environmental Laboratory (INEEL). In the second part of the project, the Sr isotope results were analyzed quantitatively and combined with existing hydraulic head data through numerical models of this system.

A state-of-the-art technique that processes fields of hydraulic head and chemical data to identify zones of unusually high or low permeability was used. This inverse method incorporates fractal geometry, which facilitates a search for both the complex structure and parameters of heterogeneous permeability distributions, using only a few unknown parameters.

Results: A suite of approximately 90 groundwater samples collected in and near the Idaho National Engineering and Environmental Laboratory (INEEL) were analyzed for Sr stable isotope ratio (^{87}Sr/^{86}Sr) and dissolved element concentrations. Subsamples of many of these were provided to researchers at Los Alamos National Laboratory (LANL), who measured ^{234}U/^{238}U ratios as part of an EMSP program project. Clear patterns in the spatial distribution of ^{87}Sr/^{86}Sr and ^{234}U/^{238}U ratios strongly suggest relatively fast groundwater flow in an elongate zone passing through the center of the southern INEEL boundary, and slower flow on both sides of this zone. Concentrations of 14 dissolved elements provided additional information on regional flow patterns and helped to highlight the unique properties of the isotope ratios as groundwater tracers.

The second focus of the project used computer models to analyze the ^{87}Sr/^{86}Sr and hydraulic head data quantitatively. SUTRA, an established groundwater flow/solute transport/reaction code was embedded in IFSINV, an inverse model based on Iterated Function Systems, yielding a code that can use observed Sr isotope data and hydraulic head data to infer the existence and locations of fast flow paths. A traditional zone-based inverse method was also developed, in which the location of a potential fast flow path was specified a priori. The models confirmed the hypothesis suggested by the ^{87}Sr/^{86}Sr data - that the observed pattern can be produced by the existence of a relatively fast flow zone passing through the southern boundary of the INEEL flanked by slower flow zones. Furthermore, it demonstrated that the lack of a similar pattern in the head data did not obviate the fast path hypothesis. The head patterns expected near a fast flow zone are more complicated and not as readily apparent as the $^{87}Sr/^{86}Sr$ patterns. The contributions of the modeling part of the study are in demonstrating methods for simultaneous, quantitative interpretation of head and water chemistry data and illustrating the complementary nature of the two data types. The modeling results suggest that geochemical data can be more easily interpreted as indicators of preferential flow zones than hydraulic head data.

GRANTEE: Indiana University

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Grant: DE-FG02-91ER14175

Basin Nonlinear Dynamics and Self-Organization

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Objectives: The goal of this project is the development of new models and rate laws to describe mechanical processes as these play a central role in the creation and dynamics of fracture zones and faults.

Project Description: Fracture zones and faults play a key role in many nonlinear basin phenomena including episodic fluid flows, self-organized compartments and chaotic fault mechanical and fluid flow processes. We are developing a new multi-phase flow law that more realistically captures the changing geometry of the phases within the pore space and the coupling of this changing geometry and the overall flow-through.

Results: *A Forward Model of Three-Dimensional Fracture Orientation and Characteristics:* A forward modeling approach to simulate the extension/closure and orientation statistics of evolving fracture networks has been developed. A representative set of putative fractures of a range of orientations is introduced and the time-dependent properties of each realized fracture are calculated. The volumetric strain caused by fracturing allows for a self-limiting feedback that we account for using a nonlinear incremental stress rheology. The anisotropic fracture permeability is obtained using the predicted fracture network statistics. Thus, the couplings between stress, rock deformation (notably fracturing), and hydrology are accounted for. The statistical aspect of fracture network dynamics is described by assuming a probability distribution that characterizes variations in rock strength within a nominally uniform lithology. The dependence of fracture density and length on the rate of fluid pressure or stress variation is thereby captured. Embedding the model in a 3-D basin simulator, we can illustrate the dynamical nature of the location and character of fracture zones in a sedimentary basin.

Failure, Memory and Cyclic Fault Movement: Faulting is typically a two-timescale process; *i.e.*, rapid failure and slow (chemical) healing. Once failed, a rock has a long memory until chemical processes have reestablished grain-to-grain contacts. The memory of rock failure can be captured by a sufficiently rich textural model and the texture must be coevolved with rock stress and deformation to yield a self-consistent model of strain hardening/weakening, fault narrowing and earthquake cyclicity. A model based on incremental stress rheology and rock texture dynamics is introduced that emphasizes the interplay of rock competency, porosity and other texture variables with stress and strain. The deformation mechanisms taken into consideration are poroelasticity and viscosity. The rheology equations are strongly coupled to the evolution equations of rock texture and pore fluid flow. The model is used to gain an understanding of several oscillatory modes of fault movement. The roles of rock competency, fluid pressure, and continuous deformation in these oscillations have been examined for various conditions.

Sedimentary Basin Deformation: An Incremental Stress Approach: A key component of sedimentary basin evolution is the spatial distribution and temporal variation of stress and deformation. The many deformation processes are inextricably bound in a tightly coupled network, which, in turn, is coupled to a myriad of basin diagenetic, thermal, and hydrologic processes. To address this 3-D complexity, we have developed a numerical simulator using a moving, adapting, accreting finite element discretization grid. Sedimentation/erosion history and the deformation at the basin lateral and bottom boundaries (*i.e.*, overall tectonics) are imposed. The finite element grid is allowed to deform and to grow and adapt with the addition of sediment to capture smaller sedimentary features. Our fully coupled model allows one to solve a number of key problems in basin and fault dynamics. These include compaction, fractured reservoir and compartment genesis and dynamics. Examples illustrating these applications are presented for idealized systems and the Piceance Basin (Colorado) and the Permian Basin (West Texas).

Salt Tectonics as a Self-Organizing Process, A Three-Dimensional Reaction, Transport and Mechanics Model: Our work places salt tectonics within the theory of nonlinear dynamical systems. Features such as waves, diapirs, and tears can be viewed as natural consequences of the symmetry-breaking instabilities and related self-organized dynamics of the deforming salt body coupled to the reaction, transport, and mechanics (RTM) of the surrounding sediments. The fundamental nonlinearities are in the surrounding-rock and salt rheology. Our work relies on a 3-D coupled RTM model that uses finite element techniques. The rheology of both rocks and salt is represented by a nonlinear incremental stress formulation that integrates poroelasticity, continuous irreversible mechanical deformation (with yield behavior), pressure solution and fracturing. In contrast to previous studies, the descriptive variables of the solid and fluid phases and the porous medium are solved from the RTM equations, and account for interactions and interdependencies between them. The model has been applied to salt waves (in 2-D) and diapirs (3-D). The role of the coupling between the spatial distribution of sediment input rate and diapir growth and stalling have been examined, as has the creation of an array of salt tectonic mini-basins.

Evolution of Gouge Grain Size Distribution -- A Markov Model: We have proposed a Markov model to describe gouge evolution. The model is based on the binary breaking of individual grains and the breaking probability is assigned to incorporate the observed gouge phenomena. The model captures the observed bimodal distribution evolution from an initially unimodal one. Using a numerical simulation of the model, parameters are calibrated with gouge evolution experiments on Ottawa sand. The model provides a new formalism for determining hydrological and mechanical properties of the fault zones including the interplay of diagenesis and the mechanics of grain breakage.

Fluid Phase Geometry Dynamics and Multi-Phase Flow in Porous Media: The dynamics of multiple fluid phases in a porous medium is determined by the changing pore-scale geometry of its phases and their interaction with the solid matrix. We have used a phenomenological approach to describing this dynamic via a new flow law that generalizes Darcy single phase and black oil-type flows. The model has two new facets. We introduce phase-geometry variables that distinguish between wetting and nonwetting phases and between phases that are discontinuous *vs.* those that are continuous on a supra-pore scale. The theory also involves a conjectured flow law, which takes this more detailed geometry into account and, as a result, allows for the distinct flow driving mechanisms associated with the various fluid phase configurations. A preliminary calibration of the model for immiscible, two-phase (aqueous and oil) systems was obtained. Numerical simulations illustrate the flow characteristics of this model and its capacity to describe phenomena not accessible to the classic black-oil model. These include wetting/nonwetting transitions, solid matrix curvature effects in single-phase regions, drag forces between phases, and the cross-over between droplet streaming flow and pore throat capillary trapping.

GRANTEE: The Johns Hopkins University

Department of Earth and Planetary Sciences
Baltimore, Maryland 21218

Grant: DE-FG02-96ER14619

The Hydrodynamics of Geochemical Mass Transport and Clastic Diagenesis: San Joaquin Basin, California

Grant Garven (410-516-8689; Fax: 410-516-7933; garven@jhu.edu) and James R. Boles (UC-Santa Barbara; 805-893-3719; Fax: 805-893-2314; boles@magic.geol.ucsb.edu)

Objectives: Deep groundwater migration plays an important role in many geologic processes, including diagenesis in sedimentary basins that directly affects other processes such as overpressuring, oil migration and sediment-hosted ore mineralization during burial because of the control on permeability and porosity. The principal objective is to quantify the hydrogeologic regimes for clastic diagenesis, using the San Joaquin basin of California to establish geologic constraints for numerical modeling at the basin and formation scale. This is a collaborative project between Prof. Jim Boles (Univ. of California, Santa Barbara) and Grant Garven (Johns Hopkins Univ.).

Project Description: Few hydrogeologic models have been developed or applied to field data sets, rigorously couple geochemical processes, or test conceptual models for diagenesis beyond abstract formation-scale numerical simulations or core-scale laboratory studies. The approach used here is to develop coupled hydrodynamic-geochemical models with computer simulations constrained by geochemical and hydrologic observations for the San Joaquin basin of California. This project has involved the compilation and general mapping of geologic, pore pressure, salinity, and temperature data for the main aquifers in the basin to build a clearer picture of flow patterns as they exist today at the regional scale. The principal task for us has been to quantify the paleohydrology and thermal history of the San Joaquin basin with a new finite-element code for simulating fluid migration and pressure changes during sedimentation, uplift, and erosion. After the hydrogeologic history has been explored in a hydrodynamic sense, we will conduct reactive-flow simulations to assess mechanisms for diagenesis and chemical mass transport in the clastic wedge. Different diagenetic fluid-flow hypotheses such as compaction dewatering, episodic pulses, meteoric invasion, and cross-formational flow are tested with the coupled hydrogeologic models through a sensitivity analysis.

Results: Geochemical and hydrologic data sets have been assembled and the co-PIs have met once in California to discuss project results and progress. A new finite-element-based code for modeling two-dimensional fluid flow and heat transport has been developed and verified mathematically against published codes. New transient hydrogeologic simulations have been made to quantify the compaction flow history during marine-terrestrial sedimentation and subsequent uplift with the onset of topography-driven flow over the several million years of basin emergence (Wilson *et al*., 1999). These hydrogeologic simulations show how hydraulic head and pore-fluid salinity evolved during initial subsidence as a forearc followed by the onset of topography-driven fluid flow with Sierran uplift. Uplift of the Coast Ranges created a second phase of regional flow across the basin. Our simulations suggested that clay dehydration created only a small degree of overpressuring. On the other hand, the distribution of salinity in the basin appears to be mostly controlled by freshwater influx and clay dehydration, and transient mass transport calculations show that marine salinities may persist for several million years after terrestrial uplift.

GRANTEE: The Johns Hopkins University

Dept. of Earth and Planetary Sciences
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Grant: DE-FG02-96ER-14616

Predictive Single-site Protonation and Cation Adsorption Modeling.

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Objectives: The overall goal of this research is to develop a predictive model of adsorption processes at the mineral-water interface that can be applied to a fundamental understanding of the role of adsorption in geochemical processes such as weathering, diagenesis, the chemical evolution of shallow and deep groundwaters and ore-forming fluids, and the fate of contaminants in groundwaters.

Project Description: The research is aimed at generating a comprehensive, internally consistent, quantitative description of proton and cation adsorption on oxides and silicates using an extended triple layer model. The model will be developed to integrate the available experimental information on proton and cation adsorption based on internally consistent assumptions. By so doing, it will considerably facilitate the comparison of experimental data from different investigators. In addition, the model will permit predictions of surface speciation to supplement the lack of experimental adsorption data for many systems of geochemical interest. In addition, it will provide a basis for extending applications of the concept of surface complexation to oxide and silicate dissolution kinetics. The proposed extended triple layer model will include: (1) Internally consistent assumptions and methods of estimating site densities and capacitances; (2) Explicit recognition of ion solvation; (3) Explicit recognition of proton attraction-repulsion; (4) Inclusion of the extended Debye-Huckel model for aqueous ionic activity coefficients; and (5) Inclusion of a geochemical thermodynamic data file for aqueous species and minerals.

Results: As part of the overall goal of placing the prediction of surface charge of oxide minerals in electrolyte solutions on a predictive basis, a new method for estimating surface site-densities has been developed. Based on idealized crystal structures, a method has been developed for choosing a specific plane slicing the crystal structure parallel to the required orientation of the surface. Estimates of the number of reactive sites based on the number of broken bonds resulted in agreement with measurements derived from tritium exchange studies. Knowledge of the site density eliminates the need to treat this parameter as a fitting coefficient.

Building on the extended triple-layer model results obtained previously, the ionic strength dependence of divalent transition and heavy metal adsorption has been investigated in detail. A major, unanticipated result has been that metal adsorption on oxide surfaces depends on the type of electrolyte. In sodium perchlorate solutions, metal adsorption is enhanced with increasing ionic strength; in sodium nitrate solutions, metal adsorption is unaffected by increasing ionic strength; and in sodium chloride solutions, metal adsorption is diminished with increasing ionic strength. Divalent and heavy metal adsorption onto many oxide surfaces appears to be accompanied by adsorption of the electrolyte anion. In this regard, the surface speciation of metals appears to be different from the corresponding aqueous speciation.

GRANTEE: The Johns Hopkins University

Department of Earth and Planetary Sciences
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GRANT: DE-FG02-95ER14074

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

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Objectives: This project is an investigation of reactions between silicate minerals and toxic metal-bearing aqueous fluids. We are specifically exploring the mechanisms of oxydation-reduction reactions at the mineral-fluid interface and transport of reactive components along the grain-boundary interface in rocks.

Project Description: This project has three main components: 1) experimental investigation of Cr and U reduction and sorption by micas; 2) high-resolution transmission electron microscopy (HRTEM) characterization of grain boundaries; and 3) experimental investigation of transport and sorption of heavy metals along grain boundaries. The first component includes development of X-ray photoelecton spectroscopy (XPS) methodologies to probe sorption behavior. The second component includes molecular-dynamical modeling of grain-boundary structures to provide insight into their transport properties. This second component also includes development of near-atomic-resolution analysis and imaging methodologies of electron-energy-loss spectroscopy (EELS), high-angle-annular-dark-field imaging (HAADF) and energy-filtered-transmission-electon-microscopy (EFTEM) in mineralogical systems. The third component combines the geochemical and mineralogical studies to elucidate transport properties and mechanisms important in Earth materials.

Results: During this first year of the three-year cycle, the geochemical work has focused on developing the XPS methodology for determining the chemical state and bonding environment of surface species in our experiments. Interpreting small shifts in binding energies (BE), $\Delta E \sim 0.3$ eV, for cations sorbed to the same silicate under different experimental conditions is complex. Binding energy shifts are affected by: 1) sorption site, 2) sorption density, 3) speciation of the sorbed cation, and 4) surface composition. Silicates are electrical insulators, which precludes an absolute BE scale. Differential dissolution of a silicate substrate can shift the BE of reference elements, and surface charging degrades analytical precision. In addition, surface composition affects BE of a sorbate. Consequently, we are developing methodology for rigorously interpreting the small BE shifts we are finding.

The mineralogical component of the project has centered on HRTEM imaging and modeling of a range of silicate-silicate and silicate-oxide grain. This work shows that boundaries in crystalline rocks typically consist of low-index facets, and are tight and semicoherent. Faceting juxtaposes densely packed planes, thereby minimizing interfacial energy. Periodically arrayed combinations of defects such as vacancies, interstitials, stacking faults, and dislocations, accommodate the misfit of abutting lattices. Many of these defects create through-going channels on the scale of the structural tunnels in many zeolites (0.3–1 nm diameter). These channels constitute nanopores, and by analogy with zeolites they may form a transport network for rapid intercrystalline exchange.

GRANTEE: Kent State University

Department of Geology
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GRANT: DE-FG02-96ER14668

Microbial Dissolution of Iron Oxides

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Objectives: The overall goal of this research is to determine the mechanisms whereby an aerobic *Pseudomonas sp.* bacterium acquires Fe from Fe(III)(hydr) oxides. Specific objectives are to characterize the types of attachment features used by the microorganism, and to determine how dissolution varies with mineral surface properties.

Project Description: The overall objective of this research is to determine the mechanisms of Fe release during microbially enhanced Fe (III) (hydr)oxide dissolution by an aerobic bacterium. Understanding the mechanisms whereby microorganisms acquire Fe in aerobic environments is fundamental to a wide range of bio-geo-chemical phenomena. For example, given that hydrous Fe(III) oxides adsorb an array of organic and inorganic components, understanding microbial dissolution is key to modeling pollutant transport phenomena. This research utilizes atomic force microscopy (AFM) and scanning electron microscopy (SEM) to characterize the types of attachment features used by the microorganisms to attach to mineral surfaces, and the structures of dissolution features that form upon reaction. An additional goal is to determine how dissolution varies as a function of hydrous Fe(III) oxide surface structure, micromorphology, and surface area. These research objectives represent important first steps towards understanding microbially mediated dissolution mechanisms.

Results: Although microorganisms have been shown to play important roles in the weathering of Fe(III)-(hydr)oxide minerals, little is known regarding microbial-mineral interactions in aerobic environments. Our research focused on determining the rates and mechanisms by which obligate aerobic *Pseudomonas* bacteria obtain Fe from geologic materials. In research conducted in collaboration of Dr. L. Hersman (LANL), we have grown colonies of *Pseudomonas* species in suspensions of Fe(III)-(hydr)oxides in which the mineral materials are the only sources of Fe. The bacteria could only grow to population sizes great than those of controls by acquiring Fe from the solid phase. Enhanced microbial growth in the presence of the Fe(III)-(hydr)oxides provided evidence that the bacteria enhanced dissolution in order to acquire Fe. Atomic-force microscopy (AFM), scanning electron microscopy (SEM), and epifluorescence microscopy showed that the bacteria colonize mineralogic aggregates, forming networks of fiber-like attachment features intertwined through amorphous-looking 'ooze'. In addition, close associations were observed between bacterial flagella and growth-medium salts (as determined by SEM/EDS) that precipitate on drying, which suggests that the flagella are hydrophilic. Our SEM, AFM, and epifluorescence images concur with, and further enhance, our understanding of the importance of microbial adhesion to mineral surfaces.

GRANTEE: Lehigh University

Department of Earth and Environmental Sciences
Bethlehem, PA 18015

GRANT: DE-FG02-95ER14507

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

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Objectives: This project is an investigation of reactions between silicate minerals and toxic metal-bearing aqueous fluids. We are specifically exploring the mechanisms of oxydation-reduction reactions at the mineral-fluid interface and transport of reactive components along the grain-boundary interface in rocks.

Project Description: This project has three main components: 1) experimental investigation of Cr and U reduction and sorption by micas; 2) high-resolution transmission electron microscopy (HRTEM) characterization of grain boundaries; and 3) experimental investigation of transport and sorption of heavy metals along grain boundaries. The first component includes development of X-ray photoelecton spectroscopy (XPS) methodologies to probe sorption behavior. The second component includes molecular-dynamical modeling of grain-boundary structures to provide insight into their transport properties. This second component also includes development of near-atomic-resolution analysis and imaging methodologies of electron-energy-loss spectroscopy (EELS), high-angle-annular-dark-field imaging (HAADF) and energy-filtered-transmission-electon-microscopy (EFTEM) in mineralogical systems. The third component combines the geochemical and mineralogical studies to elucidate transport properties and mechanisms important in Earth materials.

Results: During this first year of the three-year cycle, the geochemical work has focused on developing the XPS methodology for determining the chemical state and bonding environment of surface species in our experiments. Interpreting small shifts in binding energies (BE), $\Delta E \sim 0.3$ eV, for cations sorbed to the same silicate under different experimental conditions is complex. Binding energy shifts are affected by: 1) sorption site, 2) sorption density, 3) speciation of the sorbed cation, and 4) surface composition. Silicates are electrical insulators, which precludes an absolute BE scale. Differential dissolution of a silicate substrate can shift the BE of reference elements, and surface charging degrades analytical precision. In addition, surface composition affects BE of a sorbate. Consequently, we are developing methodology for rigorously interpreting the small BE shifts we are finding.

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GRANTEE: University Of Maryland

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GRANT: DE-FG02-94ER14467

Theoretical Studies on Metal Species in Solution and on Mineral Surfaces

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Objectives: This study utilizes the techniques of computational quantum chemistry to study the structures, energetics and properties of various metal species in solution or absorbed on mineral surfaces. Focus in the past year has been on inorganic and organometallic complexes of Hg, on Na-aluminate ion pairs, on Be and Al hydrolyzed and polymerized species and upon silicate and aluminosilicate cage species which serve as containers for various cations and as models for mineral surfaces.

Project Description: To understand the mechanisms of dissolution of minerals and formation of ore deposits one must understand the structures and properties of metallic species in aqueous solution. In the first three years of this project we calculated the structures, energetics and spectral properties of a number of different Au, As and Sb sulfide, chloride and hydroxide species. Calculating the properties of such species in the gas-phase is relatively easy -- the difficult problem is to describe with accuracy their interaction with the solvent water. More recently, we have studied Hg compounds, both purely inorganic species such as Hg chlorides and sulfides and organometallic methyl-Hg species. Aluminosilicate species are also a continuing interest, from a geochemical point of view addressing the effects of water upon melt properties as well as the modeling of aluminosilicate surfaces, and from a materials science point of view, as an opportunity for suggesting possible new materials with interesting properties.

Results: We have calculated the structures, stabilities and visible-UV spectra for a large numer of CH_3HgL species at high quantum mechanical levels, both in the gas-phase and in "supermolecules" with attached waters, designed to simulation hydration effects, in order to establish which species will be thermodynamically stable but will undergo photodecomposition by sunlight in natural water systems. We find that $CH_3HgH_2O^+$ is the most probable species for sunlight-induced decomposition, with a calculated energy for the maximum of its singlet-triplet absorption of about 5.0 eV. This low-energy triplet state is calculated to be dissociative, decomposing to CH_3 and $HgOH^{2+}$. For the Hg species HgL_2, with $L=F^-$, Cl^-, OH^-, SH^-, and CN^- we established that reliable absolute and relative formation enthalpies can be calculated using gas-phase calculations and supermolecule approachs to hydration effects. A model molecule as small as $Hg_3S_2(SH)_2$ has been found to reproduce many of the structural features of cinnabar and to serve as a model for its dissolution in pure water, SH^- rich water, S-rich water and solutions containing various halide species. The adsorption of I^- onto the surface of cinnabar can also be understood using this model.

A study of the Na-aluminate species $Al(OH)_3$, $Al(OH)_4^-$ and $NaAl(OH)_4$ with full incoroporation of both enthalpic and entropic hydration effects has established that hydrated $Al(OH)_4^-$ will be the dominant species at near neutral pH. The stable $Al(OH)_3$ species is actually $Al(OH)_3H_2O$, and the $NaAl(OH)_4$ species is actually a solvent separated ion-pair. Both species have unique spectroscopic signatures, which may make possible their identification. This work has been submitted to *Geochimica et Cosmochiumica Acta*. Work is now proceeding on the analogous Na-silicate ion pairs, to establish structures and properties and to understand how the synthesis of zeolite minerals may be influenced by such interactions.

In collaboration with William Casey and Brian Phillips of the University of California at Davis, we are studying the mechanism for the exchange of water between the first coordination sphere and bulk solvent for various Al-water, ligand species. Our calculated energetics and NMR shieldings are beginning to be reconciled with the experimental data, but good agreement has not yet been obtained. In the course of this work, it became clear that for both aqueous Al^{3+} and Be^{2+} there were a number of hydrolyzed and polymerized species that differed in both stability and metal NMR shielding. We have since shown that there is an opposition between the two effects, with hydrolysis deshielding the metal nuclei while polymerization shields them. Thus, a hydrolyzed, oligomerized species may have a metal NMR shielding almost identical to that of the unhydrolyzed monomeric parent. This work has been submitted to *J. Magn. Reson.* Armed with this knowledge, and with a determination to consider a full representation of both the 1st and 2nd coördination spheres about the metal, we are returning to the question of ligand exchange on Al^{3+} complexes.

We have also established that double four-ring aluminosilicate clusters, such as $Si_4Al_4O_{12}H_8^{4-}$, can serve as stable containers for Ti^{4+} and Zr^{4+} and that such species exhibit unusual structural and spectral propertties about the metal atom. Spectral signatures have been established to identify such materials and studies on the incorporation of other open-shell transition metal ions is proceeding

Dr. Michele Clark (Chem. and Biochem, UMCP), in a study of the solubility of Cu and As in equilibrium with Cu and As sulfide minerals, has identified a new species CuAsS(SH)(OH) leading to enhanced solubilities. We are studying this, and a series of simpler Cu^+ (also Ag^+ and Au^+) species to establish structures and relative stabilities.

GRANTEE: Massachusetts Institute Of Technology

Department of Earth, Atmospheric, and Planetary Sciences
Cambridge, MA 02139-4307

Grant: DE-FG02-97ER14760

Evolution of Pore Structure and Permeability of Rocks under Hydrothermal Conditions

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Objectives: The goal of the project is to understand the mechanisms and kinetics of evolution of pore structure and transport properties in porous rocks and granular aggregates under hydrothermal conditions and under hydrostatic and triaxial loading.

Project Summary: Pore structures and transport properties of rocks, including fluid permeability and electrical conductivity, can be altered in the Earth by a wide variety of diagenetic, metamorphic, and tectonic processes. To provide fundamental information on the way that pore structure changes, measurements of transport properties are conducted on samples while subject to elevated temperature and pressure. The samples and conditions of measurement are designed, if possible, to isolate a single mechanism, *e.g.*, roughening by diagenetic reaction, or compaction by plastic flow. Extensive optical and scanning microscope observations of the pore structure are done to quantify changes in surface roughness, porosity, and pore dimensions. Computations using network techniques and cellular automata help to model the mechanisms of porosity evolution. A better understanding of these processes is important for improving resource recovery, predicting rates of metamorphism, understanding fault mechanics and fault stability, and estimating rates of deformation by pressure solution.

Results: An elevated temperature bomb was constructed to make permeability measurements at pressures of 150 MPa and 300°C and to monitor changes in permeability as a function of reaction time. With certain restrictions, the bomb can also be used for resistivity measurements. Five *in situ* alteration experiments were conducted on synthetic samples of sintered glass beads.

Initial porosity varied between 5% and 35%. Run temperatures were 190-250°C; each run lasted for 2 to 7 days. All experiments showed a decrease in permeability of several orders of magnitude (from ~100 mDarcy to 10 µDarcy). Microstructural examination of the post-experimental samples suggested two mechanisms for the large permeability reduction: First, pore space was reduced due to formation of less dense daughter phases (*i.e.*, natrosilite, quartz, and perhaps gmelinite and amorphous Na-Ca-silicates). Second, the surfaces are roughened owing to material redistribution during dissolution and growth. The alteration products showed large fibrous to webby overgrowths with an increased surface area. In natural samples, such overgrowths are known to reduce the permeability drastically. Microstructure studies show that, in general, the pore/solid interface in porous rocks is rough, and in fact, some authors contend that the pore/solid interface is a self-affine fractal. To include roughness in a network model, the hydraulic conductivity of pipes with varying circular cross-section was calculated using the lattice-gas method for the case of pipes with a sinusoidally varying radius. The amplitude of the sinusoidal variations varied from zero (*i.e.*, straight tube) to 0.8 times the average radius. The longitudinal wavelength ranged between 0.15 and 7.9 times the average radius. The hydraulic conductivity was observed to decrease significantly with amplitude (*i.e.*, up to 2 orders of magnitude). At very short wavelengths, (*i.e.*, rough pore walls) the tube appeared to be approximately equivalent to a straight tube with a radius equal to the minimum radius. At long wavelengths, the Reynolds equation applied.

GRANTEE: University Of Michigan

Department of Geological Sciences
Ann Arbor, MI 48109-1063

Grant: DE-FG02-96ER14615

Combined Noble Gas and Stable Isotope Constraints on Nitrogen Gas Sources within Sedimentary Basins

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Objectives: To combine the information provided by both noble gas and stable isotope systematics in order to constrain the origin of nitrogen gas sources, transport behavior and mass balance within sedimentary basin systems.

Project Summary: Nitrogen is one of the major non-hydrocarbon gases found in natural gas reservoirs. Many regions in which the gas fields have a high-nitrogen content also show a relationship between the concentration of nitrogen and crustal-radiogenic helium. The crustal He will be associated with crustal ^{40}Ar and ^{21}Ne. Noble gases derived from other sources such as the air dissolved in groundwater and magmatic sources can be quantified from the noble gas isotopic composition. Combined with the distinct elemental abundance patterns it is possible to resolve the extent of crustal, mantle and atmosphere-derived noble gas involvement in these systems.

The Kansas/Texas Hugoton/Panhandle giant gas field has perhaps the best-documented He/N_2 relationship of any system. This program focuses on samples from these and neighboring fields which preserve different but distinct regional He/N_2 ratios. The noble gas and stable isotope composition are compared to enable us to identify any regional nitrogen gas isotopic end members; quantify the extent of their contribution to the sedimentary fluid regime; constrain the conditions for deep nitrogen release and transport; and by comparison with samples which show rare gas abundance fractionation, identify the mechanism of fractionation (*i.e.*, mass-dependent transport fractionation, solubility/phase fractionation) and assess its impact on the stable isotope systematics.

Results: We have completed analysis on samples from producing wells giving full geographic coverage of the entire Hugoton-Panhandle system. We show that the crustal derived He is directly proportional to the groundwater derived Ne and that the Nitrogen has two sources, one that is associated with the groundwater and crustal He, and another that is not associated with the noble gases. Using the noble gases we have identified the nitrogen isotopic composition of these end-member components and are currently assessing the origin of both nitrogen components based on this information. A simple conceptual model linking the regional groundwater system to He-associated nitrogen occurrence in natural gases is being developed. In addition to the He/N_2 study we have expanded our understanding of the way in which magmatic noble gases are input into shallow fluid systems (Ballentine, *Earth and Planet. Sci. Lett.* 1997).

GRANTEE: University Of Michigan

Department of Geological Sciences
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GRANT: DE-FG02-94ER14412

Applications of ICP Magnetic Sector Multicollector Mass Spectrometry to Basic Energy Research

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Objectives: To accurately determine the ages of, and source of components in, hydrothermal mineralization and diagenesis in order to evaluate the mechanisms responsible for the formation of economic base metal and hydrocarbon accumulation. To understand the controls on the chemistry of the oceans with particular reference to hafnium. To determine the mechanisms of entrapment of pollutants in sediments.

Project Description: This research project will develop the new technique of ICP multicollector mass spectrometry and apply the methods to a variety of problems in low temperature geochemistry. These will include new methods of dating sulfides such as long-lived isotopic chronometers (^{115}In-^{115}Sn) and higher sensitivity applications of established geochronometers, such as Lu-Hf dating of phosphates. Laser ablation in situ isotopic measurements should be possible for dating and determining the origins of components in low temperature overgrowths and fine grained diagenetic minerals, such as U-Pb measurements of zircon, anatase and sphene and Sr isotopic measurements in carbonates and feldspars. High sensitivity Hf isotopic studies of seawater and metalliferous sediments will be used to evaluate the Hf isotope geochemistry of the oceans. Precise isotope dilution measurements of transition metals and platinum group elements in dust, seawater and sediments will be used to evaluate the controls on the chemistry of the oceans and the mechanisms of entrapment of pollutants in sediments.

Results: The following has already been accomplished with this new technique: The Hf-W chronometer has provided new age constraints for the Earth's core, the Moon, the Martian core and a variety of chondrites, achondrites and iron meteorites. The first precise in situ measurements of Sr isotopic composition using an ultra-violet wavelength laser have now been made and are in excellent agreement with the results obtained with an infrared wavelength laser but are achieved withhigher sensitivity. The Hf isotopic compositions of Mn crusts have been shown to provide a record of hydrothermal contributions to the oceans. In situ measurements of the Pb isotopic compositions of Mn crusts have been shown to provide a record of oceanic paleocirculation and a possible link with changes in erosion related to climate change. New techniques for the chemical separation and measurement of the concentrations of platinum group elements and Re, Te, In, Sn, and Cd are resulting in accurate measurements of their abundances in the Earth. These will provide the groundwork for precise measurements of these chalcophile and siderophile elements in fluids. New U-Th techniques have been developed and are being applied to the dating of soils, marine carbonates and Mn crusts.

GRANTEE: University Of Minnesota, Twin Cities

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GRANT: DE-FG03-91ER14212

Magma Rheology, Mixing of Rheological Fluids, Molecular Dynamics Simulation, and Lithospheric Dynamics

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Objectives: Mixing efficiency in complex rheology, molecular dynamics of complex fluids and micro-scale Rayleigh-Taylor instabilities, effects of complex rheology in lithospheric dynamics.

Project Description: This project will improve our understanding of the thermal, chemical, dynamical and mechanical state of the continental crust and subcrustal lithosphere with particular focus on the interactions between the various subsystems. The work plan includes: (1) rheological laboratory measurements on melts and magmatic suspensions; (2) Determination of the thermodynamical and transport properties of molten silicates by MD simulations; (3) Mixing processes of rheological fluids in convection and visualization of complex processes; (4) Coupling between mantle convection with temperature-dependent and non-Newtonian rheology and mantle diapirs on the thermal regime and subsidence curves of rift-related basins; (5) The dynamical influences of lithospheric phase transitions on the thermal-mechanical evolution of sedimentary basins; (6) The development of stress fields and criteria for faulting in the crust; (7) Modeling of heat and mass transport driven by thermal and compositional heterogeneities in porous media; and (8) Open system geochemical modeling of magmatic systems.

Results: Results described below are for the University of Minnesota part of this project. Additional results are given in the summary of activities can be found in the summary of activities by the University of California, Santa Cruz team led by F.J. Spera. Molecular dynamics calculations have been carried out on binary systems consisting up to 3 million particles interacting via two-body Lennard-Jones potentials We have studied the various stages of the Rayleigh-Taylor instability in microscale covering an area of around 250,000 Å^2. We have observed from these simulations the development of hydrodynamic instabilities. A free surface is introduced by deploying an overlying void in the computational domain. We can observe the fingering instability as a result of the dynamical interaction between the two ensembles of particles. For equally sized particles a spontaneous " fluctuation driven" mixing process with a long spin-up time is observed. These molecular-dynamics results suggest the possibilities of upscaling the Rayleigh-Taylor instabilities into the mesosopic regime. This work can be found in *Computers in Physics*, Vol. 12, No. 6, 595-600, 1998.

We have proposed a line method, akin to the contour dynamics technique, which is an extension of the particle method but with the particles redistributed dynamically at each timestep. We have used up to one million particles per line and ten lines to investigate the dynamical and structural properties of mixing for both Newtonian and non-Newtonian temperature-dependent viscosity convection in 2-D geometry. The spatial structures and the time history of the lines formed in Newtonian convection are very different from those produced in non-Newtonian convection, which has the tendency for producing long-lived, horizontal structures. Efficient mixing in the upper mantle would be inhibited by non-

Newtonian convection due to the large viscosity variations across the plumes. This work has been published in *Geophysical Res. Lett.*, Vol. 25., No. 16, 3205-3208, 1998.

Different regimes of compaction driven flow have been studied within the framework of a poro-viscoelastic medium. A single dimensionless parameter, the Deborah number D_e, has been identified, which allows us to portray the solution from the purely viscous matrix limit ($D_e << 1$) to the poro-elastic ($D_e >> 1$) limit. In viscous limit the evolution of a porosity disturbance (porosity wave) is governed by the nonlinear convection-diffusion equation, while in the poroelastic limit it evolves according to a Burgers-like nonlinear advection equation. In both regimes porosity waves with higher amplitude propagate faster. However, in the viscous limit porosity waves go through each other in soliton-like fashion, while in the poro-elastic limit they coalesce and thus enhance melt segregation. The introduction of other variables, such as chemistry, would elicit different responses in the flow for low and high De, allowing for the possibilities of different feedback situations. This work has been published in *Geophys. Res. Lett.*, Vol. 25, No. 17, 3239-3242, 1998. We have also studied the effects of viscous heating involving heterogeneous media, which occurs in the interaction between the mantle-lithosphere-crust during the delamination of the mantle lithosphere. High ratesof viscous heating are found in the corner flow regions, where the deformation rate is the greatest. The weak lower crust is sheared between the upper crust and the mantle lithosphere, giving rise to a second type of viscous heating with high dissipation rates several hundred times the chondritic value. Much greater dissipation rates are found in the shear interaction between heterogeneous media with different non-Newtonian rheologies than in the shear heating inside a single non-Newtonian or Newtonian homogeneous medium. High spatial resolution of at least 2 km or finer is needed to resolve the sharp variations of viscous heating near the interface of the two layers. This paper has appeared in *Geophys. Res. Lett.*, Vol. 26., No. 4, 513-516, 1999.

More information can be found in *curriculum vitae* of Prof. Yuen's web site at http://banzai.msi.umn.edu

GRANTEE: National Academy of Sciences, Board on Earth Sciences and Resources

The National Academies
2101 Constitution Ave., N.W.
Washington, DC 20418

GRANT: DE-FG02-97ER14810

Board on Earth Sciences and Resources and its Activities

C. M. Schiffries (through December 1998) and A. R. de Souza (202-334-2744; Fax: 202-334-1377; adesouza@nas.edu)

Objectives: The purpose of the Board on Earth Sciences and its committees is to provide a focal point for National Research Council activities related to Earth science policy.

Project Description: The Board addresses the following strategic Earth science issues: identifying the frontiers of basic and applied research in the Earth sciences; strengthening multidisciplinary programs and integrated approaches to research; assessing mineral and energy resources; investigating human interactions with the Earth; understanding environmental change; improving access to and use of scientific and geospatial data and information; evaluating breakthrough technologies for mitigating environmental problems; and enhancing Earth science education.

Results: During FY 98, the Board on Earth Sciences and Resources produced 10 reports. In addition to producing reports, the board and its standing committees convened meetings to exchange information among scientists, engineers, and policy makers from government, university, and industry. Also, the board cosponsored a forum to commemorate the 50th anniversary of the American Geological Institute.

GRANTEE: University Of Nevada, Reno

Department of Geological Sciences
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GRANT: DE-FG03-98ER14885

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

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Objectives: Our main objective is to find applicable equations of flow and transport in faulted and fractured zones based on their three-dimensional structure.

Project Description: We are developing an appropriate set of mathematical tools that can be used to evaluate the results of field tests in fractured and faulted rock Previous hydraulic equations were based on a finite-sized representative elementary volume and small contrasts in media properties. Newer models that use fractional-order derivatives are based on very heterogeneous and scaleless media. We are examining the relationship between these equations and the measureable properties of fully and partially water saturated media, particularly the distribution of very high and very low velocity regions. The probability densities and connectivity of these regions directly affects the order of the governing differential equation. In particular, solute transport in a highly variable velocity field has a dispersion term of order $0 < \alpha \leq 2$. This models heavy-tailed and super-Fickian transport, both of which are characteristic of tracer tests in fractured media.

We are collaborating with a team from University of Hawaii and University of Utah that is performing detailed analysis of the three-dimensional permeability structure of faults in crystalline rocks, and developing field-based mechanical models for the nucleation and growth of faults in three dimensions. We aim to take this information and build forward models of large-scale transport in these networks. This research integrates fieldwork with deterministic and stochastic modeling to gain insight into how three-dimensional hydraulic conductivity structure of a fault develops through time. This work will lead to an increased understanding of fault zones from geologic, geomechanical, and hydrologic points of view, and to the development of a methodology for building physically realistic stochastic models for fault zone hydrology.

Results: It is important to be able to predict transport in a "forward" mode. In this mode, a transport equation is built with only hydraulic and aquifer information; no tracer need be introduced. Because of the wealth of data, ease of measurement, the 1-D nature, and the very high heterogeneity, the granular MADE site aquifer is perfectly suited. At this site, the hydraulic conductivity (K) distribution has heavy (power-law) tails with exponent $\alpha = 1.1$. This leads directly to the same order of differentiation. Simple probability arguments also gave the mean velocity and dispersion coefficients, both of which are constant at all scales, so the entire equation was gained from hydraulic data alone. The predictive ability of this equation at the MADE site is essentially perfect at later times, while the traditional ADE underpredicts tritium concentrations in the leading (heavy-tailed) edge of the plume by over six orders-of-magnitude. Merely identifying the underlying statistics of the velocity distribution led to a powerful predictive tool.

All of the previous work on the fractional ADE was restricted to one dimension. Extensions to three dimensions lay the foundation for 3-D solute transport, and included the advances of 1) developing a general theory for multidimensional fractional derivatives, and 2) showing that a huge class of random movement processes with heavy tails directly implies fractional differentiation. In particular, the older multidimensional Gaussian (the solution to the traditional 2nd-order ADE) is always ellipsoidal. This is counterintuitive to how water must flow through fractures. If fractures are concentrated on preferred orientations, so too must be the plume. The 3-D generalizations describe a random process concentrated along preferred directions in any number of dimensions. In 1-D this leads to skewness, which is perfectly allowable in the fractional ADE but not the 2nd-order equation. In 2-D we can have anything from classical "footballs" to "rabbit ear" type plumes. It all depends on the fracture patterns, which become part of the governing equation.

Finally, since flow and transport also occur in unsaturated fractures, we looked at the effect of partial saturation on channeling and the effective order of differentiation. Pachepsky *et al.* (1999) theorized that transport in unsaturated detrital sediment might lead to transport features similar to fracture flow, since flow in unsaturated soil tends to self-organize in long-range "channels." Shiozawa conducted experiments (listed by Toride *et al.*: The CXTFIT code, version 2.0, Research Report 137, U. S. Salinity Laboratory, Riverside, CA., 1995), in which a chloride salt was injected as a step function into columns with homogeneous sand filled with deionized water. The fully saturated column showed nicely Fickian breakthrough at 3 depths. When the saturation was lowered to roughly 30%, the breakthrough had heavy tails and a growing dispersivity within the traditional ADE. A fractional ADE with a constant order of 1.6 and a constant dispersion coefficient models the data with half the error of the traditional ADE.

GRANTEE: University Of New Mexico

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Grant: DE-FG03-97ER14778

Continuum and Particle Level Modeling of Concentrated Suspension Flows

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Objectives: 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.

Project Description: The proposed research will elucidate the underlying physical principles that govern concentrated multiphase systems in areas essential to continued progress in geosciences. In order to be of use in real world applications, significant enhancements to currently available continuum-level suspension flow models will be required. We will use both experimentation and high performance computing to obtain microstructural information that is necessary to the development and refinement of the continuum models. For example, we expect to use this microstructural information to gain insight into the physics of particle bridge formation and collapse and particle sedimentation, which are particularly important in sand control issues found in petroleum production. Further, we expect that continuum-level modeling could eventually be directly implemented in codes currently used to predict hydraulic fracturing operations in the petroleum industry. The understanding gained about the physics of multiphase flows will, however, have much broader application in geosciences.

Results: The continuum model originally developed by Phillips *et al.* (1992) has been extended to simulate non-neutrally buoyant particles and non-Newtonian suspending fluids. The extension entails the modification of the momentum and continuity equations to allow the fluid to have a spatially varying density and an additional gravity-driven diffusion term in the particle flux equation. The model predicts the settling of particles by density-driven instabilities as well as uniform hindered settling. Generalized Newtonian equations are included in the term for viscosity, which varies locally with the concentration of particles and the shear rate. Results from the new model, which has been implemented into a general-purpose finite element computer code, are being compared with experimental measurements based on nuclear magnetic resonance (NRM) imaging. Concurrently, two other continuum-level models are being adapted for use in the same finite element computer code. In addition, a multipole-accelerated boundary element method (BEM) is being developed to simulate several thousand individual interacting particles. These simulations lead to detailed information on individual particle and fluid motion that is unobtainable through experiments, and they will aid in determining accurate continuum approximations such as the gravity-driven diffusion terms.

GRANTEE: New Mexico Institute Of Mining And Technology

Department of Earth & Environmental Science
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Grant Number: DE-FG03-96ER14589

Investigation of Permeability Upscaling

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Objectives: The goal of this research is to better understand the process of permeability upscaling. Physical and numerical experimentation forms the basis for testing conceptual and theoretical models of permeability upscaling as well as exploring alternative measures and models of this process.

Project Description: Investigation of permeability upscaling is predicated on the results of physical experimentation. These experiments are unique in that: 1) permeability data are collected over a range of different sample supports (sample volumes), each subject to consistent measurement conditions; 2) data are collected on densely sampled grids providing detailed resolution in the spatial distribution of permeability; and 3) experiments are repeated on a variety of geologic materials each differing in their structural/textural attributes. A specially designed gas minipermeameter provides a rapid, precise, and non-destructive means of collecting permeability data. By varying the size of the minipermeameter tip seal, measurements spanning five orders of magnitude on a per-volume basis are made subject to consistent boundary conditions and flow geometry. Thousands of measurements on multiple faces of meter-scale blocks of rock are collected with each of five different tip seals (0.31 - 5.08 cm ID) plus a single large tip seal (15.24 cm ID) designed to integrate over the entire sampling domain. To quantify permeability upscaling, key summary statistics are calculated from the acquired data sets and analyzed with reference to their corresponding sample support. Results are interpreted in light of the physical characteristics of the porous medium and measurement characteristics of the sampling instrument. Detailed numerical modeling is also employed to further explore and quantify the empirical upscaling behavior and to extend the studies to a broader suite of materials.

Results: Inversion of the permeability from air minipermeameter measurements is based on a numerically determined geometric factor. For a variety of reasons, we sought a more exact solution using both analytical and numerical methods. The two independent solutions agree to five significant digits and provide much improved precision over the previously published results.

We have also developed an adjoint state method for theoretically determining the spatial filter function of the air minipermeameter. We implemented this procedure with a finite element model and were able to plot the three-dimensional filter function for the tip seal design used in our current work. The function shows great sensitivity to the permeability just below the inner tip seal radius, and a lower but still significant sensitivity to the permeability just below the outer tip seal radius. The filter function also appears to be proportional to the velocity squared, a previously unreported observation for any instrument. We plan to use the derived function to better interpret the empirical filter functions we recently published [Tidwell *et al.*, *Water Resour. Res.,* 35(1), 43-54, 1999].

Finally, we derived finite element numerical solutions for a layered permeability system consisting of a surface layer with one permeability overlying a substratum with a second permeability. This solution will assist us with determining the importance of surface disturbances from sawing and other rock preparation effects on minipermeameter measurements.

GRANTEE: State University Of New York At Stony Brook

Department of Geosciences
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GRANT: DE-FG02-94ER14449

High Precision Radiometric Dating of Sedimentary Materials

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Objectives: To develop field, petrographic and geochemical criteria to allow high precision U-Pb dating of sedimentary minerals within rapidly deposited sequences of carbonate and clastic rocks.

Project Description: The original goal was to obtain radiometric ages for sedimentary material with uncertainties of three million years or less to date the times of sedimentation. We have since shown that it is possible to obtain uncertainties of 1 Ma or less.

We started with the dating of soil calcite and have since considered the potential of U-Pb dating of sedimentary apatite and lake, swamp and spring calcite. The most obvious applications for precise ages for times of sedimentation are:

1) providing more precise duration's for unconformity bound genetic packages in sequence stratigraphy;
2) more precisely calibrating the geologic time scale;
3) correlation between marine and terrestrial stratigraphic sections; and
4) correlation between fossil-rich and fossil-poor stratigraphic sections.

Results: *Dating of Syn-Sedimentary Apatite in Coprolites, Hartford Basin:* The U-Pb system for syn-sedimentary apatite occurring in coprolites from the Lower Jurassic East Berlin Formation and Shuttle Meadow Formation (Hartford Basin, CT) was studied in order to assess its potential for directly dating the timing of sedimentation. Coprolites composed of francolite (carbonate fluorapatite) were chosen due to several characteristics:

1) authigenic formation during early diagenesis;
2) enrichment in U (100’s to 1000s ppm U); and
3) elevated ^{206}Pb/^{204}Pb ratios (400 to 3900).

Initial results of the Pb isotopic compositions were encouraging. The coprolites exhibited elevated ^{206}Pb/^{204}Pb ratios, and displayed a range of values, which suggested they had potential for dating. However as more results became available it was clear that the samples suffered normal discordance, most likely due to coupled, continuous loss of Pb and radioactive daughters of U, (dominated by the ^{238}U decay chain).

Dating Late Paleozoic Lacustrine and Palustrine Carbonates Southeastern Ohio: The Upper Paleozoic strata of southeastern Ohio are cyclic and mostly non-marine with sparse biostratigraphic controls. The origin of cyclicity in the Appalachian Basin and correlation with late Paleozoic marine cycles of the mid-continent has been a subject of debate over the years. Correlation between marine sections and terrestrial sections is difficult due to the scarcity of biostratigraphic control. The age of the

Pennsylvanian – Permian boundary is 302 ± 2 Ma. Paleontologic evidence is insufficient to definitely place the Pennsylvanian – Permian boundary within the Appalachian Basin. Rather, the location of the boundary is broadly based on the correlation of cycles from the mid-continent and incursions of rare marine units in the basin. Aliquots of one lacustrine limestone from the Virgilian Monogahela Group have uniform Pb concentrations of about 2 ppm with U concentrations ranging from 16 to 30 ppm. Values of $^{206}Pb/^{204}Pb$ range from 44 to 83. The sample yields a concordant age of 268 ± 26 Ma. Considering it's relatively large uncertainty, this age is only slightly younger than the Pennsylvanian – Permian boundary. The relatively high U/Pb ratios and the suggestion of closed system behavior is encouraging, and gives reason to expect that it should be possible to develop approaches using non-marine limestones for dating the time of sedimentation more precisely.

GRANTEE: State University Of New York At Stony Brook

Department of Applied Mathematics and Statistics
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GRANT: DE-FG02ER14261

Medial Axis Analysis of Porous Media

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Objectives: The goal of this work is to develop and utilize a package of software tools to extract quantitative information on the geometry of the void and grain microstructure of rock starting from high resolution, three dimensional (*e.g.*, X-Ray microtomographic) images.

Project Description: High resolution (1 to 5 micron), three-dimensional images of rock samples are segmented to provide specific grain/pore identification for each voxel in the image. Appropriate transforms are then applied to the segmented, digitized images to produce medial axis (co-dimension two) representations of the void (or grain) structure. Geometric properties of the rock are either measured directly from the medial axis, or the axis is utilized as a search path to locate regions where measurements are to be made.

Results: A preliminary analysis [1] of the microstructure of a suite of Fontainebleau sandstones ranging from 7.5 to 22% porosity has been completed. The data samples were imaged at 5.7-micron resolution by X-ray computed microtomography; each sample studied had a volume of 3.65 cubic mm. The results indicate: exponential distributions for the nodal pore coordination number with average coordination numbers in the range of 3.3; average pore channel length (measured nodal pore center to nodal pore center) increases with decreasing porosity down to 7.5%m consistent with the percolating nature of 7.5% porosity Fontainebleau; exponential distribution of throat areas, with decreasing average throat area with decreasing porosity; an apparent log-normal distribution of of nodal pore volumes.

We are in the process of applying the analysis to larger pore volumes (46.7 cubic mm) to verify these preliminary results. Analysis has been completed for 7.5% porosity samples.

[1] W.B. Lindquist And A. Venkatarangan, Investigating 3D Geometry Of Porous Media From High Resolution Images, *Phys. Chem. Earth (A)*, 25, (1999) 593--599.

GRANTEE: State University Of New York At Stony Brook

Department of Geosciences
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GRANT: DEFG029ER14633

Surface Chemistry of Pyrite: An Interdisciplinary Approach

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Objectives: The primary goal of this research program is to understand the microscopic aspects of pyrite oxidation. Determining the charge development on pyrite surfaces and evaluating the interaction of the pyrite surface with an array of simple inorganic and organic molecules are the immediate goals. Through a combination of macroscopic observations and observations at the atomic/molecular level new insights are gained that will lead to a better understanding how pyrite reacts in a range of chemical environments.

Project Description: The charge development, interaction with inorganic and organic constituents, and the reactivity of pyrite are being investigated. Emphasis is placed on integrating macroscopic information from low-temperature techniques such as electrophoresis and microscopic information from modern surface science techniques that are used in the ultra high vacuum (UHV) environment. Using model, atomically clean "as-grown" surfaces of pyrite, electron spectroscopies in UHV are used to understand the atomic composition and the nature of the functional groups on pyrite after exposure to the aqueous solutions. The integration of the UHV and low-temperature studies will provide a complete picture of the type of surface functional groups at the pyrite surface, their acid-base behavior, and interaction with selected aqueous constituents.

Results: In the second year of this project our studies have concentrated on using advanced surface science probes to study the surface reactivity of pyrite. In our prior funding cycle, we have obtained aqueous-based electrophoresis results in a variety of environments. The present funding cycle is geared to produce a molecular-level understanding of pyrite surface reactivity that can be used in part to understand these prior results.

Reactivity of the (100) crystallographic plane of FeS_2 in oxidizing environments: XPS in conjunction with a newly constructed high-pressure reaction cell has been used to investigate the reactivity of {100} planes of pyrite in gaseous and aqueous H_2O, O_2, and H_2O/O_2 environments. These studies have shown the exposure of $FeS_2(100)$ to a H_2O/O_2 mixture produces more oxidation then the sum of the individual activities of pyrite after exposure to pure H_2O or O_2. Only after exposure to H_2O/O_2 environments, does the disulfide group of pyrite become oxidized. It is believed that the adsorption of O_2 in the H_2O/O_2 environment results in the formation of Fe^{3+} via an electron transfer step. These Fe^{3+} sites provide dissociation sites for H_2O. When H_2O is present alone, oxidation of $FeS_2(100)$ occurs solely at surface imperfections that most likely contain a small amount of Fe^{3+} in addition to FeS like sites. Reaction is limited to these regions, since there is a limited concentration of Fe^{3+} and O_2 is not present to produce more of these active sites.

Reactivity of the (111) crystallographic plane of FeS_2 in oxidizing environments: Further experiments have started to investigate the structure sensitivity of pyrite oxidation. These studies have looked at the reactivity of {111} planes of pyrite. In contrast to the behavior of $H_2O/FeS_2(100)$, the (111) plane undergoes significant oxidation in the pure H_2O environment. Furthermore, exposure of this crystal plane to a mixture of H_2O and O_2 results in more iron and sulfur oxide product than on the (100) plane under similar conditions.

GRANTEE: State University Of New York At Stony Brook

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GRANT: DE-FG02-94ER14455

Micromechanics of Failure in Brittle Geomaterials

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Objectives: 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 failure mode. 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 in geologic materials, and thereby strengthen the theoretical basis for the application of laboratory results to various technological operations of importance.

Project Description: Knowledge of the microscale characteristics and behavior of rocks is important for several energy-related applications, including global climate change and carbon management; oil field geoscience; geotechnical engineering efforts such as design and assessment of geologic nuclear waste repositories; and environmental remediation efforts at contaminated DOE and/or DoD installations. We use an integrated approach consisting of experimental rock mechanics testing, quantitative microscopy, and theoretical and numerical analyses. The experimental investigation provides a detailed understanding of the microstructure of geologic materials and how the micro-scale characteristics affect macro-scale behavior including brittle failure and mechanical compaction. Detailed and quantitative microstructural studies complement laboratory rock mechanics experiments. The results are used to formulate and evaluate theoretical and numerical models of rock deformation and failure.

Results: (1) Investigation of water-weakening effect on the strength of porous sandstones. We have obtained a relatively comprehensive database on the weakening effect of water on brittle strength and ductile compaction of several porous sandstones. The data allow us to formulate a micromechanical model to consistently interpret the dilatant and compactive failure behaviors due to presence of water and initial damage in a fracture mechanics framework. (2) Triaxial compression experiments on limestones (of a range of porosities) and detailed characterization of the failure envelopes in both the brittle and cataclastic flow regimes. We have completed a study on the relatively compact Solnhofen limestone. For the first time, a fairly complete set of data on porosity change and the brittle-ductile transition in the Solnhofen limestone has been acquired. The failure modes are associated with complex interplay of dilatancy, pore collapse and crystal plasticity processes, and several micromechanical models have successfully been employed to interpret the phenomena. (3) Micromechanics of brittle failure and cataclastic flow and the brittle-ductile transition in a sandstone of intermediate porosity (~13%). Our observations indicate significant differences with the micromechanical behavior of a weakly cemented porous sandstone, such as Berea sandstone. The microstructural observations underscore the variability of micromechanics of failure, and the comparative study has identified the microstructural control mechanisms.

GRANTEE: Northwestern University

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GRANT: DE-FG02-93ER14344

Factors Affecting Shear Strain Localization in Rocks

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Objectives: To obtain an improved understanding of the occurrence, development and evolution of shear localization zones (faults) in rocks and their relation to the macroscopic constitutive description, especially that governing multi-axial response, and microscale mechanisms of deformation.

Project Description: Because of the significance of fractures to energy production, waste disposal, and mineral technologies, prediction of their causative stresses, location, orientation, thickness and spacing becomes paramount. This project examines the applicability of a theory of localization that describes faulting as an instability of the constitutive description of homogeneous deformation. The predictions of localization depend strongly on the constitutive description; consequently, a correlative objective is to improve constitutive model, particularly those aspects governing abrupt changes in the pattern of deformation. Investigations of constitutive behavior include both phenomenological models, derived from laboratory tests, and micromechanical models, based on the growth and interaction of microcracks and resulting increase in overall compliance of the solid. Constitutive relations are calibrated by comparison with axisymmetric compression tests and then used to predict the response in more complex experiments, e.g, compression-torsion, and plane strain. Comparison of numerical studies with experiments addresses the effects of more realistic geometries and boundary conditions.

Results: A suite of axisymmetric compression experiments has been used to develop a detailed phenomenological description of the inelastic behavior of Tennessee marble. The constitutive model describes well the variation of the in-plane stress observed in a plane strain experiment. The out-of-plane stress (in the plane strain direction) is not modeled well, apparently because the inelastic normal strain in this direction is overpredicted. In plane strain, localization is predicted to occur close to peak stress, in good agreement with experiment. This constitutive framework has been implemented as a material subroutine in the commercial finite element code ABAQUS and used to investigate the development of non-uniformities for geometries and platen friction simulating plane strain and axisymmetric compression tests. The results demonstrate that although nominal stress strain curves are not affected significantly by details of geometry or platen friction typical in experiments, the onset and location of localization are. Surprisingly, deformation in the plane strain geometry is more uniform up to localization than in the axisymmetric geometry, in which significant variations in mean stress occur.

GRANTEE: Oklahoma State University

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Grant: DE-FG03-99ER14944

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

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Objectives: The objective is to develop a quantitative understanding of critical fundamental processes controlling two-phase flow and transport in fractures, based on detailed physical experiments and high-resolution numerical simulations. This understanding may subsequently be abstracted for use in conceptual models applied to large-scale problems in petroleum extraction, isolation of hazardous or radioactive waste, remediation of contaminated subsurface media and CO_2 sequestration.

Project Description: Under two-phase immiscible flow conditions, the phase geometry associated with each phase controls the fluid flow and solute transport characteristics. The phase geometry is in-turn determined by a combination of the aperture variability, the capillary and viscous effects inherent in the two-phase flow processes themselves and external forces such as gravity. If one of the fluids can slightly dissolve in the other, then transport of the dissolved fluid also influences phase geometry.

In this collaborative project between Sandia National Laboratories, Oklahoma State University and University of Colorado at Boulder, systematic physical experimentation is coupled with concurrent numerical simulation to explore the factors controlling phase structure, flow, transport and inter-phase mass transfer in rough-walled fractures. A high-resolution light-transmission technique has been developed to facilitate acquisition of accurate experimental measurements of aperture, phase geometry and solute concentrations in transparent analog fractures. Use of this technique will lead to data of unprecedented accuracy for evaluating current understanding of invasion, flow and transport processes, and motivate refinement of theoretical concepts.

Results: A Modified Invasion Percolation (MIP) algorithm has been developed and comprehensively tested, to simulate phase invasion processes influenced by capillary and gravity forces. An essential feature of the MIP algorithm in the context of application to rough-walled fractures is the incorporation of an in-plane curvature term. The inclusion of this term is critical to obtaining phase structures that correspond closely with experimentally measured phase structures. The in-plane curvature term is not incorporated in previously proposed approaches such as standard percolation (SP) or traditional invasion percolation (IP, incorporating only an out-of-plane curvature across the aperture).

To allow a meaningful experimental evaluation of current conceptual models of flow, transport, and inter-phase mass transfer, aperture measurement errors were minimized and quantified. Each component of the light transmission system was evaluated with respect to its contribution to measurement error and the individual errors were combined to yield estimates of the total error at any location within the flow field. This effort indicated that minimizing aperture measurement errors requires a trade-off between precision errors resulting largely from signal noise and accuracy errors resulting from the nonlinearity of light absorbance by the dye used for measurements. The optimal measurement process is fracture and system specific and thus must be carefully evaluated for each new fracture or measurement system.

A careful re-evaluation of saturated and unsaturated flow experiments in rough-walled fractures is in progress, to identify the sources of discrepancy between experimental results and numerical simulations employing the Reynolds equation. It is expected that these efforts will lead to unambiguous and comprehensive evaluations of the Reynolds equation. Several issues related to the numerical implementation of the Reynolds equation and the adequacy of the data resolution are also being investigated.

A series of experiments on solute transport in partially saturated fractures was carried out. These experimental results highlight the importance of solute diffusion into and out of low velocity regions adjacent to the entrapped non-flowing phase. Because of these low velocity regions, the front edge of a solute plume appears to be more influenced by flow channeling and the tail portion appears to be stretched out. These experimental results will be compared against numerical simulations of solute transport to better understand the importance of the low velocity regions.

GRANTEE: University Of Oklahoma

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GRANT: DE-FG03-96ER14643

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

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Objectives: The goal of this project is to develop paleomagnetic methods for dating diagenetic events in sedimentary rocks. Specific objectives include testing the hypotheses that fluid flow (*e.g.*, basinal fluids, hydrocarbons), clay diagenesis and organic matter maturation are viable mechanisms for the occurrence of pervasive chemical remanent magnetizations (CRMs) that are commonly observed in sedimentary systems.

Project Description: Investigations of diagenetic processes such as fluid migration and the maturation of organic matter commonly lack temporal control. The ability to constrain the time of oil migration, for instance, would be of significant benefit for exploration. The paleomagnetic dating method is based on a genetic connection between diagenetic processes and the precipitation of authigenic magnetite. Isolation of the magnetization carried by the magnetite and comparison of the corresponding pole position to the apparent polar wander path allows the timing of diagenetic events to be determined. The research involves paleomagnetic field and laboratory tests to constrain appropriate chemical and physical conditions for magnetite authigenesis.

Results: Work completed this past year provides further evidence for chemical remanent magnetizations (CRMs) in sedimentary rocks that resulted from fluid migration, organic matter maturation and clay mineral transformations. For example, we have been testing the hypothesis that increasing rank of Carboniferous age coals towards the northwest part of an elongate east-west synclinal foreland basin in the South Wales Coalfield is a consequence of orogenic fluids. If orogenic fluids caused the observed anthracitisation (which is higher rank than expected based on burial depth alone), then it is possible that limestones that rim the basin would carry a remagnetization and exhibit a diagenetic trend similar to the coals. Paleomagnetic (a pervasive, post-folding CRM residing in magnetite) and geochemical (elevated $^{87}Sr/^{86}Sr$ values) results support alteration via orogenic fluids in the eastern part of this basin. However, whilst a synfolding CRM (possibly acquired during Variscan deformation) is observed in the western part of this basin, strontium isotope values that are essentially co-eval with respect to early Carboniferous seawater are inconsistent with this model. An additional test for a connection between CRMs and fluid migration was conducted on a set of samples from dolomite veins and associated rocks that occur in the Dalradian Schist in northwestern Scotland and Northern Ireland. The origin of these veins is uncertain and their age has been suggested as either Devonian or Permian. Our paleomagnetic results clearly indicate that the veins contain a CRM residing in hematite and that this magnetization was acquired during the late Permian/early Triassic. Associated red and gray schists contain the same magnetization. These results and concurrent petrographic and geochemical studies suggest pervasive magnetization resulting from fluid flow through the region.

Field and laboratory tests have provided new evidence for thermally induced diagenetic processes that result in magnetizations in sedimentary rocks. Jurassic age, organic-rich, carbonate-cemented sandstones around a Tertiary dike on the Isle of Skye, Scotland indicate changes in magnetic mineralogy and magnetite grain size in the contact zone. Specimens within 85 cm of this 90-cm thick dike contain a Teriary magnetization equivalent in direction to the thermal remanent magnetization in the dike, whereas at greater distances the sandstone does not carry a stable remanence. Based on isothermal remanent magnetization (IRM) measurements, thermal decay of triaxial IRMs and S-ratio determinations, magnetite is the dominant magnetic phase in the sediment except within 8 cm of the dike, where hematite predominates. Maximum unblocking temperatures (Tb_{max}) for the magnetization are higher than predicted by a thermal cooling model at distances greater than 40 cm, although Tb_{max} values are not corrected for gradual cooling of the dike and are, therefore, overestimates. Trends in rock magnetic parameters (increasing magnetic susceptibility and anhysteretic remanence [ARM]) are consistent with an increasing contribution of single domain/pseudo-single domain magnetite towards the dike. A dramatic increase in saturation IRM (SIRM) accompanied by a decrease in ARM/SIRM values suggest an increase in multi-domain magnetite near the dike (<25 cm). Low temperature experiments confirm the presence of magnetite and indicate the presence of abundant superparamagnetic magnetite. Changes in coercivity of remanence/coercive force and the character of the hysteresis loops are consistent with changes in the relative amounts of the different magnetite size fractions towards the dike. The onset of changes in the magnetite grain size budget starting at 85 cm suggests that chemical processes contributed to the natural remanent magnetization at temperatures as low as 230^{o}C. Petrographic and geochemical studies suggest that hydrothermal fluids did not pervasively alter the contact zone. Utilizing the dike as an analog for thermal processes that occur during burial, the results of this study suggest that relatively low burial depths are sufficient to cause magneto-chemical changes.

The smectite to illite transformation is another diagenetic process that may create CRMs in magnetite. Our recent paleomagnetic, rock magnetic and geochemical results from Mesozoic, organic-lean carbonates in the Vocontian Trough, southeast France, support a hypothesized acquisition of a CRM during burial diagenesis of smectite and are inconsistent with an orogenic fluid remagnetization mechanism. The geographic and vertical distribution of a widespread normal polarity, prefolding magnetization, which resides in magnetite, parallels the burial diagenesis of clays. A prefolding but secondary reverse polarity component is present in some areas and may reflect acquisition of the magnetization through a reversal. Rock magnetic results suggest that the characteristic magnetization resides in a mix of grain sizes, probably including single domain magnetite. Based on this and the presence of the reversed component, the magnetization is interpreted to be a CRM. Fold, conglomerate and reversal tests indicate that this CRM is pervasive throughout the basin. The CRM is absent only where there is no evidence for clay diagenesis, is well developed where smectite has completely altered to illite, and is poorly developed where significant smectite is still present. Strontium isotope results do not support alteration by orogenic fluids in this basin. The results indicate that burial diagenesis of clays is a viable remagnetization mechanism for limestones in the Vocontian Trough.

GRANTEE: The Pennsylvania State University

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GRANT: DE-FG02-96ER14634

Zeolite Thermodynamics and Kinetics

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Objectives: To measure the thermochemical properties and evaluate the kinetic factors that control dissolution, crystallization, and hydration of Na-, K-, Ca-, and Mg-zeolites in hydrothermal environments. This research is basic to understanding diagenesis, low-grade metamorphism, and alteration of sediments and volcanics as in repository behavior.

Project Description: Carried out are closed-system equilibrium and open-system kinetic experiments on purified natural zeolites. In the closed-system experiments, solubilities of zeolites are measured to about 300ºC and 200 bars on analcime and cation-exchanged clinoptilolite and mordenite. From these data, thermodynamic parameters are evaluated for Na-, K-, Ca-, and Mg-end-member and intermediate compositions at known water contents and Si/Al ratios.

Rates of congruent zeolite-water reactions are determined using a hydrothermal flow-through system, which is advantageous because reaction rates can be measured under fixed fluid composition, flow rate, temperature, and pressure. By evaluating the partitioning of water between vapor and zeolite hydration for isovolumetric systems at each temperature and pressure, data are also obtained on the degree of zeolite hydration at high temperatures at pressures near the liquid-vapor curve of pure water. This method permits kinetic evaluations of rates of reactions, such as among clinoptilolite + analcime + albite.

Results: Completed now are rate measurements for clinoptilolite-water and analcime-water reactions and on the nucleation and growth of analcime from precursor Na-clinoptilolite to about 300° C. Also solubility measurements now include data on Ca-clinoptilolite and mordenite from which thermodynamic characteristics have been extracted.

Near equilibrium, analcime dissolution rates increase with undersaturation. Farther from equilibrium, they apparently are constant, independent of saturation state. At fixed temperature and saturation state, dissolution rates vary slightly with the aqueous Si/Al ratio. The Arrhenius temperature dependence gives an apparent activation energy of 11.7±1.5 kcal/mol and an activation energy of 8.8 kcal/mol. The intensive parameters, water-vapor pressure, temperature, and degree of hydration are necessary to define equilibrium with clinoptilolite + water. The clinoptilolite hydration reaction is reversible and fast, within minutes, and, with liquid water, causes progressive dehydration with increasing temperature. From 25 to 250ºC, hydration of Na- and K-clinoptilolite decreases by about 50% along the water-vapor curve of pure water. This greatly affects the free energy of formation, which for zeolites is very dependent on the water content and on the composition of the aluminosilicate framework

Such zeolite reactions define the transition from zeolite to greenschist metamorphic regimes, and are characterized by the release of water and silica and large, negative molar volume changes. The data indicate that the reaction of clinoptilolite to anacime is favored when aqueous silica concentrations are equal to quartz saturation, and above 50°C, when saturated with cristobalite. The geologic persistence of clinoptilolite to near 175°C is attributable to slow kinetics rather than to equilibria with aqueous silica concentrations because analcime is slow to nucleate close to the clinoptilolite-analcime stability boundary although growth rates, measured separately, may be faster.

GRANTEE: The Pennsylvania State University

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Grant: DE-FG02-95ER14547.A000

Dissolution of Feldspar in the Field and Laboratory

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Objectives: In this project, three questions are being investigated concerning the dissolution of feldspar under ambient conditions: 1) What are the structures of altered layers on crystalline and glassy feldspars dissolved in the laboratory? 2) What techniques can be used to investigate near-equilibrium dissolution of feldspar? 3) How are the weathering rates of feldspar affected by internal porosity and surface coatings?

Project description: One of the most debated questions today in low-temperature geochemical kinetics centers upon the rate and mechanism of dissolution of feldspar, the most common mineral in the crust. In this project, the mechanisms of feldspar dissolution are investigated by emphasizing experiments with feldspar glass and crystal while comparing surface and solution chemistry. Surface sensitive analytical techniques (x-ray photoelectron spectroscopy, secondary ion mass spectrometry, Auger electron spectroscopy, atomic force microscopy) are used on samples reacted not only in the laboratory, but also in natural field settings. Specifically, laboratory work focuses on the structure of altered surface layers on feldspars, the rate of dissolution of feldspar crystal and glass in near-equilibrium and dilute solutions, and the presence of porosity and surface coatings on feldspars. In a complementary field project, the use of Sr concentrations and isotopic ratios are used to calculate feldspar dissolution rates.

Results: Altered layers and dissolution of crystalline and glassy albite have been investigated along with two suites of glasses with variable Na:Si:Al ratios. Rates of dissolution are a strong function of alumina content. For albite, the rate of dissolution of glass and crystal are equal within a factor of 2. Glasses of composition similar to minerals may therefore provide an excellent opportunity for investigation of the kinetics of aluminosilicate phases. Surface evolution of albite glass and crystal plates has also been studied using atomic force microscopy. Surface roughness increases during dissolution. Roughness of surfaces has also been measured by BET adsorption measurement of specific surface area (SSA) of powders. For samples showing negligible porosity (Amelia albite, San Carlos olivine), BET SSA can be calculated from, $\log (SSA) = b - m \log (d)$, where d = grain diameter, $b = 5.1 \pm 0.3$ and $m = 0.98 \pm 0.15$. For samples showing BET SSA greater than predicted by the preceding equation, SSA increased with porosity. If internal SSA contacts near-equilibrium pore solutions in natural systems, then perhaps internal area is nonreactive compared to external surface. If this is true, then the porosity in most primary silicates implies that BET surface area measurements may *overestimate* the surface area relevant for interface-limited kinetics.

GRANTEE: Purdue University

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Grant: DE-F602-93-ER14391

Effects of Micro- and Macro-Scale Interfaces on Seismic Wave Propagation in Rock and Soil

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Objectives: The objective of this proposal is to determine the effects of multi-scale heterogeneity on seismic wave propagation through soils and rocks. Specifically, we will address (1) heterogeneity within a fracture; (2) heterogeneity from multiple fractures and fracture networks; and (3) discontinuities in unconsolidated and poorly consolidated media.

Project Description: Soils and rocks are open, multiphase, biogeochemical systems that play an important role in the production of oil and gas, the maintenance of environmental quality, and the geotechnical stability of a site. They consist of solid, liquid, and gaseous phases that produce heterogeneity on multiple length scales that may vary temporally because of participation in the hydrogeologic and tectonic cycles. Because the physical heterogeneities can change in time, active monitoring techniques need to be developed for quantifying the changes in soils and rocks. Some sources of heterogeneity in soils and rocks arise from the physical structure of these media, such as pore and grain distributions, grain contacts, cracks, fractures, stratification, and laminae, as well as heterogeneity from the distribution of fluids within the structural components of these media. Achievement of the proposed research objective depends on the determination of the effect of micro-scale phenomena on macro-scale measurements through the combination of laboratory experiments and numerical analyses

Results: Experimentally measured compressional wave anisotropy caused by the presence of a single fracture and multiple parallel fractures was compared to theoretical predictions based on the displacement discontinuity theory. The comparison between the theoretically predicted transmission coefficients and the experimentally determined values enabled the inverstigation of the robustness of the displacement discontinuity theory for obliquely incident compressional waves on a single fracture and on multiple parallel fractures. The following behavior was observed which is predicted by the analytical solution for plane-wave propagation across a displacement discontinuity: (1) at high frequencies the group time delay is not as sensitive to changes in stiffness as transmitted amplitudes; (2) the transmission coefficient decreases in magnitude with increasing frequency; (3) the transmission coefficient decreases for glancing angles of incidence to the fracture; and (4) that a discontinuity in the value of the transmission coefficient should occur at the orientation when the trajectory of a wave crosses additional fractures. However, the experimental data did not match the predictions of the theory; single values of normal and tangential fracture specific stiffness could not be used to fit the transmission data for all angles of incidence for all frequencies. Further effort is needed to explore the frequency dependent fracture stiffness. If the frequency dependence gives an indication of the distribution of asperities or contact regions in a fracture, this information could be used to predict the hydraulic properties of fractures.

GRANTEE: Rensselaer Polytechnic Institute

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GRANT: FG02-94ER14432

Transport Phenomena in Fluid-Bearing Rocks

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Objectives: The goal of this project is to provide insight into the phenomena leading to geochemical transport in the Earth's crust and upper mantle in the presence of C-O-H fluids. There are two principal thrusts: 1) characterization of grain-scale permeabilities of fluid-bearing rocks whose microstructures result from protracted mineral-fluid interaction at conditions where the minerals are soluble and grain coarsening is effective; and 2) development and implementation of techniques for measuring diffusion coefficients of aqueous solutes (and mineral solubilities) at deep-crustal conditions.

Project Description: This is a multifaceted program of experimental research on the behavior and properties of aqueous fluids and the rocks that contain them at depths exceeding ~20 kilometers in the Earth. The objectives described in the preceding paragraph are pursued using solid-media, high pressure-temperature techniques developed during the initial grant period (1994-1997). The two main thrusts of the proposed work — solute diffusion and rock permeability — are viewed as complementary aspects of the problem of fluid-assisted mass transport that are important for different reasons: diffusion determines the efficacy of mass transport through a stationary fluid, and permeability controls the velocity of fluid flow in response to a given pressure gradient (mineral solubility is important in both cases because of its contribution to the total flux of dissolved material).

A conventional piston-cylinder apparatus is used to achieve the P-T conditions of interest (0.5-2.0 GPa; 500-1000°C). In the permeability studies, metal-jacketed synthetic rocks are prepared by high P-T treatment leading to near-equilibrium microstructures in the presence of aqueous fluid. After quenching and depressurization, the samples are mounted for permeability characterization at room conditions using conventional gas-flow techniques. For the diffusion and solubility measurements, specially designed diffusion cells are heated and pressurized at mid- to deep-crustal conditions. These cells are machined from solid silver and consist of two chambers (~0.05-0.1 cm^3) connected by a platinum capillary through which diffusion occurs at the experimental conditions. Diffusive transport—driven by a small difference in temperature between the two chambers—is quantified after each experiment by measuring the time-integrated mass of material transported.

Results: Efforts during the past year were directed mainly at the permeability aspects of the project in order to bring to completion a study of monomineralic quartzites and marbles containing ~0.3 - 20 volume % aqueous fluid. The principal finding is that rocks exhibiting equilibrium microstructure are remarkably well described by the Kozeny-Carman equation, $k=(d^2\phi^3)/C$, where k is permeability, d is grain diameter, ϕ is porosity or fluid fraction, and C is a constant (in our case 200). This agreement with a simple model developed for packed spheres and similar materials is somewhat anticlimactic, but it is also very satisfying in the sense that until now the exponent on ϕ (and the value of C) was unknown. Previous estimates of the exponent from models and experiments on other materials had yielded values ranging from 1 to 7. Confirmation of the cubic dependence will allow modelers of fluid flow deep in the

Earth (where equilibrium microstructure can be expected) to accurately incorporate an analytical expression for a key parameter controlling flow.

GRANTEE: Rice University

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GRANT: DE-FG03-95ER14552

Transition Metal Catalysis in the Generation of Petroleum and Natural Gas

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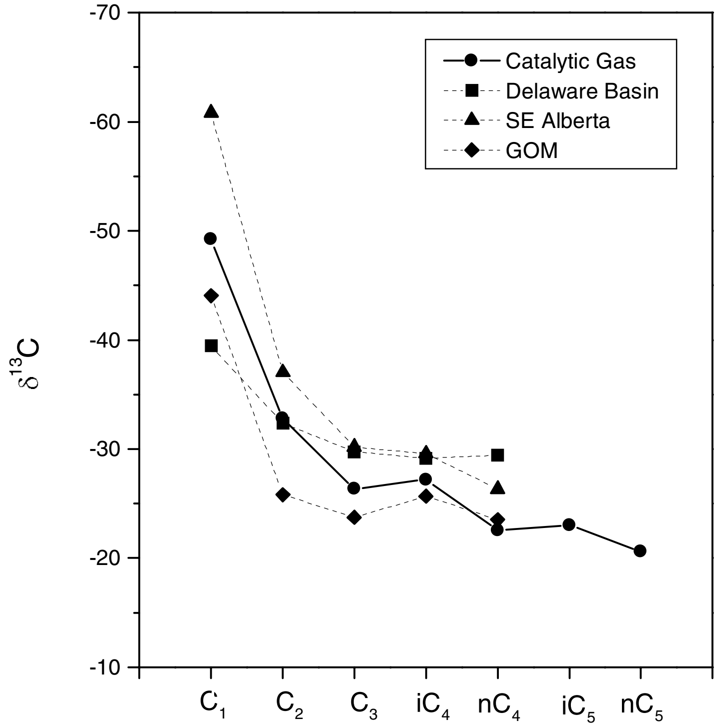
Objectives: This project started on the hypothesis that the light hydrocarbons in petroleum are formed catalytically from the transition metals in carbonaceous sedimentary rocks. The conventional view that oil and gas are the products of thermal cracking was viewed inadequate given the stability of hydrocarbons and the fact that laboratory attempts to duplicate the process had been unsuccessful. The transition metals are ubiquitous in organic sediments and could, in theory, become catalytically active during diagenesis, promoting the formation of lighter hydrocarbons and natural gas. This project's objective was to test this idea and to explore generally the catalytic properties of transition metals under realistic geologic conditions.

Project Description: Various natural sources of transition metals including the asphaltene fraction of petroleum, source rocks, and minerals (takovite and chlorite) are being analyzed for catalytic activity. Pure transition metal complexes (metal porphyrins, acetylacetonates, oxides and sulfides) are also under study. Reactions are being conducted in gas manifold systems under steady-state and batch reactor conditions and products analyzed by high-resolution gas chromatography.

Results: Crude oil is believed to be unstable in the Earth, thermally cracking to natural gas at temperatures > 150°C. Although the process (crude oil → gas) is well documented geologically, it has never received convincing support in the laboratory. Petroleum hydrocarbons are surprisingly stable and their cracking products do not resemble natural gas.

We have found crude oil to catalytically decompose to gas under mild laboratory conditions (Mango & Hightower, *Geochim. Cosmochim. Acta.* 61, 5347, 1997). Like natural gas in deep basins, it becomes progressively enriched in methane: initially 80% (wet gas) to a final composition of 100% methane (dry gas). Catalytic gas exhibits the carbon isotopic signature of natural gas (Figure) and is thus indistinguishable from natural gas. The reaction is catalyzed by transition metal oxides (V, Fe, Co, and Ni), compounds that had earlier shown activity in gas generation from olefins (Mango *et al., Nature*, 368, 535, 1994; Mango, *Org. Geochem.* 24, 977, 1996). Most crude oils contain sufficient metals to promote complete decomposition to gas at temperatures > 150°C. The key unknown is their catalytic state (active or inactive) in the subsurface. We suspect metal-clay diagenesis and the reducing conditions in reservoir rocks as the critical factors in activation.



The carbon isotopic compositions of catalytic gas (solid line), and three natural gases (dotted lines). The *Catalytic Gas* is the 4.5 hr product from: crude oil + H_2 + NiO/SiO_2, 200°C. The profiles labeled *GOM, SE Alberta,* and *Delaware Basin* are natural gases from the Gulf of Mexico, Alberta, Canada, and the Delaware Basin, respectively (James, *AAPG Bul.,* 1983).

To our knowledge, the reaction (crude oil → natural gas) is unprecedented and unexpectedly robust (Co/SiO_2 gives 0.26 g CH_4/(g Co day) at 200°C and 0.01 g CH_4/(g Co day) at 150°C) with significant implications regarding the stability of petroleum in sedimentary basins. The existence or non-existence of oil in the deep subsurface may not depend on the thermal stability of hydrocarbons as currently thought. The critical factor could be the subsurface conditions that activate transition metals and sustain the catalytic decomposition of oil to natural gas.

GRANTEE: Rutgers, The State University Of New Jersey

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GRANT: DE-FG02-97ER14755

Calorespirometry: A New Approach to Quantify Pollutant Reactions in Soil and Sediments

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Objectives: The objectives of this project are to elucidate mechanisms of abiotic degradation of key xenobiotic organic compounds in soils, and minerals and to develop a calorespirometric method coupled with spectroscopy, to measure kinetic and thermodynamic parameters for the degradation reactions.

Project Description: The monitoring and development of soil remediation technologies to restore Superfund sites are important DOE goals for this decade. Abiotic transformation of pollutants is often ignored in remediation scenarios, but nonetheless can contribute significantly to detoxification. Manganese oxides are environmentally reactive in subsurface environments as a result of their adsorptive and redox properties. They are known to catalyze the degradation of organic pollutants adsorbed to their surfaces by both redox and proton-mediated mechanisms. A variety of these minerals is being synthesized with varying specific surface areas. The reaction of the minerals with chlorinated organic compounds, such as: 2,4-D and atrazine are being investigated by calorespirometry combined withUV-visible diffuse reflectance spectroscopy, Fourier-transform infrared spectroscopy, Raman spectroscopy, electron spin resonance spectroscopy, gas chromatography-mass spectrometry and liquid chromatography, to identify and quantify the mechanisms of these interactions.

Results: Recently we have studied the abiotic degradation of atrazine adsorbed from ethyl ether solutions on synthetic δ-MnO_2 (water content $\approx$ 10%) by a developed Calorespirometric technique. We showed that the manganese surface engages the adsorbed herbicides in an oxidation-reduction reaction that produces Mn (II), CO_2 and heat; however, we could not calculate an activation energy for these reactions due to the presence of the organic solvent (ethyl ether), which caused inconsistent heat evolution during the reaction. We have overcome this limitation by developing a new method that uses light grinding of atrazine and δ-MnO_2 in the absence of a solvent. This mechanochemical approach facilitates the study of kinetic and thermodynamic parameters, such as the activation energy, E_a, of the short time surface-catalyzed degradation and facilitates a more detailed mass balance of gaseous products. We are in the process of analyzing the data obtained from light grinding of atrazine and δ-MnO_2 and plan to continue with alachlor and other compounds. From the preliminary experiments, a conventional semilog plot of the net heating rate against time shows approximately a linear plot, indicating that first order kinetics are applicable. The calculated Ea for the degradation of atrazine on δ-MnO_2 in the range of temperatures studied (10 to 50 ^{o}C) is around 12.6 kJ mol^{-1}. There is a large error associated with this value due to a change in order of the reaction at temperatures above 35 ^{o}C. Gas chromatography quantitation of headspace gases of the ground atrazine/δ-MnO_2 samples showed an accumulation of CO_2 over a 12- hour period with no changes in O_2 levels. Atomic absorption spectroscopy analysis of the methanol extracts showed that only trace amounts of Mn(II) was released during the reaction of the ground atrazine/δ-MnO_2 samples. HPLC and TLC analysis of the methanol extracts of the same reaction showed accumulation of atrazine dealkylated products: DEA, DIA and

DDA. Thus, part of the atrazine ground with δ-MnO_2 was transformed to DEA, DIA and DDA and CO_2. CO_2 was observed only as a secondary reaction after delakylation occurred. Therefore, oxygen cannot be involved in the mechanism of the dealkylation reaction. The mechanism of this interaction is a topic of continuing research.

The importance of this technique is that it facilitates the calculation of the E_a of the organic-mineral interaction. Once the E_a is known, we can then predict the thermodynamic stability of atrazine and similar compounds when adsorbed to minerals and /or soils.

GRANTEE: Scripps Institution Of Oceanography

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GRANT: DE-FG03-97ER14757

Joint Inversion of Acoustic and Induction Log Data for Enhanced Resistivity Structure

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Objectives: To combine several types of borehole logging data in order to enhance the resolution of geological structures. A connection between acoustic and electrical properties of the rock formations is sought which will allow for a joint inversion of different data types.

Project Description: We are developing inversion methods that combine several types of logging data to determine high-resolution images of the subsurface, for models in which the physical parameters vary both as a function of depth and distance from the borehole. The determination of a detailed model fitting the data is a large, nonlinear inverse problem, which can be solved most efficiently with approximate inverse methods. We will test several approximate inverse methods to explore the efficiency *versus* accuracy trade-off for each method.

We will also develop methods of combining sonic and electrical logging data to provide significantly improved resolution compared to that obtained from a single logging method. Effective medium methods will be developed to relate acoustic properties to electrical properties of the subsurface.

Results: To date, we have developed a regularized inversion code that solves for a two-dimensional (2D) conductivity model, given one or more types of induction logging data. The algorithm is based on Occam's inversion (Constable *et al.*, 1987; de Groot-Hedlin and Constable, 1990), which is approach to the regularization of nonlinear inversion problems. In this case, we introduce a penalty on the first derivative of the model (the “roughness”). The conductivity of the subsurface is represented by a model that is discretized into a large number of thin layers, each of which is split into a number of radial zones. Jacobean derivatives are computed using Doll's approximation.

The code has been written in modular form so that future additions, such as allowing for the inclusion of galvanic or acoustic logging data should be relatively simple. Currently, the code incorporates several options for any inversion. One has the option of inverting for either 1D or 2D conductivity structure. One also has the option of computing either exact forward responses, or approximate forward solutions that use a Taylor series approximation. There is also the option of initiating the inversion with a preferred model. Finally, our code is set up to handle any combination of induction data.

GRANTEE: Stanford University

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GRANT: DE-FG03-93ER14347-A007

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

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Objectives: This project concerns chemical interactions between aqueous metal ions and metal-oxide surfaces representative of those found in the Earth's crust. These “sorption” reactions partition the metal between fluid and solid and must be understood at a molecular level to develop both quantitative understanding of the geochemistry of mineral surfaces and the macroscopic models to predict the fate of contaminants in surface environments. Our objectives are (1) to characterize sorption by determining composition, molecular-scale structure, and bonding of the surface complexes using direct sorption measurements, synchrotron-based x-ray absorption fine structure (XAFS) spectroscopy and x-ray standing wave (XSW) fluorescence spectroscopy, x-ray photoelectron spectroscopy (XPS), and UV/Vis/IR spectroscopy; (2) to investigate how these properties are affected by the surface, the solution composition, simple organic ligands containing functional groups common in complex humic and fulvic substances, and time; and (3) to develop molecular-level and macroscopic models of sorption processes.

Project Description and Results: *(1) Grazing-Incidence (GI) XAFS Studies of Metal Ion Sorption Complexes on Single Crystal* α-Al_2O_3: Sorption of Zn(II) on sapphire (α-Al_2O_3) was studied with GI-XAFS both *in-situ* (in contact with bulk solution) and *ex-situ* in a humidified N_2 atmosphere. Our initial work was devoted to optimizing experimental conditions so we could examine sorbed species *in-situ*. We performed a series of metal-ion uptake experiments and GI-XAFS experiments as a function of total metal ion concentration, pH, and ionic strength. From this, we determined an optimal set of conditions for the *in-situ* experiments that precluded the aqueous Zn(II) signal from dominating the spectrum.

We have collected *in-situ* GI-XAFS spectra on Zn(II) sorbed on α-Al_2O_3 (0001) and (1-102) surfaces. Zn(II) was found to bind as an inner-sphere complex on both the (0001) and (1-102) surfaces of sapphire, most likely in a bidentate, edge-sharing geometry bound to an $Al(O,OH)_6$ octahedron, based on identification of an Al-shell at roughly 3 Å in all samples. In all cases, Zn(II) was found to transform from an octahedrally coordinated aqueous complex to a tetrahedrally coordinated surface complex. We also found that sample drying (*ex-situ* samples) led to a change in the sorption products observed, based on an increased first-shell Zn-O distance to ~2.05 Å and the presence of a strong third shell in the *ex-situ* horizontal spectra. While additional analysis is needed, it is possible that sample drying has led to a polymerization of Zn(II)-oxygen polyhedra on the surface.

Sorption products of dissolved Cu(II) on α-Al_2O_3 (0001) and (1-102) and α-SiO_2 (0001) were examined *ex-situ* after reaction of the substrate with solutions of 30 µM Cu(II) in 0.01 M $NaNO_3$, at pH 6. Fitting the measured EXAFS and Fourier transforms indicates backscattering from Al/Si atoms at 2.90-2.93 Å, which is consistent with a $Cu(II)(O,OH)_6$ bidentate (or tridentate) edge-sharing surface complex. The most important finding of the Cu(II) on sapphire work is that the extent of Cu uptake and the polarization dependence of the EXAFS spectra are different on the (0001) and (1-102) surfaces even though sorbed Cu(II) has similar local coordination environments on both surfaces.

(2) X-ray Standing Wave Studies of Zn(II), Pb(II), and SeO_4^{2-} Distributions in the EDL: Our long-period XSW studies were designed to provide quantitative information on the spatial distributions of metal ions at the metal oxide-aqueous solution. In our initial work, we investigated the distribution of Zn(II) in the electrical double layer at the α-Al_2O_3-aqueous solution interface. Comparison of XSW spectra for a 300 μM Zn(II) solution on α-Al_2O_3(1-102) under *in-situ* and *ex-situ* conditions verify that the method can easily distinguish between extreme types of distributions. Our latest experiments have focused on determining the distributions of aqueous Pb(II) and SeO_4^{2-} at the α-Al_2O_3(1-102)-solution and α-SiO_2(0001)-solution interfaces. These substrates are expected to have different charging characteristics as a function of pH [based on very different pH_{pzc} values for powdered quartz (2.9) and alumina (9.1)] and different overall reactivity for the complexation of the solution species.

(3) Effect of Organic Ligands on the Uptake of Cu(II) on Alumina: As part of a broader study of the influence of organic ligands on sorption of inorganic contaminants, we have used XAFS and attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopies to investigate the structure and binding mode of copper(II)-glutamate (glu) complexes at the γ-alumina-water interface within the range $4<pH<9$ at 300 K and 1 atm. EXAFS results for Cu(II) complexes formed at the (1-102) surface of α-Al_2O_3 in the presence of glutamic acid as a function of pH are consistent with the observed complexation behavior of Cu(II) and glutamic acid on high surface area γ-Al2O3 powders, based on powder EXAFS results. Polarization-dependent GI-XAFS spectra of Cu(II) sorption complexes in the presence of glutamic acid (30 μM Cu(II), 90 μM glutamic acid 0.01M $NaNO_3$) on the (1-102) sapphire surface were collected at pH 5.5 and 9.5. Analysis of the EXAFS spectra suggests that Cu(II) is complexed to two glutamic acid molecules through the amino acid moiety at pH 5.5. At pH 9.5 the EXAFS spectra are very similar to the spectra of Cu adsorbed at the sapphire surface in the absence of glutamic acid.

(4) Effect of Microbial Biofilm Coatings on Mineral Surfaces on Heavy Metal Uptake: Our preliminary experiments on Pb(II) and As(V) distributions in microbial biofilms were designed to determine if we could measure the distribution of Pb(II) partitioned into a biofilm grown on a single crystal surface and use GI-XAFS to obtain information on the speciation of Pb and As in the biofilms. We have collected XSW spectra for Pb(II) on α-Al_2O_3 (1-102) and (0001), α-SiO_2 (0001) and As(V) on α-Al_2O_3 (1-102) surfaces. In each case the substrate was prepared with a monolayer biofilm coating of *Burkholderia cepacia* prior to reaction of the oxide-biofilm system with CO_2-free 1-60 μM $Pb(NO_3)_2$ solutions (pH 6) or 30 μM Na_2HAsO_4 (pH 6) solution. Our results for 30 μM As(V) contrast strongly with the XSW profile obtained for 30 μM Pb(II) on biofilms on α-Al_2O_3(1-102) and demonstrate that the XSW technique will be a powerful tool for examining the partitioning of cations and oxoanions between the biofilm and the mineral surface under varying solution conditions. Modeling is in progress to determine the ion distributions in these biofilm systems.

(5) Effect of Aging on the Nature of Co(II) Sorption Complexes on Kaolinite: The length of aging time in mineral-water suspensions dramatically impacts metal ion fates. We have completed several studies of the effect of aging time on Co(II) surface complexes in a model system containing kaolinite in aqueous solution containing Co. One of our main findings in this system is strong evidence for dissolution of the kaolinite surface, which releases Al(III) and Si(IV). The Al(III) combines with Co(II) in solution forming a mixed Co(II)-Al(III)-hydrotalcite-like precipitate, which can effectively sequester Co(II) and can provide new reactive surfaces on which other metals may sorb.

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GRANT: DE-FG03-95ER14535/A000

Crosshole Seismic Attenuation Tomography and Attenuation Logging in Boreholes

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Objectives: The primary objective of this research project is to develop a methodology for estimating seismic attenuation from borehole data. Attenuation data is useful for estimating rock and fluid prooperties.

Project Description: The estimation of seismic attenuation is complicated by the fact that many acquisition and wave propagation effects influence the recorded signal amplitudes. We have developed an imaging method based on frequency shifts, *i.e.*, dispersion, where a downshift in the signal frequency of a signal wavelet is used as data for tomographic inversion. Frequency-shift data are less sensitive to the propagation effects that severely contaminate seismic amplitudes. As a result, the frequency-shift method is more robust than absolute amplitude processing or spectral ratios. Once local attenuation and velocity are known away from the borehole, they may be combined with logs and core data to obtain indirect estimates of reservoir properties such as porosity, saturation, and possibly permeability. The primary goal of our project is to attenuation imaging near and between boreholes. To that end, we have demonstrated our new methodology using seismic data recorded in crosswell and single well log geometries. The next phase of this project is to use this attenuation information to estimate the reservoir properties. The project makes extensive use of both numerical models and field data.

Results: We developed models that relate globally measured attenuation along a seismic ray path to the shift in signal frequency measured at a receiver. One model is exact for a Gaussian pulse propagating in a constant-Q medium. Other models are approximate for non-Gaussian pulses (*e.g.*, boxcar or triangular spectra) in media with power law frequency dependence. The models were first tested with synthetic data. We developed several synthetic modeling codes for different situations: (1) a one-dimensional and vertically layered visco-elastic model that is parameterized in terms of media Q's and velocities. (2) A one-dimensional layer-cake poro-elastic model based on Biot theory and parameterized with the elastic properties of the matrix materials and the fluid properties. (3) A two-dimensional poro-elastic model based on Biot theory. (4) And a one-dimensional radially stratified visco-elastic model for the sonic log and crosswell geometries. These models were used to simulate attenuation anisotropy in laminated media and dispersion caused by layer stratification around boreholes. The borehole model was also used to calculate the radiation patterns of borehole seismic sources.

We found that the frequency shifts provide a reliable means of estimating attenuation in simple media, large-scale heterogeneity. However, a single parameter is not sufficient to describe the attenuation behavior of seismic waves in complicated media where the bandwidth as well as the centroid frequency of the wavelet changes due for example to scattering. For example, near geological interfaces, the frequency shifts are overly sensitive to interference from multiples. The simulation tests clearly indicate the advantage of the crosswell geometry over the sonic log geometry because the latter experiences significant frequency dispersion due to scattering form near borehole layers such as casing and various profiles of mud invasion.

We successfully tested the frequency-shift method on field data sets recorded in a variety of geological settings, *e.g.*, carbonates, siliciclastics and chalks. The method shows good promise on high frequency field data (*e.g.*, greater than 1000 Hz) where the frequency shifts are easily detected. However, the method has difficulty with low frequency data (*e.g.*, less than about 500 Hz bandwidth) where the shifts have similar proportions but their magnitudes are small. We also developed and tested a three-dimensional version of the imaging method for use when the multiple boreholes and deviated wells.

We also tested the frequency-shift method on time-lapse data where we successfully imaged changes in attenuation and velocity associated with injected carbon dioxide. In this case, the data are the time-lapse changes if the frequency-shifts after inject of carbon dioxide. The time-lapse attenuation images suggest the paths of fluid flow, *e.g.*, changing fluid saturation, and thus provide indirect information on permeability.

The major difficulty encountered is the lack of calibration data on attenuation for the *in situ* images. That is, although we can now produce attenuation images it is not yet possible to calibrate these images because attenuation is rarely measured on rock samples in the lab and when measured it's done at ultrasonic frequencies.

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GRANT: DE-FG03-99ER14933-A001

Seismic Aignatures of Fluids in Anisotropic Rocks

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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: 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) response. Furthermore, geophysical characterization of fractured reservoirs via their elastic anisotropy is an extremely important economical problem, in particular for the continental United States. In tight formations, which can include sandstones, shales, carbonates, and coal, often the only practical means to extract fluids is by exploiting the increased drainage provided by fractures. The practical difficulties that must be overcome before effectively using these fractures include: locating the fracture zones, determining the position, orientation, spatial density, and connectivity of fractures, and characterizing the spatial relationships of fractures to other reservoir heterogeneities which might enhance or inhibit the fluid flow. In this project we are developing theoretical models to describe anisotropy in fractured media. Fluids play an important role in the anisotropy. The presence of fluids is a key interpretation problem for the oil and gas industry, in amplitude-versus-offset analysis and in fluid substitution modeling using Gassmann's equations.

Results: This project has just been recently funded and there are no results to date.

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GRANT: DE-FG03-86ER13601

Porous Rocks with Fluids: Seismic and Transport Properties

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Objectives: In this study we develop a model to simulate flow-limited diagenetic processes in porous media. In addition, we are measuring and modeling the elastic properties of gas hydrate and sediment that contains gas hydrates.

Project Description: 1. *Flow-Limited Diagenesis and Transport Properties of Porous Media Using the Lattice Boltzmann Method.* We use a model that combines a Lattice-Boltzmann flow simulation with pore filling mechanisms. After investigating the transport properties for each mechanism, we group the mechanisms into related classes and evaluate the results relative to commonly used emperical porosity-permeability relationships.

2. *Measuring and Modeling the Elastic Properties of Gas Hydrate and Sediment Containing Gas Hydrates.* Natural gas hydrates are nonstoichiometric crystalline solids comprised of a hydrogen-bonded water lattice and entrapped “guest” molecules, predominantly methane. Gas hydrate with methane as the guest species is stable at the pressure and temperature conditions present in the sediments beneath most of the world’s continental margins and deep inland seas and also in arctic sediments below the permafrost layer. Enormous amounts of methane are believed to be trapped in nature by hydrates; both in the hydrate crystal structure itself and in sediments beneath hydrate deposits. This large reservoir of natural gas may be a future energy resource and may play a significant role in global climate change. The formation of melting of gas hydrate also has a strong effect on sub-sea slope stability. Unfortunately, all distribution and hydrate-related methane estimates are very inexact because accurate estimates of the amount of methane hydrate *in situ* are not currently available on a regional or site specific basis. A remote sensing technique that can accurately assess the amount and distribution of hydrate in natural deposits is needed to improve these distribution and hydrate-related methane estimates.

The best technique for remotely probing sediments several hundred meters below the surface or beneath deep bodies of water is seismic reflection profiling. Interpreting seismic data to deduct the amount of gas hydrate in place requires a relation between the hydrate fraction in the sediments and the elastic properties of the hydrate-sediment composite.

Results: 1. *Flow-Limited Diagenesis and Transport Properties of Porous Media Using the Lattice Boltzmann Method.* Eight different pore-filling mechanisms related to the fluid flow were calculated during the evolution of pore geometry. After investigating the transport properties in each mechanism, we identified four distinct groups: 1. Grain boundary related; 2. Low-flux related; 3. High-flux related; and 4. Random filling mechanisms. The boundary related mechanism showed very good correlation with empirical relations (Kozeny-Carmen relation and Archie’s law). Because the empirical relations represent averaged relations of real data and theoretical models, the grain boundary can be regarded as a major factor in the diagenetic process of sedimentary rocks. Low-flux related mechanisms showed very small change in permeability even in latter stages of diagenetic processes. For this case, electric conductivity decreases faster than permeability. High-flux related mechanisms are the most efficient in reducing permeability. Since the pore filling starts in efficient flow paths, the flow simulation in this case is very slow to converge. One of the innovations was to change the iterative Lattice-Boltzmann algorithm of the flow simulation to a sparse matrix form. The matrix method showed better convergence in high flux related diagenetic mechanisms. Random filling showed an intermediate behavior between high-flux related and boundary related mechanisms. At early pore filling stages, the permeability decreases very rapidly, followed by a trend very similar to the boundary-related mechanism. This modeling enables us to efficiently explore the complicated relationship between fluid flow and evolving porosity for ranges of realistically complex pore geometry.

2. *Measuring and Modeling the Elastic Properties of Gas Hydrate and Sediment Containing Gas Hydrates.* To address the lack of data on the properties of gas hydrates, we first made propane hydrate in the laboratory by bubbling gas through water and water saturated sand in a clear walled pressure vessel. Propane was chosen as the hydrating gas because the pressure conditions were less stringent, making a glass pressure vessel practical. These experiments were all videotaped. They were a great success at demonstrating why there are so few elastic property measurements published in the literature. The reason is that it is relatively easy to make gas hydrate in the laboratory, but it is nearly impossible to create well-characterized, pure samples by bubbling gas through water, the traditional way of making samples. It is very difficult to drive the reaction to completion; so unreacted water and/or gas generally remain in the pressure vessel. With a research group at the SUGS in Menlo Park, we obtained very successful measurements of the compressional and shear wave speeds of pure, compacted, polycrystalline methane hydrate.

Next, we modeled the effect that gas hydrate formation would have on wave speeds through sediments, using theoretical effective-medium modeling. Based on existing models, we know that the effective elastic moduli of sediments strongly depend on the location of pore filling material within the pore space (*i.e.*, grain contact cement or suspended in the pore fluid). We apply three types of models: one in which the hydrate is suspended in the pore fluid, one in which the hydrate becomes a load-bearing component of the sediment framework and one in which the hydrate forms as a grain contact cement. The cementation model is appropriate only for high porosity sands, but the other two models are appropriate for both sands and ocean-bottom sediments. The models are tested against real world data from ODP hole 995 (methane hydrate in clay rich, high porosity ocean bottom sediments) and Northwest Eileen State Well #2 (methane hydrate in onshore, arctic sands beneath permafrost). In both cases, the data strongly suggest that gas hydrate forms as a load-bearing component of the sediment framework.

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GRANT: DE-FG03-98ER14904

Rock Physics for Seismic and SAR Characterization and Monitoring of Reservoir Fluids and Their Recovery

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Objectives: The future of geophysics includes the potential to track reservoir fluid distribution during the life of a field using periodic geophysical snapshots or time-lapse geophysical monitoring. To this end our research focuses on the advanced use of rock physics for interpreting remote measurements for accurate detection and monitoring of subsurface fluids using 2 methods: (a) seismic, both surface and borehole; and (b) differential interferometric synthetic aperture satellite radar (DInSAR) measurements.

Project Description: We are conducting analyses of experimental data to determine the variation in seismic properties as a function of pressure and water saturation. We are also exploring quantitative methods to estimate rock properties from one or more seismic observables. Finally, we are exploring the use of extracting reservoir rock properties from subsidence measurements made using synthetic aperture radar.

Results: *Seismicresearch:* Pore pressure and fluid detection from compressional and shear-wave data. By analyzing experimental data we show that in many rock-dry rocks, the Poisson's ratio (PR) decreases with differential pressure (confining minus pore pressure). In many liquid-saturated rocks, the opposite is true: PR increases with decreasing differential pressure. This means that in gas-saturated rocks, PR decreases with increasing pore pressure and in liquid-saturated rocks it increases with increasing effective pressure. We confirm the generality of the observed effect by theoretically reproducing it *via* effective medium modeling. This effect can be used as a new tool for seismic pore pressure and pore fluid monitoring during production as well as for overpressure detection from surface seismic, cross-well, sonic logs and measurements ahead of the drill bit.

Quantifying information and uncertainty of rock property estimation from seismic data. We consider quantitative methods to estimate rock properties from one or more seismic observables. We first explore well and laboratory data, as well as rock physics model parameters, and clarify the effects of rock properties on various combination s of seismic attributes. We then introduce statistical formulations of information theory and Bayes decision theory to quantitatively describe the information about rock properties carried by seismic attributes, as well as the estimation uncertainty about the rock properties. We also present a method of combining stochastic simulation and Bayes inversion for quantifying information about rock properties provided by seismic reflectivity. Finally, we explore multi component seismic data and compare how P-S converted wave data can reduce uncertainty about rock properties.

SAR research: Land subsidence over Belridge and Lost Hills oil fields, Southern California, observed by differential SAR interferometry. Land subsidence over the Belridge and Lost Hills oil fields, Southern California in 1995 and 1996, was measured using space borne interferometric synthetic aperture radar (InSAR). The detailed deformation maps clearly show that there are strong correlations between oil production and surface subsidence. However, the relation between the absolute values of oil production and surface subsidence is not linear, which indicates that besides absolute production volume, reservoir properties such as rock compressibility, permeability, fluid viscosity, are also essential factors in forming the final pattern of surface subsidence. Therefore, it may be possible to infer those reservoir properties when precise surface subsidence measurements are easily available from InSAR techniques.

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GRANT: DE-FG03-94ER14462

Development of Fracture Networks and Clusters: Their Role in Channelized Flow in Reservoirs and Aquifers

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Objectives: Prediction of the spatial distribution of permeability in subsurface aquifers and reservoirs as determined by structural heterogeneities is a challenging problem for water resources and waste management in hydrogeology and for both exploration and production in the oil and gas industry. To address this problem we are carrying out an integrated plan to map structural heterogeneities (deformation bands, joints, sheared joints, and faults) in an analogue reservoir and developing conceptual models for the evolution of these structures. Furthermore, we are studying the signature of the ancient chemically reactive flow systems within the Aztec Sandstone. The spatial distribution of chemical alteration formed from these reactive fluids reflects their flow pathways, and enables us to infer the *in situ* permeabilities of the structures with which the fluids interacted

Project Description: We are following a methodology based on documentation using detailed field mapping, analysis using FEM flow models, and mini-permeameter field measurements. This three-pronged attack is enabling us to determine: 1) the slip distribution along the fault; 2) the segmentation tendencies of a mature fault zone and variation of the gouge and fault core thickness; 3) the mechanism(s) for propagation and growth of the fault; 4) the distribution of the secondary fractures along the entire fault; 5) the relationship between alteration fronts and head contours or the water table; 6) the differences between subsurface (*in situ*) hydraulic properties and surface (present day) properties; 7) the nature and physical mechanisms of conductivity enhancement or degradation during shearing of joints; 8) the effect of joint connectivity on flow localization; and 9) the integrated effect of joints, sheared joints, deformation bands, and faults on bulk permeability anisotropy of the Aztec Sandstone.

Results: *(1) Fault Development from Localized Shearing of Joint Zones:* We documented the structural evolution of a class of faults formed by localization of shear strain along pre-existing zones of joints in sandstone as a function of slip magnitude and initial conditions. The initial joint zones occur as planar sub-parallel arrays of closely spaced joints in echelon arrangements. Subsequent shearing of these zones results in formation of heterogeneous structures composed of a damaged core and a hierarchy of secondary fractures. Fragmentation within the fault core occurs at different scales; at the microscopic scale it is due to frictional sliding along sheared joints. At the macroscopic scale it occurs through intersection of sheared joints and secondary splay fractures produced by shearing. As slip accumulates, strain localization produces a through-going damaged core within which mean fragment size and porosity are reduced. The fracture hierarchy formed within the core and in the fault periphery is produced by an iterative process of shearing of joints forming splay fractures, which are later sheared forming a new generation of joints. The style of deformation and fault architecture are controlled by the original joint zone geometry.

(2) Fluid Flow in Fractured Sandstone: We have two major results to report in this category:
(2.1) Joint and deformation band permeability: Joints and deformation bands are structural heterogeneities that can strongly influence the spatial distribution and magnitude of fluid flow through a deformed rock mass. The perspective offered here provides a unifying conceptual framework for analyzing and interpreting the influence of joints and deformation bands on groundwater flow paths in porous sandstone. Fluid flow through joints can be represented by an equivalent porous media (EPM), conceptually replacing viscous drag of fluids on the fracture walls with a macroscopic flow law through granular material. This representation preserves volumetric flow rates, average fluid velocity, and joint geometry while allowing for exchange of fluid with a permeable matrix and for flow directions that do not parallel the joint trace. We propose a modification of the EPM model that adds an irreducible flow rate equal to the unperturbed matrix flow rate at small fracture apertures. Using this modified EPM model, joint aperture can be directly converted to a joint permeability and both the direction and magnitude of fluid flow through a joint in a permeable matrix can be predicted from Darcy's Law. Deformation bands are zones of grain size reduction whose influence on flow can also be described by Darcy's Law. Representing joints with the modified EPM model results in a mathematically consistent hydraulic continuum between joints and deformation bands, with joints as zones of increased permeability and deformation bands as zones of decreased permeability. Fluid flow in and around both features can be represented with a single unifying equation, and models of fluid flow pathways can be extended to cover both kinds of structures.

Joints and deformation bands produce characteristic perturbations in the flow field. Joints display low hydraulic gradients along their length and steep gradients in the matrix near their tips. In comparison, deformation bands have steep hydraulic gradients within the band and lower gradients in the adjacent matrix. Finite element simulations of fluid flow through discrete fracture systems based on field observations from the Aztec Sandstone indicate that increasing fracture permeability or decreasing deformation band permeability both lead to increased localization of flow paths.

(2.2) Fault zone permeability: This work produced conceptual models for fault zone growth based on an understanding of the deformation processes involved and the fault zone architecture. Though heterogeneous, these faults are all composed of various combinations of joints, sheared joints, and fault rock, which are their fundamental structural elements. Fault permeability is assessed through determination of the permeability of each of these elements. Effective block permeabilities for a fault zone are determined using numerical fluid flow simulation. A detailed fault map of the principle structural elements is compiled then discretized into representative sized blocks. Joints are modeled as thin, highly permeable inclusions using a cubic flow law assumption to estimate joint permeability. Matrix, gouge, and sheared joint permeabilities are obtained through digital image analysis of samples and Kozeny-Carman based petrophysical relations between porosity, grain size, and permeability. A finite difference solution of the heterogeneous/anisotropic fluid flow equation with constant boundary conditions is used to estimate the fault normal and fault parallel components of the effective permeability tensor. Results indicate that formation of a low permeability barrier along the damaged fault core restricts fault normal flow as slip increases; high permeability conduits may develop in the fault periphery due to increased joint density with increasing slip magnitude. In general increasing slip is correlated to decreasing fault normal permeability and increasing fault parallel permeability.

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GRANT: DE-FG05-95ER14497

Development of Laser-Based Resonance Ionization Techniques for ^{81}Kr and ^{85}Kr in the Geosciences, II

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Objectives: (1) Bring into operation a new analytical methodology for ^{81}Kr and ^{85}Kr, (2) identify performance limitations and implement improvements in reproducibility, accuracy, throughput and sample size, and (3) initiate research in the geosciences.

Project Description: Cosmogenic ^{81}Kr (2.3×10^5 year half-life; 20,000 to 1,000,000 year dating range) and anthropogenic ^{85}Kr (10.8 year half-life; 0.1 to 40 year dating range) are potentially useful for aiding our understanding of processes in the environment, including dating of polar ice and very old ground water, ocean circulation, and modern water flow patterns. Their chemical inertness should simplify interpretation of results. The only ^{81}Kr measurements from natural samples to date are a handful of results from old groundwater and polar ice using the laser-based analytical technique under development here, although a few measurements of ^{85}Kr from 200 liter water samples using decay counting have been demonstrated. This new technique should permit ^{85}Kr measurements using only 1- to 5-liter samples and ^{81}Kr measurements from 10- to 20-liter samples. It is a multi-step process involving: (1) degassing of the water sample; (2) separating Kr from the recovered gas; (3 & 4) two isotopic enrichments reducing interfering isotopes by $>10^8$; and (5) detecting the rare isotope in a time-of-flight mass spectrometer. The sensitivity, element specificity, and immunity to isobaric interference of resonance ionization (100 ^{85}Kr atom detection limit) are utilized to detect the few thousand analyte atoms remaining in the sample.

Results: During this fiscal year, progress on instrumentation was primarily on steps (3), (4) and (5). The reduced dispersion of the first enrichment system [step (3)] permits monitoring a stable isotope, (^{80}Kr during ^{85}Kr enrichments; ^{86}Kr during ^{81}Kr enrichments) which significantly improves quantitation. Two movable Faraday cups were designed and installed for this. Tests of the redesigned sample collector, Faraday cup, and detector assembly of the second enrichment system [step (4)] solved earlier inconsistencies in sample collection efficiency. This eliminated an empirically derived (and variable) "fudge factor," dramatically improving quantitation of this historically troublesome step. Although delivery of the new laser system was scheduled for November 1997, delays in the completion of the Science and Engineering Research Building on the main campus, and staff turnover at the laser manufacturer, resulted in spring 1998 delivery, and acceptance only by September 1998.

In addition to the collaboration established earlier with the Waterloo Centre for Groundwater Research, Ontario, collaboration was established with the Ground Water Institute of the University of Memphis. From information in their data bank and recent tritium data, a site was selected at the Shelby County Landfill where follow-on ^{85}Kr measurements would be valuable in confirming suspected "windows" in the confining layer of the Memphis Sand Aquifer, a potential contamination pathway to this major regional water resource.

GRANTEE: Temple University

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GRANT: DEFG029ER14644

Surface Chemistry of Pyrite: An Interdisciplinary Approach

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Objectives: The primary goal of this research program is to understand the microscopic aspects of pyrite oxidation. Determining the charge development on pyrite surfaces and evaluating the interaction of the pyrite surface with an array of simple inorganic and organic molecules are the immediate goals. Through a combination of macroscopic observations and observations at the atomic/molecular level new insights are gained that will lead to a better understanding how pyrite reacts in a range of chemical environments.

Project Description: The charge development, interaction with inorganic and organic constituents, and the reactivity of pyrite are being investigated. Emphasis is placed on integrating macroscopic information from low-temperature techniques such as electrophoresis and microscopic information from modern surface science techniques that are used in the ultra high vacuum (UHV) environment. Using model, atomically clean "as-grown" surfaces of pyrite, electron spectroscopies in UHV are used to understand the atomic composition and the nature of the functional groups on pyrite after exposure to the aqueous solutions. The integration of the UHV and low-temperature studies will provide a complete picture of the type of surface functional groups at the pyrite surface, their acid-base behavior, and interaction with selected aqueous constituents.

Results: In the second year of this project our studies have concentrated on using advanced surface science probes to study the surface reactivity of pyrite. In our prior funding cycle, we obtained aqueous-based electrophoresis results in a variety of environments. The present funding cycle is geared to produce a molecular-level understanding of pyrite surface reactivity that can be used in part to understand these prior results.

Reactivity of the (100) crystallographic plane of FeS_2 in oxidizing environments:
XPS in conjunction with a newly constructed high-pressure reaction cell has been used to investigate the reactivity of {100} planes of pyrite in gaseous and aqueous H_2O, O_2, and H_2O/O_2 environments. These studies have shown the exposure of $FeS_2(100)$ to a H_2O/O_2 mixture produces more oxidation then the sum of the individual activities of pyrite after exposure to pure H_2O or O_2. Only after exposure to H_2O/O_2 environments, does the disulfide group of pyrite become oxidized. It is believed that the adsorption of O_2 in the H_2O/O_2 environment results in the formation of Fe^{3+} via an electron transfer step. These Fe^{3+} sites provide dissociation sites for H_2O. When H_2O is present alone, oxidation of $FeS_2(100)$ occurs solely at surface imperfections that most likely contain a small amount of Fe^{3+} in addition to FeS like sites. Reaction is limited to these regions, since there is a limited concentration of Fe^{3+} and O_2 is not present to produce more of these active sites.

Reactivity of the (111) crystallographic plane of FeS_2 in oxidizing environments:
Further experiments have started to investigate the structure sensitivity of pyrite oxidation. These

studies have looked at the reactivity of {111} planes of pyrite. In contrast to the behavior of $H_2O/FeS_2(100)$, the (111) plane undergoes significant oxidation in the pure H_2O environment. Furthermore, exposure of this crystal plane to a mixture of H_2O and O_2 results in more iron and sulfur oxide product than on the (100) plane under similar conditions.

GRANTEE: Texas A&M University

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GRANT: DE-FG03-ER14887

Fluid-Assisted Compaction and Deformation of Reservoir Lithologies

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Objectives: This research addresses the volumetric creep compaction, chemical reaction processes, and distortional deformation of fine-grained quartz aggregates and quartz-clay mixtures subjected to aqueous fluids at temperatures, effective pressures and stress states representative of diagenetic conditions. Specific goals include 1) determination of the transition from isochemical brittle deformation to fluid-assisted solution-transfer creep, 2) identification of the mechanisms of solution-transfer creep, and 3) evaluation of mechanical and chemical rate laws for clastic reservoir lithologies.

Project Description: The compaction and diagenesis of sandstones that form reservoirs to hydrocarbons depend on mechanical compaction processes, fluid flow at local and regional scales, and chemical processes of dissolution, precipitation and diffusional solution transport. Using an experimental approach, the rates of compaction and distortional deformation of quartz and quartz-clay aggregates exposed to reactive aqueous fluids at varying stress states are under investigation. Pore fluid compositions and reaction rates during deformation are measured and compared with creep rates, and acoustic emissions and microstructures of specimens are used to determine the contributions of mechanical and chemical processes to deformation and pore-structure evolution.

Results: Short-term hydrostatic compaction experiments on sand specimens performed at room temperature and confining pressures P_c of up to 260 MPa while maintaining a constant pore pressure P_p of 10 MPa exhibit subtle inflection points in effective pressure-volumetric strain curves associated with grain failure by Hertzian cracking. From the grain sizes of these specimens and inferred starting porosities, our results are in satisfactory agreement with previous determinations of critical P^* values for unconsolidated sand and glass spheres of comparable $f \cdot R$ (where f is porosity and R is the grain radius). Sand specimens subjected to effective pressures (34.5 MPa) well below P_e^* at a temperature of 150°C exhibit slow creep compaction. One specimen of St Peter sand was loaded without any pore fluid present, and it exhibits early transient compaction qualitatively similar to transient creep observed for fluid-saturated samples, though creep rates drop to such low values that they challenge our ability to measure them.

In all other long-term compaction experiments, distilled water was introduced at one end of the specimen at a pore pressure of 12.4 MPa and silica was measured in pore fluid exiting the opposite specimen end at a rate of ~0.12 ml/hr. SiO_2 concentrations of fluids exiting samples at $P_e = 0$ are very close to the equilibrium solubility at P_p while those at $P_e = 34.5$ MPa are 5-10% greater. Comparisons between rates of dissolved SiO_2 loss and creep rates for St. Peter sand specimens suggest that volumetric strains of these samples can be accounted for almost entirely by silica loss and grain convergence, assuming that dissolution occurs only at grain contacts and that internal precipitation is negligible.

GRANTEE: University Of Texas

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GRANT NO.: DE-FG03-97ER14812

High-Resolution Temporal Variations in Groundwater Chemistry: Tracing the Links Between Climate, Hydrology, and Element Mobility in the Vadose Zone.

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Objectives: To evaluate the extent to which radiogenic and stable isotopic and trace element variations in speleothems and modern groundwater from the same aquifer provide a means to reconstruct temporal changes in groundwater geochemistry, flow routes, and corresponding climatic controlling processes.

Project Description: This study is using cave calcite deposits (speleothems) and modern groundwater samples to develop a new approach, integrating Sr, Nd, C, O, H and U-series isotope variations with other geochemical and hydrologic tracing tools, to provide 1) improved sensitivity in reconstructing temporal records of groundwater evolution, and 2) a new perspective on the links between climate variability, hydrology, soil evolution, and groundwater chemistry. An understanding of controls on the modern hydrologic system provides a framework within which to interpret the speleothem record. Groundwater, soils, rainfall, speleothem and aquifer rocks are sampled in selected catchments using low-contamination procedures, and analyzed by mass spectrometry. Two karst aquifers were selected for intensive study to achieve the aims of this project. The results are presented below for each aquifer.

Results: *Barbados, W. I. aquifer*: Part of this research effort deals with the use of different methods of estimating recharge and inferring the spatial and seasonal distribution of recharge to the Pleistocene limestone aquifer on Barbados. A new method has been developed to estimate recharge based on oxygen isotope variations in rainwater and groundwater. Significantly, inter-annual recharge variations indicate that recharge is dependent on the distribution of rainfall throughout the year rather than total annual rainfall. Consequently, a year when rainfall occurs primarily during the peak wet season months (August through November) may have more recharge than a year when rainfall is more evenly distributed through the year. Isotopic mass balance indicates that monthly rainfall less than 195 mm will all be taken up by evapotranspiration. These results lay important groundwork for analysis of rainfall/recharge variations over different time scales based on isotopic records under construction from Barbados speleothems from the same aquifer.

Edwards aquifer, Texas: We have established a sampling and analysis program for speleothem, water, rock and soil samples from ten caves across the region. This regional sampling is designed to address an issue of long-standing importance in the application of speleothems to studies of paleoclimate: Do speleothem records preserve local variations in the hydrology of individual caves, or do they preserve regional climatic signals? Reconnaissance geochronologic analyses demonstrated a total period of record available in the speleothem samples from the present back to approximately 350,000 years. Based on these analyses, construction has begun of a detailed and precise chronologic and stable isotope sequence for selected samples that cover key time intervals, including transitions into and out of the glacial maximum periods that occurred at 60 and 18 ka.

GRANTEE: University Of Texas

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GRANT: DE-FG03-96ER14596

Integrated 3-D Ground-penetrating Radar, Outcrop, and Borehole Data Applied to Reservoir Characterization and Flow Simulation

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Objectives: 3-D ground-penetrating radar (GPR) is used for characterization of the geometry of a clastic hydrocarbon reservoir analog. Sedimentologic mapping and porosity and permeability measurements from core plugs extracted from cliff-faces and boreholes allow population of the model with realistic flow parameters. The final step is 3-D flow simulation through the model to evaluate the effects of flow barriers and baffles to hydrocarbon production.

Project Description: Existing reservoir models are based on 2-D outcrop studies; their 3-D apsects are inferred from correlation between well data, and so are inadequately constrained for reservoir simulations. Field study sites are in the Cretaceous Ferron Sandstone in Utah. Detailed sedimentary facies maps of cliff faces define the geometry and distribution of reservior flow units, barriers, and baffles at the outcrop. High-resolution 3-D ground-penetrating radar (GPR) images extends these reservoir characteristics into 3-D, to allow development of realistic 3-D reservoir models. Models use geometrical information from the mapping and the GPR data, petrophysical data from surface and cliff-face outcrops, lab analyses of outcrop and core samples, and petrography. Flow simulation in the final models will illustrate the applicability of reservoir analog studies to well siting and reservoir engineering for maximization of hydrocarbon production.

Results: The focus of activity in this first project year was data acquisition. Data acquired included: measurements of topography of the surface and cliff-faces; photomosaics; mapping of major bounding surfaces of the architecural elements and their internal features; stratgraphic and gamma ray sections; core plug profiles; continuous coring of four 16-meter holes; permeability measurements; 2-D GPR data (on a 450 x 650 m grid); and 3-D GPR data on two (30 x 27 m and 30 x 51 m) grids.

A new and unique aspect of the project is that most of the geologic mapping and all of the topographic mapping is being done digitally in the field in real time using global positioning systems (GPS), and reflectorless laser rangefinders.

Preliminary results indicate the existance of four main architectural elements, which, from bottom to top are (1) low-sinuosity bedload dominated fluvial, (2) high-sinuosity tidally influenced fluvial, (3) estuarine, and finally, (4) tidal.

GRANTEE: University Of Texas

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GRANT: DE-FG03-97ER14772

Thermohaline Convection in The Gulf of Mexico Sedimentary Basin, South Texas

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Objectives: The objectives of this study are: 1) to evaluate if observed heat flow anomalies in the Gulf of Mexico sedimentary basin, if reconfirmed by extensive data analysis, can be accounted for by conduction alone or if convection is a significant perturbing factor; 2) to determine if the present potential field is amenable to convection hypotheses; and 3) to develop fluid and heat flux histories compatible with both compiled and newly collected data.

Project Description: In order to test the hypotheses posed to address the objectives stated above, we have compiled an extensive data base of fluid pressures, water chemistries, and formation temperatures from industrial data services, state well records, and the published literature; installed these data on a G.I.S. for analysis; analyzed selected drill cores and cuttings for their mineralogy; obtained samples from which we have collected thermal conductivity, radiogenic heat production, and porosity/bulk density data; analyzed several major commercial and governmental computer codes for possible utilization; and written several codes to simulate heat conduction and analyze the propensity for free convection. We are presently continuing to collect thermal property data; validating the temperature and pressure data to infer predevelop-ment conditions; calculating areal buoyancy gradients; and implementing a 2-D/3-D model to simulate the study area's temperatures and pressures.

Results: Over 25,000 data points, reflecting basin pressures and temperatures at depths of up to nearly 5 kilometres (over 16,000 feet) have been assembled for the study area. Analysis of these data reconfirmed the thermal anomalies discerned from earlier, much smaller databases. The pressure data reveal that petroleum production has created significant depressurization that extends beyond the immediate petroleum reservoirs. This has implications for regional subsidence trends and in the analysis of predevelopment fluid potentials. The much more sparse water chemistry data reveal several areas with significant buoyancy gradients. The collected thermal property data yielded several interesting results. First, radiogenic heat production, although small, is significant and should be accounted for in simulation models. Secondly, sandstone and muddy sandstone thermal conductivities correlate well with the quartz content and poorly with porosity, although porosity is the variable that has been utilized in most previous models. The analysis of shale cuttings indicated significant shrinkage; laboratory measurements of shale thermal conductivity, porosity, and bulk density may be suspect. Preliminary numerical modeling to date, which uses the real data as produced, indicate that convection is a significant factor in geological time for regional scale heat transport.

GRANTEE: University Of Utah

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GRANT: DE-FG03-93ER14313

High Resolution Imaging of Electrical Conductivity using Low-Frequency Electromagnetic Fields

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Objectives: The project seeks to determine means of increasing the resolution of low frequency electromagnetic techniques by means of an optimal use of *a-priori* information

Project Description: The research concentrates on enhancing the resolution of EM probing without sacrificing depth of investigation through better understanding the nature of the EM response and its relationship with other sources of geological information. This is accomplished through:

1) Improvement of Modeling Algorithms.
Forward and inverse modeling algorithms of increasing power and versatility permit subtle data features to be modelled, thus increasing the amount of resolution provided by a given data set.

2) Knowledge Adaptive EM Survey Design.
EM experimental design should use the known conductivity structure to optimize resolution of the unknown target. Borehole information, baseline data, or hypothesized structure can all be used to optimize source waveforms, array weighting, or array phasing.

3) Solution Space Characterization.
Geophysical targets should be refined as much as possible using independent geological or engineering information.

Results: *Improvement of Modeling Algorithms.*
References [3] and [4] discuss the adaptation of FDTD techniques to modeling a geophysical situation in which high conductivity contrasts are encountered. Such could be used to model situations where EM probing is executed in the presence of metallic objects.

Knowledge Adaptive EM Survey Design.
Reference [1] discusses the extension of adaptive focussing theory to the EM inversion problem. In particular, optimal sources give optimal gradient directions for imaging. Reference [2} demonstrates EM focussing for delineation of a conductive target.

Solution Space Characterization.
Reference [5] demonstrates that for a composite of two materials of known complex conductivities, a hierarchy of inverse bounds is available. These bounds can form the basis of a random material inversion.

References:

[1] Cherkaeva, E. and Tripp, A.C., 1998, Optimized sources in the inverse electromagnetics problem: PIERS 98.

[2] Furse, C., Johnson, D., Tripp, A.C., and Cherkaeva, E., 1998, Optimization of a cross-borehole prospecting technique for delineation of buried conductive ore deposits in a resistive host: IEEE Antennas and Propagation Summer Symposium

[3] Johnson, D., Furse, C., and Tripp, A.C., 1998, FDTD modeling of the borehole EM response of a conductive ore deposit in a lossy dielectric: presented at the 68th Annual SEG conference.

[4] Furse, D., Johnson, D., and Tripp, A.C., 1998, Application of the FDTD method to geophysical simulations: invited column (*Advances in CEM*, ed. M. Piket-May), Applied Computational Electromagnetics Society Newsletter.

[5] Tripp, A.C., Cherkaeva, E., and Hulen, J., 1998, Bounds on the complex conductivity of geophysical mixtures: *Geophysical Prospecting*, v. 46, issue 6, p. 589 - 601.

GRANTEE: Utah State University

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GRANT: DE-FG03-98ER14851

Big Hole Drilling Project: Characterization of Fault Zone Properties from *In-Situ* Analyses

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Objectives: We examine the *in situ* hydraulic properties of faulted sandstones to evaluate the impacts such faults have on the subsurface fluid flow regimes. We use our data to develop stochastic models to predict the spatial distribution of faults, and to establish methods for extrapolation of the permeability architecture of faulted rocks.

Project Description: We examine the hydraulic properties of the well-exposed Bighole in central Utah. We have completed the second year in a 3-year project funded primarily by the U.S. Department of Energy (DOE). Auxiliary funds contributed by a group of corporate sponsors for this first year of work (Phase I) enabled us both to obtain the DOE funding and to enhance the project so that the results would be of greater value to the petroleum industry. We drilled five core holes through the fault zone, collected geophysical logs from all core holes, logged the core, performed mini-permeameter, whole-core and in-situ hydraulic tests of rocks in and around the fault zone.

Results: We drilled five core holes through the fault, collected geophysical logs from all core holes, and logged the core in the field. The five holes yielded a total continuously cored length of nearly 400 meters (1300 ft). A comprehensive suite of geophysical logs run in the holes includes sonic, resistivity, gamma ray, deviation, density, neutron, acoustic televiewer, caliper and SP. Preliminary interpretation of the geophysical logs is complete and shows interesting relationships between geophysical signatures and the faulted rocks. The drill core has yielded detailed core logs, structural analysis results and core photographs. Mini-permeameter testing and whole-core (2.5 in and 1.0 in diameter) permeability/porosity/density testing is under way. Test results, geophysical data, core information and a structural analysis of faults in the core will be included in the Phase I final report. The holes were drilled at two sites: the "tip" site, where extrapolation of Shipton's fault displacement data suggests a dip-slip displacement of 2 to 3 m, and the site where 8 m of dip slip can be measured in the outcrop ("the 8 m site"). Core recovery from the five holes was very good to excellent. Most importantly, recovery of fault zone materials (regions approximately 40 to 60 feet [12 to 18 m] long in each hole) was very good to excellent. Intact core was obtained from the central fault core, subsidiary faults and the regions where the borehole log signatures suggest the presence of fault-affected rocks over distances of several tens of feet. All core was oriented, and the orientation of the structures in the core has been measured.

GRANTEE: Utah State University

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GRANT: DE-FG03-95ER14526

Growth of Faults and Scaling of Fault Structure

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Objectives: We extended our prior research on the three-dimensional structure of small faults in crystalline rock to examine how faults grow in three-dimensions; to systematically examine the mechanics and geometries of faults a few meters to a few kilometers long. We use this knowledge to develop physically based stochastic models for predicting the geometry of faults over a wide range of scale, and for analyzing their hydraulic behavior.

Project description: To achieve these objectives, we documented the geometry and slip distribution of small faults, and compare those attributes to those of small faults to assess how fault geometry and slip distribution scale. We also documented and compared the style and extent of deformation near the ends of strike-slip faults and normal faults that range in length from several meters to several kilometers to assess how fault tip deformation scales. The structure near the ends of small faults resembles the structure where small faults are linked, and we expect information on the structure near the ends of large faults will provide insight into how linkages develop along large faults and how these linkages change with scale. Finally, we compare the style and extent of deformation near the ends of small faults and large faults with that predicted by elasticity theory and cohesive zone theory.

Results: Analyses of structure and microstructures of small faults with 10 cm to 50+ m of slip in the Sierra Nevada Range, California, when compared to microstructures of the San Gabriel and Punchbowl faults, southern California are remarkably similar. The primary difference is that the fault cores of the latter faults are 10-20 cm thick; however, at the thin-section scale many of the microstructures and deformation mechanisms are the same. This similarity across such a wide range of slip suggests that the deformation mechanisms responsible for slip localization develop very early in the fault history, and may continue to operate along extremely narrow surfaces over the history of the fault. Models for fault growth thus should emphasize the mechanics of linkage of faults, as the dominant processes of slip along an individual fault may be set in at the very early stages of fault development. The three-dimensional structure of the faults can be inferred by mapping of numerous small faults, and we show that the small faults consist of a starter elliptical crack that propagated at its tips by slip along curved splays. Irregular displacement profiles along the faults suggests that faults up to 200 m long may grown in patches, with non-uniform slip distribution across the fault.

GRANTEE: Virginia Polytechnic Institute & State University

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GRANT: DE-FG05-89ER14065

Experimental Studies in the System H_2O-CH_4-"Petroleum"-Salt Using Synthetic Fluid Inclusions

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Objectives: The objective of this project is to experimentally determine the pressure-volume-temperature-composition (PVTX) relationships of fluids in the C-O-H-NaCl system over the complete range of PTX conditions encountered in crustal energy, resource, and waste-related environments. These data are used to develop equations of state to predict the behavior of these fluids in crustal rocks and to interpret results obtained from natural fluid inclusions.

Project Description: Volumetric (PVT) data provide the fundamental information needed to understand the physical and chemical behavior of fluids in energy, resource and waste-related environments. Further, these data represent the basis for developing and testing empirical or theoretical equations of state to predict the thermodynamic properties of fluids over crustal PTX conditions. In this study the PVTX properties of fluids in the C-O-H-NaCl system are being experimentally determined using the synthetic fluid inclusion technique. With this technique, fluids of known composition are trapped as inclusions by healing fractures in quartz at known temperatures and pressures. Recent efforts have focused on fluids representing the H_2O-CH_4-NaCl system. Phase relations and P-T locations of isochores in the H_2O-CH_4-NaCl system are obtained by observing the temperatures and modes of homogenization of the synthetic fluid inclusions during subsequent heating and cooling experiments in a fluid inclusion stage mounted on a petrographic microscope.

Results: During FY98 a technique was developed to produce synthetic fluid inclusions containing known concentrations of methane. Aluminum carbide and water in known amounts are added to platinum capsules and sealed with an arc welder. When loaded into an autoclave and heated, the aluminum carbide reacts with water to produce methane and aluminum oxide.

These synthetic inclusions with known water-methane compositions were used to develop a technique for determining the compositions of natural methane-bearing aqueous fluid inclusions, based on the Raman spectra obtained at homogenization to a one-phase fluid. The Raman spectra of synthetic fluid inclusions were obtained using a Dilor XY microprobe equipped with a 5-watt argon-ion laser. The ratio of the areas under the methane and water peaks were determined, and this ratio was related to the known methane concentration to develop an empirical equation that can be used to determine compositions of natural inclusions from hydrocarbon reservoirs. The equation is valid for methane concentrations greater than about 500 ppm, and over the temperature range from ambient to 350°C and pressures up to about 200 MPa.

GRANTEE: University Of Washington

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GRANT: DE EG03-97ER-14781

Electromagnetic Imaging of Fluids in the San Andreas Fault

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Objectives: To obtain high-resolution images of the electrical resistivity of the San Andreas fault (SAF) zone. This will permit the fault zone architecture and fluid distribution to be constrained.

Project description: There is increasing evidence that fluids may play a significant role in the earthquake rupture process. However, the difficulty of directly observing fluids in active fault zones currently limits progress in understanding these processes. Magnetotelluric (MT) data collected in 1994 at Parkfield and Carrizo Plain showed that the fault zone at these locations has very different electrical structure.

To further examine how these differences might be related to fault zone seismicity, a two-phase program of MT data acquisition and interpretation is being undertaken. In the first phase, data will be collected on additional profiles across the SAF at Middle Mountain, Parkfield to obtain a three-dimensional image of the electrical resistivity in this area. In the second phase, a three-dimensional survey of the central creeping section of the SAF near Hollister will be undertaken. These surveys will allow the distribution of fluids within the fault zone to be determined, and to show how these distributions vary between segments with different seismic behavior.

Results: Magnetotelluric data were collected during October 1997 in the Parkfield area. This included two densely sampled profiles that crossed the fault zone on Middle Mountain, and more widely spaced sites to constrain both the deeper fault zone structure and the regional structure. The combined 1994 and 1997 data were then inverted. The resulting resistivity models indicate that the low resistivity wedge that was observed close to the 1966 epicenter is present along the entire length of Middle Mountain. This feature is interpreted as being a damaged zone saturated with saline ground water. The base of this wedge is at a depth of approximately 3 km and corresponds with the depth at which microseismicity begins. The data are inconsistent with a low resistivity fault that extends all the way through the upper crust. The resistivity models for the San Andreas Fault on Middle Mountain have been used to determine the optimal location for deep scientific drilling into the SAF at this location. Magnetotelluric data were also collected on a profile across the San Andreas Fault in the Cholame Valley, near the en echelon offset. The shallow sedimentary basin was well imaged and observed to deepen to the west. In contrast to Middle Mountain, no low resistivity wedge was detected in the fault zone at this location.

GRANTEE: University Of Wisconsin

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GRANT: DE-FG02-93ER14328

Comparative Studies of Physiochemically and Biologically Mediated Reactions at Mineral Surfaces

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Objectives: The goal of this research is to identify and quantify the microbial contributions to rates and mechanisms of weathering reactions at interfaces between organisms and minerals. Specifically, we are testing the hypothesis that both small organic molecules and extracellular polymers can substantially influence both silicate dissolution rates and secondary mineral formation.

Project Description: This work builds on a model for microbe-mineral interactions developed by high-resolution characterization of the intact interface between communities of microorganisms (the lichen-rock association) and mineral surfaces. Initial studies defined a series of zones in which distinct processes operate over millimeter to sub-millimeter distances. Our research includes experiments designed to quantify phenomena in each of these zones. Firstly, confocal scanning laser microscopy (CSLM) was used to quantify the extent to which microorganisms can modify the pH of their environments. Experiments were then conducted with a variety of minerals, in the presence or absence of cells or organic molecules, to measure the magnitudes of the effects. Secondly, cryogenic field-emission scanning electron microscopy (FESEM) of high pressure frozen samples was used to define the association between microbes, cell surface polymers, and primary and secondary minerals. Dissolution experiments were then conducted to measure effects of polymers in association with dissolving minerals. Energy-filtered transmission electron microscopy (EFTEM) and electron energy loss spectroscopic (EELS) imaging are used to map element distribution patterns on the few nanometer scale.

Results: Measurement of pH gradients within micron-wide microbially colonized fractures that showed that solution pH can be depressed by up to 3-4 units relative to bulk solution. Consequently, experiments on the weathering of apatite, as well as biotite and feldspar, were conducted. The effects of specific organic acids and natural byproducts of microbial growth on release of ions were measured. A compilation of two years worth of experimental results indicates that mineral weathering rates may be accelerated by up to about two orders of magnitude. Apatite dissolution reactions are important because they are the primary means by which phosphate is supplied to the biosphere. Results confirmed that the primary control is proton activity, but that organic molecules can also modulate rates by up to an order of magnitude, especially at near-neutral pH. The distribution of extracellular polymers on mineral surfaces was characterized by high-resolution electron microscopic methods that ensure preservation of hydrated materials. Experiments using model polysaccharides demonstrated inhibition or acceleration of dissolution rates by up to three orders of magnitude, depending upon solution pH. Solution chemical data implied retention of Al relative to Si. This is attributed to selective binding of Al by polymers. Because this may represent the first stage of polymer-mediated clay crystallization, we conducted additional studies on the role of organic molecules in clay formation under laboratory conditions.

GRANTEE: University Of Wisconsin

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GRANT: DE-FGO2-98ER14850

Deformation and Fracture of Poorly Consolidated Media

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Objectives: The objective of this research is to investigate the process of hydraulic fracturing and of borehole breakout formation in poorly consolidated granular rock. Specifically we are interested in studying the mechanisms leading to these two types of borehole failure, and establishing whether either or both could be used as *in situ* stress indicators in high porosity weak rocks.

Project description: For borehole breakout studies we employ a specially fabricated biaxial loading cell mounted inside a compression loading machine, which allow us to carry out drilling of axial boreholes (diameters of 14-40 mm) in rock blocks (150x150x230 mm) already subjected to a state of true triaxial *in situ* stress. Berea sandstone of 24-26% porosity, other sandstones, and artificial granular material of similarly high porosity are tested. For hydraulic fracturing experiments we use cylindrical rock specimens (100x150 mm) mounted in a triaxial vessel through which we apply lateral and axial loads, as well as pore pressure and borehole fluid pressure.

Results: In this initial year of the project we first designed, fabricated, and calibrated a new biaxial loading cell. This cell enables the application of two independent mutually perpendicular stresses (each up to 110 MPa) to rectangular rock blocks.

We also performed a series of physical and mechanical properties tests on the high porosity Berea sandstone obtained from an Ohio quarry. Based on our tests, the rock can be classified as weak, highly porous and permeable, with a definite non-linear triaxial strength criterion. We have completed ten experiments of breakout-inducing drilling under a pre-existing triaxial state of stress simulating *in situ* conditions. Borehole failures are demonstrably unlike any observed in rocks such as granite and limestone. In the latter rocks breakouts are the result of dilatant inter- and intra-granular cracking parallel to the largest horizontal stress, leading to the well known 'dog ear' or 'V'-shaped breakout cross sections. In the presently tested sandstone, breakouts appear to be the culmination of a non-dilatant debonding of the grains at the points of highest stress concentration due to the reduced cementing matrix material (as inferred from the very high porosity). This failure mechanism leads to fracture-like or slot-like breakouts orthogonal to maximum compression, an orientation that is counter-intuitive, but reasonable if one realizes the non-dilatant nature of the failure. These breakout fractures extend for large distances from the borehole wall and could be a major source of 'sand production' in petroleum-producing wells.

The breakout fractures in the present tests are noticeably varying in length depending on the state of applied far-field stress, but their width is consistently limited to 5-7 grain diameters.

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GRANT: DE-FG02-93ER14389

Microanalysis of Stable Isotope Ratios in Low Temperature Rocks

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Objectives: To further develop microanalytical techniques for stable isotope analysis and to employ them to decipher the complex effects of superimposed hydrothermal events in modern and fossil geothermal systems (Long Valley, Yellowstone, Skye).

Project Description: This study focuses on samples of altered volcanic rocks from the Long Valley Exploratory Well, CA and other drilling and outcrop samples from Long Valley and Yellowstone, and on hydrothermally altered granites from related rocks from the Isle of Skye. New techniques allow analysis of stable isotope ratios in ultra-small samples and oxygen isotope ratio can now be contoured across single crystals. Mineral zonation patterns provide new insights into the process of water/rock interaction: mechanisms of exchange, timing, degree of equilibration, variability of fluid fluxes, and fluid sources. Enhanced understanding of these processes is essential for improving computer models of fluid flow through hot rocks.

At the Long Valley caldera and at Yellowstone, these results provide information on the nature of magma chambers at depth, the size of the modern geothermal resource, and the volcanic hazards. On the Isle of Skye, Scotland, samples of granite from beneath an ancient, deeply eroded caldera provide further insights for active systems.

Results: In the past year, a new airlock sample chamber has been developed that permits analysis of oxygen isotope ratio from reactive materials by laser including: whole rock powders, clays, glass, pumice, and hydrothermally altered feldspars. New procedures have also been developed to analyze quartz by laser.

At Long Valley, microanalysis of oxygen isotope ratios demonstrates a normal geothermal gradient beneath the resurgent Dome (Long Valley Exploratory Well) and an inverted gradient beneath the east moat. These results document shallow lateral flow of heated meteoric waters probably due to convection driven by post 500Ka intrusions beneath the Resurgent Dome.

At Yellowstone, samples have been collected of 24 units erupted over the past 2Ma. Zircon has been shown to preserve the best record of primary magmatic composition and some quartz is altered. Zircon concentrates have been separated from large 20 kg samples of each unit and they are being carefully analyzed to detect inheritance.

At Skye, oxygen isotope analysis of zircons has shown that most granites formed from isotopically light magmas. These data document a more complex and protracted history of hydrothermal alteration and magmatic interaction than was previously detected by analysis of quartz or feldspar. Samples have been collected for comparison from other plutons of the British Tertiary Igneous Province (Arran, Mull) that stitch domains with basement ages from Archean to Phanerozoic. The evolved oxygen isotope compositions do not correlate to basement and are dominated by processes in the shallow crust.

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GRANT: DE-FG02-98ER14852

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

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Objectives: The objective of the grant is to to evaluate the effect of rock microstructure on poroelastic properties of fractured rock and on multiphase fluid flow.

Project Description: Laboratory and theoretical work is being undertaken to predict the coupled deformation and fluid-flow behavior of a fractured rock mass based on a description of the rock microstructure at the pore and grain scale. The laboratory effort is to measure a complete set of poroelastic constants over a range of confining and pore pressures. A special endcap allows control of the internal fluid pressure to place the sample in a drained, undrained, or unjacketed condition. The theoretical analysis for wave propagation is based on a dual-porosity model, which can effectively treat the strong contrast of deformation and fluid-transport properties between fracture and matrix porosity in rock.

Results: A complete set of transversely isotropic poroelastic constants was measured on Berea sandstone at thirteen pore-pressure and hydrostatic stress pairs. The linear compressibilities for drained and undrained conditions decreased in a non-linear manner as the effective stress increased. As the effective stress increases, the anisotropy decreases until the sample behaves isotropically at the higher effective stresses. The unjacketed compressibilities show little anisotropy.

The double porosity theory of Berryman and Wang (1995) was extended to the dynamic case. Effects that are usually attributed to squirt flow under partially saturated conditions can be explained alternatively in terms of the double-porosity model. The validity of Gassmann's equation relating the drained and undrained bulk moduli was investigated by fitting the crack and pore distribution in a rock into the dual-porosity model.

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GRANT: DE-FG02-94ER14435

Robust, Controlled Leverage Magnetotelluric Data Analysis

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Objectives: To develop an improved understanding of the causes of bias and variability in magnetotelluric response function estimates, particularly in the presence of source field problems and cultural noise, to develop new processing methods which will eliminate these problems, and to apply tensor decompositions for galvanic distortion to the response functions in an automatic fashion.

Project Description: Over the past decade, collaboration with D.J. Thomson of AT&T Bell Laboratories has resulted in major improvements to Magnetotelluric data processing methodology, including robust remote reference algorithms that eliminate outliers in the electric field and extension of the jackknife to obtain nonparametric estimates of confidence limits. However, these methods do fail under some circumstances. This research will focus on further advances, which will be driven by analysis of diverse types of data, including those of interest in industry.

The major problems to be addressed include:

1) Investigating the efficacy of multiple remote references.
2) Designing algorithms that control the influence of extreme data in the magnetic as well as the electric field (which conventional robust algorithms cannot do).
3) Tests of the hypothesis that statistically based data sorting can remove many of the confounding influences that sometimes affect Magnetotelluric data.
4) Tests of the importance of magnetic field galvanic distortion in a variety of data.

Results: A robust, controlled-leverage algorithm has been developed which automatically removes the influence of outlying electric field data (as for conventional robust methods) and also controls the leverage effects of unusual magnetic field data. The latter is accomplished by weighting based on the size of the diagonal elements of the hat matrix, and has necessitated the derivation of the statistical distribution of this quantity for Gaussian data which has evidently not been done previously. The algorithm has been extended to allow multiple instead of single remote references. This involves computing the projection of the local magnetic field from all of the remote sites, and reduces to the conventional remote reference method when only a single reference site is available. In addition, the projection operation is performed robustly, opening up a new way of removing cultural noise in the local magnetic field if the remote site is not affected by it. The multiple remote reference, robust, controlled leverage algorithm with jackknife error estimates has been programmed and is being tested with a variety of data to refine the approach. The past year has been devoted to testing and debugging of this algrorithm, and to its application in a variety of places with a diversity of data.

An X-windows GUI has been completed, that greatly simplifies setting up and executing runs, and in particular facilitates viewing graphical output from a run. Without such an interface, it is very difficult to look at the statistical output from a run, and hence understand what is going on.

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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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Objectives: Constrain the role of water and minerals during organic transformations responsible for the conversion of oil to natural gas at elevated temperatures and pressures

Project Description: 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 in the presence of water and minerals at elevated temperatures and pressures. These experiments differ from previous studies by the addition of naturally occurring mineral assemblages that buffer redox conditions and the activity of aqueous sulfur species. Results from these experiments will be used to assess the relative influence of reactions regulated by thermodynamic equilibrium and chemical kinetics. In addition, the contribution of water derived hydrogen and oxygen to the production of methane and carbon dioxide will be determined.

Results: Extensive efforts have been directed at developing analytical and experimental methodologies to be used for this study. A bench-top gas chromatograph mass spectrometer was modified for quantitative analysis of gases dissolved in water and oil using a custom-built purge-and-trap device. In addition, a flexible gold hydrothermal reaction cell was designed and constructed to allow sampling of coexisting oil and water phases at the *in situ* temperature and pressure of an experiment.

Experiments reacting a medium weight crude oil from Eugene Island in the U.S. Gulf Coast with excess water and a pyrite-pyrrhotite-magnetite or a hematite-magnetite-pyrite mineral assemblage were conducted at 300 to 350°C and 350 bars. The abundance of aromatic and aliphatic hydrocarbons, volatile species such as CO_2, H_2S, and C_1-C_6 hydrocarbons, phenols, organic acids, ammonia, and alcohols in both the oil and aqueous phases were quantitatively determined at *in situ* conditions. Interpretations based on these preliminary results suggest that the stability of petroleum in the presence of liquid water is strongly influenced by the redox state of the chemical system. Specifically, petroleum decomposition through a series of oxidation reactions that ultimately produce carbon dioxide and methane are enhanced under oxidizing conditions. Accordingly, the stability of petroleum in natural environments may be regulated by the presence of redox sensitive inorganic sedimentary components.

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GRANT: DE-FG02-89ER13466

Organic Geochemistry of Outer Continental Margins and Deep-Water Sediments

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Objectives: 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.

Project Description: Our current research focuses on utilization of organic compounds in elucidating mechanisms, rates, and consequences of subsurface fluid flow processes. Our group at Woods Hole, in collaboration with the Geochemical and Environmental Research Group (GERG) at Texas A&M, has been the principal organic geochemical arm of the Global Basin Research Network since its formation in 1989. The GBRN is a distributed network of scientists working to understand the coupled physical and chemical processes that control fluid movement in sedimentary basins.

Results: Previous work provided evidence for on-going oil and gas injection (termed dynamic migration) into reservoirs of Eugene Island Block 330 (EI330) and areas to the south along the Louisiana Gulf Coast shelf edge and slope. Two major processes produce alterations to reservoired oils: biodegradation in shallower reservoirs and gas washing in all reservoirs. In "gas washing", oil in reservoirs is "washed" with multiple volumes of upward migrating gas. The amount of gas involved and the depth from which it originates is calculated from equations of state describing gas-oil phase behavior. Oil and gas compositions from individual reservoirs together and pressure-volume-temperature data from initial well testing are used as input data. Initial results show that EI330 oils have been washed with about 10 to 14 volumes of gas. This process, together with oil biodegradation, is probably responsible for the observed hydrocarbon compositional changes that occur in some, but not all, EI330 oils on short time-scales (5-10 year). The result of these two processes working together is a very dynamic system involving the disappearance of heavier n-alkanes *via* biodegradation accompanied by the appearance oflighter n-alkanes *via* gas washing.

A critical question: is this "remigration" merely a localized phenomenon or could it be part of a larger scale process? What volumes and flow rates of hydrocarbons are involved? Many lines of evidence indicate a widespread phenomenon involving upward migration of large volumes of gas, which is not limited to the Gulf of Mexico. Even though this process can be very large volumetrically, it is often difficult to detect because it is highly localized and possibly episodic. Therefore, research this year focused partially on developing a method for continuous detection and measurement of this upward seepage at the seafloor which is much more accessable to long term monitoring that the subsurface. Such a device would be useful in petroleum exploration, could be used to detect episodic petroleum migration, and would provide a better measure of overall upward petroleum fluxes than measurements on subsurface oil and gas reservoirs. Seafloor oil and gas seepage is much more widespread than subsurface trapping; only 2% of generated oil and gas is ever trapped in a producible reservoir, while about 54% in lost at the sediment surface into the overlying ocean.

Under the current project, a simple *in situ,* continuous fluorescence detector was tested utilizing a commercially available CTD (compensated temperature depth) unit that is normally used to examine chlorophyll along with salinity and temperature in the surface ocean. Here, the instrument was operated instead along the ocean bottom in a suspected oil and gas seep area. The device is relatively small and can be easily deployed *via* a cable from the ship for vertical water column measurements or from a submersible for continuous *in situ* measurements along the bottom. Scientific "cruises of opportunity" were used to test the instrument, first in the Gulf Coast Green Canyon oil seep area, utilizing the manned submersible, the Johnson Sealink, and secondly in the Gulf of California Guaymas Basin, utilizing the unmanned submersible, Jason. In Guaymas, hydrothermal heating of organic-rich sediments continuously generates oil and gas. Initial results show that: a) CTD fluorescence is an excellent tool for finding very localized ocean bottom oil and gas seepages and could easily be deployed to explore large areas of the ocean from both manned and unmanned submersibles, and b) fluorescence signals caused by seafloor venting of oil and gas are very localized, often occurring on less than a one-meter scale. Seafloor oil and gas seeps would have been easily missed without near-bottom continuous CTD fluorescence profiles.

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Mineral Dissolution and Precipitation Kinetics: A Combined Atomic-Scale and Macro-Scale Investigation

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Objectives: Our objectives are to build and test an atomic force microscope (AFM) capable of operation at up to 150°C and 6 atm. pressure, and to apply this AFM to direct, *in-situ*, and real-time observation of step dynamics during dissolution and growth of minerals at elevated temperature and pressure.

Project Description: This project combines atomic-scale and macro-scale approaches to the study of mineral-fluid interaction in order to significantly improve our understanding of, and ability to predict the course of, mineral dissolution and precipitation processes. With the successful construction of a hydrothermal atomic force microscope (HAFM), we can measure rates of dissolution and precipitation, determine activation energies, measure rates of step motion across surfaces (including anisotropy), and investigate step-step interactions that affect rate. Such data can then be used to address many questions concerning the exact forms for rate laws near and far from equilibrium, the microscopic interpretation of these rate laws in terms of dissolution and precipitation mechanisms.

Figure The hydrothermal atomic force microscope at Lawrence Livermore National Laboratory.

Results: After extensive design and construction work, the HAFM was successfully operated at elevated temperature and pressure in November 1997. Calcite dissolution was observed at 143°C and 90 psi in aqueous solution under static conditions. Shortly after this, flow-through capabilities were added. This initial success led to the publication of the initial design in an article for the Review of Scientific Instruments (Higgins, S.R., Eggleston, C.M., Knauss, K.G., and Boro, C.O., 1998, A hydrothermal atomic force microscope for imaging in aqueous solution up to 150°C, *Rev. Sci. Instr.* 69(8), 2994-2998). A second HAFM was built and installed at Lawrence Livermore National Laboratory, and is pictured in Figure 1. Temperature and flow controllers are seen to the left, an electronics interface is seen behind. The microscope itself in the foreground and consists of a gas-pressurized base containing stepper motor for coarse approach, middle section containing the cylindrical piezoelectric scanner element, atop the microscope is a third-party laser optical head adapted for our HAFM. The passivated titanium fluid cell, with thermocouple and inlet-outlet ports, is visible inside the front of the optical head.

Findings made using the HAFM in research work on barite ($BaSO_4$) (001) dissolution subsequent to the successful first operation of the HAFM include:

1) unbounded monomolecular layer steps created by etch pit coalescence on the barite (001) surface during dissolution retreat at much higher velocities than monolayer steps bounded within etch pits;
2) [120] steps retreat more rapidly than [010] steps, but both step orientations have about the same activation energy for step motion within error;
3) nucleation of etch pits had a much lower activation energy than step retreat, so that with increasing temperature the slope of etch pit walls decreases;
4) a two-dimensional birth-and-spread model of etch pit formation best describes the overall macroscopic dissolution rate if the nonrandom pit nucleation at defects is taken into account.

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GRANT: DE-FG02-95ER14522

A Field Experiment on Plants and Weathering

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Objectives: For 1998 the objectives were to: (1) study the effects on rock weathering and the geochemical cycling of elements resulting from experimental deforestation; (2) extend our theoretical calculations of how long-term carbon cycling affects the levels of atmospheric O_2 and CO_2; and (3) study how O_2 is consumed and CO_2 is given off to the atmosphere by the weathering of organic matter in ancient shales.

Project description: (1) The chemical composition of drainage waters from experimental plots at the Hubbard Brook Experimental Forest Station in New Hampshire continued to be analyzed. Descriptions of the plots are given in the 1997 and earlier reports. In May 1998 the trees were cut down and all stems and foliage removed from the pine-covered plot. Changes in water flow and chemistry, as a result of the tree cutdown, were monitored on a weekly basis over the year. (2) Our computer modeling of the long-term carbon cycle was continued and it focused on the effects of changes in the rates of burial of organic carbon and sulfide on the evolution of atmospheric O_2. (3) Weathering profiles developed on high-carbon black shales were collected and analyzed for total organic carbon as a function of depth from the outcrop surace into the unaltered host rock. Also kerogen was separated and analyzed via FTIR and NMR techniques.

Results: After the pine trees were cut down we found much higher autumn water discharge and, most surprisngly, the release of voluminous dissolved chloride after a lag of a few months. It is not normally considered as a nutrient element stored within the root mass and explanation of this Cl^- release is somewhat of a mystery.

Our carbon cycle calculations suggest that the fractionation of carbon isotopes during photosynthesis should be affected by changes in atmospheric O_2. This provides much-needed negative feedback to the modeling of the evolution of O_2.

Organic carbon loss as a result of shale weathering ranged from 60 to 100%. FTIR and NMR analyses of separated kerogen show the presence of oxygen-containing functional groups (*e.g.*, carbonyl) on the weathered material. Comparison of young (post-glacial) and old weathering proifiles indicates that the attainment of a steady state concentration-*vs.*-depth profile is rapid. This suggests that the rate-limiting step in organic matter weathering is the uncovering and exposure of kerogen to oxygen.

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GRANT: DE-FG02-90ER14153

Reactive Fluid Flow and Applications to Diagenesis, Mineral Deposits, and Crustal Rocks

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Objectives: To initiate new: modeling of coupled fluid flow and chemical reactions of geologic environments; experimental and theoretical studies of water-rock reactions; collection and interpretation of stable isotopic and geochemical field data at many spatial scales of systems involving fluid flow and reaction in environments ranging from soils to metamorphic rocks.

Project Description: Theoretical modeling of coupled fluid flow andchemical reactions, involving kinetics, has been employed to understand the differences between equilibrium, steady-state, and non-steady-state behavior of the chemical evolution of open fluid-rock systems. The numerical codes developed in this project treat multi-component, finite-rate reactions combined with advective and dispersive transport in multi-dimensions. The code incorporates heat, mass, and isotopic transfer in both porous and fractured media. Experimental work has obtained the kinetic rate laws of pertinent silicate-water reactions and the rates of Sr release during chemical weathering. *Ab-initio* quantum mechanical techniques to obtain the kinetics and mechanisms of silicate surface reactions. Geochemical field-based studies were carried out on the Wepawaug metamorphic schist, on the Irish base-metal sediment-hosted ore system, in the Dalradian metamorphic complex in Scotland, and on weathering in the Columbia River flood basalts. The geochemical and isotopic field data, and the experimental and theoretical rate data, were used as constraints on the numerical models and to determine the length and timescales relevant to each of the field areas.

Results: A reactive fluid-flow model was developed to examine the role of kinetically controlled quartz dissolution and precipitation on the evolution of sandstones in near-surface crustal environments. Thermal buoyancy induced flows tend to channelize in high-permeability zones, where non-equilibrium effects are especially pronounced. Kinetic effects moderate “runaway” dissolution in downwelling zones.

A detailed model was developed to calculate isotopic changes in zoned minerals and in fluids being transported in crustal flow systems. The model captures finite rates of intra-grain diffusion, as well as accurately calculating the effects of dissolution and precipitation.

A flow and reaction model of metamorphic reactions of siliceous dolomites was created. The kinetic based formulation includes multiple minerals and reactions in a two-dimensional porous medium surrounding a heat source. Significant overstepping of univariant curves can occur.

Field samples suggest that basalt weathers considerably faster than granites. Results of experiments measuring the dissolution rate and Sr release rate of biotite and phlogopite indicated that ^{87}Sr is preferentially released relative to ^{86}Sr, leading to weathering solutions with higher ^{87}Sr/^{86}Sr ratios than the reacting mineral. Iron oxidation was found to be the limiting step in biotite dissolution.

A computer model describing the potential influence of the weathering of the Columbia River Basalt suggests that the weathering of this province could have caused the major inflection in the marine Sr isotopic record that occurred 15 million years ago.

A one-dimensional model of coupled heat transport, fluid transport, porosity feedback, and metamorphism was used to investigate how dehydration reactions may influence pore fluid pressure along fault zones. Overstepping of dehydration reactions can lead to a sudden increase in pore pressure that can lead to tensile failure of the rock.

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DOE/OBES Geosciences Research: Historical Budget Summary

(Thousands of dollars)

	FY 94	FY 95	FY 96	FY 97	FY 98
Total, on-site	10,353	10,442	10,865	10,826	10,263
Total, off-site	8,477	7,937	8,815	9,705	11,226
Total, operating	18,830	18,379	19,680	20,521	21,489
Equipment	1,262	1,141	1,258	1,450	1,256
Total GEOSCIENCES	20,092	19,520	20,938	21,971	22,745

ON-SITE INSTITUTIONS

Institution	**FY 94**	**FY 95**	**FY 96**	**FY 97**	**FY 98**
Argonne National Laboratory	533	655	600	620	620
Brookhaven National Laboratory	363	460	528	350	425
Idaho National Laboratory	121	119	65	40	40
Los Alamos National Laboratory	1,881	2,241	1,960	2,096	1,509
Lawrence Berkeley National Laboratory	2,253	1,875	2,197	2,170	2,320
Lawrence Livermore National Laboratory	1,743	1,921	1,940	1,915	1,421
Oak Ridge Inst for Sci and Ed					85
Oak Ridge National Laboratory	1,163	1,140	1,251	1,195	1,228
Pacific Northwest Laboratory	664	665	684	600	770
Sandia National Laboratory	1,545	1,345	1,616	1,725	1,845
Grand Junction Project Office	87	-	-	-	-
Total, on-site	**10,353**	**10,442**	**10,865**	**10,826**	**10,263**

OFF-SITE INSTITUTIONS

Institution	**FY 94**	**FY 95**	**FY 96**	**FY 97**	**FY 98**
Alaska, Univ of (Lee)	-	49	98	-	-
Alaska, Univ of (Eichelberger)	112	-	-	-	-
Am. Geolog. Inst. (Davin)	36	40	42	-	-
AM. Muus. NY (Mathez)	37	72	69	85	98
Arizona St. (Buseck)	-	126	132	139	-
Arizona St. (Hervig/Williams)	62	86	59	74	83
Boston Univ. (Klein)	-	71	74	77	123
Brown U (Yund)	302	-	152	-	-
Cal Tech (Clayton)	142	55	-	-	-
Cal Tech. (Stolper)	153	123	140	142	146
Cal Tech. (Wasserburg)	388	400	400	400	465
Calif, Univ. of Berk (Helgeson)	349	-	185	192	195
Calif, Univ. of Berk (Nishiizumi)	-	-	-	160	164
Calif, Univ of Berk (Sposito)	-	-	-	67	70
Calif. Univ. of Davis (Casey)	-	-	110	108	104
Calif, Univ. of Davis (Lesher)	66	75	-	-	-

Institution	**FY 94**	**FY 95**	**FY 96**	**FY 97**	**FY 98**
Calif, Univ of Davis (Navrotsky)	-	-	-	150	-
Calif, Univ. of Davis (Rock)	78	-	151	134	138
Calif, Univ. of LA (Harrison)	100	105	111	119	123
Calif, Univ. of LA (McKeegan)	85	-	44	-	-
Calif. Univ. of SB (Boles)	-	-	20	31	16
Calif. Univ. of SB (Spera)	-	82	75	76	89
Calif, Univ of Santa Cruz (Wu)	-	-	-	-	278
Calif, Univ of San Diego (DeGroot-Hedlin)	-	-	-	49	58
Carnegie Inst of Wash (Hemley)	-	-	-	-	37
Chicago, Univ. of (Richter)	247	-	-	183	141
Chicago, Univ. of (Sutton/Rivers)	458	-	341	418	429
Chicago, Univ. of (Sutton)	127	138	159	131	137
Colo, Univ. of (Ge)	179	179	13	86	-
Colo, Univ. of (Rajaram)	-	-	79	124	-
Colo, Univ. of (Rundle)	-	109	114	120	130
Colo, Univ. of (Smyth)	10	-	-	-	-
Colo, Univ. of (Spetzler)	145	126	132	152	161
Colo Sch Mines (Larner)	97	-	-	-	-
Col Sch of Mines (Tsvankin)	-	-	-	-	230
Columbia Univ. (Broecker)	-	131	137	134	154
Columbia Univ. (Walker)	103	113	-	-	-
Conn. Univ. of (Torgersen)	19	76	65	68	79
Delaware, Univ. of (Wood)	90	108	109	111	124
Desert Res. Inst. (Tyler)	-	-	80	148	
Duke Univ (Malin)	-	-	-	-	44
Florida, Univ. of (Ladd)	-	-	-	-	85
Florida, So. Univ of (Compton)	56	-	-	-	-
Florida St., Univ. of (SCC)	214	-	-	-	-
Geophys. Lab, CIW (Bell)	89	92	-	-	-
Georgia Tech (Dove)	-	91	91	39	86
Hawaii, Univ. of (Martel)	-	81	79	84	130
Headquarters Services	1	-	-	-	-
Illinois, Univ of (T. Johnson)	-	-	-	138	-
I.R.I.S. (Simpson)	-	211	211	-	-
Indiana, Univ. of (Ortoleva)	-	100	102	108	141
John Hopkins Univ.(Garven)	-	-	67	70	77
Johns Hopkins Univ.(Sverjenski)	-	-	118	105	108
Johns Hopkins Univ.(Veblen)	-	156	156	163	110
Kent State Univ (Maurice)	-	-	-	33	34
Lehigh Univ. (Ilton)	-	44	44	37	115
Lehigh Univ. (Moses)	-	-	123	-	-
Maine Science & Tech (Shehata)	-	-	-	340	-
Maryland, Univ. of (Tossell)	35	-	28	56	47
Miami, Univ. of (Eberli)	169	155	-	-	-
Michigan, Univ. of (Ballentine)	-	-	69	71	69
Michigan, Univ. of (Halliday)	147	172	207	226	200

Institution	FY 94	FY 95	FY 96	FY 97	FY 98
Minn. Univ of (Yuen)	-	82	78	76	91
MIT (B. Evans)	-	-	-	185	188
MIT (Madden)	70	74	-	-	-
MIT (Toksoz)	374	367	-	-	150
NASA (Blankston)	100	-	113	95	113
NAS/NRC (Benson/Crowley)	10	-	-	-	-
NAS/NRC (Phillips)	121	-	-	-	-
NAS/NRC (Price/Schiffries)	100	100	100	100	100
Nevada, Univ of (Long)	-	-	-	-	106
New England Res (S. Brown)	-	-	-	-	211
New Mexico Inst. Min. Tech.(Wilson)	-	-	30	64	-
New Mexico, Univ of (Ingber)	-	-	-	-	76
New Mexico, Univ. of (Miller)	-	100	100	-	-
NY, City Univ. of CC (Koplik)	121	125	98	98	100
NY, State Univ. of SB (Hanson)	121	126	131	-	155
NY, State Univ. of SB (Lindquist)	22	33	33	35	50
NY, State Univ. of SB (Schoonen)	-	-	48	51	54
NY, State Univ. of SB (Wong)	69	70	71	99	100
Northwestern Univ. (Rudnicki)	72	85	-	88	148
Notre Dame Univ (Pyrak-Nolte)	61	65	78	81	83
Ohio St. Univ (Adler)	161	-	43	-	-
Okla, Univ. of (Elmore)	-	112	158	-	219
Oregon St. Univ (Egbert)	-	-	41	-	-
Penn St. Univ. (Barnes)	-	-	81	87	93
Penn St. Univ. (Brantley)	-	115	117	107	200
Penn St. Univ. (Brantley) conf.	-	-	10	-	-
Princeton Univ (Navrotsky)	145	150	150	-	-
Purdue Univ. of (Johnson)	-	-	-	-	130
Renesselaer Polytech. Inst. (Watson)	144	140	146	-	181
Rice Univ. (Mango)	97	136	105	109	111
Rust Geotech, Inc. (Fukui)	-	87	87	35	-
Rutger Univ (Cheney)	-	-	-	75	75
Santa Fe Inst. (Rundle)	11	-	-	-	-
Calif. Univ. of So (Aki)*	155	-	112	-	-
Stanford Univ. (Brown)	204	210	-	247	259
Stanford Univ. (Harris)	-	115	120	125	-
Stanford Univ. (Liou)	-	80	-	-	-
Stanford Univ. (Nur)	173	185	193	196	211
Stanford Univ. (Nur)	-	-	-	-	150
Standard Univ. (Pollard)	210	224	232	250	195
Stanford Univ. (Segall)	83	83	-	-	-
Stanford Univ. (Zoback)	72	38	-	-	-
Temple Univ. (Strongin)	-	-	76	49	52
Tennessee Univ. of (Thonnard)	-	100	82	69	-
Texas, Univ of at Aus(Banner)	-	-	-	-	152
Texas, Univ. of at Aus (Hardage)	-	170	175	175	-

Institution	**FY 94**	**FY 95**	**FY 96**	**FY 97**	**FY 98**
Texas, Univ of at Aus (Land)	104	-	-	-	-
Texas, Univ of at Aus (Nelson)	5	-	-	-	-
Texas, Univ of at Aus (Sharp)	48	-	-	61	58
Texas, Univ of Dallas (McMechan)	-	-	164	124	162
Texas, A&M Univ. (Kronenberg)	156	167	-	-	184
USGS (Bredehoeft)	30	-	-	-	-
USGS (Russ)	126	-	-	-	-
Utah, Univ. of (Tripp)	59	64	55	57	60
Utah St. (Hestir)	-	99	160	157	73
Utah St (Evans)	-	-	-	-	129
VPI & SU (Bodnar)	133	104	100	104	122
Washington, Univ. of (Booker)	247	-	116	-	-
Washington, Univ of (Booker-conf)	-	-	-	-	8
Wasington, Univ. of (Unsworth)	-	-	-	96	97
Washington St. Univ.-R (Reidel)	5	-	-	-	-
Washington Univ, St. Louis (Shock)	24	53	75	80	106
Wisconsin, Univ of (Bahr)	46	49	-	-	-
Wisconsin, Univ of (Banfield)	98	-	104	139	149
Wisconsin, Univ of (Haimson)	10	-	-	-	125
Wisconsin, Univ. of (Valley)	142	149	-	148	153
Wisconsin, Univ of (Wang)	-	60	-	-	50
WHOI (Chave)	91	91	55	-	-
WHOI (Eglinton)	275	-	135	-	-
WHOI (Seewald)	-	-	-	130	79
WHOI (Whelan)	180	191	195	200	205
Wyoming, Univ. of (Eggleston)	-	-	81	56	56
Yale Univ. (Berner)	-	78	91	92	177
Yale Univ. (Lasaga)	-	207	290	295	240
Other	85	87	90	244	222
Total, Offsite	**8,477**	**7,937**	**8,815**	**9,705**	**11,226**