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Summaries of FY 1995 Geosciences Research

December 1995

U.S. Department of Energy

Office of Energy Research
Office of Basic Energy Sciences
Division of Engineering and Geosciences

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Germantown, MD 20874

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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 programs. The Geosciences Research Program includes research in geophysics, geochemistry, resource evaluation, 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 by accessing the URL address *http://www.er.doe.gov/production/bes/geo/geohome.html.*

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 earth's 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 AND EXOGEOCHEMISTRY

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 fluid–rock systems.

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

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**

A. Mineral–Fluid Interactions: Experimental Determination of Atomic-Scale Processes Using Synchrotron Radiation *(Ronald P. Chiarello [708-252-9327; Fax 708-252-9373; E-mail chiarello@cmt.anl.gov] and Neil C. Sturchio)*

Objectives: The objective of this program is to advance the basic understanding of rock–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 techniques with high-brilliance synchrotron radiation. This approach applies techniques developed recently by physicists for basic studies of surface phenomena and semiconductor properties. 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 in chemically controlled conditions. During the past year, experiments were conducted to characterize the atomic structure of the calcite (104) cleavage plane in contact with water, and to observe changes in this structure as a function of solution composition and time, using crystal truncation rod measurements. This work required the development of a new reflection geometry x-ray cell having a thin (micron-scale) water layer above the calcite surface. X-ray reflectivity and diffraction techniques were used to determine the growth rate, compositional evolution, and crystallographic characteristics of a $(Ca,Cd)CO_3$ solid solution precipitated heterogenously onto calcite. The x-ray standing-wave technique (at Bragg diffraction angle) was used to determine the lattice locations of Mn and Sr in calcite and Zn sorbed onto the calcite surface from aqueous solution, by triangulation from three different diffraction planes, in collaboration with M. J. Bedzyk (Northwestern University) and colleagues.

B. Geochemistry of Organic Sulfur in Marine Sediments *(A. Vairavamurthy [516-282-5337; Fax 516-282-5526] and B. Manowitz [516-282-2458; Fax 516-282-5526])*

Objectives: The broad objectives are to understand the geochemical mechanisms of sulfur incorporation into sedimentary organic matter, to study the changes in the abundance and forms of sulfur during early diagenesis in various organic-rich sedimentary environments, and to examine the influence of sulfur incorporation in the preservation of sedimentary organic matter.

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. The fundamental geochemical issue in this matter is the mechanism of sulfur incorporation into sedimentary organic matter. Although there is compelling evidence to indicate that reactions of reduced inorganic sulfur species with organic molecules occur during the early stages of diagenesis and under very mild conditions, the molecular mechanisms are still not well understood. Previously, hydrogen sulfide has been considered to be the primary sulfur reactant for organic sulfur formation in sediments. Recently, evidence is emerging that H_2S oxidation products, especially polysulfides, are also important. The roles of elemental sulfur, sulfite, and thiosulfate in the formation of organic sulfur are still not clear. 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 sulfide oxidation to understand the formation of different oxidation intermediates, and (4) analytical methods development. An important goal of this project is to use synchrotron-radiation-based x-ray absorption near-edge-structure (XANES) spectroscopy for characterization and determination of sulfur species, in addition to other state-of-the-art techniques.

Results: Recently, we established sulfonates as an important class of organic sulfur in marine sediments. Currently, one of our areas of research is directed toward understanding the origins of sulfonates in sediments. XANES analysis revealed that sulfonates are the dominant forms of sulfur in most marine phytoplankton species. These results are remarkable because reduced sulfur is thought to be the most abundant sulfur form in these organisms. Thus, it is possible that sedimentary sulfonates have a biological origin in addition to an origin in geochemical mechanisms involving reactions between H_2S oxidation intermediates (sulfite and thiosulfate) and functionalized organic molecules.

Measurements of sulfur speciation of the organic-rich sediments off the coast of Chile were conducted to better understand the early diagenetic distribution of various sulfur species, including sulfonates. Our results of this study and earlier ones indicate that organic polysulfides are the dominant fraction of organic sulfur in early diagenetic sediments. The distribution of organic sulfides in the vicinity of the oxic–anoxic interface, where intermediates from H_2S oxidation were likely to be generated most abundantly, strongly suggests they were formed by the geochemical pathway involving reactions between (inorganic) polysulfides and functionalized organic molecules. The sub-surface maximum for sulfonates appearing just above that of organic polysulfides also indicates their geochemical origin. These results strongly support the view that the partial oxidation products of H_2S play a dominant role in incorporating sulfur into sedimentary organic matter. Since these oxidation products are generated maximally at the oxic–anoxic interface, which usually lies above the hydrogen sulfide maximum, the oxidation intermediates will have the first chance to react with reactive molecules present in the deposited organic matter rather than hydrogen sulfide. This hypothesis may explain the dominance of organic polysulfides in geochemical systems.

CONTRACTOR: **IDAHO NATIONAL ENGINEERING LABORATORY**
Idaho Falls, Idaho 83419

CONTRACT: **SBQ040**

CATEGORY: **Geophysics and Earth Dynamics**

PERSON IN CHARGE: **J. Epstein**

A. Frictional Process Zones in Compressive Fracture *(J. Epstein [208-526-6874; Fax 208-526-0690; E-mail esj@inel.gov] and L. Koo [208-526-0464; Fax 208-526-0690; E-mail lts@inel.gov])*

Objectives: The purpose of this project is to investigate the fracture of quasi-brittle materials which exhibit friction along their crack faces under varied degrees of shear and compression loading. Success in this endeavor will lead to an improved class of frictional constitutive relations useful to the modeling of underground joints. Relative to the U.S. Department of Energy mission areas, these improved slip models are applicable to underground storage facilities such as the Yucca Mountain Project, whose NRC certification requires a validated means for predicting the long-term behavior of tunnel slip planes.

Project Description: Using a combined experimental and theoretical approach, a series of homogeneous specimens have been fabricated made of pure Solnhofen limestone, marble, Nevada tuff and *bimaterial* systems consisting of Solnhofen bonded to PMMA. These compressional fracture specimens have no initial crack mouth opening such that under compression shear a singular slip field develops with no pre-elastic compression effects normally encountered with an artificial saw-cut crack. A floating biaxial frame has been developed to apply independent degrees of shear and compression to the crack up to initiation. Diagnostics include a 4-beam moiré interferometry system to map the X,Y, and 45-degree in-plane displacement fields local to the crack face with a sensitivity of 0.4 microns. Also employed is a coupled acoustic emission loading system to control unstable crack growth in the specimens. The measured in-plane displacement fields are compared to complex function solutions incorporating frictional sliding along the crack face for homogenous and bimaterial cases. The final product will be verified semi-closed form solutions for frictional slip along crack faces that can be input into larger numerical geo-models.

Results: Several homogeneous specimens of Solnhofen limestone have been fabricated and tested under varied degrees of independently applied shear to compressional loading. Mixed-mode crack initiation has consistently occurred at a shear to normal load ratio corresponding to the measured coefficient of frictional (0.6–7) as measured by Sandia Labs. These initiation results indicate a uniform frictional locking effect dominated by the crack face much larger than the singular region of the tips. Once slip occurs it vastly overwhelms the K_{II} initiation value for the Solnhofen material, thus initiating the crack. The in-plane X and Y displacement fields have been measured to determine the crack face opening profile. This profile has been compared to a complex variables solution incorporating the friction as a non-singular term. A solution has also been derived for the bimaterial crack under shear and compression incorporating the effects of friction. Bimaterial samples have been fabricated consisting of Solnhofen limestone bonded to PMMA. This material mismatch should be sufficiently strong to vary the frictional process zone along the crack face as compared to the pure Solnhofen sample and should yield significant fundamental insight on the behavior mismatched jointed media. These specimens are being tested in the same fashion as the homogeneous specimens. Energies to fracture will be extracted from these bimaterial tests as a function of shear to normal load ratio.

measure particle accelerations at various positions in the plate. Particle motion measurements made along a profile crossing the fracture have confirmed that the interface waves have elliptically polarized particle motions. The model is being adapted to investigate the effects of a fracture of finite length, multiple fractures, and fractures with variable stiffness.

B. Effects of Heterogeneity on the Mechanical Properties of Rock *(L. R. Myer [510-486-6456; Fax 486-5686; E-mail myer@lbl.gov], N. G. W. Cook, and K. T. Nihei)*

Objectives: The objective of this work is to develop a fundamental understanding of the effects of microstructural and macrostructural heterogeneity on the nonlinear, hysteretic deformation and failure of rock loaded in compression.

Project Description: This work examines the mechanical process in rock that control how rocks deform and fail under compressive loading. Laboratory measurements on a suite of sedimentary rocks are being performed to determine how variability in rock microstructure (e.g., grain shape, size, cementation, tensile strength and packing geometry) produces local stress concentrations which, in turn, produce intergranular frictional sliding and extensile microcracking. Laboratory work includes stress–strain, pore compressibility, and seismic properties measurements. Microstructure at any particular state of stress is preserved for SEM analysis using a Wood's metal impregnation technique. Numerical studies using a boundary element code and a Lagrangian discontinuous deformation analysis code are also being conducted in parallel with the experiments to quantify the effects of stochastic variations in grain strength, size, and packing geometry on the nucleation and coalescence of microcracks.

Results: A laboratory investigation of the effects of intergranular frictional sliding in sandstone on the static (large strain) and dynamic (small strain) moduli was completed for uniaxial stress, uniaxial strain, and hydrostatic states of stress. From these measurements, the elastic moduli obtained from small strain unloading excursions from the loading part of the static stress–strain curve were observed to be nearly identical to the dynamic stress–strain curve obtained by integrating the elastic moduli computed from measured ultrasonic velocities. This result clearly illustrates that the difference between the elastic moduli obtained from static and dynamic tests is primarily due to the difference in the applied strain amplitude and not due to the frequency of the applied stress, and, furthermore, underscores the importance of intergranular frictional sliding effects in the analysis of rock deformation. Laboratory work has continued with an investigation of the effects of frictional sliding on the pore compressibility of rocks subjected to different loading paths. Measurements on Berea sandstone indicate that initial differential loading followed by hydrostatic loading can significantly increase the pore compressibility. Analysis of these measurements is being performed to illuminate the micromechanical processes that produce this observed shear enhanced pore compressibility.

Numerical studies continued with boundary element simulations of crack growth in granular rock models consisting of two-dimensional packings of cylindrical grains of variable size, strengths, and moduli. A parametric study to determine how the magnitude of grain dilatation which occurs after a grain is fractured controls the subsequent failure of surrounding grains was performed. This study revealed that dilatation of a failed grain is an important mechanism for transferring local stresses to neighboring grains. If the dilatation of the failed grain is small, than microcracking will tend to progress perpendicular to the maximum compressive stress. However, if the dilatation is large, microcracks will form parallel the direction of the maximum compressive stress.

As a first step toward the development of a class of numerical simulators capable of modeling rock deformation and failure processes such as frictional sliding, grain debonding, grain rotation, and grain fracture, a Lagrangian Discontinuous Deformation Analysis (LDDA) finite-element code is being developed. At present, LDDA is capable of modeling discrete grains that interact along discrete boundaries. Each grain is modeled as a continuous elastic body, and intermittent pressing need to interpret an increasing amount of field data available to us. This data is now in the frequency domain, at only a few frequencies, and can only be interpreted with the products of tasks 2 and 3. However, the evident success of the q-domain tomographic imaging process strongly argues for the development of a suitable wideband borehole system (task 4).

Results: The summary of this year's research consists of improvement of the q-domain imaging method, Born inversion, and 3-D nonlinear inversion.

The wavefield transform method (q-domain) has been extended to include frequency-domain data and the result was presented at the SEG International Exposition and 64th Annual Meeting ("Wavefield transform of electromagnetic fields," K. H. Lee, G. Xie, T. M. Habashy, and C. Torres-Verdin, Los Angeles, CA, October 23–28, 1994). Further investigation in the transform method shows that there is a simple theoretical relationship between the phase of electromagnetic field and the traveltime in the q-domain. This relationship is well understood when the medium is homogeneous. When the medium is heterogeneous, however, this relationship is nonlinear and requires a great deal of information, in the form of frequency- or time-domain data, to yield appropriate spatial resolution in velocity in the q-domain.

Further research in the Born inversion and 3-D nonlinear inversion has resulted in two publications in *Geophysics* and one in *The Leading Edge*. The 3-D nonlinear inversion requires many forward model calculations using the integral equation. The computational efficiency involved in this process is not optimum at this point.

E. Non-Linear Elasticity and Seismology *(V. A. Korneev [510-486-7214; E-mail korneev@ccs.lbl.gov], T. V. McEvilly [510-486-7347; Fax 510-486-5686; E-mail mcevilly@ccs.lbl.gov], and L. R. Johnson [510-486-4173; E-mail lrj@ccs.lbl.gov])*

Objectives: Nonlinear wave propagation has long been a fruitful area of research in the field of acoustics. Initial measurements for earth materials have revealed that the basic nonlinear behavior is quite profound, and this has caused considerable interest in nonlinear wave propagation effects in the earth. A program in this area of research has been under way at LBL for two years and it includes components of theoretical, laboratory, and field investigations to better understand basic nonlinear elastic phenomena in earth materials. The research also addresses the phenomenon of elastic scattering in wave propagation. Methods are sought for characterizing the nonlinear parameters of rocks through observations of elastic wave propagation.

Project Description: It is very difficult to separate nonlinear waves from multiple harmonics generated by the source, and time-domain solutions become desirable. Use of the direct Fourier transform technique is prohibited by the nonlinearity of the equations of motion. Therefore, a special study was performed for the purpose of predicting the nonlinear behavior of elastic pulses. Another theoretical investigation studied the nonlinear interactions of two elastic waves. If collimated beams intersect in a spherical volume, there are 54 possible combinations, of which only 10 result in resonant scattering. We have used available in-house field data in a search for effects of nonlinear elasticity. In addition, we conducted one field experiment explicitly for detection of nonlinear wave propagation in conjunction with a previously planned Vertical Seismic Profile at the DOE Nevada Test Site, and we analyzed a special data set acquired by Los Alamos National Laboratory in West Texas in an attempt to verify nonlinear wave propagation during a seismic reflection profile. The scattering of elastic waves by different kinds of obstacles has been another subject of intensive investigation. Theoretical investigations and numerical simulations are being used to design field experiments where the basic predictions of the localization phenomenon can be tested in the earth. If it can be shown that this process plays an active role in seismic wave propagation, then the next stage is to develop methods of accurately estimating the relevant parameters for earth materials.

Results: Time-domain solutions were obtained for 1-D nonlinear elastic wave propagation problems using

Seismic Imaging

- Borehole tomography
- 3-D travel-time inversion for velocity and attenuation
- Microearthquakes for process monitoring
- High-resolution reflection profiling

Visualization

- Effective depiction of 3-D structures, subsurface processes, complex wave propagation
- In-field, near-real-time display and experiment control

Results: CCS supports a wide range of research projects, from deep earth structure to high-resolution crosswell tomography, ranging from the most basic investigations to those directed to the most applied technologies. The best demonstration of this wide range of content is in the CCS research output. Major accomplishments flow largely from the breadth of research support provided by CCS, and the cross-fertilization of applications and fundamental studies. Primary strengths lie in elastic wave generation and propagation, inverse methods, data processing and tomographic imaging methods. The list of recent publications, produced with CCS support to varying degrees, displays the range of research accomplishments. The list of PhD thesis topics developed with some CCS resource support adds about four entries per year and they reflect the integration of a wide spectrum of research interests in such a way that applications are readily evident and easily pursued by the more problem-directed researchers in CCS.

G. Controls on Pull-Apart Basin Evolution: Integrated Geological, Geophysical and Modeling Studies *(Patrick L. Williams [510-486-7156; Fax 510-486-4159; E-mail plw@ccs.lbl.gov] and Thomas V. McEvilly)*

Objectives: In a variety of Earth science and technology problems including petroleum production, aquifer characterization, contaminant studies, and tectonic hazards analysis, it has become critically important to identify and characterize in three dimensions the sedimentary character and tectonic structure of sedimentary basins. This project is developing a better understanding and predictive capability for the three-dimensional (3-D) structure of extensional sedimentary basins. The purpose of this work is the integration of surface geology and high-resolution subsurface geological and geophysical data in full 3-D basin representation.

Project Description: This project is directed at the development of a predictive capability for recovery of the 3-D structure of pull-apart basins. Stage one of this work is the integration of surface geology and high-resolution subsurface geological and geophysical data in full 3-D basin representation. This project will complete 3-D representations, or "empirical models," of the bounding geometry, structural elements, stratigraphy, and sedimentology of selected basins. This provides a point of departure (and constraints) for stage two of the project: the development of a new generation of 3-D numerical or "theoretical mechanical basin models." The development of realistic mechanical models of an extensional basin's evolution will require the encoding of accurate basin geometries and deformation history. Subsequent modeling will test how fault geometry and fault displacement affect basin structure in three dimensions.

Results: Development and application of landform and substrate imaging and characterization techniques and the analyses of these landform and subsurface data have been the primary products of this project, and several publications are in progress. Our studies of specific pull-apart basins in the San Francisco Bay area have contributed directly to the understanding of tectonic (earthquake) hazards to structures including industrial facilities, transportation structures, and lifelines. With industry participation, we are demonstrating the capability of advanced imaging tools for investigations of subsurface structure for environmental remediation and characterization of geological hazards.

While the focus of this activity is toward the improvement of fundamental understanding, e.g., the na-gas from depths of a few kilometers, and when combined with observations of anomalous seismic activity, is suggestive of a recent intrusive event.

(2) Calcium isotopic fractionation in nature is known to be relatively small in comparison to that of oxygen and sulfur but there has previously been no successful attempt to discover whether it is systematic, or what mechanisms are responsible for the fractionation. New measurements show that biological fractionation is the major source of Ca isotopic fractionation in nature, and that the fractionation is systematic and dependent primarily on trophic level. There are small isotopic variations in igneous rocks, but insufficient data exist to determine the sources of variability. We have set up procedures for measuring Ca isotopic variations using the ^{44}Ca/^{40}Ca ratio expressed as permil variations (∂^{44}Ca) from a standard value based on typical terrestrial igneous rocks and average meteorites. The ∂^{44}Ca values of samples are determined using a double spike (^{42}Ca + ^{48}Ca) technique; analytical uncertainty of the ∂^{44}Ca value is ±0.15 permil. The ∂^{44}Ca value of seawater (+0.9) is the highest value measured thus far. Marine organisms vary systematically from values as high as +0.1 to +0.5 for foraminiferal calcite, to values as low as –2.5 for a porpoise bone. The primary determinant of ∂^{44}Ca in the bone and shell material of marine organisms appears to be trophic level; the magnitude of temperature-dependent fractionation is much smaller. Terrestrial organisms have lower ∂^{44}Ca values than marine organisms of approximately similar mass and trophic level. The high ∂^{44}Ca of seawater appears to be a result of sedimentary sequestering of light Ca.

(3) A new method of uranium–thorium–lead (U–Th–Pb) radiometric age dating for Quaternary rocks was developed. The approach uses an instrumental mass discrimination correction for Pb isotope ratios, which allows small enrichments of radiogenic ^{206}Pb and ^{208}Pb to be detected at the level of 0.001%. Igneous rocks hosting minerals with a range in ^{238}U/^{204}Pb values of 100 can be dated with uncertainties of approximately ±15–20 kyr. A Quaternary rhyolite dated at 1.19 Ma by Ar–Ar yields a ^{238}U–^{206}Pb age of 1.03 ± 0.10 Ma. A Holocene dacite (9.5 Ka) has uniform ^{206}Pb/^{207}Pb to within ±0.002% in groundmass phases, but 1-mm plagioclase phenocrysts have lower ^{206}Pb/^{207}Pb by 0.105 ± 0.002%, indicating contamination of the magma after plagioclase crystallization. High-precision ^{206}Pb/^{207}Pb ratios may be a useful new tool for petrogenetic studies.

(4) Models of ^{87}Sr/^{86}Sr ratio evolution in groundwater systems that contain both rapidly exchanging and slowly dissolving solid phases were developed and used to constrain integrated flow rates of groundwater under the Lawrence Berkeley National Laboratory. At LBNL, ^{87}Sr/^{86}Sr ratios increase markedly over tens of meters along presumed flow paths. The dissolved Sr is close to isotopic equilibrium with the exchangeable (leachable) Sr in the rock, but the overall pattern reflects the changes in whole rock ^{87}Sr/^{86}Sr along the flow paths. The data require that flow velocities be ≤10 cm/yr, and are consistent with corrected radiocarbon ages.

(5) Stable isotope geochemistry of low-temperature clay minerals is being studied to define the effects of temperature, phase transitions, and fluid composition on the hydrogen and oxygen isotopic compositions of clay minerals formed at low temperatures (<150°C). The purpose is to enable the use of stable isotope compositions of authigenic clay minerals for studies of low-temperature fluid flow (i.e., oil field brines, groundwater flow), weathering, and paleotemperature reconstruction. Analysis of smectite samples from drill holes from the East Rift Zone of Kilauea Volcano of Hawaii indicates that the clays formed at temperatures ranging from 96 to 322°C and demonstrate the potential use of clays for stable isotope thermometry at low temperatures.

B. Thermodynamics of High-Temperature Brines *(K. S. Pitzer [510-486-5456; Fax 510-642-6911; E-mail kspitzer@lbl.gov])*

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 natu-

XANES results ruled out the possible formation of Se(0) in the ponded waters, and also indicated that formation of organo-Se compounds was insignificant. The latter result is consistent with the XANES study conducted with Pickering and Brown. Recently, XANES studies of Se-contaminated sediments which have been subjected to various chemical extractions have also been initiated with G. E. Brown, Jr., and A. L. Foster (Stanford University). This work will compare Se speciation by direct XANES versus by sequential chemical extraction. In another application of micro-XANES, spatially and temporally resolved reduction of Cr was studied in soil.

ture. Mapping of seismic shear wave velocity may be useful for delineating low-permeability zones in the reservoir which are apparently associated with high smectite content. When swelling clays in the decomposed sandstone are allowed to adsorb water, shear moduli can drop as much as 50%, when compared to a dry, unreactive sandstone. The clay component can be as small as 10% by volume to cause large effects. The shear modulus decreases even further at high strains. These results imply that extrapolations of ground motion assuming elastic response at the site underpredict the motion caused by the Northridge main shock by a factor of two or three.

A numerical model which accounts for friction at internal surfaces has been developed to simulate shear hysteresis at intermediate strains. The simulation solves the equation of motion for a one-dimensional nonlinear spring element, and is specified by a strain-dependent shear modulus defect. This simple model reproduces hysteretic attenuation, strain-softening behavior, and slope discontinuities in agreement with experiment for fractured grainite. The effect of adhesion forces will be added to account for thin fluid films adsorbed onto internal surfaces. When complete, this constitutive model will generate input consistent with laboratory meaurements for finite difference and element simulation of wave propagation and strong ground motion in nonlinear materials.

B. Effects of Heterogeneity on the Fracture of Rock *(S. C.Blair [510-422-6467; Fax 510-423-1057; E-mail blair@s55.es.llnl.gov] and L. R. Myer [Lawrence Berkeley Laboratory, 510-486-6456])*

Objective: The objective of this research is to understand how microscale (or grain-scale) heterogeneity affects macroscopic mechanical behavior of rocks, and to study the process of progressive fracture of rock in compression, and evaluate the role of crack interaction in rock deformation and fracture. Moreover, this work also aims to investigate the relationship of static to dynamic moduli (in collaboration with LBL) and to characterize the role of heterogeneity at a variety of scales in fracture and the scaling properties of rocks.

Project Description: This project is concerned with simulation of rock deformation and fracture at grain and larger scales. A field-theory model for rock fracture has been developed and is being used to perform two types of studies: a parameter-sensitivity analysis to determine how heterogeneity in different microscale parameters affects behavior in the simulated compression tests, and a detailed analysis of the process of fracture in a few selected trials to interrogate the macroscopic stress–strain curve and determine how the macroscopic stress–strain behavior is related to the formation of cracks. Finally, percolation theory in being used to analyze output from the model, in order to investigate scaling relationships in fracture processes.

Results: Results show that the model produces realistic stress–strain curves and implicitly predicts the development of shear-type fractures, even though a simple crack element that does not include shear stress is used. This implies that the en-echelon nature of cracking observed in rocks in compression may be due to the local heterogeneity in the rock, and that local heterogeneity may lead to crack interactions along macroscopic surfaces that are similar to those caused by shear localization and that are often observed in real experiments.

Results also show that the model exhibits an implicit size effect that closely matches laboratory and field data for the dependence of sample strength on sample size. This is an inverse power-law relation with exponent similar to that obtained in analysis of laboratory and field data on rock strength. No assumption of flaw size is needed to generate this effect, and the effect is assocated with a decrease in the stress level required to create crack interaction, as the size of the lattice increases. This may be because a larger population of sites offers more possible ways for cracked sites to interact and a larger number of ways for a weak path to be formed.

The model was also used to relate macroscopic stress–strain behavior to the formation of microcracks and to strain energy due to cracks. Analysis shows strain softening to be associated with crack extension. Two patterns of cracking were found, including spatially uncorrelated, non-interacting cracks that have little

CATEGORY: **Geochemistry**

PERSON IN CHARGE: **F. J. Ryerson**

A. Thermodynamic and Transport Properties of Aqueous Geochemical Systems

(Joseph A. Rard [510-422-6872; Fax 510-422-0208] and Donald G. Miller [510-422-8074; Fax 510-422-6363; E-mail dmiller@llnl.gov])

Objectives: The objectives are to (1) measure precise and accurate osmotic/activity coefficients, 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. Being measured are osmotic/activity coefficients and solubilities by the isopiestic method, densities by pycnometry and vibrating densitometry, and diffusion coefficients by Rayleigh and Gouy interferometry.

One goal is to measure highly accurate data for systems involving geochemical brines, radioactive waste isolation, 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. Transport data are being analyzed as Onsager transport coefficients and osmotic/activity coefficients are being analyzed using extended Pitzer's equations, which should be capable of yielding reliable estimates for mixtures.

Results: A few additional diffusion experiments were performed for aqueous K_2SO_4 at 25°C, using the high-precision Gosting diffusiometer at Texas Christian University, to supplement our previous results. The photographic plates from these experiments were analyzed with our automated plate reader. Diffusion experiments were also performed at two compositions of NaCl + Na_2SO_4 at 25°C. A new analysis method was programmed for the computer controlling the automatic plate reader so that photographic plates could be read with higher precision. One plate for K_2SO_4 was reread by this newer method. In general the two methods give good agreement for the diffusion coefficient but the newer approach gives somewhat better statistical precision and internal consistency.

Isopiestic experiments were completed at 25°C for aqueous $CaCl_2$ solutions up to 10.253 $mol{\cdot}kg^{-1}$, which is about 2.8 $mol{\cdot}kg^{-1}$ above saturation, and for H_2SO_4 from 0.27470 to 0.70512 $mol{\cdot}kg^{-1}$. All three isopiestic chambers are now being used for aqueous H_2SO_4 + $MgSO_4$ mixtures at 25°C. Experiments have been performed at molality fractions for H_2SO_4 of 6/7, 5/7, and 4/7; 114 data points have been measured covering the water activity range of $0.8850 \leq a_w \leq 0.4893$. These experiments are being extended to higher and to lower molalities.

A major amount of time was spent writing papers for publication in journals. During this period six were published; three more were submitted for publication, of which two are in press. These include an analysis of the emfs of cells containing aqueous H_2SO_4, a detailed thermodynamic model for aqueous NaBr valid from the freezing temperatures to over 300°C and to high pressures, ternary solution diffusion coefficients at 30° for some compositions of aqueous NaCl + $MgCl_2$, an intercomparison of the precision and accuracy of diffusion coefficients for a ternary solution derived from Rayleigh and Gouy interferometry, and testing of various mixing approximations for densities and for electrical conductances based on binary solution data.

has proved to be a problem for some minerals during the experiments (especially under hydrous conditions) and is being addressed by varying P–T conditions, the characteristics of the reservoir, and fluid composition.

C. Experimental Determination of Mineralogical Controls on U–Th–Pb Redistribution: Implications for Crust/Mantle Differentiation *(H. F. Shaw [510-423-4645; Fax 510-423-1057; E-mail shaw4@llnl.gov] and F. J. Ryerson [510-422-6170; Fax 510-422-1002; E-mail ryerson@s91.es.llnl.gov])*

Objectives: The objective of this work is to determine mineral/aqueous fluid and mineral/silicate liquid partition coefficients for a suite of trace elements (U, Th, Hf, Zr, Nb, Ta, Sr, Ba, Rb, and Pb) under conditions relevant to fluid metasomatism and partial melting in the upper mantle. The results of the project will provide important constraints on the petrogenetic interpretation of trace element, U–Th–Pb, and U-series disequilibrium data obtained on igneous rocks, particularly those formed in subduction-zone environments.

Project Description: Along with the formation of the earth's core, the differentiation of the crust and mantle represents the major chemical fractionation process occurring on the earth. The nature of this process has been constrained by a wide variety of trace element and isotopic analyses of crust- and mantle-derived samples. Effective utilization of these data requires a quantitative understanding of the fractionation of the elements of interest between minerals and both silicate melts and aqueous fluids. For many elements, however, the relevant mineral/melt partition coefficients are poorly known and there is an almost complete lack of data for the partitioning of trace elements between minerals and aqueous fluids. The experimental data generated in this project will provide quantitative information of the partitioning of trace elements of geologic interest between minerals and melts and aqueous fluids, with emphasis on the partitioning of U, Th, Pb, and the high-field-strength elements (Zr, Hf, Nb, Ta). Partition coefficients for elements of interest are being obtained as a function of fO_2, T, P, and fluid or melt composition. Experimental charges are produced using standard and newly developed techniques that utilize one-atmosphere gas-mixing furnaces and high-pressure piston–cylinder devices. The trace element composition of the charges is being measured primarily by quantitative ion microprobe techniques, supplemented by electron microprobe analyses and solid-source mass spectrometry.

Results: The partitioning of U, Th, Pb, Ba, Sr, Nb, and Ta between aqueous fluids (with and without added Cl^- and CO_3^{2-}) and rutile, clinopyroxene, orthopyroxene, pyrope, olivine, and pargasitic amphibole under upper mantle conditions has been studied. Using these data, together with literature data for Sr and Pb isotopic compositions of Pacific island arc basalts (IABs), the calculated composition of a fluid in equilibrium with the average Pacific IAB source is $^{87}Sr/^{86}Sr = 0.7036$, $^{207}Pb/^{204}Pb = 15.57$, Sr ~500 ppm, and Pb ~30 ppm. The subarc fluid composition is consistent with a mixture of fluids from both altered MORB (~96 wt%) and sediment (~4 wt%), with ~96% of the Sr from the former, and ~70% of the Pb from the latter. Although the mass fraction of sediment-derived fluid in the subarc fluid may be minor, sedimentary input for Ba (0–50%), Th (53–88%), U (61–83%), in addition to Pb, can be significant. Our results are consistent with, and provide additional support for, models of slab input to IAB sources. Preliminary results indicate that metasomatism by water-rich fluids and silicate melts will produce similar but distinguishable trace element signatures in island-arc basalts (IABs).

Experiments were conducted to determine partition coefficients for Ti, Rb, Ba, Sr, Zr, Nb, Ta, Hf, Pb, U, and Th between pargasitic amphibole and a synthetic hydrous silicate liquid. Rb, Ba, Nb, and Ta are dramatically less compatible in pyroxene than in amphibole, while other elements, such as Th, U, Hf, and Zr, have similar compatibilities. Because of these differences, liquids produced by small degrees of partial melting of amphibole-bearing mantle sources, or by high-level fractionation of amphibole, should have distinctively lower Th-normalized Rb, Ba, Nb, and Ta concentrations than melts from amphibole-free systems.

constraints. A paper on these results has been submitted to the *Journal of Applied Mechanics*. In collaboration with researchers at Princeton, New York University, and the University of Utah, we have developed a method for obtaining rigorous bounds on the shear modulus of viscoelastic composites such as rocks that contain mixtures of two viscoelastic constituents. This work extends and completes the previous work of the collaborators on the bounds for the bulk modulus of viscoelastic composites, and furthermore shows how well various realizable theoretical models produce results consistent with the bounds. A paper describing this work is currently being written for publication. In collaboration with researchers at the University of Wisconsin, we have 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. The first part of this work has been accepted for publication in the *Journal of Geophysical Research*.

B. Deployment of a Borehole Seismometer at the KTB Drilling Site *(Paul Kasameyer [510-422-6487; Fax 510-422-3925; E-mail kasameyer1@llnl.gov])*

Objective : The purpose of this trip was to install a seismic monitoring system in a 4-km-deep borehole adjacent to the KTB 9.1-km borehole, and to use that instrument to record explosions and natural and operationally induced earthquakes at this depth.

Project Description: The KTB project is a decade-long project to develop drilling and measurement capabilities to explore deep in the continental crust, and to use those techniques to study a major European suture zone. The latest scientific efforts in that project were a 3-D seismic survey, and a hydrofrac and induced seismicity experiment. Cooperation with the KTB project is one goal of the US Continental Scientific Drilling Program. This project was funded to deploy a borehole seismometer that had been originally constructed for the Geothermal Technology Division of DOE to monitor these activities at 4-km depth where the frequency content is not limited by passage through the near-surface.

Results: The LLNL borehole seismometer system was refurbished and outfitted with new sensors. The system was emplaced at a depth of 3830 m and deployed there for four days, continuously recording three components of seismic data at a sample rate of 1000 Hz.

The LLNL borehole sensor has three characteristic features: first, the sensors are sensitive to ground acceleration and therefore have a relatively low high-frequency noise floor compared to more conventional seismometers that respond to earth velocity. Second, the sensors have no downhole amplification, so they can be used at higher temperatures. Third, the system was designed to clamp into a well-cemented metal casing of known diameter. A second system, designed by Geostock, a French company, was deployed in the hole immediately after we removed our system. The Geostock tool had high-frequency seismometers, downhole amplifiers, and clamps in the open portion of the hole. Consequently, this experiment provided the opportunity to compare these two design approaches for deep-hole seismic recording.

Our borehole system recorded approximately six “large” events, and several “small” events. The large events included four explosions that were part of a deep 3-D seismic survey, with several hundred surface seismometers. We recorded the time-history of the down-going energy so that it can be effectively removed from the surface recordings in order o produce better reflection images, a local quarry blast, and a local earthquake. The origin of the smaller events was not known. Preliminary results showed that the LLNL tool was more subject to 50-Hz interference than was the Geostock tool, and that the LLNL tool had a lower instrumental noise floor above 60 Hz. Low-frequency noise on the tool made detection of regional seismic signals very difficult. The data were forwarded to the KTB seismologists for final analysis.

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

(P. A. Berge [510-423-4829; Fax 510-423-1057; E-mail berge@s44.es.llnl.gov], J. G. Berryman [510-423-2905; Fax 510-422-1002; E-mail berryman@s123.es.llnl.gov], D. Elata [510-423-8281; Fax 510-422-1002; E-mail elata@llnl.gov], I. Tsvankin, Colorado School of Mines [303-273-3060; Fax 303-273-3478; E-mail ilya@dix.mines.edu], K. Larner, Colorado School of Mines [303-273-3428; Fax 303-273-3478; E-mail klarner@dix.mines.edu], and F. Muir, Stanford Univ. [415-723-9390; Fax 415-723-1188; E-mail francis@pangea.stanford.edu]

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 reflection 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 find 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 seismic reflection data in vertically inhomogeneous, transversely isotropic media. These results have been submitted for publication in *Geophysics* and for presentation at the Society of Exploration Geophysicists annual meeting. Currently, Colorado School of Mines researchers are using their codes to process seismic data and to produce estimates of some of the anisotropy parameters. Results from research at Stanford include the development of a new theoretical model that describes the anisotropic behavior of certain shales. This work was submitted for publication in the *Journal of Seismic Exploration*. LLNL investigators have shown that constraints on anisotropy parameters for models of layered rocks contain information about lithology. These results have been submitted for presentation at the Society of Exploration Geophysicists annual meeting. LLNL and Stanford researchers are currently developing and analyzing additional theoretical models of rocks to determine how anisotropy parameters are related to rock properties and how these relationships constrain lithology. The Stanford/LLNL group is also determining what information from seismic reflection data is necessary and sufficient for correlating anisotropy parameters and lithology.

structure and fill; geometry and internal structure of the composite pluton underlying the caldera; and the structure and composition of the middle to lower crust beneath the pluton. A majority of the effort will involve collecting and interpreting seismic data to be used in imaging the subsurface structure beneath the caldera. Active seismic data will be collected along three lines, each about 170 km in length. Seismic sources include vibroseis explosions along each line. The reflection, wide-angle reflection, and refraction data from these six lines will be interpreted to obtain a detailed image of the crust beneath the Jemez volcanic field. In addition, two passive seismic arrays, consisting of up to 50 seismic instruments, will be set up to record teleseisms. The teleseismic data will be used to constrain the mid-crustal and upper-mantle seismic structure. Part of the teleseismic array will consist of one or more sub-arrays, with instrument spacing of as little as 1 km. Converted phases recorded on these sub-arrays are being analyzed to obtain more constraints on locations of velocity anomalies in the crust. The existing gravity datasets are being supplemented with new data. Gravity and magnetotelluric data will be analyzed along with the seismic data.

Results: The first active phase of the experiment, consisting of one seismic line of length 160 km, was completed in 1993. Both passive phases of the experiment have now been completed. The second passive phase, involving the deployment of 50 three-component seismometers for a period of about 4 months, was completed during FY1995. Permitting for the second active phase consisting of two seismic lines to be conducted during the fall of 1995 is nearly complete.

Analysis of the passive data from the first experiment using a travel-time tomographic technique has indicated the existence of a low-velocity body beneath the center of the caldera at a depth of between 8 and 12 km. This anomaly is substantially smaller than but better resolved than the one found from previous studies using fewer instruments. The existence of this anomaly is consistent with the data collected during the first active phase of the project. Analysis completed to date on the active data do not give a good constraint on the horizontal location of the anomaly. An anomaly located near the crust-mantle boundary is also consistent with both active and passive datasets. This low-velocity anomaly was unexpected.

C. Imaging of Reservoirs and Fracture Systems Using Microearthquakes Induced by Hydraulic Injections *(L. House [505-667-1912; Fax 505-667-8487; E-mail house@lanl.gov] and M. Fehler)*

Objectives: This work aims to characterize and image hydraulically fractured rock volumes using arrival times and waveforms of microearthquakes induced by the fracturing.

Project Description: In spite of the extensive use of hydraulic fracturing by the oil and gas and geothermal industries, the fluid paths created by the fracturing are usually not well known. That information is crucial, however, for most effectively exploiting the fractured reservoirs. Hypocenters of the induced microearthquakes give some information about the fluid paths, but do not provide the spatial resolution or amount of detail that are needed.

This study is developing analysis methods to extract more information about the fluid system created by hydraulic fracturing from the arrival times and waveforms of microearthquakes induced by the fracturing. Microearthquakes are much more energetic sources, particularly for shear waves, than the artificial sources used in active experiments. Moreover, because they are distributed throughout the rock volume to be interrogated, they provide better resolution of the rock properties than would be possible with artificial sources.

Two principal analysis methods are used. First is a velocity tomography approach that simultaneously determines a three-dimensional velocity structure and new hypocenters for the earthquakes. The creation of fluid paths within the rock will decrease both the compressional and the shear wave velocities within the fracture system, but particularly the shear wave velocity. The velocity tomography is intended to identify these changes. Second, conspicuous secondary seismic phases that arrive after the direct P and S waves stringer, explaining in part why the rock does not exhibit anomalously high conductivity at 0.1 MPa (1 atm) pressure. The observations indicate that carbonaceous material may exert a primary control on crustal electrical conductivity because it may be present as interconnected arrays in grain boundaries or microfractures or in megascopic, through-going fractures.

CATEGORY **Geochemistry**

PERSON IN CHARGE: **D. Janecky**

A. Search for Evidence of Large Comet or Asteroid Impacts at Extinction Boundaries

(M. Attrep, Jr. [505-667-0088; Fax 505-665-4955; E-mail mattrep@lanl.gov])

Objectives: Identify the signatures in the geological record large-body impacts and/or massive volcanism in relation to the known extinction boundaries in the fossil record. In addition, we also investigate the environmental consequences of local releases of ultra-high amounts of energy (impacts), help establish and develop the field of chemostratigraphy, and establish geochemical time markers in the geological record. We also take advantage of our unique analytical capabilities and these unique geological markers to investigate trace-element migration of the chemical element as a mean to understand the dynamics of the nuclear waste storage/burial strategies.

Project Description: Our analytical methodology to accomplish these tasks is the use of radiochemical neutron activation analysis to measure the platinium group elements. In particular, we measure iridium at the 1–3 part per trillion level.

Results: For the past year we have concentrated on sites where there are suspected impact sites. These include the Ames Structure in Oklahoma (Devonian). We have found a modest iridium enrichment in samples from this site that correlate to the backwash in the inner structure. This work is being done in collaboration with the Dr. Ken Johnston at the Oklahoma Geological Survey. We have analyzed for iridium in core samples from the Manson structure and in the suspected ejecta material in South Dakota. No iridium enrichment was found, indicating that the meteorite was a type that did not contain iridium. The Manson related work has been done in collaboration with Dr. Maureen Steiner (University of Wyoming) and Dr. Gene Shoemaker (USGS). These studies are being finalized. We have been working with Prof. Henning Dypvik, University of Oslo, and have analyzed suspected ejecta (Myklegardfjellet Bed in Greenland) and core samples from the Mjolnir Structure in the Barents Sea. The suspected impact corresponds to the Jurassic–Cretaceous boundary. We have observed some evidence that the structure may have been caused by an impact. The core samples showed a marked increase in iridium at the level that would correspond to the low-angle ejecta. We also have several other collaborations: Alamo Breccia in Nevada with Dr. John Warme, Colorado School of Mines, and possible impact structure at the Devonian Mississippian in collaboration with Dr. Don Woodrow Hobart and William Smith College, NY. We have continued our collaboration in numerous investigations at the Frasnian–Famennian (China, Canada and Europe) in collaboration with Dr. Kun Wang and Prof. H. H. J. Geldzetzer in Canada. Samples from Prof. S. Chatterjee, Texas Tech University, are being analyzed for evidence of the K–T boundary in the Deccan Traps.

models, coupled fracture and matrix permeability models, lattice gas automata models, and large-scale hydrologic models.

Results: Development of labeled organic compounds focused initially on use of deuterium. Working with industry, commercial sources are being developed for relatively large amounts of isotopically labeled compounds. A range of labeled compounds are on hand for laboratory experiments and relative large quantities of labeled compounds have been utilized for experiments by an industrial collaborator. The choice of stable isotope labeled organic molecules as tracers provides significant advantages in simultaneous multicomponent analysis; however, it also requires a commensurate emphasis in complex analytical methods. Development of GC/MS analyses for environmental samples and expertise developed through analytical work for oil shale processing programs, along with continuously improving analytical equipment, has been combined to successfully complete analyses of labeled organic compounds in solutions, including fresh to brine salinities, gas and liquid petroleum matrices.

Detailed evaluation of our initial multicomponent tracer experiment below the Mammoth Terraces in Yellowstone National Park indicates general consistency between a range of simple tracers as a function of the first acid dissociation constants and internally consistent changes in dispersion and peak shape. Laboratory HPLC experiments are providing information on processes that produce complex peak shapes, similar to some found in the field experiment. In collaboration with Mobil Exploration & Producing US, two multiwell, multicomponent tracer experiments were initiated in petroleum reservoirs. Analyses of the thousands of samples collected over a one-year time frame reveal a snapshot of field operation, tracer transport/reactions and variability of produced petroleum fraction. Similarly, detailed analyses and laboratory experiments with conventional rhodamine-WT tracer provided information on complex chemical and spectroscopic changes which were observed during an environmental demonstration experiment.

D. ^{230}Th–^{238}U Disequilibrium in Geologic Systems Using Solid Source Mass Spectrometry

(M. T. Murrell [505-667-4299; Fax 505-665-4955; E-mail mmurrell@lanl.gov], K. W. W. Sims, and S. J. Goldstein)

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

Project Description: Previously, we have developed mass spectrometric methods for measuring ^{230}Th/^{238}U, ^{226}Ra/^{230}Th, ^{228}Ra/^{232}Th, and ^{231}Pa/^{235}U disequilibria which have significant advantages over decay counting methods. Current emphasis is using these techniques to better understand the behavior of U-series members in magmatic and aqueous systems. These issues are critical to understanding the mechanisms that control dynamic geologic processes, such as the formation of the Earth's crust.

Results: We have adapted the mass spectrometric procedures for radium and barium originally developed for our NBS instruments for use on our commercial instrument (Fisons Sector 54-30). We have also modified our separation chemistry, which originally involved pressurized ion exchange columns, for use with the commercially available Sr-Spec resin and columns (Eichrom Industries). This should allow this procedure to be used by commercial laboratories for verifying compliance in NORM regulatory issues.

Previously, we determined precise U–Th and Sm–Nd isotopic ratios and concentrations in a series of systematic lavas from Hawaii, which have trace-element and petrological characteristics indicating that they span a large range of melt fraction. Based upon this work, we concluded that U/Th fractionation in Hawaiian basalts can be understood in terms of simple batch melting of a garnet peridotite source with melt fractions of 0.5% to 6.5% (Sims et al., *Science*, 1995). The consistency of the isotopic and major-element data would suggest that the melt generation and segregation rates are short relative to the half life of ^{230}Th. In order to further refine our understanding of this timescale, we have measured Ra in the same young series of Hawai-

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Summaries of FY 1995 Geosciences Research

December 1995

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Office of Energy Research
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Division of Engineering and Geosciences
Germantown, MD 20874

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CONTENTS

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 programs. The Geosciences Research Program includes research in geophysics, geochemistry, resource evaluation, 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 by accessing the URL address *http://www.er.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 the long-term fundamental knowledge base necessary to provide for energy technologies of the future.

Future energy technologies and their individual roles in satisfying the nation's energy needs are uncertain in their particulars. 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 these 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:

- Geophysics and Earth Dynamics.
- Geochemistry.
- Energy Resource Recognition, Evaluation, and Utilization.
- Hydrogeology and Exogeochemistry.
- Solar–Terrestrial Interactions.

The following outline of current research in these categories is intended to be illustrative and evolves with time and progress in these 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. Also, 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 earth's 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 AND EXOGEOCHEMISTRY

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 fluid–rock systems.

C. ***Perturbations of Fluid Flow.*** Research on the physicochemical dynamics and chemical transport of fluid–rock 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 earth's 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**

A. Mineral–Fluid Interactions: Experimental Determination of Atomic-Scale Processes Using Synchrotron Radiation *(Ronald P. Chiarello [708-252-9327; Fax 708-252-9373; E-mail chiarello@cmt.anl.gov] and Neil C. Sturchio)*

Objectives: The objective of this program is to advance the basic understanding of rock–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 techniques with high-brilliance synchrotron radiation. This approach applies techniques developed recently by physicists for basic studies of surface phenomena and semiconductor properties. 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 in chemically controlled conditions. During the past year, experiments were conducted to characterize the atomic structure of the calcite (104) cleavage plane in contact with water, and to observe changes in this structure as a function of solution composition and time, using crystal truncation rod measurements. This work required the development of a new reflection geometry x-ray cell having a thin (micron-scale) water layer above the calcite surface. X-ray reflectivity and diffraction techniques were used to determine the growth rate, compositional evolution, and crystallographic characteristics of a $(Ca,Cd)CO_3$ solid solution precipitated heterogenously onto calcite. The x-ray standing-wave technique (at Bragg diffraction angle) was used to determine the lattice locations of Mn and Sr in calcite and Zn sorbed onto the calcite surface from aqueous solution, by triangulation from three different diffraction planes, in collaboration with M. J. Bedzyk (Northwestern University) and colleagues.

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CATEGORY:	**Geochemistry**
PERSONS IN CHARGE:	**B. Manowitz** and **M. A. Vairavamurthy**

A. Sulfur Speciation in Sedimentary Macromolecular Organic Matter by X-Ray Absorption Spectroscopy *(B. Manowitz [516-282-2458; Fax 516-282-5526] and M. A. Vairavamurthy [516-282-5337; Fax 516-282-5526])*

Objectives: This project focuses on the use of x-ray absorption spectroscopy for understanding sulfur speciation in sedimentary macromolecular organic matter in a collaborative project with Woods Hole Oceanographic Institution titled "The role of sulfur in the formation and diagenesis of macromolecular matter in sediments." A major objective is to quantitatively speciate sulfur forms in sediments and in the products of diagenesis to complement information obtained with other techniques such as gas chromatography.

Program Description: In marine sediments, sulfur is intimately involved in organic matter diagenesis. Several recent studies suggest an important role for sulfur in the formation of macromolecular organic matter in sediments. The experimental and theoretical approaches used in this project are based on the premise that macromolecularly bound sulfur can be represented by model structures which differ in such linkage type (inter-molecular bridges vs intra-molecular bonds), as well as the number of linkages per molecule and the number of sulfur atoms in each linkage. Studies will be conducted to understand whether the degree of sulfur cross-linking controls the molecular-size distribution in sulfur-rich organic matter. X-ray absorption spectroscopy for sulfur will be performed in X-19A beam line at the National Synchrotron Light Source. The K-edge XANES spectra will be collected as fluorescence spectra. Quantitative analysis will be performed by computer simulation using spectra of model compounds.

Results: X-ray absorption spectroscopy was used, in conjunction with a variety of other techniques (including pyrolysis-gas chromatography, ^{13}C NMR spectrometry, and elemental analysis), to examine variations in sulfur speciation during thermal maturation of Monterey shale. Samples comprised total sediments, kerogens, and bitumens obtained from a series of hydrous pyrolysis experiments conducted at temperatures ranging from 125 to 360°C at 350 bars pressure.

Based on these measurements, it was possible to recognize three distinct temperature regimes, within which the type and amount of sulfur in the analyzed fractions underwent transformations: (1) between 150 and 225°C, a significant proportion of kerogen-bound sulfur is lost probably due to the collapse of polysulfide bridges; (2) between 225 and 275°C, cleavage of –S–S– and –S–C– linkages within the kerogen is believed to occur, resulting in substantial production of polar sulfur-rich bitumen; (3) above 275°C total bitumen yields as well as the proportion of bitumen sulfur decrease, while C–C bond scission leads to increased yields of saturated and aromatic hydrocarbons.

The results from this study clearly and quantitatively establish a link between organically bound sulfur, and more specifically, organic polysulfides, and the low-temperature evolution of soluble petroleum-like products (bitumen) from sulfur-rich source rocks.

B. Geochemistry of Organic Sulfur in Marine Sediments *(A. Vairavamurthy [516-282-5337; Fax 516-282-5526] and B. Manowitz [516-282-2458; Fax 516-282-5526])*

Objectives: The broad objectives are to understand the geochemical mechanisms of sulfur incorporation into sedimentary organic matter, to study the changes in the abundance and forms of sulfur during early diagenesis in various organic-rich sedimentary environments, and to examine the influence of sulfur incorporation in the preservation of sedimentary organic matter.

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. The fundamental geochemical issue in this matter is the mechanism of sulfur incorporation into sedimentary organic matter. Although there is compelling evidence to indicate that reactions of reduced inorganic sulfur species with organic molecules occur during the early stages of diagenesis and under very mild conditions, the molecular mechanisms are still not well understood. Previously, hydrogen sulfide has been considered to be the primary sulfur reactant for organic sulfur formation in sediments. Recently, evidence is emerging that H_2S oxidation products, especially polysulfides, are also important. The roles of elemental sulfur, sulfite, and thiosulfate in the formation of organic sulfur are still not clear. 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 sulfide oxidation to understand the formation of different oxidation intermediates, and (4) analytical methods development. An important goal of this project is to use synchrotron-radiation-based x-ray absorption near-edge-structure (XANES) spectroscopy for characterization and determination of sulfur species, in addition to other state-of-the-art techniques.

Results: Recently, we established sulfonates as an important class of organic sulfur in marine sediments. Currently, one of our areas of research is directed toward understanding the origins of sulfonates in sediments. XANES analysis revealed that sulfonates are the dominant forms of sulfur in most marine phytoplankton species. These results are remarkable because reduced sulfur is thought to be the most abundant sulfur form in these organisms. Thus, it is possible that sedimentary sulfonates have a biological origin in addition to an origin in geochemical mechanisms involving reactions between H_2S oxidation intermediates (sulfite and thiosulfate) and functionalized organic molecules.

Measurements of sulfur speciation of the organic-rich sediments off the coast of Chile were conducted to better understand the early diagenetic distribution of various sulfur species, including sulfonates. Our results of this study and earlier ones indicate that organic polysulfides are the dominant fraction of organic sulfur in early diagenetic sediments. The distribution of organic sulfides in the vicinity of the oxic–anoxic interface, where intermediates from H_2S oxidation were likely to be generated most abundantly, strongly suggests they were formed by the geochemical pathway involving reactions between (inorganic) polysulfides and functionalized organic molecules. The sub-surface maximum for sulfonates appearing just above that of organic polysulfides also indicates their geochemical origin. These results strongly support the view that the partial oxidation products of H_2S play a dominant role in incorporating sulfur into sedimentary organic matter. Since these oxidation products are generated maximally at the oxic–anoxic interface, which usually lies above the hydrogen sulfide maximum, the oxidation intermediates will have the first chance to react with reactive molecules present in the deposited organic matter rather than hydrogen sulfide. This hypothesis may explain the dominance of organic polysulfides in geochemical systems.

C. Measurement of Fluid Flow and Fluid–Rock Interactions Using Synchrotron Computed Microtomography *(K. W. Jones [516-282-4588; Fax 516-282-5271; E-mail kwj@bnl.gov] and W. B. Lindquist)*

Objectives: The objective of this project is to study microgeometry, fluid flow, and fluid–rock interactions in geological specimens using the nondestructive technique of synchrotron computed microtomography (CMT). The work is carried out using high-intensity x-ray beams produced at the National Synchrotron Light Source. An area x-ray detector makes it possible to obtain volume images with up to 10^9 voxels and a spatial resolution better than 10 m.

Project Description: The CMT is used to measure the microgeometry of rocks at pore-scale dimensions. The results are used to determine values for porosity, permeability, connectivity, and other rock properties. Theoretical predictions for fluid flow can then be made and verified based on realistic rock properties at a microscopic scale. Models for rock properties can be made and used to link microscopic and macroscopic models. The experiments are intimately linked to the development of a CMT system which provides integration of data acquisition, tomographic section reconstruction, and visualization with a three-dimensional viewing system. Ultimately, the experimental technologies developed will be used at the Argonne National Laboratory (ANL) Advanced Photon Source (APS) so as to benefit from the higher brilliance of that third-generation synchrotron photon source. It will be feasible to obtain information at rates which will greatly improve the ability for measurements of flow kinetics and other time-dependent phenomena.

Results: Presently emphasis is placed on investigation of sandstones and other rocks found in petroleum reservoirs. Information is obtained on pore structure porosity, permeability, connectivity, and the specific minerals found in the rocks. Initial experiments related to fluid transport were undertaken. Several theoretical analyses of the experimental structures were completed.

Visualization of the structures found using CMT is important. Hence, a project to incorporate true three-dimensional visualization into the CMT system has been designed in collaboration with Mobil Research & Development and GTE. The new system, to be in operation during FY 1996, will facilitate not only viewing the structure, but will also help in validation of theoretical fluid-flow calculations.

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CATEGORY: **Geophysics and Earth Dynamics**

PERSON IN CHARGE: **J. Epstein**

A. Frictional Process Zones in Compressive Fracture *(J. Epstein [208-526-6874; Fax 208-526-0690; E-mail esj@inel.gov] and L. Koo [208-526-0464; Fax 208-526-0690; E-mail lts@inel.gov])*

Objectives: The purpose of this project is to investigate the fracture of quasi-brittle materials which exhibit friction along their crack faces under varied degrees of shear and compression loading. Success in this endeavor will lead to an improved class of frictional constitutive relations useful to the modeling of underground joints. Relative to the U.S. Department of Energy mission areas, these improved slip models are applicable to underground storage facilities such as the Yucca Mountain Project, whose NRC certification requires a validated means for predicting the long-term behavior of tunnel slip planes.

Project Description: Using a combined experimental and theoretical approach, a series of homogeneous specimens have been fabricated made of pure Solnhofen limestone, marble, Nevada tuff and *bimaterial* systems consisting of Solnhofen bonded to PMMA. These compressional fracture specimens have no initial crack mouth opening such that under compression shear a singular slip field develops with no pre-elastic compression effects normally encountered with an artificial saw-cut crack. A floating biaxial frame has been developed to apply independent degrees of shear and compression to the crack up to initiation. Diagnostics include a 4-beam moiré interferometry system to map the X,Y, and 45-degree in-plane displacement fields local to the crack face with a sensitivity of 0.4 microns. Also employed is a coupled acoustic emission loading system to control unstable crack growth in the specimens. The measured in-plane displacement fields are compared to complex function solutions incorporating frictional sliding along the crack face for homogenous and bimaterial cases. The final product will be verified semi-closed form solutions for frictional slip along crack faces that can be input into larger numerical geo-models.

Results: Several homogeneous specimens of Solnhofen limestone have been fabricated and tested under varied degrees of independently applied shear to compressional loading. Mixed-mode crack initiation has consistently occurred at a shear to normal load ratio corresponding to the measured coefficient of frictional (0.6–7) as measured by Sandia Labs. These initiation results indicate a uniform frictional locking effect dominated by the crack face much larger than the singular region of the tips. Once slip occurs it vastly overwhelms the K_{II} initiation value for the Solnhofen material, thus initiating the crack. The in-plane X and Y displacement fields have been measured to determine the crack face opening profile. This profile has been compared to a complex variables solution incorporating the friction as a non-singular term. A solution has also been derived for the bimaterial crack under shear and compression incorporating the effects of friction. Bimaterial samples have been fabricated consisting of Solnhofen limestone bonded to PMMA. This material mismatch should be sufficiently strong to vary the frictional process zone along the crack face as compared to the pure Solnhofen sample and should yield significant fundamental insight on the behavior mismatched jointed media. These specimens are being tested in the same fashion as the homogeneous specimens. Energies to fracture will be extracted from these bimaterial tests as a function of shear to normal load ratio.

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CATEGORY **Geophysics and Earth Dynamics**

PERSON IN CHARGE: **S. M. Benson**

A. Energy Partitioning of Seismic Waves in Fractured Rock *(L. R. Myer [510-486-6456; Fax 486-5686; E-mail myer@lbl.gov], N. G. W. Cook, and K. T. Nihei)*

Objectives: The objectives of this work are to: (1) investigate the partitioning of energy between seismic body waves, guided waves, and scattered waves produced by sources of finite size and bandwidth which are transmitted, reflected, and channeled along single and multiple fractures; (2) determine optimum source and receiver configurations for exciting and detecting these waves; (3) determine the effects of spatial variations in the fracture properties on seismic wave propagation; and (4) examine the effects of a finite-length fracture on seismic waves.

Project Description: A combination of analytic, numerical, and laboratory modeling is being conducted to determine the effects of single and multiple fractures on body waves and guided waves. Analytic work is being conducted to determine the frequency-dependent velocities and particle motions of trapped and leaky fracture guided waves. Numerical simulations are also being performed using a dynamic boundary element code to analyze the generation of fracture guided waves from a polarized, bandlimited source. The predictions of the analytic and numerical modeling are being tested in the laboratory using two-dimensional (plane stress) physical models that enable measurement of both velocities and particle motions. The laboratory measurements are also being used to investigate the effects of finite length and variable stiffness fractures, both of which are difficult to analyze analytically and numerically.

Results: Analysis of the modal determinant for a single, infinitely long fracture embedded in an elastic medium revealed that the determinant can be reduced to two fracture interface wave dispersion equations, both with mathematical forms similar to the classic free-surface Rayleigh wave equation. The two fracture interface waves have either symmetric (i.e., extensional) or antisymmetric (i.e., flexural) wave motion with elliptically polarized particle displacements. The symmetric fracture interface wave has a cut-off frequency above which it is a normal mode and below which it exists as a leaky mode. At zero frequency, the leaky symmetric interface wave degenerates to a compressional body wave.

A two-dimensional dynamic boundary element code capable of modeling elastic wave propagation in an elastic media containing a fracture of arbitrary stiffness was developed for investigation of the conversion of body waves of finite bandwidth and wavefront curvature into fracture interface waves. Numerical boundary element simulations for a line source located on the fracture plane show clear evidence of the symmetric and antisymmetric fracture interface waves predicted by the analytic theory and, in addition, fracture head waves and a fracture compressional wave. All of these waves were observed to be sensitive to the stiffness of the fracture.

The predictions of the plane wave analysis and the numerical studies have been confirmed in the laboratory using two-dimensional fracture models. The modeling is performed on a thin acrylic sheet. A collinear array of holes are drilled to model the fracture. A two-component miniature accelerometer is used to measure particle accelerations at various positions in the plate. Particle motion measurements made along a profile crossing the fracture have confirmed that the interface waves have elliptically polarized particle motions. The model is being adapted to investigate the effects of a fracture of finite length, multiple fractures, and fractures with variable stiffness.

B. Effects of Heterogeneity on the Mechanical Properties of Rock *(L. R. Myer [510-486-6456; Fax 486-5686; E-mail myer@lbl.gov], N. G. W. Cook, and K. T. Nihei)*

Objectives: The objective of this work is to develop a fundamental understanding of the effects of microstructural and macrostructural heterogeneity on the nonlinear, hysteretic deformation and failure of rock loaded in compression.

Project Description: This work examines the mechanical process in rock that control how rocks deform and fail under compressive loading. Laboratory measurements on a suite of sedimentary rocks are being performed to determine how variability in rock microstructure (e.g., grain shape, size, cementation, tensile strength and packing geometry) produces local stress concentrations which, in turn, produce intergranular frictional sliding and extensile microcracking. Laboratory work includes stress–strain, pore compressibility, and seismic properties measurements. Microstructure at any particular state of stress is preserved for SEM analysis using a Wood's metal impregnation technique. Numerical studies using a boundary element code and a Lagrangian discontinuous deformation analysis code are also being conducted in parallel with the experiments to quantify the effects of stochastic variations in grain strength, size, and packing geometry on the nucleation and coalescence of microcracks.

Results: A laboratory investigation of the effects of intergranular frictional sliding in sandstone on the static (large strain) and dynamic (small strain) moduli was completed for uniaxial stress, uniaxial strain, and hydrostatic states of stress. From these measurements, the elastic moduli obtained from small strain unloading excursions from the loading part of the static stress–strain curve were observed to be nearly identical to the dynamic stress–strain curve obtained by integrating the elastic moduli computed from measured ultrasonic velocities. This result clearly illustrates that the difference between the elastic moduli obtained from static and dynamic tests is primarily due to the difference in the applied strain amplitude and not due to the frequency of the applied stress, and, furthermore, underscores the importance of intergranular frictional sliding effects in the analysis of rock deformation. Laboratory work has continued with an investigation of the effects of frictional sliding on the pore compressibility of rocks subjected to different loading paths. Measurements on Berea sandstone indicate that initial differential loading followed by hydrostatic loading can significantly increase the pore compressibility. Analysis of these measurements is being performed to illuminate the micromechanical processes that produce this observed shear enhanced pore compressibility.

Numerical studies continued with boundary element simulations of crack growth in granular rock models consisting of two-dimensional packings of cylindrical grains of variable size, strengths, and moduli. A parametric study to determine how the magnitude of grain dilatation which occurs after a grain is fractured controls the subsequent failure of surrounding grains was performed. This study revealed that dilatation of a failed grain is an important mechanism for transferring local stresses to neighboring grains. If the dilatation of the failed grain is small, than microcracking will tend to progress perpendicular to the maximum compressive stress. However, if the dilatation is large, microcracks will form parallel the direction of the maximum compressive stress.

As a first step toward the development of a class of numerical simulators capable of modeling rock deformation and failure processes such as frictional sliding, grain debonding, grain rotation, and grain fracture, a Lagrangian Discontinuous Deformation Analysis (LDDA) finite-element code is being developed. At present, LDDA is capable of modeling discrete grains that interact along discrete boundaries. Each grain is modeled as a continuous elastic body, and intermittent contact between grains is captured with slideline finite elements using a perturbed Lagrangian multiplier technique. The code is being extended to include fracture and finite rotations. Although this code is still in its development stage, it is anticipated that its capabilities will allow investigation of all aspects of static and dynamic mechanical failure processes that occur in rock.

C. Transport in Single Fractures (Graph Theory) *(Larry Myer [510-486-6456; Fax 510-486-5686; E-mail gemei@myer.lbl.gov], N. G. W. Cook, and G. Yang)*

Objectives: This research will provide a level of understanding of multiphase flow in fractures sufficient to develop algorithms that can be used to analyze and quantitatively predict transport properties in fractures in the field.

Project Description: The mathematics of graph theory is used to characterize the topology of the fracture void space and calculate flow through it. The focus of the work is on single fractures. The general approach is to create a network which captures the important topological characteristics of the flow paths in a single fracture. Graph theory techniques are then used to develop highly efficient algorithms for solving network flow problems.

Results: Second-year studies focused on two-phase distribution under different capillary pressures (imbibition and drainage processes) and identification of preferred flow channels. Given an aperture distribution for a single fracture, a graph theory model has been employed to simulate the transport properties of the fracture. In the processes of imbibition and drainage, the connectivity of each phase at a particular capillary pressure can be sought out by the priority-first search algorithm of graph theory. Then the flow path in each phase can be identified, and flow equations can be established and solved in an optimal manner. The preferred paths make major contributions to the transport properties of a fracture. On the other hand, the imbibition-drainage curves and the hysteresis cycles can reveal the connectedness of the apertures with different heights. The flexibility of graph theory techniques is obvious, but its efficiency is even more impressive. The problem we calculated took tens of minutes to complete, while just a few years ago this size of problem (100×100) was considered as a practical limit using traditional percolation theory (Lenormand et al., 1990). Graph theory is a useful tool when the connectivity is equally important as conductivity.

D. High-Resolution Imaging of Electrical Conductivity Using Low-Frequency Electromagnetic Fields *(K. H. Lee [510-486-7468; Fax 510-486-5686; E-mail KHLee@lbl.gov], H. F. Morrison, and A. Becker)*

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: In spite of great progress in EM methods 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 the following 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. (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. This data is now in the frequency domain, at only a few frequencies, and can only be interpreted with the products of tasks 2 and 3. However, the evident success of the q-domain tomographic imaging process strongly argues for the development of a suitable wideband borehole system (task 4).

Results: The summary of this year's research consists of improvement of the q-domain imaging method, Born inversion, and 3-D nonlinear inversion.

The wavefield transform method (q-domain) has been extended to include frequency-domain data and the result was presented at the SEG International Exposition and 64th Annual Meeting ("Wavefield transform of electromagnetic fields," K. H. Lee, G. Xie, T. M. Habashy, and C. Torres-Verdin, Los Angeles, CA, October 23–28, 1994). Further investigation in the transform method shows that there is a simple theoretical relationship between the phase of electromagnetic field and the traveltime in the q-domain. This relationship is well understood when the medium is homogeneous. When the medium is heterogeneous, however, this relationship is nonlinear and requires a great deal of information, in the form of frequency- or time-domain data, to yield appropriate spatial resolution in velocity in the q-domain.

Further research in the Born inversion and 3-D nonlinear inversion has resulted in two publications in *Geophysics* and one in *The Leading Edge*. The 3-D nonlinear inversion requires many forward model calculations using the integral equation. The computational efficiency involved in this process is not optimum at this point.

E. Non-Linear Elasticity and Seismology *(V. A. Korneev [510-486-7214; E-mail korneev@ccs.lbl.gov], T. V. McEvilly [510-486-7347; Fax 510-486-5686; E-mail mcevilly@ccs.lbl.gov], and L. R. Johnson [510-486-4173; E-mail lrj@ccs.lbl.gov])*

Objectives: Nonlinear wave propagation has long been a fruitful area of research in the field of acoustics. Initial measurements for earth materials have revealed that the basic nonlinear behavior is quite profound, and this has caused considerable interest in nonlinear wave propagation effects in the earth. A program in this area of research has been under way at LBL for two years and it includes components of theoretical, laboratory, and field investigations to better understand basic nonlinear elastic phenomena in earth materials. The research also addresses the phenomenon of elastic scattering in wave propagation. Methods are sought for characterizing the nonlinear parameters of rocks through observations of elastic wave propagation.

Project Description: It is very difficult to separate nonlinear waves from multiple harmonics generated by the source, and time-domain solutions become desirable. Use of the direct Fourier transform technique is prohibited by the nonlinearity of the equations of motion. Therefore, a special study was performed for the purpose of predicting the nonlinear behavior of elastic pulses. Another theoretical investigation studied the nonlinear interactions of two elastic waves. If collimated beams intersect in a spherical volume, there are 54 possible combinations, of which only 10 result in resonant scattering. We have used available in-house field data in a search for effects of nonlinear elasticity. In addition, we conducted one field experiment explicitly for detection of nonlinear wave propagation in conjunction with a previously planned Vertical Seismic Profile at the DOE Nevada Test Site, and we analyzed a special data set acquired by Los Alamos National Laboratory in West Texas in an attempt to verify nonlinear wave propagation during a seismic reflection profile. The scattering of elastic waves by different kinds of obstacles has been another subject of intensive investigation. Theoretical investigations and numerical simulations are being used to design field experiments where the basic predictions of the localization phenomenon can be tested in the earth. If it can be shown that this process plays an active role in seismic wave propagation, then the next stage is to develop methods of accurately estimating the relevant parameters for earth materials.

Results: Time-domain solutions were obtained for 1-D nonlinear elastic wave propagation problems using a five-constant theory, and the strongest nonlinear effects are obtained for the case of single compressional wave propagation, for single compressional or shear wave propagation through a longitudinally pre-stressed elastic material, and for shear wave propagation in a shear pre-stressed elastic material. Estimates of the size of these effects indicate that nonlinear phenomena are likely to be observable in real seismic data. For the interacting beams, except for the interactions of SH waves, the amplitudes of the scattered waves are directly proportional to the nonlinear elastic constants. The scattered waves form conical beams at specific scattering angles. The width of the beams is directly proportional to the size of the interaction volume and inversely proportional to the scattered wavelength. Analytical expressions for the scattering coefficients were obtained for all possible types of interactions, as well as expressions for the scattering angles and their limiting bounds. Sample calculations suggest that scattered waves with amplitudes which are a significant proportion of the primary wave amplitude may arise at moderate strain levels in rock, although this result must be conditioned by the fact that attenuation was not included in the analyses. General results for the scattering problem of an arbitrary elastic wave incident upon a spherically symmetric inclusion, expressed in the form of canonical scattering coefficients, were obtained for the cases of incident P waves and incident S waves. Optical theorems relating the scattering cross-section to the amplitude of the scattered field in the forward direction were also derived for both of these cases. Analytical expressions for scattering coefficients of a homogeneous elastic sphere, a sphere filled by fluid, and a spherical cavity were obtained, and scattering cross-sections were calculated for these different types of obstacles.

F. CCS: Center for Computational Seismology *(T. V. McEvilly [510-486-7347; Fax 510-486-5686; E-mail mcevilly@ccs.lbl.gov], E. L. Majer [510-486-6709; E-mail elm@ccs.lbl.gov], and L. R. Johnson [510-486-4173; E-mail lrj@ccs.lbl.gov])*

Objectives: CCS provides a specially equipped and staffed computational facility to support and advance a wide-ranging program of seismological research. Beyond computers, work stations, seismic processing packages, and visualization capabilities, it is a physical facility in which scientists pursuing individual research interact with other scientists and technical support staff. The data management and processing techniques at CCS are integrated with the data acquisition instrumentation in the Geophysical Measurements Facility (GMF), within which field projects are designed and managed. The goal for CCS is a well-maintained geophysical computing facility to support cutting-edge research in seismology.

Project Description: The Center for Computational Seismology (CCS) serves as the core data processing, computation, and visualization facility for seismology at LBL. CCS was founded in FY82 with VAX 11/780 hardware and DISCO reflection processing software to maintain a state-of-the-art computing environment in support of various seismological and other geophysical research programs at LBL and to develop in this environment new methods for investigating Earth's subsurface structure and processes along with methods for visualizing results. Since the original VAX installation, CCS has progressed through a CONVEX era to the present distributed configuration.

A wide range of research projects rely upon CCS resources for development and application of methods for characterization, process definition, and process monitoring in the rock–fluid–thermochemical subsurface environment. Consequently, CCS research spans a range from the most fundamental investigations to those driven by the most applied technologies. CCS supports basic research in three general areas:

Wave Propagation, Source Studies, and Inverse Theory

- Theoretical, numerical, laboratory, and field studies of wave propagation in media with complex scattering and elastic properties
- Moment-tensor inversion for earthquake and explosion sources
- Solutions for geophysical inverse problems

Seismic Imaging

- Borehole tomography
- 3-D travel-time inversion for velocity and attenuation
- Microearthquakes for process monitoring
- High-resolution reflection profiling

Visualization

- Effective depiction of 3-D structures, subsurface processes, complex wave propagation
- In-field, near-real-time display and experiment control

Results: CCS supports a wide range of research projects, from deep earth structure to high-resolution crosswell tomography, ranging from the most basic investigations to those directed to the most applied technologies. The best demonstration of this wide range of content is in the CCS research output. Major accomplishments flow largely from the breadth of research support provided by CCS, and the cross-fertilization of applications and fundamental studies. Primary strengths lie in elastic wave generation and propagation, inverse methods, data processing and tomographic imaging methods. The list of recent publications, produced with CCS support to varying degrees, displays the range of research accomplishments. The list of PhD thesis topics developed with some CCS resource support adds about four entries per year and they reflect the integration of a wide spectrum of research interests in such a way that applications are readily evident and easily pursued by the more problem-directed researchers in CCS.

G. Controls on Pull-Apart Basin Evolution: Integrated Geological, Geophysical and Modeling Studies *(Patrick L. Williams [510-486-7156; Fax 510-486-4159; E-mail plw@ccs.lbl.gov] and Thomas V. McEvilly)*

Objectives: In a variety of Earth science and technology problems including petroleum production, aquifer characterization, contaminant studies, and tectonic hazards analysis, it has become critically important to identify and characterize in three dimensions the sedimentary character and tectonic structure of sedimentary basins. This project is developing a better understanding and predictive capability for the three-dimensional (3-D) structure of extensional sedimentary basins. The purpose of this work is the integration of surface geology and high-resolution subsurface geological and geophysical data in full 3-D basin representation.

Project Description: This project is directed at the development of a predictive capability for recovery of the 3-D structure of pull-apart basins. Stage one of this work is the integration of surface geology and high-resolution subsurface geological and geophysical data in full 3-D basin representation. This project will complete 3-D representations, or "empirical models," of the bounding geometry, structural elements, stratigraphy, and sedimentology of selected basins. This provides a point of departure (and constraints) for stage two of the project: the development of a new generation of 3-D numerical or "theoretical mechanical basin models." The development of realistic mechanical models of an extensional basin's evolution will require the encoding of accurate basin geometries and deformation history. Subsequent modeling will test how fault geometry and fault displacement affect basin structure in three dimensions.

Results: Development and application of landform and substrate imaging and characterization techniques and the analyses of these landform and subsurface data have been the primary products of this project, and several publications are in progress. Our studies of specific pull-apart basins in the San Francisco Bay area have contributed directly to the understanding of tectonic (earthquake) hazards to structures including industrial facilities, transportation structures, and lifelines. With industry participation, we are demonstrating the capability of advanced imaging tools for investigations of subsurface structure for environmental remediation and characterization of geological hazards.

While the focus of this activity is toward the improvement of fundamental understanding, e.g., the nature of subsurface fluid flow, the propagation of extensional faults in the upper crust, the extent and nature of surface deformation in extensional provinces, this project has a number of direct applications and practical fall-outs: (1) 500 km of high-definition marine seismic reflection data have been collected for study of basins, faults, and the tectonic hazards to bridges in the SF Bay Area. (2) Our work on a small pull-apart basin in Fremont, California, has provided a high-definition plan and sectional structural model for this basin. The Pull-Apart project enhances prior USGS-funded studies of the "archeological record" of Hayward fault earthquakes. (3) We also have advised industrial facilities (oil refineries, land fills), California DOT, and municipalities in regard to the geological hazards associated with a large pull-apart feature, San Pablo Basin, north of Oakland, California. (4) We have developed a model of pull-apart controls to geothermal energy production and brought that model to the attention of industrial and U.S. Navy geothermal producers. (5) As new understanding of complex active fault patterns in the Bay Area and southern California evolves, we have provided various reports to local and national media.

CATEGORY **Geochemistry**

PERSON IN CHARGE: **S. M. Benson**

A. Integrated Isotopic Studies of Geochemical Processes *(Donald J. DePaolo [510-486-4975, 510-643-7686; Fax 510-486-5686, E-mail depaolo@garnet.berkeley.edu or djdepaolo@lbl.gov] and Mack Kennedy [510-486-6451, Fax 510-486-5686, E-mail bmkennedy@lbl.gov])*

Objective: 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, 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 improving geological characterization for energy development and regulatory purposes, and at improved subsurface characterization of natural rock and fluid systems.

Results: (1) Isotopic measurements of He were made in high-CO_2 soil gas on the flanks of Mammoth Mountain, a quiescent (?) Quaternary volcano on the southwest rim of the Long Valley caldera in east-central California. The high-CO_2 soil gas is causing anomalous coniferous forest mortality, which was initially noted in 1990 and presently totals at least 30 ha. Soil-gas CO_2 concentration in tree-kill areas can exceed 90% compared to <1% in nearby healthy forested areas. Helium isotopic composition of the fumarolic discharge indicates an increase in the flux of magmatic CO_2 and He, rapid transport (10 m/d) of the magmatic gas from depths of a few kilometers, and when combined with observations of anomalous seismic activity, is suggestive of a recent intrusive event.

(2) Calcium isotopic fractionation in nature is known to be relatively small in comparison to that of oxygen and sulfur but there has previously been no successful attempt to discover whether it is systematic, or what mechanisms are responsible for the fractionation. New measurements show that biological fractionation is the major source of Ca isotopic fractionation in nature, and that the fractionation is systematic and dependent primarily on trophic level. There are small isotopic variations in igneous rocks, but insufficient data exist to determine the sources of variability. We have set up procedures for measuring Ca isotopic variations using the ^{44}Ca/^{40}Ca ratio expressed as permil variations (∂^{44}Ca) from a standard value based on typical terrestrial igneous rocks and average meteorites. The ∂^{44}Ca values of samples are determined using a double spike (^{42}Ca + ^{48}Ca) technique; analytical uncertainty of the ∂^{44}Ca value is ±0.15 permil. The ∂^{44}Ca value of seawater (+0.9) is the highest value measured thus far. Marine organisms vary systematically from values as high as +0.1 to +0.5 for foraminiferal calcite, to values as low as –2.5 for a porpoise bone. The primary determinant of ∂^{44}Ca in the bone and shell material of marine organisms appears to be trophic level; the magnitude of temperature-dependent fractionation is much smaller. Terrestrial organisms have lower ∂^{44}Ca values than marine organisms of approximately similar mass and trophic level. The high ∂^{44}Ca of seawater appears to be a result of sedimentary sequestering of light Ca.

(3) A new method of uranium–thorium–lead (U–Th–Pb) radiometric age dating for Quaternary rocks was developed. The approach uses an instrumental mass discrimination correction for Pb isotope ratios, which allows small enrichments of radiogenic ^{206}Pb and ^{208}Pb to be detected at the level of 0.001%. Igneous rocks hosting minerals with a range in ^{238}U/^{204}Pb values of 100 can be dated with uncertainties of approximately ±15–20 kyr. A Quaternary rhyolite dated at 1.19 Ma by Ar–Ar yields a ^{238}U–^{206}Pb age of 1.03 ± 0.10 Ma. A Holocene dacite (9.5 Ka) has uniform ^{206}Pb/^{207}Pb to within ±0.002% in groundmass phases, but 1-mm plagioclase phenocrysts have lower ^{206}Pb/^{207}Pb by 0.105 ± 0.002%, indicating contamination of the magma after plagioclase crystallization. High-precision ^{206}Pb/^{207}Pb ratios may be a useful new tool for petrogenetic studies.

(4) Models of ^{87}Sr/^{86}Sr ratio evolution in groundwater systems that contain both rapidly exchanging and slowly dissolving solid phases were developed and used to constrain integrated flow rates of groundwater under the Lawrence Berkeley National Laboratory. At LBNL, ^{87}Sr/^{86}Sr ratios increase markedly over tens of meters along presumed flow paths. The dissolved Sr is close to isotopic equilibrium with the exchangeable (leachable) Sr in the rock, but the overall pattern reflects the changes in whole rock ^{87}Sr/^{86}Sr along the flow paths. The data require that flow velocities be ≤10 cm/yr, and are consistent with corrected radiocarbon ages.

(5) Stable isotope geochemistry of low-temperature clay minerals is being studied to define the effects of temperature, phase transitions, and fluid composition on the hydrogen and oxygen isotopic compositions of clay minerals formed at low temperatures (<150°C). The purpose is to enable the use of stable isotope compositions of authigenic clay minerals for studies of low-temperature fluid flow (i.e., oil field brines, groundwater flow), weathering, and paleotemperature reconstruction. Analysis of smectite samples from drill holes from the East Rift Zone of Kilauea Volcano of Hawaii indicates that the clays formed at temperatures ranging from 96 to 322°C and demonstrate the potential use of clays for stable isotope thermometry at low temperatures.

B. Thermodynamics of High-Temperature Brines *(K. S. Pitzer [510-486-5456; Fax 510-642-6911; E-mail kspitzer@lbl.gov])*

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 350°C and pressures to 1 kbar. The new calorimeter has been tested and measurements will proceed for the mixing of NaCl(aq) with $CaCl_2$(aq).

Results: 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 equation received support also from the Chemical Sciences Division of BES, DOE. Also, an earlier equation for NaCl–H_2O was tested against the equilibrium data for the reaction: brucite = periclase + H_2O at 2 kbar and temperatures from 590 to 670°C with excellent agreement. These data had not been considered when the equation was developed.

C. Uses of Synchrotron X-Ray Methods in Earth Sciences Research on Contaminant Transport

(T. K. Tokunaga [510-486-7176; Fax 510-486-5686; E-mail tktokunaga@lbl.gov])

Objectives: Contaminant transport is being studied using the synchrotron x-ray microprobe and XANES. Spatially and temporally resolved speciation provided with these methods is being directed toward better understanding trace element partitioning in soil, sediment, and rock systems. This first year's research has focused on diffusion and reduction of selenium at boundaries between sediments and ponded waters.

Project Description: Predicting transport of trace elements between various environmental compartments is currently often unsuccessful, partly due to lack of relevant information at compartment boundaries. Without *in situ* spatially and temporally resolved chemical information, transport between compartments can only be described with system-specific, nonmechanistic, mass transfer models. Boundaries between surface waters and underlying sediments are important zones for transport and reaction in wetlands and other aquatic environments. Previous experiments (collaborations with G. E. Brown, Jr., and I. J. Pickering) showed that reduction of soluble Se(VI) to insoluble Se(0) can occur within a narrow (several mm) zone at the interface between ponded waters and sediments. That study emphasized application of XANES for tracking Se reduction in bulk sediments, and suggested the need for spatially resolved chemical information at sediment–pond boundaries. Other previous work (collaborations with S. R. Sutton and S. Bajt) suggested that Se micro-XANES could provided the needed spatially resolved information on valence distributions at this important boundary. The present study employs Se micro-XANES for tracking Se diffusion and reduction at ponded water–sediment boundaries.

Results: This project began October 1, 1994. Activities to date (conducted primarily at NSLS) include (1) a micro-XANES experiment for tracking Se(VI) diffusion into sediments, (2) micro-XANES experiments for directly measuring Se(VI) reduction at pond–sediment boundaries, and (3) a transient Cr micro-XANES experiment in sediment. The micro-XANES experiment for determining Se(VI) diffusivities in sediments is being combined with conventional, macroscopic diffusion experiments, and is in progress. The micro-XANES experiment on Se transport and reduction at pond–sediment boundaries has been completed. Results show reduction of Se(VI) to Se(IV), and ultimately to Se(0) within specific zones in the sediments. The location of the active reduction zone was within the surface 2 mm in an extremely reducing sediment, while it was displaced several mm deeper in a less reducing sediment. These results are consistent with diffusion-limited transport calculations. Micro-

XANES results ruled out the possible formation of Se(0) in the ponded waters, and also indicated that formation of organo-Se compounds was insignificant. The latter result is consistent with the XANES study conducted with Pickering and Brown. Recently, XANES studies of Se-contaminated sediments which have been subjected to various chemical extractions have also been initiated with G. E. Brown, Jr., and A. L. Foster (Stanford University). This work will compare Se speciation by direct XANES versus by sequential chemical extraction. In another application of micro-XANES, spatially and temporally resolved reduction of Cr was studied in soil.

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CATEGORY: **Geophysics and Earth Dynamics**

PERSON IN CHARGE: **F. J. Ryerson**

A. Basic Research on Nonlinear Elastic Phenomena in Rock *(B. P. Bonner [415-422-7080; Fax 415-423-1057; E-mail bonnerl@llnl.gov], joint research with T. J. Shankland and P. A. Johnson, LANL, and T. V. McEvilly and L. Myer, LBL)*

Objective: As rocks are loaded by finite stresses, their mechanical response can no longer be approximated by a linear relation—Hooke's law. The objective of this project is to determine the conditions, e.g., rock morphology, strain amplitude, and fluid saturation, etc., which control the magnitude of the nonlinear response at low frequencies, and thus determine if nonlinear effects can be exploited for seismic applications such as rock mass characterization, strong motion prediction, and advanced imaging methods.

Project Description: This project is part of an integrated theoretical and experimental effort directed at quantifying and modeling nonlinear response under conditions relevant near the earth's surface. It is well known that features of the microstructure, including pores, macro and micro fractures, and the composition and position of pore fluid phases control rock properties such as seismic velocity, shear strength, and permeability. Little is known about how rock responds to moderate stress at seismic frequencies. This component of the project makes use of a unique laboratory apparatus, a torsional oscillator, to apply moderate stresses to rock samples to determine how the low-frequency nonlinear response and microstructural characteristics are related. The nonlinear response in shear is determined by measuring the amplitude dependence of the shear modulus and attenuation and vibration distortion caused by the nonlinear sample. These fundamental laboratory experiments are relevant to several applications, including improved simulations of the strong motions associated with explosions and earthquakes, new methods of rock characterization using finite amplitude seismic sources, and the possibility of a low-frequency, directed source created by nonlinear wave mixing. Such a source would be useful in boreholes and would be ideal for imaging with seismic tomography.

Results: Previous measurements demonstrated that strong nonlinear effects often occur in rock and are associated with the presence of defects such as fractures or microfractures or of fluid phases. Low-frequency torsion measurements are now being made to characterize nonlinear shear response for rocks which do not meet the usual criteria for mechanical tests; that is, homogeneous and chemically inert and with relatively simple mineralogy. Sample materials include low-porosity argillites and graywackes from the Geysers geothermal field and partially decomposed sedimentary rocks (sandstones and siltstones) from the site of a freeway interchange that collapsed during the Northridge earthquake. The objectives of the experiments are to understand the mechanisms responsible for reductions in shear modulus and increases in attenuation with amplitude for these "difficult" materials. The results indicate that the usual assumption of chemical neutrality of the pore fluid, commonly made in analyzing mechanical response, is violated for these rocks and is accentuated for measurements at low frequency. Argillite from the Geysers softens when water saturated because swelling smectite loosens the structure. Mapping of seismic shear wave velocity may be useful for delineating low-permeability zones in the reservoir which are apparently associated with high smectite content. When swelling clays in the decomposed sandstone are allowed to adsorb water, shear moduli can drop as much as 50%, when compared to a dry, unreactive sandstone. The clay component can be as small as 10% by volume to cause large effects. The shear modulus decreases even further at high strains. These results imply that extrapolations of ground motion assuming elastic response at the site underpredict the motion caused by the Northridge main shock by a factor of two or three.

A numerical model which accounts for friction at internal surfaces has been developed to simulate shear hysteresis at intermediate strains. The simulation solves the equation of motion for a one-dimensional nonlinear spring element, and is specified by a strain-dependent shear modulus defect. This simple model reproduces hysteretic attenuation, strain-softening behavior, and slope discontinuities in agreement with experiment for fractured grainite. The effect of adhesion forces will be added to account for thin fluid films adsorbed onto internal surfaces. When complete, this constitutive model will generate input consistent with laboratory meaurements for finite difference and element simulation of wave propagation and strong ground motion in nonlinear materials.

B. Effects of Heterogeneity on the Fracture of Rock *(S. C.Blair [510-422-6467; Fax 510-423-1057; E-mail blair@s55.es.llnl.gov] and L. R. Myer [Lawrence Berkeley Laboratory, 510-486-6456])*

Objective: The objective of this research is to understand how microscale (or grain-scale) heterogeneity affects macroscopic mechanical behavior of rocks, and to study the process of progressive fracture of rock in compression, and evaluate the role of crack interaction in rock deformation and fracture. Moreover, this work also aims to investigate the relationship of static to dynamic moduli (in collaboration with LBL) and to characterize the role of heterogeneity at a variety of scales in fracture and the scaling properties of rocks.

Project Description: This project is concerned with simulation of rock deformation and fracture at grain and larger scales. A field-theory model for rock fracture has been developed and is being used to perform two types of studies: a parameter-sensitivity analysis to determine how heterogeneity in different microscale parameters affects behavior in the simulated compression tests, and a detailed analysis of the process of fracture in a few selected trials to interrogate the macroscopic stress–strain curve and determine how the macroscopic stress–strain behavior is related to the formation of cracks. Finally, percolation theory in being used to analyze output from the model, in order to investigate scaling relationships in fracture processes.

Results: Results show that the model produces realistic stress–strain curves and implicitly predicts the development of shear-type fractures, even though a simple crack element that does not include shear stress is used. This implies that the en-echelon nature of cracking observed in rocks in compression may be due to the local heterogeneity in the rock, and that local heterogeneity may lead to crack interactions along macroscopic surfaces that are similar to those caused by shear localization and that are often observed in real experiments.

Results also show that the model exhibits an implicit size effect that closely matches laboratory and field data for the dependence of sample strength on sample size. This is an inverse power-law relation with exponent similar to that obtained in analysis of laboratory and field data on rock strength. No assumption of flaw size is needed to generate this effect, and the effect is assocated with a decrease in the stress level required to create crack interaction, as the size of the lattice increases. This may be because a larger population of sites offers more possible ways for cracked sites to interact and a larger number of ways for a weak path to be formed.

The model was also used to relate macroscopic stress–strain behavior to the formation of microcracks and to strain energy due to cracks. Analysis shows strain softening to be associated with crack extension. Two patterns of cracking were found, including spatially uncorrelated, non-interacting cracks that have little effect on macroscopic deformation, and spatially correlated interacting cracks associated with extension or linking of larger cracks. These cause strain-softening and large changes in crack strain energy.

C. The Role of Carbon and Temperature in Determining Electrical Conductivity of Basins, Crust, and Mantle *(A. G. Duba [510-422-7306; Fax 510-423-1057; E-mail alduba@llnl.gov]; joint research with T. J. Shankland, LANL [505-667-4907; Fax 505-667-8487; E-mail shankland@lanl.gov]; and E. A. Mathez, American Museum of Natural History [212-769-5379; Fax 212-769-5339; E-mail mathez@amnh.org])*

Objectives: The intent of this work is to comprehend the electrical conduction mechanisms in carbon-bearing rocks and in mantle minerals for the purpose of relating electrical conductivity (σ) 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 as carbon, fluids, or ore minerals at the lower temperatures of the crust and basins. Thus, one research approach is to measure σ 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.

Results: Electrical conductivity of a water-saturated schist, collected from a surface outcrop near the Denali Fault Zone in the Yukon–Tanana terrane of south-central Alaska, increases slightly with pressure to about 200 MPa. Thus, the accepted hypothesis that electrical conductivity of saturated crustal rocks decreases with pressure is not necessarily true. Detailed petrographic examination of one sample, a quartz–mica–garnet–schist, revealed the presence of a stringer of carbonaceous material generally less than 10 µm thick within one of the muscovite layers. The stringer extends for about 2 cm along the foliation and is probably responsible for the anomalous conductivity change with pressure. The carbonaceous stringer together with its host muscovite layer are deformed and broken around a rotated garnet porphyroclast. We interpret this to indicate that the carbonaceous material formed by fluid deposition in a fracture formed within the muscovite layer, possibly during the main phase of metamorphism and deformation. The mica and carbon stringer were then deformed by a non-coaxial deformation responsible for rotation of the garnet porphyroclasts. The deformation was accommodated by plastic deformation of quartz, indicating that it occurred in the ductile regime under conditions at least equivalent to greenschist facies metamorphism. This result demonstrates that the carbonaceous stringer was present at depth. Brittle deformation on the microscopic scale is observed in the rock and interpreted to have been caused by subsequent unloading due to uplift. The brittle deformation broke the connectivity of the carbon stringer, explaining in part why the rock does not exhibit anomalously high conductivity at 0.1 MPa (1 atm) pressure. The observations indicate that carbonaceous material may exert a primary control on crustal electrical conductivity because it may be present as interconnected arrays in grain boundaries or microfractures or in megascopic, through-going fractures.

CATEGORY: **Geochemistry**

PERSON IN CHARGE: **F. J. Ryerson**

A. Thermodynamic and Transport Properties of Aqueous Geochemical Systems

(Joseph A. Rard [510-422-6872; Fax 510-422-0208] and Donald G. Miller [510-422-8074; Fax 510-422-6363; E-mail dmiller@llnl.gov])

Objectives: The objectives are to (1) measure precise and accurate osmotic/activity coefficients, 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. Being measured are osmotic/activity coefficients and solubilities by the isopiestic method, densities by pycnometry and vibrating densitometry, and diffusion coefficients by Rayleigh and Gouy interferometry.

One goal is to measure highly accurate data for systems involving geochemical brines, radioactive waste isolation, 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. Transport data are being analyzed as Onsager transport coefficients and osmotic/activity coefficients are being analyzed using extended Pitzer's equations, which should be capable of yielding reliable estimates for mixtures.

Results: A few additional diffusion experiments were performed for aqueous K_2SO_4 at 25°C, using the high-precision Gosting diffusiometer at Texas Christian University, to supplement our previous results. The photographic plates from these experiments were analyzed with our automated plate reader. Diffusion experiments were also performed at two compositions of NaCl + Na_2SO_4 at 25°C. A new analysis method was programmed for the computer controlling the automatic plate reader so that photographic plates could be read with higher precision. One plate for K_2SO_4 was reread by this newer method. In general the two methods give good agreement for the diffusion coefficient but the newer approach gives somewhat better statistical precision and internal consistency.

Isopiestic experiments were completed at 25°C for aqueous $CaCl_2$ solutions up to 10.253 $mol \cdot kg^{-1}$, which is about 2.8 $mol \cdot kg^{-1}$ above saturation, and for H_2SO_4 from 0.27470 to 0.70512 $mol \cdot kg^{-1}$. All three isopiestic chambers are now being used for aqueous H_2SO_4 + $MgSO_4$ mixtures at 25°C. Experiments have been performed at molality fractions for H_2SO_4 of 6/7, 5/7, and 4/7; 114 data points have been measured covering the water activity range of $0.8850 \le a_w \le 0.4893$. These experiments are being extended to higher and to lower molalities.

A major amount of time was spent writing papers for publication in journals. During this period six were published; three more were submitted for publication, of which two are in press. These include an analysis of the emfs of cells containing aqueous H_2SO_4, a detailed thermodynamic model for aqueous NaBr valid from the freezing temperatures to over 300°C and to high pressures, ternary solution diffusion coefficients at 30° for some compositions of aqueous NaCl + $MgCl_2$, an intercomparison of the precision and accuracy of diffusion coefficients for a ternary solution derived from Rayleigh and Gouy interferometry, and testing of various mixing approximations for densities and for electrical conductances based on binary solution data.

B. Uranium, Thorium, Lead, and Oxygen Diffusion in Rock-Forming Minerals: Implications for Reactive Transport

(F. J. Ryerson [510-422-6170; Fax 510-422-1002; E-mail ryerson@s91.es.llnl.gov] and K. D. McKeegan, Univ. of California at Los Angeles [310-825-3580; Fax 310-825-2779; E-mail kdm@argon.ess.ucla.edu])

Objectives: The spatial distributions of isotopes of elements such as uranium, thorium, lead, and oxygen, observed on a microscale, can be utilized to constrain thermal histories of crustal rocks and the extent of their interactions with fluids. There are two requirements necessary for application of this idea to real geologic systems: first, microanalytical techniques must be employed to quantitatively measure the isotopic or elemental heterogeneities, and second, fundamental diffusion data must be experimentally determined in order to know the rates at which equilibrium between fluid (either melts or aqueous fluids) and host rocks can be approached as a function of various external conditions.

Project Description: The diffusion coefficients for uranium, thorium, lead, and oxygen will be determined in a number of different minerals under a variety of external conditions. The experimental diffusion runs are performed at the Lawrence Livermore National Laboratory and the analytical phase of the work is done at UCLA using the Cameca ims 1270 ion microprobe. Techniques for the *in situ* measurement of either experimentally induced or naturally occurring variations of isotopic and elemental concentrations are being developed for the UCLA ion microprobe.

Results: Most of our effort this past year has been dedicated toward continued development of the Cameca ims 1270 for measurements of isotopic and inter-element ratios on a ~10-mm spatial scale. A new instrument control system, based on a SPARC computer, has been installed and data acquisition and analysis software, written in LabVIEW, has been debugged. Along with our modified detector system, the new instrument control software has been important for improving precision and accuracy of isotope ratio measurements and depth-profiling capabilities. Techniques have been developed for the determination of U, Th, and Pb concentrations in monazite with better than 2% accuracy and for *in situ* measurements of O and C stable isotopic abundances in carbonates and silicates with permil precision.

Th–Pb age determinations on 15-mm spots of individual monazite grains from the Manaslu pluton have demonstrated that Pb inheritance can be widespread in leucogranite monazite. In several cases, complex microdistributions in age have been observed within an individual monazite grain. Further measurements at a finer spatial resolution (~1 mm) are being undertaken to determine if these heterogeneities can be interpreted as diffusion gradients that, with application of the appropriate diffusion law for Pb in monazite, can yield detailed thermochronological information. In collaboration with Daniel Farber, we have conducted experiments to measure Pb diffusion rates in monazite. The lead diffusion experiment was performed by immersing a polished sample of synthetic $PrPO_4$ monazite in PbS within a sealed SiO_2 glass capsule; the quenched PbS can be removed from the surface, which appears unaffected. Profiles consistent with the solution to Fick's Law for the imposed boundary conditions yield diffusion coefficients in the 10^{-20} $m^2\ s^{-1}$ range. We are currently performing experiments with gem-quality natural monazites.

Oxygen isotopic disequilibrium can be utilized as a tracer of the extent of fluid–rock interactions provided that spatially resolved isotopic data can be obtained and that the processes and rates of isotopic exchange quantified. We have developed an ion probe method for measurement of $^{18}O/^{16}O$ ratios in ~10-mm spots of insulating samples with a typical precision of ~1‰. So far this method has been applied to a study of carbonate cement formation from drill core samples obtained from petroleum reservoirs in the San Joaquin valley, CA. Ongoing calibration work for quartz, pyroxene, olivine, garnet, and feldspar will allow application of this technique to a broad range of problems. At the same time, we are engaged in a series of experiments to determine oxygen self-diffusion rates in garnet, olivine, and pyroxene under both anhydrous and hydrous conditions as a function of temperature and oxygen fugacity. The preservation of highly polished surfaces (necessary for the depth-profiling analyses) has proved to be a problem for some minerals during the experiments (especially under hydrous conditions) and is being addressed by varying P–T conditions, the characteristics of the reservoir, and fluid composition.

C. Experimental Determination of Mineralogical Controls on U–Th–Pb Redistribution: Implications for Crust/Mantle Differentiation *(H. F. Shaw [510-423-4645; Fax 510-423-1057; E-mail shaw4@llnl.gov] and F. J. Ryerson [510-422-6170; Fax 510-422-1002; E-mail ryerson@s91.es.llnl.gov])*

Objectives: The objective of this work is to determine mineral/aqueous fluid and mineral/silicate liquid partition coefficients for a suite of trace elements (U, Th, Hf, Zr, Nb, Ta, Sr, Ba, Rb, and Pb) under conditions relevant to fluid metasomatism and partial melting in the upper mantle. The results of the project will provide important constraints on the petrogenetic interpretation of trace element, U–Th–Pb, and U-series disequilibrium data obtained on igneous rocks, particularly those formed in subduction-zone environments.

Project Description: Along with the formation of the earth's core, the differentiation of the crust and mantle represents the major chemical fractionation process occurring on the earth. The nature of this process has been constrained by a wide variety of trace element and isotopic analyses of crust- and mantle-derived samples. Effective utilization of these data requires a quantitative understanding of the fractionation of the elements of interest between minerals and both silicate melts and aqueous fluids. For many elements, however, the relevant mineral/melt partition coefficients are poorly known and there is an almost complete lack of data for the partitioning of trace elements between minerals and aqueous fluids. The experimental data generated in this project will provide quantitative information of the partitioning of trace elements of geologic interest between minerals and melts and aqueous fluids, with emphasis on the partitioning of U, Th, Pb, and the high-field-strength elements (Zr, Hf, Nb, Ta). Partition coefficients for elements of interest are being obtained as a function of fO_2, T, P, and fluid or melt composition. Experimental charges are produced using standard and newly developed techniques that utilize one-atmosphere gas-mixing furnaces and high-pressure piston–cylinder devices. The trace element composition of the charges is being measured primarily by quantitative ion microprobe techniques, supplemented by electron microprobe analyses and solid-source mass spectrometry.

Results: The partitioning of U, Th, Pb, Ba, Sr, Nb, and Ta between aqueous fluids (with and without added Cl^- and CO_3^{2-}) and rutile, clinopyroxene, orthopyroxene, pyrope, olivine, and pargasitic amphibole under upper mantle conditions has been studied. Using these data, together with literature data for Sr and Pb isotopic compositions of Pacific island arc basalts (IABs), the calculated composition of a fluid in equilibrium with the average Pacific IAB source is $^{87}Sr/^{86}Sr = 0.7036$, $^{207}Pb/^{204}Pb = 15.57$, Sr ~500 ppm, and Pb ~30 ppm. The subarc fluid composition is consistent with a mixture of fluids from both altered MORB (~96 wt%) and sediment (~4 wt%), with ~96% of the Sr from the former, and ~70% of the Pb from the latter. Although the mass fraction of sediment-derived fluid in the subarc fluid may be minor, sedimentary input for Ba (0–50%), Th (53–88%), U (61–83%), in addition to Pb, can be significant. Our results are consistent with, and provide additional support for, models of slab input to IAB sources. Preliminary results indicate that metasomatism by water-rich fluids and silicate melts will produce similar but distinguishable trace element signatures in island-arc basalts (IABs).

Experiments were conducted to determine partition coefficients for Ti, Rb, Ba, Sr, Zr, Nb, Ta, Hf, Pb, U, and Th between pargasitic amphibole and a synthetic hydrous silicate liquid. Rb, Ba, Nb, and Ta are dramatically less compatible in pyroxene than in amphibole, while other elements, such as Th, U, Hf, and Zr, have similar compatibilities. Because of these differences, liquids produced by small degrees of partial melting of amphibole-bearing mantle sources, or by high-level fractionation of amphibole, should have distinctively lower Th-normalized Rb, Ba, Nb, and Ta concentrations than melts from amphibole-free systems.

Using mineral–melt partition coefficients determined in this project, the isotopic evolution of the uranium-series nuclides ^{238}U, ^{230}Th, ^{226}Ra, and ^{231}Pa during partial melting in an ascending column of mantle was modeled. The observed [^{230}Th] and [^{231}Pa] excesses in e-MORB and n-MORB can be generated by initiating melting in the garnet stability field at varying depths, and these excesses can be preserved during equilibrium transport of the melt at geologically reasonable rates through the overlying spinel lherzolite.

CATEGORY: **Energy Resource Recognition, Evaluation, and Utilization**

PERSON IN CHARGE: **F. J. Ryerson**

A. Linear and Nonlinear Mechanics of Rocks *(J. G. Berryman [510-423-2905; Fax 510-422-1002; E-mail berryman@s123.es.llnl.gov], P. A. Berge [510-423-4829; Fax 510-423-1057; E-mail berge@s44.es.llnl.gov] and D. Elata [510-423-8281; Fax 510-422-1002; E-mail elata@llnl.gov])*

Objectives: Our major 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. This project exploits these as well as other new results, with the expectation that new insight into the linear and nonlinear mechanics of rocks will result. Such insight may prove important for understanding earthquake source mechanisms and for oil field engineering practices related to drilling and pumping. Also, such information is important for interpretation of both seismic and electrical field data.

Project Description: Modeling of idealized two-mineral component rocks will be one of the main thrusts of the effort. Recent advances show that it is possible to compute all the compressibilities (jacketed, unjacketed, jacketed pore, and unjacketed pore) exactly for certain models. Although very general results on effective-stress rules for various physical properties of rocks have already been published, more explicit applications to examples of well consolidated and poorly consolidated rocks have now been studied and will soon be reported. The new approach based on exact results offers promise of analytical and/or numerical modeling capability from linear to semilinear to fully nonlinear deformation of rocks, including rocks containing cracks, within the same basic theoretical framework. These types of results are of interest in the oil and gas industry, as they play a significant role in interpretation of AVO (amplitude versus offset) data used as direct hydrocarbon indicators. 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.

Results: We have developed a unified approach for deriving effective medium theories, and demonstrated the range of applicability and relationships between implicit and explicit schemes. A paper on this work is currently under review at the journal *Mechanics of Materials*. 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. In collaboration with Stanford researchers, we have developed a new approximate analytical solution describing the pressure dependence of contact stiffnesses for coated spheres, which can be used to describe the elastic behavior of cemented sandstones. These results have also been submitted for publication in the journal *Mechanics of Materials*. We also show that theoretical models for granular rocks must be modified to avoid violating thermodynamic constraints. A paper on these results has been submitted to the *Journal of Applied Mechanics*. In collaboration with researchers at Princeton, New York University, and the University of Utah, we have developed a method for obtaining rigorous bounds on the shear modulus of viscoelastic composites such as rocks that contain mixtures of two viscoelastic constituents. This work extends and completes the previous work of the collaborators on the bounds for the bulk modulus of viscoelastic composites, and furthermore shows how well various realizable theoretical models produce results consistent with the bounds. A paper describing this work is currently being written for publication. In collaboration with researchers at the University of Wisconsin, we have 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. The first part of this work has been accepted for publication in the *Journal of Geophysical Research*.

B. Deployment of a Borehole Seismometer at the KTB Drilling Site *(Paul Kasameyer [510-422-6487; Fax 510-422-3925; E-mail kasameyer1@llnl.gov])*

Objective : The purpose of this trip was to install a seismic monitoring system in a 4-km-deep borehole adjacent to the KTB 9.1-km borehole, and to use that instrument to record explosions and natural and operationally induced earthquakes at this depth.

Project Description: The KTB project is a decade-long project to develop drilling and measurement capabilities to explore deep in the continental crust, and to use those techniques to study a major European suture zone. The latest scientific efforts in that project were a 3-D seismic survey, and a hydrofrac and induced seismicity experiment. Cooperation with the KTB project is one goal of the US Continental Scientific Drilling Program. This project was funded to deploy a borehole seismometer that had been originally constructed for the Geothermal Technology Division of DOE to monitor these activities at 4-km depth where the frequency content is not limited by passage through the near-surface.

Results: The LLNL borehole seismometer system was refurbished and outfitted with new sensors. The system was emplaced at a depth of 3830 m and deployed there for four days, continuously recording three components of seismic data at a sample rate of 1000 Hz.

The LLNL borehole sensor has three characteristic features: first, the sensors are sensitive to ground acceleration and therefore have a relatively low high-frequency noise floor compared to more conventional seismometers that respond to earth velocity. Second, the sensors have no downhole amplification, so they can be used at higher temperatures. Third, the system was designed to clamp into a well-cemented metal casing of known diameter. A second system, designed by Geostock, a French company, was deployed in the hole immediately after we removed our system. The Geostock tool had high-frequency seismometers, downhole amplifiers, and clamps in the open portion of the hole. Consequently, this experiment provided the opportunity to compare these two design approaches for deep-hole seismic recording.

Our borehole system recorded approximately six "large" events, and several "small" events. The large events included four explosions that were part of a deep 3-D seismic survey, with several hundred surface seismometers. We recorded the time-history of the down-going energy so that it can be effectively removed from the surface recordings in order o produce better reflection images, a local quarry blast, and a local earthquake. The origin of the smaller events was not known. Preliminary results showed that the LLNL tool was more subject to 50-Hz interference than was the Geostock tool, and that the LLNL tool had a lower instrumental noise floor above 60 Hz. Low-frequency noise on the tool made detection of regional seismic signals very difficult. The data were forwarded to the KTB seismologists for final analysis.

C. Compositional Kinetic Modeling of Oil and Gas Formation *(Alan K. Burnham [510-443-8779; 510-423-7914; E-mail burnham1@llnl.gov])*

Objectives: This work develops and tests models of petroleum generation, migration, and thermal stability. These models are used to reduce petroleum exploration risk and costs through integrated basin analysis, which combines many aspects of geology, geophysics, geochemistry, and hydrology to determine where and when oil is generated, migrates, and accumulates.

Project Description: Oil- and gas-generation kinetics and oil-destruction kinetics are measured by a variety of techniques, including isothermal hydrous pyrolysis, temperature-programmed pyrolysis using various detectors, and sealed capillary tube pyrolysis. An increasing portion of the effort is directed toward understanding the kinetics of oil cracking to better understand the floor for oil survival and formation mechanisms of natural gas. Mathematical techniques and computer programs of varying complexity are developed to predict oil and gas generation and composition and their expulsion from the source rock. Compositional approaches are tested against geological data. Many of the experiments involve industrial collaborators.

Results: The previous summary reported that a new nucleation kinetic model was more appropriate for interpretation of pyrolysis data from well-preserved algal kerogen. During the past year, the temperature calibration was inproved for one of our pyrolysis apparatus, resulting in quantitative agreement between isothermal and constant-heating-rate pyrolysis rates in a fluidized bed and a Pyromat micropyrolyzer. A more complete statistical comparison of various kinetic models confirmed that the nucleation model fits the best, as well as being the most reliable at reaching a global minimum during non-linear regression analysis. Microscopic analysis of all samples confirmed the presence of well-preserved algal bodies in all samples having the nucleation characteristics.

The previous summary also reported the first measurements of intrinsic decomposition rate of hexadecane within a complex oil matrix by the use of isotopically labeled compounds. The past year expanded upon these results by examining a wider range of pyrolysis conditions and by a more thorough analysis of the cracked samples. First, rate constants at additional temperatures indicated that the activation energy of hexadecane cracking in oils is similar to that of pure hexadecane, even through it is somewhat slower. Second, good agreement was obtained between cracking rates in autoclaves (high pressure) and glass capillaries (modest pressure). Third, analysis of cracked oil and control hexadecane samples by gas chromatography–mass spectrometry and nuclear magnetic resonance indicated a difference in products from the hexadecane cracking. Neat hexadecane forms high-molecular-weight addition products from alkylation of olefin products by primary and secondary alkyl radical products, while no such products were detected when an oil matrix is present. This result is consistent with our earlier hypothesis that labile hydrogen within the oil more efficiently caps radicals than hexadecane itself and limits the propagation chain reactions. Fourth, isotopic analysis of the gas products from one of the autoclave experiments was used to deduce the gas product distribution from the labeled hexadecane, with the result that it is similar to neat hexadecane and different from the bulk oil. Finally, added water in one of the autoclave experiments had little effect on reaction rates or products except that a large increase in CO_2 production and a minor increase in H_2 production occurred. Apparently, water is serving to some extent as a hydrogen donor during cracking, with the water oxygen converted to CO_2.

D. Velocity Analysis, Parameter Estimation, and Constraints on Lithology for Transversely Isotropic Sediments *(P. A. Berge [510-423-4829; Fax 510-423-1057; E-mail berge@s44.es.llnl.gov], J. G. Berryman [510-423-2905; Fax 510-422-1002; E-mail berryman@s123.es.llnl.gov], D. Elata [510-423-8281; Fax 510-422-1002; E-mail elata@llnl.gov], I. Tsvankin, Colorado School of Mines [303-273-3060; Fax 303-273-3478; E-mail ilya@dix.mines.edu], K. Larner, Colorado School of Mines [303-273-3428; Fax 303-273-3478; E-mail klarner@dix.mines.edu], and F. Muir, Stanford Univ. [415-723-9390; Fax 415-723-1188; E-mail francis@pangea.stanford.edu]*

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 reflection 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 find 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 seismic reflection data in vertically inhomogeneous, transversely isotropic media. These results have been submitted for publication in *Geophysics* and for presentation at the Society of Exploration Geophysicists annual meeting. Currently, Colorado School of Mines researchers are using their codes to process seismic data and to produce estimates of some of the anisotropy parameters. Results from research at Stanford include the development of a new theoretical model that describes the anisotropic behavior of certain shales. This work was submitted for publication in the *Journal of Seismic Exploration*. LLNL investigators have shown that constraints on anisotropy parameters for models of layered rocks contain information about lithology. These results have been submitted for presentation at the Society of Exploration Geophysicists annual meeting. LLNL and Stanford researchers are currently developing and analyzing additional theoretical models of rocks to determine how anisotropy parameters are related to rock properties and how these relationships constrain lithology. The Stanford/LLNL group is also determining what information from seismic reflection data is necessary and sufficient for correlating anisotropy parameters and lithology.

CONTRACTOR: **LOS ALAMOS NATIONAL LABORATORY**
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CONTRACT: **W-7405-ENG-36**

CATEGORY: **Geophysics and Earth Dynamics**

PERSON IN CHARGE: **M. Fehler**

A. New Methods for Modeling and Processing Seismic Data (ACTI) *(M. Fehler [505-667-1925; Fax 505-667-8487; E-mail fehler@seismo5.lanl.gov], Ru-Shan Wu [Univ. of California at Santa Cruz], N. Bleistein [Colorado School of Mines], and M. N. Toksoz [Massachusetts Institute of Technology])*

Objectives: To develop and test new methods for modeling and processing seismic data of importance to the oil and gas industry.

Project Description: As new oil and gas reserves become more difficult to find and expensive to drill for, there is increased interest in obtaining ever better images of the earth beneath increasingly complicated structures. The demand for processing large seismic datasets to obtain high-quality images has thus become of critical importance. This project consists of three parts, each addressing a significant issue in analysis of seismic data that is relevant to petroleum exploration. The three parts are: (1) Fast 3D Modeling and Prestack Depth Migration Using Multi-Screen Wave Propagator. We are developing and testing the use of a multi-screen (phase-screen for acoustic waves, complex-screen for elastic waves) algorithm as a backpropagator for 3D pre-stack migration in laterally heterogeneous media. The method is a wide-angle one-way elastic wave propagator that neglects reverberations and adopts a fast dual-domain (space and wavenumber) implementation. (2) Statics Estimation for Complex Media Using Prestack Migration. Development and testing of a method for estimating statics in complex terrain by iterative use of migration. (3) True Amplitude Dip Moveout. An investigation of amplitude effects of non-planar interfaces on DMO by high-frequency asymptotic analysis of the application of a DMO formalism to Kirchhoff-approximate data for a single reflector.

Results: This is a new project. We have had a meeting with industrial participants on part of the project and laid the groundwork for technical progress in the project. Preliminary work has been done on developing a formalism for determining the limits of reliability of the phase screen method.

B. Jemez Imaging and Tomography Experiment (JITEX) *(M. Fehler [505-667-1925; Fax 505-667-8487; E-mail fehler@seismo5.lanl.gov] and W. S. Baldridge)*

Objectives: To obtain insight into volcanic and crustal-forming processes by constructing a model of the crust and upper mantle beneath the Valles Caldera that incorporates data from as many geophysical and geological disciplines as possible.

Project Description: The project is focused on obtaining an improved understanding of the origin, evolution, and modern thermal regime of a major intraplate magmatic system. Insight into how crustal forming processes occur in mid-continental volcanic systems will also be obtained. Geophysical data are being used to test models for the geometry of the caldera structure and fill; geometry and internal structure of the composite pluton underlying the caldera; and the structure and composition of the middle to lower crust beneath the pluton. A majority of the effort will involve collecting and interpreting seismic data to be used in imaging the subsurface structure beneath the caldera. Active seismic data will be collected along three lines, each about 170 km in length. Seismic sources include vibroseis explosions along each line. The reflection, wide-angle reflection, and refraction data from these six lines will be interpreted to obtain a detailed image of the crust beneath the Jemez volcanic field. In addition, two passive seismic arrays, consisting of up to 50 seismic instruments, will be set up to record teleseisms. The teleseismic data will be used to constrain the mid-crustal and upper-mantle seismic structure. Part of the teleseismic array will consist of one or more sub-arrays, with instrument spacing of as little as 1 km. Converted phases recorded on these sub-arrays are being analyzed to obtain more constraints on locations of velocity anomalies in the crust. The existing gravity datasets are being supplemented with new data. Gravity and magnetotelluric data will be analyzed along with the seismic data.

Results: The first active phase of the experiment, consisting of one seismic line of length 160 km, was completed in 1993. Both passive phases of the experiment have now been completed. The second passive phase, involving the deployment of 50 three-component seismometers for a period of about 4 months, was completed during FY1995. Permitting for the second active phase consisting of two seismic lines to be conducted during the fall of 1995 is nearly complete.

Analysis of the passive data from the first experiment using a travel-time tomographic technique has indicated the existence of a low-velocity body beneath the center of the caldera at a depth of between 8 and 12 km. This anomaly is substantially smaller than but better resolved than the one found from previous studies using fewer instruments. The existence of this anomaly is consistent with the data collected during the first active phase of the project. Analysis completed to date on the active data do not give a good constraint on the horizontal location of the anomaly. An anomaly located near the crust-mantle boundary is also consistent with both active and passive datasets. This low-velocity anomaly was unexpected.

C. Imaging of Reservoirs and Fracture Systems Using Microearthquakes Induced by Hydraulic Injections *(L. House [505-667-1912; Fax 505-667-8487; E-mail house@lanl.gov] and M. Fehler)*

Objectives: This work aims to characterize and image hydraulically fractured rock volumes using arrival times and waveforms of microearthquakes induced by the fracturing.

Project Description: In spite of the extensive use of hydraulic fracturing by the oil and gas and geothermal industries, the fluid paths created by the fracturing are usually not well known. That information is crucial, however, for most effectively exploiting the fractured reservoirs. Hypocenters of the induced microearthquakes give some information about the fluid paths, but do not provide the spatial resolution or amount of detail that are needed.

This study is developing analysis methods to extract more information about the fluid system created by hydraulic fracturing from the arrival times and waveforms of microearthquakes induced by the fracturing. Microearthquakes are much more energetic sources, particularly for shear waves, than the artificial sources used in active experiments. Moreover, because they are distributed throughout the rock volume to be interrogated, they provide better resolution of the rock properties than would be possible with artificial sources.

Two principal analysis methods are used. First is a velocity tomography approach that simultaneously determines a three-dimensional velocity structure and new hypocenters for the earthquakes. The creation of fluid paths within the rock will decrease both the compressional and the shear wave velocities within the fracture system, but particularly the shear wave velocity. The velocity tomography is intended to identify these changes. Second, conspicuous secondary seismic phases that arrive after the direct P and S waves provide the information needed to identify and locate features in the rock that scatter seismic waves effectively. These features are presumed to be major fluid pathways.

Results: Recent new results from this work have included initial analysis of a new microearthquake data set collected from a hydraulic fracture in sedimentary rock. This hydraulic fracture was seismically monitored by strings of geophone packages in two monitoring wells. A total of 25 three-component geophone packages were emplaced in each of the two monitoring wells, which provided many more monitoring packages than had been used for any previous hydraulic fracturing. Although most of the detected microearthquakes are fairly small in size, several hundred are large enough to locate reliably. Microearthquake hypocenters form a linear trend aligned at about N75E. Although the injection was into a sandstone characterized as laterally uniform, the trend of the hypocenters shows a distinct break that does not appear to result from a fault. Initial analysis of the microearthquake waveforms suggests there are coherent scattering features. If subsequent fuller analysis confirms the scatterers, they may be able to be imaged using the diffraction stacking methods previously developed.

D. The Role of Carbon and Temperature in Determining Electrical Conductivity of Basins, Crust, and Mantle *(T. J. Shankland [505-667-4907; Fax 505-667-8487; E-mail shankland@lanl.gov]; joint research with A. G. Duba, LLNL [510-422-7306; Fax 510-423-1057; E-mail alduba@llnl.gov] and E. A. Mathez, American Museum of Natural History [212-769-5379; Fax 212-769-5339; E-mail mathez@amnh.org])*

Objectives: The intent of this work is to comprehend the electrical conduction mechanisms in carbon-bearing rocks and in mantle minerals for the purpose of relating electrical conductivity(σ) 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 as carbon, fluids, or ore minerals at the lower temperatures of the crust and basins. Thus, one research approach is to measure σ 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; texture of carbon distribution is mapped with electron microscopy in the same samples used for conductivity measurement.

Results: Electrical conductivity of a water-saturated schist, collected from a surface outcrop near the Denali Fault Zone in the Yukon–Tanana terrane of south-central Alaska, increases slightly with pressure to about 200 MPa. Thus, the accepted hypothesis that electrical conductivity of saturated crustal rocks decreases with pressure is not necessarily true. Detailed petrographic examination of one sample, a quartz–mica–garnet–schist, revealed the presence of a stringer of carbonaceous material generally less than 10 µm thick within one of the muscovite layers. The stringer extends for about 2 cm along the foliation and is probably responsible for the anomalous conductivity change with pressure. The carbonaceous stringer together with its host muscovite layer are deformed and broken around a rotated garnet porphyroclast. We interpret this to indicate that the carbonaceous material formed by fluid deposition in a fracture formed within the muscovite layer, possibly during the main phase of metamorphism and deformation. The mica and carbon stringer were then deformed by a non-coaxial deformation responsible for rotation of the garnet porphyroclasts. The deformation was accommodated by plastic deformation of quartz, indicating that it occurred in the ductile regime under conditions at least equivalent to greenschist facies metamorphism. This result demonstrates that the carbonaceous stringer was present at depth. Brittle deformation on the microscopic scale is observed in the rock and interpreted to have been caused by subsequent unloading due to uplift. The brittle deformation broke the connectivity of the carbon stringer, explaining in part why the rock does not exhibit anomalously high conductivity at 0.1 MPa (1 atm) pressure. The observations indicate that carbonaceous material may exert a primary control on crustal electrical conductivity because it may be present as interconnected arrays in grain boundaries or microfractures or in megascopic, through-going fractures.

CATEGORY **Geochemistry**

PERSON IN CHARGE: **D. Janecky**

A. Search for Evidence of Large Comet or Asteroid Impacts at Extinction Boundaries

(M. Attrep, Jr. [505-667-0088; Fax 505-665-4955; E-mail mattrep@lanl.gov])

Objectives: Identify the signatures in the geological record large-body impacts and/or massive volcanism in relation to the known extinction boundaries in the fossil record. In addition, we also investigate the environmental consequences of local releases of ultra-high amounts of energy (impacts), help establish and develop the field of chemostratigraphy, and establish geochemical time markers in the geological record. We also take advantage of our unique analytical capabilities and these unique geological markers to investigate trace-element migration of the chemical element as a mean to understand the dynamics of the nuclear waste storage/burial strategies.

Project Description: Our analytical methodology to accomplish these tasks is the use of radiochemical neutron activation analysis to measure the platinium group elements. In particular, we measure iridium at the 1–3 part per trillion level.

Results: For the past year we have concentrated on sites where there are suspected impact sites. These include the Ames Structure in Oklahoma (Devonian). We have found a modest iridium enrichment in samples from this site that correlate to the backwash in the inner structure. This work is being done in collaboration with the Dr. Ken Johnston at the Oklahoma Geological Survey. We have analyzed for iridium in core samples from the Manson structure and in the suspected ejecta material in South Dakota. No iridium enrichment was found, indicating that the meteorite was a type that did not contain iridium. The Manson related work has been done in collaboration with Dr. Maureen Steiner (University of Wyoming) and Dr. Gene Shoemaker (USGS). These studies are being finalized. We have been working with Prof. Henning Dypvik, University of Oslo, and have analyzed suspected ejecta (Myklegardfjellet Bed in Greenland) and core samples from the Mjolnir Structure in the Barents Sea. The suspected impact corresponds to the Jurassic–Cretaceous boundary. We have observed some evidence that the structure may have been caused by an impact. The core samples showed a marked increase in iridium at the level that would correspond to the low-angle ejecta. We also have several other collaborations: Alamo Breccia in Nevada with Dr. John Warme, Colorado School of Mines, and possible impact structure at the Devonian Mississippian in collaboration with Dr. Don Woodrow Hobart and William Smith College, NY. We have continued our collaboration in numerous investigations at the Frasnian–Famennian (China, Canada and Europe) in collaboration with Dr. Kun Wang and Prof. H. H. J. Geldzetzer in Canada. Samples from Prof. S. Chatterjee, Texas Tech University, are being analyzed for evidence of the K–T boundary in the Deccan Traps.

B. Dating Young Surfaces Using Cosmogenic He and Ne *(Jane Poths [505-665-2636; Fax 505-665-6637; E-mail jpoths@lanl.gov])*

Objectives: To understand quantitatively the processes affecting use of cosmogenic noble gases as chronometers for dating young (<0.5 Ma) surfaces.

Project Description: Geomorphic surfaces start accumulating cosmogenic He and Ne once they are created, e.g., by flood or volcanic eruption. The concentrations of cosmogenic He and Ne, and hence surface exposure ages, can be determined for minerals separated from these surfaces by ultra-sensitive mass spectrometry. Through investigating the ages of a set of carefully selected surfaces, we are both tackling specific geomorphic problems and testing the assumptions inherent in this new technique. These tests are being performed on surfaces of lava flows, stone pavements, and paleo-shorelines in the arid Southwestern U.S. and Mexico. Our approach includes: (1) comparison with dates from other experimental techniques, (2) determining reproducibility for multiple samples from a single surface, and (3) use of He/Ne ratios to identify additional components and check for gas loss. The results provide the eruption history of volcanic fields, insight into the mechanism for formation of stone pavements, and the timing of climatic events recorded by lake high stands.

Results: One thrust of this year's work has been to determine the timing of volcanism for the ten volcanic centers of the San Quintin volcanic field in Baja California, Mexico. The surface exposure ages fall in two groups; three centers cluster at 25 ka and are suggestive of structural control on timing and location of volcanism. After a hiatus, the remaining centers erupted between 84 to 165 ka. Encouragingly, several Ar–Ar ages and surface exposure ages agree within uncertainties. Another thrust has been to investigate stone pavement formation. Surface exposure ages were determined on pavement clasts and their source lava flows for five flows in two volcanic fields. For each flow, several individual clasts and the parent flow yield identical ages. This strongly suggests that stone pavements are created and maintained at the surface. This is true even for clasts that have exposure ages of 260 ka, implying that stone pavements are some of the oldest and best preserved surfaces in the desert landscape. A third thrust has been to investigate the use of plagioclase as a phase for surface exposure dating. In two out of three cases, ^{21}Ne dates for plagioclase are significantly younger than those for co-existing olivine, implying that plagioclase is not suitable for surface exposure dating.

C. Tracer Tomography in Geological Reservoirs *(David R. Janecky [505-665-0253; Fax 505-665-4955; E-mail janecky@lanl.gov] and W. Dale Spall [505-667-2772])*

Objectives: This project is developing and demonstrating approaches to evaluate large-scale porous flow heterogeneities and integrated chemical processes by focusing on multicomponent injected tracers, coupled with detailed characterization of natural chemical compositional variability in space and time. Coupled processes of interest include spatially distributed flow, dispersion, sorption, partitioning, displacement, and chemical reactions. Applications and basic geochemical information tailored to petroleum reservoir, geothermal, and environmental systems are being developed in consultation with industry.

Project Description: New classes of conservative and reactive nonradioactive organic tracers for both laboratory and field experiments are being defined and tested using stable isotopic labeling schemes. Laboratory experiments, including chromatography and core floods, provide basic geochemical information in well-constrained systems, which isolate aspects of natural processes for evaluating and quantifying flow and reaction processes.

Interpretation of multicomponent tracer information in a consistent, integrated framework requires integration of computational models, including classical and non-equilibrium thermodynamics chromatographic models, coupled fracture and matrix permeability models, lattice gas automata models, and large-scale hydrologic models.

Results: Development of labeled organic compounds focused initially on use of deuterium. Working with industry, commercial sources are being developed for relatively large amounts of isotopically labeled compounds. A range of labeled compounds are on hand for laboratory experiments and relative large quantities of labeled compounds have been utilized for experiments by an industrial collaborator. The choice of stable isotope labeled organic molecules as tracers provides significant advantages in simultaneous multicomponent analysis; however, it also requires a commensurate emphasis in complex analytical methods. Development of GC/MS analyses for environmental samples and expertise developed through analytical work for oil shale processing programs, along with continuously improving analytical equipment, has been combined to successfully complete analyses of labeled organic compounds in solutions, including fresh to brine salinities, gas and liquid petroleum matrices.

Detailed evaluation of our initial multicomponent tracer experiment below the Mammoth Terraces in Yellowstone National Park indicates general consistency between a range of simple tracers as a function of the first acid dissociation constants and internally consistent changes in dispersion and peak shape. Laboratory HPLC experiments are providing information on processes that produce complex peak shapes, similar to some found in the field experiment. In collaboration with Mobil Exploration & Producing US, two multiwell, multicomponent tracer experiments were initiated in petroleum reservoirs. Analyses of the thousands of samples collected over a one-year time frame reveal a snapshot of field operation, tracer transport/reactions and variability of produced petroleum fraction. Similarly, detailed analyses and laboratory experiments with conventional rhodamine-WT tracer provided information on complex chemical and spectroscopic changes which were observed during an environmental demonstration experiment.

D. ^{230}Th–^{238}U Disequilibrium in Geologic Systems Using Solid Source Mass Spectrometry

(M. T. Murrell [505-667-4299; Fax 505-665-4955; E-mail mmurrell@lanl.gov], K. W. W. Sims, and S. J. Goldstein)

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

Project Description: Previously, we have developed mass spectrometric methods for measuring ^{230}Th/^{238}U, ^{226}Ra/^{230}Th, ^{228}Ra/^{232}Th, and ^{231}Pa/^{235}U disequilibria which have significant advantages over decay counting methods. Current emphasis is using these techniques to better understand the behavior of U-series members in magmatic and aqueous systems. These issues are critical to understanding the mechanisms that control dynamic geologic processes, such as the formation of the Earth's crust.

Results: We have adapted the mass spectrometric procedures for radium and barium originally developed for our NBS instruments for use on our commercial instrument (Fisons Sector 54-30). We have also modified our separation chemistry, which originally involved pressurized ion exchange columns, for use with the commercially available Sr-Spec resin and columns (Eichrom Industries). This should allow this procedure to be used by commercial laboratories for verifying compliance in NORM regulatory issues.

Previously, we determined precise U–Th and Sm–Nd isotopic ratios and concentrations in a series of systematic lavas from Hawaii, which have trace-element and petrological characteristics indicating that they span a large range of melt fraction. Based upon this work, we concluded that U/Th fractionation in Hawaiian basalts can be understood in terms of simple batch melting of a garnet peridotite source with melt fractions of 0.5% to 6.5% (Sims et al., *Science*, 1995). The consistency of the isotopic and major-element data would suggest that the melt generation and segregation rates are short relative to the half life of ^{230}Th. In order to further refine our understanding of this timescale, we have measured Ra in the same young series of Hawaiian basalts. If the timescale of melt generation and segregation rates are comparable to the half-life of ^{226}Ra (1600 a), then one would expect that this isotope should be super-enriched in these rocks due to the ingrowth of ^{226}Ra in the matrix during basalt genesis. In fact, all samples show Ra enrichment relative to Th and, as with U/Th fractionation, Th/Ra fractionation varies with the basalts major and trace-element chemistry. Tholeiites from Mauna Loa and Kilauea which represent larger degree partial melts, show almost no U/Th fractionation but about 10% enrichment of Ra over Th; alkali basalts from Hualalai, show about 10% U/Th fraction and 25–30% Th/Ra fractionation; whereas the silica-undersaturated basanites of Haleakala show the most U/Th fractionation, 20–30%, and large degrees of Th/Ra fractionation, up to 45%. These enrichments of Ra relative to Th are significant and will be modeled as to the temporal effects of melt generation and segregation. This project represents a collaboration with Donald DePaolo at LBL/UCB.

In an effort to investigate the nature of ^{234}U/^{238}U fractionation observed in waters associated with silicic tuffs, we analyzed samples from the Apache Leap Tuff near Superior, Arizona. Samples were obtained along a generalized flow path including an ephemeral stream, fracture zones near the surface, matrix pore water, a perched aquifer, and a point where the aquifer discharges into a mine tunnel. ^{234}U/^{238}U activity ratios range from 1.4 to 6.2 in these samples. Data interpretation is still in the preliminary phase, but selective leaching is apparently occurring at this site near the surface in soils and fracture zones, where residence time is limited. As these waters percolate down through the rock matrix, total U concentration increases but ^{234}U/^{238}U does not. If these data are representative of selective leaching in the Apache Leap Tuff, then multiple ^{234}U/^{238}U fractionation mechanism must be present. This project represents a collaboration with Ernest Hardin at the University of Arizona.

CATEGORY: **Energy Resource Recognition, Evaluation, and Utilization**

PERSON IN CHARGE: **Grant Heiken**

A. Operation of a Sample Management System for the Continental Scientific Drilling Program

(G. Heiken [505-667-8477; Fax 505-665-3285; E-mail heiken@lanl.gov] and Larry Fukui, Rust Geotech, Inc., Core Repository, P.O. Box 14000, Grand Junction, CO 81502 [970-248-6172]

Effective sample management is part of the Continental Scientific Drilling Program (CSDP), an interagency collaboration. Curatorial policies and procedures for sample curation were established early in the program. Eventually, a DOE curation facility was set up in DOE facilities in Grand Junction, Colorado. Operations continue to provide sample management of cores and cuttings from CSDP thermal regimes coreholes and of cores and cuttings from DOE-sponsored geothermal drilling. Most recently, the Grand Junction facility has published a "Handbook of Procedures—Petrology Laboratory and Core and Sample Repository," which is available to any investigator upon request to Larry Fukui.

CATEGORY: **Solar–Terrestrial Interactions**

PERSON IN CHARGE: **S. Peter Gary**

A. Energy Transport in Space Plasma *(S. P. Gary [505-667-3807; Fax 505-665-3332; E-mail pgary@lanl.gov])*

Objective: 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 distribution functions and parameters observed by Los Alamos plasma instruments on scientific spacecraft as well as computer simulations are used to carry out fundamental studies of plasma instabilities and associated transport in and near the solar wind, the Earth's bow shock, and the terrestrial magnetosphere.

Results: The most important accomplishment of this program in 1994 was the development of a prediction for the temperatures of anisotropic warm protons observed near 10 electron volts (eV) in the outer magnetosphere. Under the assumptions that hot (keV) protons drive the electromagnetic proton cyclotron instability and that this mode is the heating source for the warm protons, one-dimensional hybrid computer simulations were used to determine the nonlinear consequences of instability growth on initially cool protons. From an ensemble of such simulations, a scaling law for the warm proton temperature as a function of the hot proton properties has been developed. Comparison against observations from Los Alamos plasma instruments on a geosynchronous satellite has shown that the simulation results provide a good description of warm proton temperatures measured in the outer magnetosphere. This scaling relation may be able to describe the heating of cool ionospheric protons in large-scale computer models of plasmaspheric refilling, and, if so, may significantly improve the predictive accuracy of such models.

B. The Solar Wind–Magnetospheric Interaction *(J. Birn [505-667-9232; Fax 505-665-3332; E-mail jbirn@lanl.gov])*

Objectives: The goal of this research is to further the understanding 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 large-scale structure and dynamics 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: Major achievements in 1994 concerned the role of plasma anisotropies and their reduction through a microscopic instability in the dynamics of the magnetotail. Anisotropic magnetofluid simulations were used to investigate the influence of several models of anisotropy reduction on the dynamic evolution of the magnetotail, concerning both the substorm growth phase and the substorm expansive phase. The plasma models included one which is fully isotropic, the double adiabatic model in which pressures parallel and perpendicular to the background magnetic field are completely uncoupled, and a model in which small-scale instabilities impose an upper bound on the anisotropy. In this last model, anisotropies that exceed this bound are reduced on a short Alfvenic timescale. The major effects of the growth phase, resulting from an externally applied electric field, are a localized increase in current density and a reduction in the magnitude of the magnetic field strength in the near-Earth neutral sheet; both of these effects are more pronounced for the more isotropic plasma models. For the expansive phase magnetotail model the development of a generalized tearing instability occurs faster and the substorm wedge currents grow stronger when the plasma model is closer to isotropy. During both phases the plasma anisotropy model strongly influences the spatial variation of the magnetic field in the neutral sheet and hence the location where reconnection occurs and a neutral line forms. Both the driven and the unstable anisotropic models develop mirror-type anisotropies in the boundary regions of the plasma sheet and the adjacent lobes, while the center region of the plasma/current sheet remains close to isotropy.

C. Energetic Particle Acceleration *(G. D. Reeves [505-665-3877; Fax 505-665-4414; E-mail reeves@lanl.gov])*

Objectives: The goal of this research is to develop a better understanding of the Earth's energetic particle environment near geosynchronous orbit.

Project Description: This effort concerns the analysis of data from a series of geosynchronous spacecraft which carry Los Alamos energetic particle detectors. The energies measured range from tens of 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 in the realm of cosmic rays and is therefore well suited to the study of energetic particles which can penetrate the Earth's magnetic field such as galactic cosmic rays and particles produced in solar flares.

Results: In 1994 we continued our study of the magnetic connectivity between the ionosphere and the magnetosphere. We compared particle spectra obtained at geosynchronous orbit (20,000 km altitude, equatorial orbit) and with the DMSP satellites (800 km, polar orbit). We identified 102 conjunctions with good spectral matches and compared the resulting mapping with six widely used magnetic field models. Surprisingly, we found that no single magnetic field model emerged as a clear "winner." Systematic over-stretching of the magnetic field was found in all models and, while none of the models had enough dynamic range to account for all measurements, all models predicted a clear magnetic relationship between magnetospheric substorm activity and auroral processes.

We also investigated the energization of relativistic electrons in co-rotating high-speed solar wind streams from coronal holes and studied the relationship between magnetic storms and substorms. One interesting result showed distinct differences between energetic particle injections observed during storms and those observed during substorms. Storm-related injections seem to be more global, more periodic, and more efficient at accelerating ions to energies above 1 MeV than substorms. This calls into question the commonly held view that a magnetic storm is simply the summed effect of a series of substorms.

CONTRACTOR: **OAK RIDGE NATIONAL LABORATORY**
Lockheed Martin Energy Systems, Inc.
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CONTRACT: **DE-AC05-84OR21400**

CATEGORY: **Geochemistry**

PERSON IN CHARGE: **B. R. Appleton**

A. Thermodynamic Mixing Properties of C–O–H–N Fluids *(J. G. Blencoe [423-574- 7041; Fax 423-574-4961; E-mail jblencoe@blencoe.chem.ornl.gov], J. C. Seitz, and L. M. Anovitz)*

Objectives: Thermodynamic data for C–O–H–N fluids (hydrothermal waters, natural gas, etc.) are insufficient in quantity and quality to permit formulation of accurate equations of state for natural fluids in the Earth's crust, which are composed predominantly of H_2O, CO_2, CH_4, H_2 and N_2. Such equations find wide application in solving geochemical problems, including geothermal and hydrocarbon reservoir hydrodynamics modeling, thermochemical calculations of the stabilities of hydrocarbons and alteration minerals, permeability changes in reservoirs, contaminant transport, and global cycling of greenhouse gases.

Project Description: Experiments are performed with H_2O, CO_2, CH_4, N_2, and mixtures of these gases at pressure–temperature conditions similar to those encountered in deep aquifers, sedimentary basins, and geothermal fields. The pressure–volume–temperature (PVT) relationships of pure gases, binary, and ternary mixtures are determined with unprecedented precision in a unique vibrating-tube densimeter designed to perform in the range 50-450°C and 100–3500 bars. The pressure–temperature–composition (PTX) relationships of gas mixtures are studied in another unique facility, a hydrogen-service, internally heated pressure vessel capable of operation with several thousand bars of hydrogen pressure, with an overall operating range up to 10 kilobars at 100 to 1200°C. Novel Raman spectroscopic studies of gas mixtures, performed in collaboration with scientists at Washington University and the U.S. Geological Survey, complement these approaches. Equations of state are developed from the experimental results, coupled with literature data.

Results: An equation of state has been developed for binary and ternary mixtures in the CO_2–CH_4–N_2 system in the range 0–400°C and 0–1000 bars pressure, based on our current and previous PVT experimental results. The new equation reduces to the ideal gas law at the limit of low pressure, is readily extrapolatable to higher pressures, and is modular in that improved equations of state for the pure end member gases can be easily incorporated. Abundant new data on the PVT properties of binary mixtures in the CO_2–CH_4–N_2 system have been collected at 400°C and 100–1000 bars using our vibrating-tube-densimeter. We have initiated modifications to the densimeter to permit the investigation of water–gas mixtures.

PTX measurements of H_2O+CO_2 and H_2O+N_2 mixtures have been investigated at 500 bars and 475°C over a wide range of water mole ratios in our internally heated pressure vessel, from which the activity–composition relationships of these mixtures can be determined. New methods of generating nitrogen gas from cobalt, nickel, and copper nitrides facilitate these experiments. We have also developed a unique small-volume sample chamber which isolates both the experimental charges and a newly designed hydrogen pressure sensor from the bulk pressure vessel atmosphere. These improvements together with a new cryogenic-manometric gas analysis system have resulted in PTX measurements of unprecedented accuracy and precision.

In collaboration with Jill Pasteris at Washington

University and I Ming Chou of the U.S. Geological Survey, we have succeeded in using molecular dynamics simulations to produce synthetic Raman spectra of C–O–H–N gas mixtures, which can be compared with the observed spectra to refine molecular interaction models and gas mixture equations of state. We have also performed detailed Raman spectral measurements of individual gas-rich fluid inclusions from the Crystal Graphite Mine in Montana. Estimates of the gas compositions and internal pressures in these inclusions from the microRaman measurements are consistent with results from conventional, but far more laborious, approaches.

B. Fundamental Research in the Geochemistry of Geothermal Systems *(D. J. Wesolowski [423-574-6903; Fax 423-574-4961; E-mail dqw@ornl.gov], J. Horita, D. R. Cole, S. M. Fortier, and P. Benezeth)*

Objectives: The objective of this project is to provide fundamental information on geochemical reactions which play pivotal roles in a wide range of geological processes, but which 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–S isotopes, and melt–mineral–volatile 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 Technology Development Program.

Results: Current topics within this project include the aqueous geochemistry of aluminum, which affects permeability development and scaling in geothermal systems, and the effects of dissolved salts on the partitioning of the stable isotopes of hydrogen and oxygen 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.

Using a newly constructed hydrogen-electrode concentration cell, we have demonstrated for the first time ever that the pH of a solution and the solubility of a mineral phase can be simultaneously measured at temperatures to 250°C. Using this approach, we have studied the solubility of boehmite, AlOOH, in 0.03 to 1.0-molal sodium chloride solutions from 100 to 250°C in solutions with pH ranging from 2 to 10. The solubility of this phase is controlled by the reaction $AlOOH + (3-n)H^+ \rightarrow Al(OH)_n^{3-n} + (2-n)H_2O$, with n varying from 0 to 4. Continuous pH monitoring permits us to observe the rate of approach to equilibrium between the mineral and the solution as pH is changed by titrating either acid or base into the cell, as well as the achievement of an equilibrium state. Reversed equilibrium solubilities have been obtained across the pH range studied. The results obtained compare well with extrapolations of our previous work at lower temperatures and with recent literature data at low ionic strength.

In collaboration with scientists of the Atomic Energy Agency of Argentina, we have developed a quasitheoretical model for the partitioning of the stable isotopes of oxygen and hydrogen between pure water liquid and vapor from 0 to 374°C, based on our previous experimental results and selected literature data. The effects of addition of 0- to 6-molal NaCl to water on the liquid–vapor partitioning of oxygen and hydrogen isotopes have been determined from 0–350°C. The isotope salt effects are shown to increase with increasing temperature above about 150°C, an unexpected result which now appears to be related to the dramatic increase in the critical temperature of a water solution as salt is added. The effects of 0- to 6-molal $CaCl_2$ have also been determined to 200°C. The effects of this salt on both oxygen and hydrogen isotope partitioning are much larger than the monovalent NaCl for equimolal solutions. Experiments involving the exchange of oxygen and hydrogen isotopes between water and several minerals (calcite, strontianite, brucite) at 200 to 450°C demonstrate that the liquid–mineral partitioning of both oxygen and hydrogen isotopes undergoes the same shift upon addition of salts to the solution as does the liquid–vapor partitioning. This proves our hypothesis that the isotope salt effects are related to the activity/concentration ratios of the isotopic water molecules ($H_2{}^{16}O$, $H_2{}^{18}O$, and $HD^{16}O$) in the liquid phase as a function of salinity.

C. Ion Microprobe Studies of Diagenesis *(L. R. Riciputi [423-576-4839; Fax 423-576-8559; E-mail riciputilr@ornl.gov], D. R. Cole, and R. Ripperdan)*

Objectives: The principal objective of this research is to use elemental and isotopic compositions, and mineralogical relationships, to quantify the mass transfer processes influencing porosity, permeability, and fluid chemistry during diagenesis of carbonates and clastics. Development of ion probe methodologies for elemental and isotopic analysis of geological materials has been a secondary objective.

Project Description: In this project, the micron-scale spatial resolution, elemental and isotopic imaging, and quantitative trace element and isotope ratio capabilities of ORNL's Cameca 4f ion microprobe are being developed and used in studies of fluid–rock interactions in sedimentary basins. The probe studies are augmented by information obtained from a variety of other geochemical techniques, including conventional gas-source isotope ratio mass spectrometry, electron microprobe, scanning electron microscopy, neutron activation, and fluid inclusion microthermometry. These techniques are currently being applied to: (1) investigations of sulfate reduction and sedimentary sulfide formation in hydrocarbon reservoir rocks and their relationship to hydrocarbon migration; (2) the formation of diagenetic iron oxides associated with large-scale fluid migration events in and near sedimentary basins; and (3) the use of ion probes to obtain precise measurements of the $^{18}O/^{16}O$ and $^{34}S/^{32}S$ ratios in clastic, primary precipitated, and diagenetic minerals in sedimentary rocks.

Results: Fifty core samples from the Obed Formation of the Alberta oil and gas province have been examined. Trace element analyses of diagenetic sulfides show no clear correlation with their sulfur isotopic compositions, although the latter readily permit differentiation of bacterially mediated sulfate reduction from thermogenic sulfate reduction processes during early and late diagenesis, respectively. Thermogenic sulfide formation is related to greater burial depths during late diagenesis, and is clearly associated with the generation of sour, H_2S-rich natural gas. A large number of conventional bulk sulfur isotope analyses of these sulfides performed by our collaborators at the University of Alberta failed to distinguish these two origins of sedimentary sulfides, demonstrating the need for the greater spatial and textural resolution provided by the ion probe studies. We have also obtained Pb isotope ratio data from these sulfides, and we are continuing these studies with the hope of age-dating individual diagenetic and fluid-migration events.

In collaboration with T. C. Onstott of Princeton University, we are examining sedimentary sulfides collected from deep (>5 km) drill holes as part of DOE's Office of Health and Environmental Research, Subsurface Science Program. The aim of the OHER program is to determine the depth of the biosphere in the solid earth, and to investigate the utility of deep-subsurface microorganisms in hydrocarbon extraction and environmental remediation. A number of the samples studied exhibit very large (>100 per mil) variations in $^{34}S/^{32}S$ ratios in sulfides within a single thin section. Because biological sulfate reduction typically leads to extremely low ^{34}S contents in resultant sulfides, we may be able to use this approach to prove that biologically mediated reactions are indeed occurring at great depth in sedimentary basins. We have also detected extreme $^{34}S/^{32}S$ variations in sulfides from the North Sea oil and gas province, obtained in collaboration with scientists at Exxon Production Research, Queens University in Belfast, and the Scottish Universities Research Reactor Center.

Over 800 analyses of $^{18}O/^{16}O$ ratios in electrically insulating silicates, sulfides, phosphates, and carbonates have now been performed using the Cameca 4f ion probe. Novel analysis procedures developed in this project have enabled consistently high precision, close to the ±0.6 per mil limit imposed by counting statistics.

D. Experimental Studies of Fundamental Stable Isotope Exchange Reactions

(D. R. Cole [423-574-5473, Fax 423-574-4961, E-mail me@cole.chem.ornl.gov], S. M. Fortier, J. Horita, and D. J. Wesolowski)

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 focused on: (1) the oxygen isotope partitioning between aqueous fluids and the minerals hematite, Fe_2O_3, and magnetite, Fe_3O_4, in the 100–500°C range; and (2) the exchange rates and equilibrium fractionations of hydrogen and carbon isotopes among gaseous species in the system H_2O–CO_2–CH_4–H_2. Novel experimental methods are used to promote recrystallization and/or synthesis of the iron minerals, and natural and synthetic catalysts for exchange among the C–O–H gases are investigated.

Results: A series of experiments in which magnetite, Fe_3O_4, was synthesized by different reaction mechanisms at 300–450°C all give water–magnetite fractionations which vary by only a few per mil over this temperature range and are consistent with several published semitheoretical models based on quantum mechanics. The most promising of these is the reaction of iron powder with pure water in silver–palladium alloy capsules which permit escape, by diffusion through the capsule walls, of hydrogen formed by the reaction $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$. Interestingly, this is exactly analogous to the corrosion of steel in fossil and nuclear power plant steam generation systems. Thus, the kinetics of this process, as well as the equilibrium oxygen fractionation factors, are of interest to the power generation industry as well as the geoscience community.

Magnetite was also synthesized by reduction of extremely fine-grained hematite (Fe_2O_3) starting material in the presence of dilute acetic acid solutions. Perfect octahedral and dodecahedral magnetite crystals up to 100 microns in diameter were grown from the submicron hematite starting material. Because acetic acid is the most abundant soluble organic component in sedimentary basin brines, the ability of this and related compounds to facilitate the formation of magnetite is of great interest in field studies of authigenic magnetite formation, in which alteration of the remnant rock magnetism has been used to age-date large-scale basinal fluid migration events.

Equilibrium water–magnetite oxygen isotope fractionation factors obtained in the 300–450°C range from both types of synthesis experiments are similar. Conventional bulk isotopic analyses of the run products by laser-fluorination were augmented by ion microprobe analyses of individual mineral grains. The two types of analyses gave essentially the same results, within experimental error. This is the first time that ion probe measurements have been used to obtain a mineral–water isotope fractionation factor. This approach has great promise, because it may permit the determination of equilibrium fractionation factors from experiments which involve only a few percent of overall isotopic exchange, as is typical for minerals which react very slowly (most silicates and oxides) and at low temperatures where exchange rates for all minerals are slow.

Hematite–water fractionations have been obtained by partial exchange experiments between water and extremely fine-grained hematite starting material at 300°C. This and our previous results at 150 and 350°C exhibit a temperature trend that is consistent with recent semitheoretical models. The degree of partial exchange observed at all temperatures is sufficient to permit refinement of the fractionation factor as a function of temperature.

Carbon isotope exchange ($^{13}C/^{12}C$) between CO_2 and CH_4 has been found to be extremely sluggish in the absence of catalysts, with only 0.01% exchange observed after 26 days at 400°C and 0.2% after 7 days at 500°C. Silica gel, dehydrated zeolites, and graphite increase the exchange rates by more than an order of magnitude. These materials may mimic natural catalysts in sedimentary and igneous rocks. A variety of metals (Pt, Ni, Rh, Pd) have been found to be even more effective as catalysts for this exchange reaction. Using such catalysts, which may have a natural analog in metal-rich hydrocarbon source rocks such as black shales, we have obtained an equilibrium fractionation factor between CH_4 and CO_2 of 20.4 per mil at 400°C, as compared with the calculated semitheoretical value of 18.5 per mil. Therefore, investigation of natural and synthetic catalysts may permit experimental determination of the equilibrium fractionation of these geologically important gases in the 200–600°C range, and may also permit quantification of residence times of gases in hydrocarbon reservoirs.

E. Potentiometric Studies of Geochemical Processes *(D. J. Wesolowski [423-574-6903; Fax 423-574-4961; E-mail dqw@ornl.gov], R. E. Mesmer, and P. Benezeth)*

Objectives: The objective of this project is to utilize ORNL's unique, high-temperature, hydrogen-electrode, potentiometric cells to study aqueous reactions which involve exchange of hydrogen ions (i.e., changes in pH).

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

Results: A variety of activities were initiated and completed during this period. In collaboration with Dr. Scott Wood of the University of Idaho, we determined the formation constants for Nd^{3+}–acetate complexes in 0.1-molal NaCl solutions from 25 to 250°C to aid in interpretation of diagenetic and alteration effects on rare earth element distributions in sedimentary and igneous rocks. With Dr. Michael Machesky of the Illinois State Water Survey, we continued our measurements of the adsorption/desorption of H^+ on the surface of the mineral rutile, TiO_2, in 0.01- to 1.0-molal NaCl solutions from 25 to 250°C, as a test case for the study of the surface properties of more abundant rock-forming minerals. With Dr. Richard Kettler of the University of Nebraska, and his student Moira Ridley, we examined the complexation of Cd^{2+} and Al^{3+} by oxalate and malonate, two naturally occurring difunctional carboxylic acids, to help in modeling of elemental migration and permeability changes in organic-rich sedimentary basin brines.

Also in collaboration with Dr. Kettler and Ms. Ridley, we have initiated an extensive investigation of the complexation of Al^{3+} by sulfate. Sulfuric acid is the principal contributor to acidified stream, lake, and soil waters caused by both acid rain (burning of sulfur-rich fossil fuels) and acid mine drainage (oxidation of pyrite associated with coal and metal mining). Our preliminary results from potentiometric titrations indicate that the formation constants of the first and second aluminum sulfate complexes, $Al(SO_4)^+$ and $Al(SO_4)_2^-$, increase by more than an order of magnitude as temperature decreases from 50 to 5°C. A preliminary study of the dissolution rates of gibbsite, $Al(OH)_3$, in sulfuric acid versus hydrochloric acid at the same pH (3.0), temperature (5.0°C), and ionic strength (0.1-molal NaCl), indicates that the rate of dissolution of the aluminum mineral is also increased by more than an order of magnitude in the sulfate solution relative to the chloride solution. Thus, not only is the equilibrium solubility of aluminum minerals predicted to be much higher in low-temperature sulfate solutions than in sulfate-free solutions at the same pH, but the release rates of aluminum to the solution are also much higher. Since Al^{3+} concentration in soil and lake waters (derived from aluminum-rich clay particles) is one of the major contributors to biological toxicity, these studies have an important environmental impact associated with the extraction and burning of fossil fuels, particularly in sensitive ecosystems such as tundra and high-altitude or high-latitude forests. Also, the permeability of sedimentary rocks, which contain abundant aluminosilicates, may also be controlled in part by aluminum–sulfate interactions.

F. Mechanisms and Rates of Oxygen Isotope Exchange in Mineral–Fluid Systems

(D. R. Cole [423-574-5473; Fax 423-574-4961; E-mail me@cole.chem.ornl.gov], L. R. Riciputi, and S. M. Fortier)

Objective: The major objective of this research is to measure the rates of both oxygen isotope and chemical exchange between minerals and fluids controlled by surface reactions which lead to the growth and dissolution of minerals.

Project Description: There are many documented case histories of natural fluid–rock interaction systems that indicate: (1) isotope disequilibrium may be more widespread than previously realized; (2) isotope disequilibrium can occur at high as well as low temperatures; (3) different minerals exhibit varying susceptibilities to retrograde exchange; and (4) the mechanisms of chemical and isotope exchange are varied and depend on the prevailing conditions (temperature, fluid chemistry, etc.). This research is focused on the experimental determination of rates of oxygen isotope exchange and mineral growth in the carbonate–quartz–feldspar–fluid system at temperatures of 300 to 700°C and pressures up to 3 kilobars. These results will allow extrapolation to lower temperatures appropriate for studies of fluid–rock interactions in sedimentary basins, geothermal systems, waste repositories, etc.

Results: Experimental results have been obtained on the degree of oxygen isotope exchange between carbonates and NaCl-bearing solutions at 300°C and pressures of 0.1 and 1.0 kilobars. Calcite was reacted with isotopically distinct waters containing 0-, 1-, 3-, and 5-molal NaCl for periods of up to 3024 hours. The degree of exchange toward equilibrium increases with increasing salinity. Similar experiments have been performed with $SrCO_3$ and $BaCO_3$. Detailed SEM imaging indicates that strontianite underwent extensive recrystallization with an 8-fold increase in grain size in 5-molal NaCl, while calcite grain size increase was only 1.4-fold at the same conditions. These results suggest that the natural logarithm of the degree of oxygen isotope exchange toward equilibrium varies linearly with ratio of average "new" grain diameter to initial grain diameter, and that the calcite growth rate follows the cube root of time.

We have continued our experimental and theoretical evaluation of the systematics of carbon and oxygen isotope exchange between calcite, CO_2, and H_2O. New experimental results were obtained on the competing rate effects of recrystallization and solid-state diffusion, as a function of fluid composition. 1–3-millimeter chips of Iceland Spar calcite were reacted at 700°C with either pure water with 98% ^{18}O, or a mixture of this water containing 4 mole percent CO_2, for durations of 72 hours at 3 kilobars, and 18 hours at 1 kilobar. Depth profiles of ^{18}O parallel to the c-axis were obtained with our Cameca 4f ion microprobe. When compared with numerical simulations using published rates of diffusion of carbon and oxygen in calcite, the measured profiles establish that intracrystalline transport of these elements is more rapid than predicted when H_2O is present, indicating that a significant portion of the isotope exchange occurs via chemical reaction, in which water accelerates solid-state recrystallization of the calcite. SEM examination reveals an extensive microtopography developed on grain surfaces. These results seriously challenge currently available diffusion coefficients at elevated temperatures and pressures.

An empirical model describing the kinetics of oxygen isotope exchange in silicates and carbonates recrystallizing under hydrothermal conditions has been established for temperatures of 300–500°C. The equation is $\ln(r) = a + b(U') + c/T$, where r is the isotope exchange rate constant (moles of oxygen per meter^2 per second), T is the absolute temperature, a-b-c are constants unique to individual mineral groups (e.g., framework silicates, sheet silicates, etc.), and U' is the mineral's electrostatic lattice energy normalized to the number of cations in the mineral. This equation permits estimation of the isotope exchange rates for a large number of minerals and is valid over the range of temperatures and fluid compositions in the input experimental data. Accuracy in calculated values of ln(r) are ±0.42, ±0.15, ±0.10, and ±0.27 for framework, chain, and sheet silicates, and carbonates, respectively.

CONTRACTOR: **PACIFIC NORTHWEST LABORATORY**
Richland, Washington 99352

CONTRACT: **DE-AC06-76RLO 1830**

CATEGORY: **Geochemistry**

PERSON IN CHARGE: **S. Rawson**

A. Surface Structure and Chemistry of Carbonate Minerals

(Donald R. Baer [509-375-2375; Fax 509-375-5965; E-mail dr_baer@pnl.gov],
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Objectives: The purpose of this program is to develop a fundamental, microscopic understanding 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 CO_2 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 understanding will eventually provide insights into the behavior of these materials in natural systems.

The approach to meeting program goals involves three interdependent area efforts: 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 environments.

Results: Atomic force microscopy (AFM) has been used to examine the surface structure of $CaCO_3$ $(10\bar{1}4)$ surface in different aqueous solutions with atomic resolution.

From these images, it appears that the cleaved calcite $(10\bar{1}4)$ surface exhibits a relaxed (1×1) structure in which the carbonate group within the surface unit cell reorients itself. *Ab initio* density-functional computations and glancing incidence x-ray diffraction measurements of this surface are currently being performed to determine if this relaxation is inherent to the calcite surface or is induced by the aqueous solution.

The dissolution of calcite under a variety of solution conditions has also been examined using AFM. The dissolution on the cleavage $(10\bar{1}4)$ surface has been found to proceed via pit growth. These pits are typically a single atomic layer deep and their growth is anisotropic as a result of differing atomic configurations at the pit step edges. The dissolution step velocities measured by AFM are 3.5 nm/sec and 1.4 nm/sec for the fast and slow directions, respectively. AFM measurements of the pits' size dependence on temperature yield apparent dissolution activation energies for the fast and slow directions of 0.61 eV and 0.64 eV. Other interesting features of these pits include the fact that the pit velocity is constant over time, that the pits maintain their crystallographic shape, with straight edges, over time, and that the presence of impurities in the aqueous solution can significantly alter the surface morphology during dissolution.

In an attempt to understand the microscopic factors controlling dissolution, two models were examined. The first is the analytical "terrace-ledge-kink" (TLK) model (Burton et al.., 1951; Lothe and Hirth, 1959) which relates the velocities of pit edge retreat to the frequency of "double-kink" and "kink" site formation. In this model, many different pit morphologies are possible depending upon the relative magnitudes of the double-kink and kink site formation frequencies. As a result, it is easily shown in this model that the maintenance of crystallographically shaped pits with straight edges and a constant velocity retreat requires a delicate balance in the frequency of double-kink and kink site formation referred to as the "double-kink annihilation regime." This model also indicates that the constant-velocity phenomena is exhibited only after the pits reach a size that is significantly greater than the size of the fundamental atomic building blocks of the surface. Pits smaller than this accelerate as they dissolve. This prediction has not yet been verified experimentally because of the difficulty of imaging nanoscale pits with the AFM.

To investigate this quantitatively, a Kinetic Monte Carlo (KMC) model was constructed from one originally developed to describe growth phenomena (Weeks and Gilmer, 1979). Using a simple two-parameter KMC model in which the activation energy for the removal of a surface species is based upon its near-neighbor coordination, all of the available experimental data were reproduced, including the temperature dependence of pit size and the evolution of pit size as a function of time. The model also reproduces the acceleration regime for small pits predicted by the TLK model, as well as the transition to a constant-velocity regime for pits significantly larger than the atomic dimensions of the surface. Finally, the fundamental microscopic rates for the elementary pit dissolution surface processes were derived from this model.

Current efforts in this area are now concentrated on elucidating the role solution impurities play in changing the pit morphology during dissolution.

B. Theoretical Characterization of the Physics and Chemistry of Soil Minerals

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Objectives: This program is designed to provide the theoretical basis for understanding the molecular scale processes that drive subsurface transport. Research in this area is specifically designed to investigate the microscopic properties of minerals and mineral interfaces that directly affect the macroscopic transport contaminants through the subsurface.

Project Description: This work is focused on identifying critical or controlling aspects of atomic-scale phenomena that influence the behavior of complex geochemical systems on longer length and time scales. This information can be used to understand the timescale at which an event becomes most probable and to fix the initial conditions of more macroscopic models such as those found in reactive transport theory.

This research effort is based upon a fully integrated theoretical approach which combines methods from *ab initio* quantum mechanics and classical mechanics. *Ab initio* and first-principle quantum mechanical methods implemented on massively parallel computer architectures are used to investigate such phenomena as adsorption, dissociative chemisorption, diffusion, and desorption on the internal and external surfaces of oxide, metal oxide, and aluminosilicate minerals. Molecular dynamics and molecular mechanics techniques are employed, in conjunction with the quantum mechanical calculations, to study interfacial dynamics and ensemble effects.

This research program is jointly supported by OBES/Geosciences and OBES/Chemical Sciences.

Results: The complex nature of subsurface geochemistry is apparent even with studies of well-defined water/oxide interfaces. Calculations on MgO (001) indicated that water weakly physisorbs, at low temperatures on a perfect surface, but surface hydroxylation, resulting from the chemidissociation of water, is endothermic. However, the computed energetics clearly indicate that both adsorption and dissociation processes are exothermic at "corner" and "edge" defect sites. Recent experimental data has indicated that binding energy of water on MgO(001) is ~14–15 kcal/mol, consistent with the calculations.

Studies on ZnO have investigated the bulk, clean $(10\bar{1}0)$ surface, and CO adsorbed on the $(10\bar{1}0)$ surface using periodic Hartree–Fock theory. Investigations of the bulk material probed the relative stability of the zincblende, wurtzite, and rocksalt phases confirmed the only experimental measurement of the zincblende/rocksalt phase transition pressure (9.0 GPa experimental, 8.6 GPa theory). A computed relaxed structure of the $(10\bar{1}0)$ surface was compared to LEED data and showed both quantitative and qualitative disagreement with the experimental findings of a large dimer tilt angle (11±5) and no significant shorting of the ZnO bond length. Calculations for the CO/ZnO interface revealed a bond length contraction and subsequent frequency increase which are interpreted to result from a very small charge transfer from anti-bonding molecular orbitals in the CO to the Zn atoms. This strengthening of the intramolecular bond is unusual and has important implications for the catalytic properties of the surface.

The relaxed geometry of α-Al_2O_3 (0001) was computed and based solely upon the reported non-bonded oxygen distances a number of relaxed surfaces are possible. The empirical data suggests that H_2O would only weakly physisorb (reversibly) on this surface at low temperatures. In rather sharp contrast, the theoretical studies indicate a number of physisorption configurations and at least one strong chemisorption site (water oxygen down over a surface aluminum; bound by approximately 28 kcal/mol).

C. Structure and Reactivity of Ferric Oxide and Oxyhydroxide Surfaces

(James R. Rustad [509-372-6313; Fax 509-375-2718; E-mail jr_rustad@pnl.gov] and
Andrew R. Felmy [509-372-6296; Fax 509-375-2718; E-mail ar_felmy@pnl.gov])

Objectives: The objectives of this program are to (1) develop the capability to create molecular models of hydroxylated ferric oxide and oxyhydroxide surfaces, (2) use these models to better understand the relationship between surface 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. For many solutes, measurement of sorption density versus aqueous concentration suggests the presence of a heterogeneous array of surface sites having a range of affinities for the probing solute. Crystallographic differences in coordination and geometrical pattern of surface oxide sites are a fundamental aspect of this heterogeneity. In this project, the effects of crystallographic heterogeneity on adsorption are evaluated using computational molecular models. These results are then used to produce a more robust thermodynamic description of adsorption at the mineral–water interface.

Results: A model describing the interactions of ferric iron with oxide ions, hydroxide ions, and water was developed and parameterized using a combination of empirical and theoretical information on Fe–O–H potential energy surfaces. The model was constructed to describe as accurately as possible Fe–O, Fe–OH, Fe–OH_2, OH–H_2O, and H_2O–H_2O interactions in gas and condensed phases. The model was tested by predicting the bulk structures of goethite, akaganeite, lepidocrocite, hematite, proton-ordered ice, gas-phase water clusters, the proton affinities of water and hydroxide ion, and structure and acidity of solvated $Fe(H_2O)_6$. The model was then applied to goethite (100), (010), (001), (110), and (021) surfaces using infinite slabs parallel to these crystallographic directions. The lowest-energy protonation scheme for each of these neutral surfaces was identified. Gas-phase proton affinities and acidities were computed by creating proton vacancies and interstitials at various sites on the slabs. To relate these energies to stability constants for surface protonation reactions, energies were computed for hydrolyzed ferric iron species in solution for which stability constants are known. The stability constants showed a very good linear relationship with the energies of the complexes as computed using the Fe–O–H model. This relationship was applied to compute equilibrium constants for proton equilibria on surface hydroxide and aqua sites. The surface stability constants were incorporated into a thermodynamic speciation code to calculate the extent of proton adsorption as a function of pH. Using the unmodified relationship, the predicted point of zero charge was too low by approximately one log unit, but the shape of the calculated curve was quite close to that of the experimental curve. If a term accounting for differential solvation between the surface and aqueous complexes is fit to the point of zero charge, the titration data are well reproduced. A most interesting result is that the stability constants involving protonation/deprotonation of surface Fe_3OH, Fe_2OH, and FeOH groups are all very similar. The lack of variability was interrupted by the (010) surface, which has a particularly acidic site partially buried in the solid.

CATEGORY: **Solar–Terrestrial Interactions**

PERSON IN CHARGE: **Nels R. Larson and Donald W. Slater**

A. DOE Insolation Studies *(N. R. Larson [509-372-6053; Fax 509-372-6397; E-mail nr_larson@pnl.gov]*

Objectives: The Insolation Studies program is focused on the determination of the amounts and spatial/temporal distributions of atmospheric aerosols and ozone using PNL-developed radiometer technology.

Project Description: Beginning in 1993 a network of Multiple Filter Rotating Shadowband Radiometers (MFRSRs) was formed for the purpose of measuring the latitudinal distributions of atmospheric aerosols and ozone. The MFRSRs make fully automated measurements of all-sky, diffuse, and direct solar beam irradiances at seven different wavelengths. They were developed at Pacific Northwest Laboratory and State University of New York at Albany for the Department of Energy. Data from the instruments allow the determination of the optical extinction caused by trace atmospheric species. This information is in turn used to compute the particle size distributions of aerosols and column amount of ozone. By measuring trends in aerosol populations and ozone amounts, the impacts on the solar resource from aerosol-generating human activities and natural perturbations, such as volcanic eruptions and wildfires, can be assessed. This information assists the evaluation of computational climate models, and will allow them to produce more accurate forecasts of how climatic changes might occur because they will be able to account better for the potentially significant radiative effects of aerosols.

Results: The physical properties and radiative effects of recently erupted stratospheric aerosols from Mount Pinatubo were characterized over the 3-year span of their presence. At mid-U.S. latitudes there were three maxima in aerosol optical depths occurring in Spring of 1992, Winter of 1992–93, and Winter of 1993–94.

The loss of direct-beam solar energy in the mid-visible region of the spectrum at those times was about 13, 9, and 3%, respectively; this reduction was enough to cause comparable losses in the output of solar energy systems that rely on direct beam focusing for energy transfer. The particle size distributions exhibited a stable mode throughout this period with sulfuric acid droplet radius of about 0.55 micrometers; this helped to contribute to new lows in ozone amounts over the U.S.

The relative amount of radiative extinction caused by aerosols in the lowest 1 km of the atmosphere was characterized in the Columbia River Basin of Eastern Washington. It was determined that about one-third to one-half of the total atmospheric column extinction results from this layer, which is the most heavily influenced by human-generated aerosols.

A new assessment of atmospheric transmission was accomplished with the goal of optimizing the performance of the MFRSR in measuring the wavelength dependence of aerosol extinction. In this study it was discovered that some of the world standard aerosol observation wavelengths can in fact be compromised by water vapor absorption. As a result, a new set of filtered detectors was obtained for installation in the latitudinal MFRSR network. Currently the network consists of units in Alaska, Washington (2), Arizona, Hawaii, and Australia (3).

B. Operation Of DOE Aeronomy Observatory *(Donald W. Slater [509-372-6049; Fax 509-372-6397; E-mail dw_slater@pnl.gov])*

Objective: The objective of this work is to broaden the understanding of the mechanisms governing the transfer of energy within the magnetosphere–atmosphere coupled system. A primary task is to investigate the response of the thermosphere to large energy influxes from the space surrounding the earth.

Project Description: This work addresses the need for critical observations to assess the understanding of, and confidence in, the current computational models used to describe energy exchange within near-earth space and the resultant atmospheric effects. Optical remote sensing techniques, using low-light-level imaging instruments developed at PNL, are used to monitor signatures of optical emissions from the upper atmosphere that are the direct result of this energy influx, and that can be used to diagnose intensity, spatial and temporal characteristics of this influx.

Results: With the development period completed for the PNL-designed low-light-level imager, operation of the instrument in routine mode began. The red line emission of atomic oxygen (630.0 nm) has been used as a diagnostic tool to define regions of the earth's upper atmosphere that experience large-scale heating due to energy influx from the magnetosphere. These features are known as stable auroral red arcs. A comprehensive review article describing research of the entire production cycle of these features, from initial energy exchange between the earth's ring current and the low-energy plasmaspheric electrons to deposition of this energy into the upper atmosphere and its effects, has been completed. The network of mobile scanning photometers that preceded the advent of the imager has been retrieved from field sites and decommissioned.

CONTRACTOR: **SANDIA NATIONAL LABORATORIES**
Lockheed–Martin
Albuquerque, New Mexico 87185

CONTRACT: **DE-AC04-94AL85000**

CATEGORY: **Geophysics and Earth Dynamics**

PERSON IN CHARGE: **M. C. Walck**

A. Micromechanics of Failure in Brittle Geomaterials *(Joanne T. Fredrich [505-844-2096; Fax 505-844-7354; E-mail fredrich@sandia.gov] and Teng-fong Wong, State Univ. of New York at Stony Brook)*

Objectives: The objectives of this project are 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 processes 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: A technique for determining three-dimensional pore structure was developed. Laser scanning confocal microscopy can be used to resolve submicron optical sections and the digital 2-D images can be analyzed using image analysis software to create 3-D reconstructions. As an application to analysis of transport properties, a quartz sandstone with a variable porosity which results from differing degrees of cementation during diagenesis was imaged; the reconstructions suggest that permeability evolution with porosity reduction is dramatically affected by a loss in connectivity with increasing cementation. Another application is the study of brittle failure processes, where the reconstructions reveal the complex pore geometry and micromechanical processes associated with increasing deviatoric compressive stresses. A paper describing this work appeared in *Science.*

Although the initial damage state is an important parameter in theories of rock failure, little data exists to evaluate the effect. A test series was performed on Westerly granite with two initial damage states: pristine and thermally cracked. Heating to 600°C causes a 2-fold increase in crack density and 75% reduction in compressive wave velocity. Unconfined compressive strength is reduced by 25%, which is consistent with results in the literature. New findings are that strength is reduced only for low minimum compressive stresses and that intrinsic rock strength is recovered when the applied stresses are sufficient to close preexisting microcracks. The results suggest that under low confining stresses, open microcracks act as nucleation sites for the growth of new microcracks which interact and lead to failure. Upon closure, normal stresses transmitted across the crack face increase their shear resistance to displacement and preclude the nucleation of microcracks. The failure process instead proceeds independently of the initial isotropic damage and microcracks must be nucleated by a different mechanism. One alternative is that grain boundaries, via an elastic mismatch mechanism, are the dominant flaws at elevated pressures; such an explanation is consistent with observations in the literature on the grain-size dependence of fracture strength in low-porosity rocks.

B. Laboratory and Theoretical Analyses of Transport Paths in Single Natural Fractures

(S. R. Brown [505-844-0774; Fax 505-844-7354; E-mail srbrown@sandia.gov], N. G. W. Cook, L. R. Myer, and G. Yang, Univ. of California at Berkeley and Lawrence Berkeley Laboratory)

Objectives: Fluid flow in fractured rock is an important phenomenon to understand in connection with energy production and containment or disposal of wastes. The objective of this project is to address several outstanding questions of the effects of void topology on flow and transport in single fractures by quantitative, visual observations and measurements of single- and two-phase flow.

Project Description: We have developed a method for obtaining precise replicas of real fracture surfaces using transparent epoxy resins. These replicas are being used to examine flow in the fracture void space using digitized optical imaging and nuclear magnetic resonance imaging (NMRI). In parallel work, we are examining single- and two-phase flow in irregular fracture aperture distributions using graph theory, effective medium theory, and percolation theory to analyze the topology of the conducting network of void space. This work emphasizes that the topology of the network is of at least as much importance as the conductance of the individual elements in determining fluid flow. The topological characteristics of the preferred paths at different scales will be analyzed to study the effects of scale on flow and dispersion in fractures. Numerical predictions based on graph theory will be compared with experimental observations of multi-phase flow.

Results: Field specimens of several natural rock joints were collected. Matched two-dimensional images of the surface topography of each fracture surface were measured, allowing the fracture aperture distributions to be calculated. Silicon rubber molds and epoxy replicas of the fracture surfaces were made. Preliminary NMRI and dye-flow experiments were done which show distinct and strong channeling of fluid flow at the millimeter-to-centimeter scale. Refinement of the measurements is in progress to allow the channel size and spatial distribution to be quantified.

A simple mathematical model of rough-walled fractures in rock has been fully developed and documented. This model requires the specification of only three main parameters: the fractal dimension, the rms roughness at a reference length scale, and a length scale describing the degree of mismatch between the two fracture surfaces. Fractured samples, collected from natural joints and laboratory specimens, have been profiled to determine the range of these three parameters in nature. This surface roughness model can be easily implemented on a computer, allowing future detailed study of the mechanical and transport properties of single fractures and the scale dependence of these properties.

In collaboration with J. B. Walsh (MIT), the mathematical model of a single fracture has been used to guide development and test statistical formulations of flow and transport in single fractures. A new "effective medium theory" (EMT) has resulted, which includes short-range spatial correlations in aperture heights. This new EMT elucidates the important geometrical parameters and physical processes controlling flow and substantially improves upon the accuracy of predictions over that of traditional versions of the theory.

In collaboration with R. L. Bruhn (Univ. of Utah), the concept of two rough surfaces contacting to form a fracture has been extended to a large scale, leading to the development of a conceptual model of the formation of voids and veins along geologic faults. This model includes progressive dilation of the fault during slip events and the elastic deformation of the surfaces normal to the fault plane (closure) as new void space develops. The model predicts vein geometries that are qualitatively similar to those observed in fault-controlled mineral deposits. The statistics of the vein system have been described and strategies for sampling of such structures by drilling were developed. The results have significant implications for evaluation of ore reserves and evaluating the fluid transport properties of faults.

In collaboration with H. W. Stockman and S. J. Reeves (SNL), predictions of the Reynolds equation for flow between rough-walled surfaces have been compared to a more exact calculation of Navier–Stokes flow based on a lattice-gas automaton method. Two-dimensional channels were constructed with an idealized sinusoidal roughness on each wall. Flow in the channels was studied by both methods for various amplitude-to-wavelength ratios of the roughness, surface separations, relative alignment or phase of the sinusoids, and Reynolds numbers. The Reynolds equation overestimates fluid velocity as the surfaces are placed together or the amplitude of the roughness increases relative to its wavelength.

C. Shear Strain Localization and Fracture Evolution in Rocks *(W. R. Wawersik [505-844-4342; Fax 505-844-7354; E-mail wrwawer@sandia.gov], D. J. Holcomb, and W. A. Olsson)*

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. Specifically, the research examines the applicability to fracture formation of a theory by Rudnicki and Rice 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, including Tennessee marble and Gosford 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 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: Confined, axial compression–torsion experiments on Tennessee marble (TM), designed to measure a set of incremental shear moduli parallel and at 45 degrees to the coordinate axes, were completed. The observed relative changes in these moduli with increasing axial deformation suggest that localization will occur sooner than predicted by isotropic constitutive models. Similar experiments were begun on Gosford sandstone (GS) in a search for vertex hardening, which is a destabilizing phenomenon. The initial results suggest that vertex hardening may occur in GS, as found earlier for TM. Thus the results from two common rock types show that more complete understanding of shear localization requires better constitutive models and associated improvement in laboratory parameter measurement.

Results from triaxial experiments on TM were analyzed to produce contour maps of the evolution of the local damage surface slope as a function of shear and mean stress, and the dilatancy parameter and plastic tangent modulus as a function of the plastic shear strain. Results are needed for calculating when the Rice–Rudnicki localization conditions are met. Acoustic emission locations were determined for plane-strain and triaxial tests on TM and GS. In plane strain, localization is evident well before peak stress. An additional four plane strain tests were run using in-plane strain control to maximize stability of the localization process.

CATEGORY: **Geochemistry**

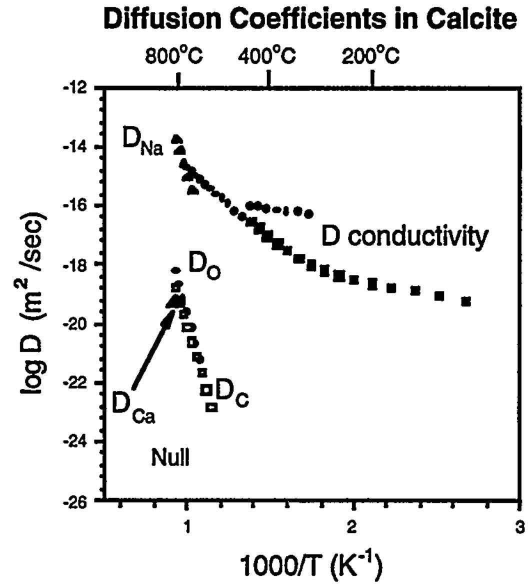
PERSON IN CHARGE: **M. C. Walck**

A. Cation Diffusion Rates in Selected Minerals *(Diana K. Fisler, Randall T. Cygan [505-844-7216; Fax 505-844-7216; E-mail rtcygan@sandia.gov], and Henry R. Westrich)*

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 require the accurate determination of cation diffusion data in silicate and carbonate minerals. 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/sec in the temperature range of 600° to 900°C. Resistive evaporation of enriched stable isotopes onto polished mineral surfaces is used to create a thin film–mineral diffusion couple. Diffusion couples are 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 accurate and reproducible diffusion coefficients: The temperature dependence of enstatite diffusion has been determined in an earlier phase of the project, and work continues on enstatite to determine the dependence of the diffusion coefficient on iron content and oxygen fugacity.

Results: Specimens of enstatite with compositions of $Mg_{0.99}Fe_{0.01}SiO_3$, $Mg_{0.91}Fe_{0.09}SiO_3$, and $Mg_{0.83}Fe_{0.17}SiO_3$ were obtained, cut, and polished parallel to the (010) crystallographic direction. The samples were then preannealed for 24 hours at 900°C and an oxygen fugacity equivalent to the IW buffer. Two additional samples of $Mg_{0.91}Fe_{0.09}SiO_3$ were preannealed at oxygen fugacities equivalent to the QFM and WM buffers to evaluate the dependence of self-diffusion on oxygen fugacity. Gem-quality calcite was obtained and polished parallel to (104) cleavage. Preliminary experiments on the stability of the calcite reveal sample decomposition at approximately 600°C and 1 bar CO_2. Subsequently, a sample assembly was constructed with a quartz tube and a manganese carbonate source to provide 30 bars of CO_2 pressure at 700°C in order to prevent decomposition of the calcite. In addition, predictions based on the "null" result for tracer diffusion by previous workers, and calculations using conductivity data and the Nernst–Einstein equation, indicate that diffusion of Ca^{2+} under dry conditions should be approximately 10^{-21} m^2/sec at 700°C.



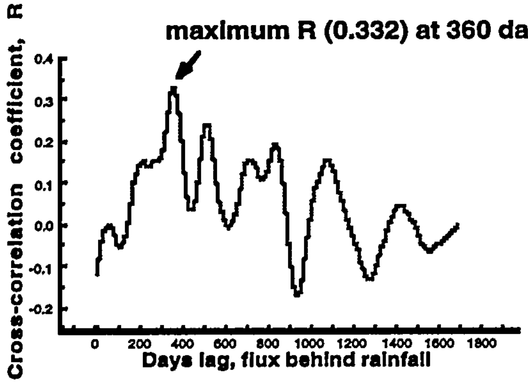
B. Isotopic and Mineralogical Indicators of Infiltration and Vertical Fluid Movement in Unsaturated Zones of Semiarid Terrain *(Steven J. Lambert [505-844-7876; Fax 505-844-7354; E-mail sjlambe@sandia.gov])*

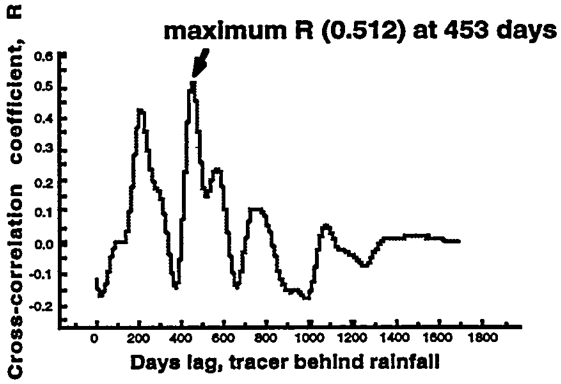
Objectives: To determine how the depth, volume, and rate of infiltration, and groundwater travel-time between surface and subsurface are governed by the seasonal distribution of episodic precipitation and storm intensity; to investigate the relationships between meteoric events and the transient and steady-components of infiltration and groundwater-recharge in a desert environment.

Project Description: This work seeks to identify climatic and hydrological parameters that govern recharge, and which potentially contribute to contaminant transport in unsaturated zones. In arid and semiarid terrain the uncertainty in the recharge term (used in water budget calculations) is commonly large; furthermore, losses due to evapotranspiration in the root zone may be significant. A natural cavern system developed in fractured limestone, underlying a desert environment, provides for direct measurement and sampling of water recharging an unsaturated zone, without the perturbations of borehole-sampling. Specifically, time-series (monthly) data are obtained for subsurface flux; concentrations of natural isotopic tracers (^{18}O and deuterium) in both the infiltrate water and surface precipitation are measured in samples collected during flux measurements. Domains of unsaturated flow, represented by variations in flux (indicative of changes in hydrostatic potential) and tracer concentration (indicative of mass transport), are then correlated with surface recharge events using local precipitation records and the variations in tracer concentration in precipitation.

Results: Monitoring of flux and $\delta^{18}O$ values of precipitation and recharge to the unsaturated zone was completed in Carlsbad Cavern, New Mexico. The record of monthly infiltration rates and $\delta^{18}O$ values at 13 permanent catchment stations is now complete through December, 1994, and the rainfall record is complete through October, 1994. δD values were also determined for infiltrate samples having the highest $\delta^{18}O$ value over the 37-month monitoring period at each station. In $\delta D/\delta^{18}O$ space the data trend is indistinguishable from the worldwide meteoric trend, providing no evidence of isotopic exchange between infiltrate water and host rock; hence, the infiltrate $\delta^{18}O$ data are not believed to be perturbed by such interaction. However, a numerical test of the correlation between $\delta^{18}O$ and infiltrate flux reveals that infiltrate at stations having lower flux and exposed to particularly long drops from ceiling to floor has undergone a small but significant isotopic exchange with moisture-saturated atmosphere, resulting in a slight enrichment (up to 0.3 ‰).

The correlations of flux and tracer concentration between surface and subsurface water reflect two discrete travel times for groundwater in different parts of the unsaturated zone: transport through the root zone from the surface to the top of a standing water-column within the subcutaneous layer (the "pulse" travel time), and mass transport from the top of the standing water-column to its bottom, representing arrival of fluid in the main unsaturated zone.





In order to determine pulse travel-times, numerical derivatives of the infiltration rate were compared with a 30-day moving average of the amounts of local rainfall accumulated in a 24-hour period, and the most significant increases in infiltration rate were ascribed to clusters of significant meteoric events. Similarly, the arrival of groundwater bearing a seasonally dependent fingerprint (lower ^{18}O for storms originating over the Pacific Ocean, higher ^{18}O for storms from the Gulf of Mexico) was used as the basis for estimating mass travel-time. The time series resulting from both the numerical derivatives of the infiltrate flux and the squares of numerical derivatives of the infiltrate $\delta^{18}O$ values were cross-correlated with the smoothed rainfall-input function. An example of these correlations, for a sampling station at ~250 meters depth, indicates a travel time of 12 months from the surface to the top of the standing water column, and 15 months from the surface through the subcutaneous layer into the main unsaturated zone.

C. An Investigation of Organic Anion–Mineral Surface Interactions During Diagenesis

(Patrick V. Brady [505-844-7146; Fax 505-844-7354; E-mail pvbrady@sandia.gov], R. T. Cygan, and H. R. Westrich)

Objectives: Mineral surface–organic acid interactions may control organic anion budgets and the coupled dissolution and growth of aluminosilicate minerals during soil formation and diagenesis. Determination of temperature-dependent adsorption of common carboxylate and phenolate functional groups will lead to an improved understanding of soil weathering and porosity evolution during diagenesis.

Project Description: The adsorption of organic anions to mineral surfaces in soils and deep basins can be understood if temperature-dependent adsorption isotherms of carboxylate and phenolate groups onto aluminosilicate surfaces are first known. Moreover, the catalytic role of adsorbed organic anions on mineral dissolution and porosity evolution in soils and during diagenesis may be reliably estimated if the mechanistic link between anion adsorption and reaction rate is quantitatively established. These hypotheses are being examined by wet-chemical measurements of the temperature-dependent adsorption of oxalate, acetate, salicylate, and benzoate onto corundum, quartz, kaolinite, albite, and enstatite. To complement this experimental program, a variety of computer-based techniques are being used to examine the molecular interactions at the mineral–solution interface, including ionic modeling, Monte Carlo docking, and molecular-dynamics simulations. Linking observed anion–surface interactions with an atomistic evaluation of reaction mechanisms and pathways will lead to a set of general rules for predicting the extent of organically mediated phase changes during diagenesis. At the same time field measurements of soil weathering in the presence and absence of organic acids are being used to determine linkages between soil biota, the silicate–carbonate cycle and global climate.

Results: (1) T-Dependent Sorption—Potentiometric titrations interpreted using the triple-layer model provide optimal proton, hydroxyl, and oxalate adsorption energies for quartz, corundum, and kaolinite surfaces at 25 and 60°C. Kaolinite binds oxalate under mildly acidic conditions ($pH < 6.5$), whereas quartz, with only Si adsorption sites, does not bind oxalate at any pH (>2). Al surface sites bind organic acids. At any pH, the degree of ionization also increases with temperature, so that changes in the electrostatic interaction favor increasing adsorption with temperature.

(2) Al–H Exchange and Precursor Formation—On the basis of dissolution experiments, proton exchange for adsorbed Al has been proposed as a precursor to activated complex formation for dissolution of aluminosilicates. Our measurements of the exchange reaction on kaolinite and albite supports this hypothesis and point to a 3:1 H:Al exchange stoichiometry.

(3) Digital Imaging of Silicate Weathering—Digital imaging of weathering intensity on ^{14}C-dated basalt flows on Hawaii has been used in tandem with meteorological records to establish a baseline temperature-dependence of long-term plagioclase weathering in the absence of organic acids of 26.2 kcal mol^{-1}.

CATEGORY: **Energy Resource Recognition, Evaluation, and Utilization**

PERSON IN CHARGE: **M. C. Walck**

A. Development of a Smart, High-Temperature Fluid-Sampling Tool *(P. Lysne [505-844-8885; Fax 505-844-3952; E-mail pclysne@sandia.gov])*

Objectives: Past fluid-sampling tools have leaked when withdrawn from holes drilled into geothermal formations. The goal of the present program is to develop a proper sampling device compatible with borehole environments in excess of the critical point of sea water (407°C, 298.5 bars); another version of the sampler is designed to gather steam samples at similar temperatures, but much lower pressures.

Project Description: Sampling devices that use one-way valves similar to those found in internal combustion engines leak when withdrawn from liquid-filled wells possessing even a modest temperature gradient. This possibility exists whenever the thermal contraction of the trapped fluid causes the pressure internal to the tool to fall below the local hydrostatic pressure in the borehole. Another issue becomes important in steam-filled wells; specifically, either sampling vessels need to be inordinately large and heated if gas-phase samples are to be collected and maintained, or, if the steam is allowed to condense, large heats-of-fusion must be accommodated within the Dewared sampling system. A final issue deals with the deployment of sampling tools. Due to the unreliability of electrical wireless at high temperature, the present samplers will be battery-operated and data stored on board. Such "memory" devices are highly reliable, but they do not transmit diagnostic information to the surface. Thus, the tools are being designed around computing systems that make them "smart." For example, the samplers can be programmed to trip when measured pressures and temperatures indicate that the tool has reached a specific state.

Results: All components of the pressure- and temperature-logging system have been tested in geothermal wells. Both measurements are traceable to national standards, and high-resolution temperature measurements have produced gradient logs that appear to be lithological indicators, perhaps due to differences in radioactive decay. The pressure measurements have been used to deduce reservoir information in geothermal wells.

Steam samples are condensed through the use of a low-temperature melting alloy, and tests in the Sandia steam plant have proved that the system is working properly. Diagnostic information on the state of the sampled material is taken as a matter of course. The sampler is ready for field work, and awaits opportunities in scientific and industrial wells.

B. 3-D Electromagnetic Data Inversion *(G. A. Newman [505 844-8158; Fax 505 844-7354; E-mail ganewma@sandia.gov])*

Objectives: Develop 3-D electromagnetic data inversion capabilities in the frequency band below 30 MHz. Use the capabilities to image the earth's electrical properties, with particular emphasis on reservoir characterization for enhanced oil production.

Project Description: Data inversion capabilities are to be developed for 2-D and 3-D reconstructions of electrical conductivity and dielectric permittivity within the earth. The inversion algorithm is to use electromagnetic (EM) data below 30 kHz arising from electric and magnetic dipole transmitters. The inversion capability will provide fundamental understanding of the earth's electrical properties and be highly useful in characterizing reservoirs with zones of mobilized oil and environmental waste site cnaracterization and remediation. The 3-D reconstruction of electrical data will be carried out using least-squares inversion. 3-D finite difference forward modeling is employed to compute model sensitivities and predicted data. Because inversion is nonlinear, the problem is solved iteratively by updating the fields from the previous electrical model update. The data inversion capability is to be tested using synthetic data with random noise. Field data will then be inverted to further access the robustness and reliability of the inversion capability.

Results: The EM inversion project has seen continued development of the 3-D finite difference scheme for the forward modeling problem; extensions include a method to efficiently model 3-D variations in dielectric permittivity and magnetic permeability and the incorporation of absorbing boundary conditions such that propagative (radar) fields can be accurately simulated. A manuscript on the general nature of the forward solution has been accepted by *Radio Science* for publication. There has also been continued development of the 3-D inverse, where the method of conjugate gradients is now being employed. This procedure allows us to construct images of the earth's electrical properties that are not underparameterized because it can efficiently invert for tens of thousands of parameters. The inversion code has been successfully applied to synthetic data with random noise using 27,000 cells in the reconstruction.

C. Effects of Microscopic Reactions and Buoyancy on Macroscopic Transport in Geologic Media: A Lattice Gas Study of Retardation and Dispersion

(Harlan W. Stockman [505-844-0975; Fax 505-844-7354; E-mail hwstock@sandia.gov])

Objectives: Use Lattice Gas Automata (LGA) to determine effects of surface reactions and buoyancy on macroscopic transport of solutes and colloids through geologic media; test common dispersion and retardation approximations.

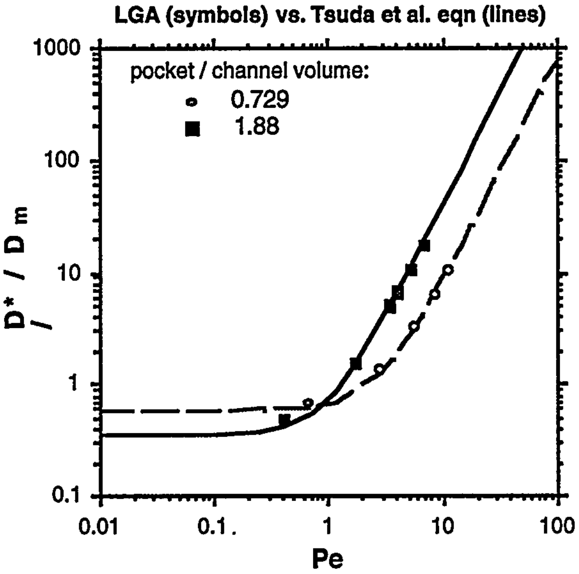
Project Description: The macroscopic dispersion and retardation coefficients can be approximated from models proposed by Turner (1958, *Chem. Eng. Sci.*, **7**, 156), Aris (1959, *Proc. Royal Soc.*, **252**A, 538) and Golay (1958, *Gas Chromat.*, 36). Overall flow can be estimated from the Reynolds equation (Brown, 1989, *JGR,* **94,** 9429). These models view the fracture or porous medium as one or more straight channels lined with stagnant dead-end pores, and use several simplifying assumptions to derive macroscopic coefficients from the microscopic geometry and molecular diffusion and sorption rates. Such approximations are widely applied, but are rarely tested for accuracy.

This project uses LGA to calculate first and second moments of solute distributions for flow through a variety of geometries, ranging from simple Turner structures to more complex, irregular fractures lined by porous walls. The results of LGA calculations are fitted to the approximations suggested by Turner and others, which yield apparent molecular diffusion and distribution coefficients. By comparing the input diffusion and distribution coefficients used in the LGA calculations, one can assess the accuracy of the approximations, estimate scaling effects, and suggest experimental strategies for obtaining greatest accuracy. This year we focused on three areas: (1) a comparison of LGA and Reynolds equation calculations; (2) a rigorous comparison of LGA against the experimental and numerical work of Tsuda et al. (1991, *Chem Eng. Sci.*, **46,** 1419) for dispersion of gas in alveolated channels; and (3) models for viscous fingering in porous media. Applications of the comparisons include modeling ^{129}I and $^{14}CO_2$ transport through wet-walled fractures in tuff, gas transport in the human lung, and the mixing of water and hydrocarbons in contaminated aquifers.

Results: The Reynolds equation is widely used to model flow in rough-walled fractures; however, the equation assumes the undulations in fracture walls have gentle slopes, and the usefulness of the Reynolds equation for real fractures is a subject of debate. We tested the accuracy of the Reynolds equation with LGA calculations for flow between sinusoidally walled fractures, as functions of sinusoid amplitude, offset between the fracture walls, wall separation, and Reynolds number (size of the inertial term). For steep-sloped sinusoids, we found the equation tended to overpredict flow rates by a factor of 2 when plate separations were approximately the same size as the amplitude. The effect of offsetting the fracture walls also induced an error of roughly a factor of two, but this error was largely compensated by applying a simple correction for the average length of the flow path. The Reynolds equation assumes Stokesian flow; our LGA runs showed that the assumption of Stokesian flow caused an error of 30% at a Reynolds number of 50.

The Turner–Aris equation (Aris 1959, *Chem. Eng. Sci.* **11**, p194) has been used to predict dispersion coefficients in porous media and the human respiratory tract. It is extremely difficult to derive a closed-form solution to the Turner–Aris equation for an arbitrary geometry, and a number of simplifying assumptions are generally made. Tsuda et al. (1991) derived analytical approximations for essentially 2-D, alveolated (pocketed) channels, and also performed finite element calculations and experiments with 1–2% SF_6 and He tracer gas in the same geometry. We were able to closely match the conditions used by Tsuda et al., and our LGA estimates of D^*/D_m (ratio of apparent to molecular diffusion coefficient) closely match the predictions of their analytical expressions and numerical models, as a function of Peclet number, as shown in the figure. However, the experimental results were often a factor of 1.1 to 2 different from the calculations. We used LGA to investigate the effects of tracer slug geometry and buoyancy, and concluded that much of the discrepancy between experiments and calculations could be due to the density difference between the carrier fluid and the tracer gas.

We have also explored use of LGA algorithms to model viscous fingering, and particularly the phenomenon of tip-splitting, in porous media. This effect ensues when a low-viscosity fluid, such as water, is intruded into a higher-viscosity fluid such as oil, and can cause unexpectedly fast intermixing and dispersion of contaminants. The modeling is very calculation-intensive, and in the past has relied on parallel-processing or lattice Boltzmann methods and Hele–Shaw approximations. We were able to increase the efficiency of the algorithm by a factor of 50, and perform useful calculations (involving up to 3 million particles) on a single-processor Pentium computer.



PART II

OFF-SITE

GRANTEE:	**UNIVERSITY OF ALASKA** Geophysical Institute Fairbanks, Alaska 99775-7320
GRANT:	**DE-FG06-86ER13530**
TITLE:	**A Study of Solar Prominences and Magnetospheric Substorms**
PERSONS IN CHARGE:	**L. C. Lee** (907-474-7410; Fax 907-474-7290; E-mail lclee@geewiz.gi.alaska.edu) and **S.-I. Akasofu**

Objectives: To examine and understand (1) formation and eruption of solar prominences, (2) formation of a very thin current sheet during the substorm growth phase, and (3) kinetic aspects of magnetic reconnection.

Project Description: This project deals with the formation of a thin current sheet and magnetic reconnection in the solar corona and in the geomagnetotail. These problems have relevance to formation and eruption of solar prominences and magnetospheric substorms. The methodology of this study encompasses mathematical analysis and computer simulations. Specifically, the following topics are addressed: (1) formation of a current sheet between two bipolar arcades and the dynamic and thermodynamic evolution of plasma in the subsequent reconnection process, (2) the equilibrium configuration of the Earth's magnetosphere under a constraint on entropy content, (3) thinning and stretching of the near-earth current sheet, (4) plasma dynamics in the neighborhood of the neutral lines (X- and O-lines) in collisionless reconnection processes.

Results: A current sheet is formed between two bipolar regions on the Sun when either parallel or antiparallel footpoint motions are applied. When magnetic reconnection takes place in the current sheet, the density enhancement above the X-line induces a thermal instability. The prominence created is topologically a Kippenhahn–Schlüter type, but is to be observed to have an inverse polarity geometry.

A two-dimensional global equilibrium configuration for the Earth's magnetotail is obtained by the magnetofrictional method. As opposed to previous studies, the entropy content in each flux tube is directly imposed as a constraint. The tail current sheets become thinner as the entropy, the entropy gradient or the open magnetic flux in the lobe increases. An "entropy antidiffusion instability" is proposed as a mechanism of current sheet thinning and dipolarization of the magnetic field.

A new formulation of adiabatic quasi-steady evolution of the geomagnetotail is developed in the presence of the dawn–dusk electrostatic field. The advection of the entropy function in the flux function space can explain the observed enhancement of entropy function in the near-earth plasma sheet. The tailward stretching of field lines leads to a dusk-to-dawn induction electric field, which nearly cancels the imposed electrostatic field. The resulting total electric field in the near-earth plasma sheet is then very small as shown by observations.

In a full particle simulation of magnetic reconnection in a thin current sheet with an electron gyroradius scale, a new dynamo process is discovered. A large amount of new magnetic flux is generated near the O-line associated with the compression of particles during magnetic reconnection. The newly created magnetic flux is about $\rho_e B_0$, where B_0 is the magnetic field far away from the current sheet and ρ_e is the electron gyroradius in terms of B_0 and the electron thermal velocity.

GRANTEE: **AMERICAN GEOLOGICAL INSTITUTE**
Alexandria, Virginia 22302-1507

GRANT: **DE-FGO5-94ER75979**

TITLE: **U.S.–Russian Geoscience Student Exchange Program**

PERSON IN CHARGE: **Edward M. Davin** (703-379-2480; Fax 703-379-7563;
E-mail lsutherl@jei.umd.edu)

Objective: Support Administration and Operation of the U.S.-Russian Student Exchange Program.

Results: On July 29, 1995, seven students who had completed their one-year training program in energy economics arrived in Washington for a program review and evaluation before returning to Moscow. Two of the students made such outstanding records at the Colorado School of Mines that the company sponsors requested them to stay a second year and complete a master's degree. The other students, on returning to Moscow, plan to take positions on the staffs of U.S. oil company sponsors.

Seven new students arrived in Washington for the 1995–96 program. This group had recently received their five-year diploma from such technical schools as the Moscow Geological Prospecting Academy, Moscow State University, etc. Following their cultural orientation at Meridian House International, Washington, DC, they will travel to Houston where they will receive a technical orientation in the offices of Exxon Exploration, Texaco Exploration and Production, Amoco Production, and Conoco. On August 19 they will arrive at their assigned universities: University of Texas–Austin and Texas A&M University, where they will spend two semesters studying energy economics. As mentioned above, two students from the 1994–95 group are returning to Colorado School of Mines.

GRANTEE:	**AMERICAN MUSEUM OF NATURAL HISTORY** Department of Earth and Planetary Sciences New York, New York 10024
GRANT:	**DE-FG02-92ER14265**
TITLE:	**The Effect of Carbon on the Mechanical and Electrical Properties of Rocks**
PERSON IN CHARGE:	**E. A. Mathez** (212-769-5379; Fax 212-769-5339; E-mail mathez@amnh.org)

Objectives: Understand how carbon films form on crack surfaces in rocks, determine how these films influence electrical conductivity, and explore the effect of growth of carbon in rocks on fracture propagation.

Project Description: Experiments will be conducted to test two hypotheses: (1) As fractures open in the time leading up to failure along a fault, carbon is deposited as a continuous film on the new mineral surfaces and electrical conductivity increases. Subsequent changes in electrical conductivity occur as the connectivity of the initial fracture network is altered by continued deformation. (2) The rate of crack growth may be enhanced by the catalytic growth of carbons. Two sets of experiments will be conducted at Lawrence Livermore National Laboratory with A. G. Duba. In the first set we shall determine if carbon is deposited on new crack surfaces during rock deformation and its effect on electrical conductivity. The latter will be monitored as a rock approaches failure in the presence of a $CO–CO_2–CH_4$ gas mixture. In the second set of experiments acoustic emission will be monitored as the rocks are loaded to failure in an inert carbon-free atmosphere of N_2, and then identical experiments will be conducted in $CO–CO_2–CH_4$ gas mixtures.

Results: This project was only recently initiated.

GRANTEE:	**ARIZONA STATE UNIVERSITY** Departments of Geology and Chemistry/Biochemistry Tempe, Arizona 85287-1404
GRANT:	**DE-FG03-95ER14533**
TITLE:	**Reaction Mechanisms of Clay Minerals and Organic Diagenesis: An HRTEM/AEM Study**
PERSONS IN CHARGE:	**Peter R. Buseck** (602-965-3945; Fax 602-965-8102; E-mail iacpzb@asuvm.inre.asu.edu) and **Huifang Xu** (602-965-7250; Fax 602-965-8102; E-mail xu@asuhrm.la.asu.edu)

Objectives: To gain an improved understanding of the microstructures and reaction mechanisms in the following reaction processes during diagenesis: (1) berthierine-to-chamosite reaction and polytype transformation in chamosite, (2) smectite illitization and mechanism for the formation of periodically interstratified illite/smectite, and (3) textural and structural evolution of the organic matter vitrinite.

Project Description: We will study 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 high-resolution transmission electron microscopy (HRTEM), analytical electron microscopy (AEM), electron-energy loss spectrometry (EELS), scanning electron microscopy (SEM), x-ray powder diffraction (XRD), and standard petrographic and geochemical techniques. We are especially interested in three subjects: (1) the berthierine-to-chamosite reaction, (2) smectite illitization, and (3) organic diagenesis.

This research will lead to an improved understanding of the states of I/S, C/B, organic matter, and detrital minerals in diagenetic environments. The results will provide important 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 certain depths, temperatures, and times. Such fundamental data will help with evaluations of basinal diagenetic patterns in hydrocarbon exploration.

Results: This project was initiated on August 1, 1995. We have no results to date.

GRANTEE: **ARIZONA STATE UNIVERSITY**
Center for Solid State Science and Department of Geology
Tempe, Arizona 85287-1704

GRANT: **DE-FG03-94ER14414**

TITLE: **A Microanalytical (SIMS) Study of the Trace Element and Isotopic Geochemistry of Diagenetic Silicates**

PERSONS IN CHARGE: **Richard L. Hervig** (602-965-3107; Fax 602-965-9004; E-mail hervig@csss.la.asu.edu) and **Lynda B. Williams** (602-965-0829; Fax 602-965-8102; E-mail Lynda.Williams@asu.edu)

Objectives: Oxygen isotope microanalyses on detrital and diagenetic quartz overgrowths are being measured by secondary ion mass spectrometry (SIMS) on spots ~10 μm in diameter. The objective of this work is to determine variation in $\delta^{18}O$ of authigenic cements that could allow a better understanding of the diagenetic processes and timing of cementation relative to hydrocarbon migration through sandstone reservoirs.

Project Description: Oxygen isotope ratios of authigenic quartz cements can help to determine the source (meteoric or basinal) or temperature of fluids present during diagenesis. Conventional bulk analyses of cements for oxygen isotopes require mineral separates or calculations using mass balance and volume estimates. This project uses SIMS to obtain microanalyses for oxygen isotope ratios of silicates *in situ*. These data allow detection of significant changes in fluid chemistry during diagenesis and fluid migration through these major hydrocarbon-producing regions of the world.

In conjunction with the oxygen isotopic measurements, boron isotope ratios of clay mineral coatings associated with quartz overgrowths are being studied. This research is being conducted to determine whether the boron isotopic ratio in clays is useful as an independent indicator of the origin (meteoric or basinal) of fluids that precipitated these diagenetic cements.

Results: Heterogeneous authigenic quartz cements have been identified in sandstone reservoirs from the Alberta Basin, U.S. Gulf Coast Basin, and the North Sea. Results from a Mississippian sandstone reservoir in the Alberta Basin and Cretaceous sandstone in the Texas Gulf Coast have a range of $\delta^{18}O$ from 20–35‰. Comparison to conventional bulk isotopic analyses suggest that such techniques underestimate the $\delta^{18}O$ of authigenic quartz. This biases the timing of diagenetic quartz precipitation toward higher temperature. SIMS results suggest that precipitation begins at low temperature from initial pore fluids with $\delta^{18}O$ similar to meteoric water, and continues during burial, increasing in rate between temperatures of 60–90°C. In the Gulf Coast reservoir, there is evidence for slowed quartz precipitation at temperatures above 110°C, which could result from the introduction of hydrocarbons.

Work on determining boron isotopic ratios in various standard clay minerals has just begun. After determining the SIMS calibrations for smectite, illite, and mixed-layered illite/smectite, analyses of these clay minerals in thin section will help establish if the precipitating fluids are basinal, and therefore constrain the range of possible oxygen isotopic values of the fluid. Together these isotopes may be a useful geothermometer.

GRANTEE: **BOSTON UNIVERSITY**
Department of Physics
Boston, Massachusetts 02215

GRANT: **DE-FG03-95ER14498**

TITLE: **Interpretation of Geodetic Crustal Strains Using Massively Parallel Supercomputer Simulations of Nonlinear Dynamical Models**

PERSONS IN CHARGE: **W. Klein** and **John B. Rundle** (Univ. of Colorado; 303-492-5642; Fax 303-492-1149; E-mail rundle@cires.colorado.edu)

Objectives: The underlying objective of this basic research is to understand the fundamental physical processes giving rise to the hazards and risks a variety of critical energy facilities face from several kinds of tectonic instabilities, notably earthquakes, volcanic eruptions, and landslides, in concert with the International Decade of Natural Disaster Reduction.

Project Description: A variety of nonlinear dynamical processes operate within the complex earth system, and are observed to display the signatures of many of the same phenomena as physical processes in other areas of physics, chemistry, and biology. In particular, scaling (fractal distributions), nonlinear thresholds and spatial interactions are all features possessed by these systems. Signatures of these processes include the appearance of scaling (geometric and dynamical fractal distributions), global and local self-organization, intermittancy (transitions from "laminar" to "turbulent" behavior), chaos, and the emergence of coherent space–time structures. The geodynamical effects observed in earthquake systems, particularly crustal straining, dynamical segmentation, and intermittent 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 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 Aperture Radar, and other field data.

Results: Although this research was only recently initiated, we have achieved major progress in understanding the origin of scaling in earthquake processes. In work accepted for publication in *Physical Review Letters,* we show that noise-driven earthquake fault systems develop a Boltzmann distribution in energy. We further show that the scaling distributions for the simulations can fall into one of two classes, involving fluctuations about either a symmetric or antisymmetric free energy well. Scaling exponents for the two classes can be readily computed from first principles, and have been verified in the simulations. The significance of this work lies in the demonstration that the scaling phenomena seen in this class of earthquake models is isomorphic to that seen in thermal and magnetic critical phenomena. We therefore predict that the nucleation phenomena for slip events (earthquakes) in the simulations will be similar and perhaps identical to that in thermal and magnetic systems. Discussions are under way on methods to test these predictions in field and laboratory data.

GRANTEE: **BROWN UNIVERSITY**
Department of Geological Sciences
Providence, Rhode Island 02912

GRANT: **DE-FG02-90ER14144**

TITLE: **Diffusional Transport and Fluid Connectivity in Mineral Aggregates**

PERSONS IN CHARGE: **R. A. Yund** and **J. R. Farver** (401-863-1931; Fax 401-863-2058;
E-mail ray@gech031.geo.brown.edu)

Objective: The objective of this study is to experimentally determine bulk diffusional transport rates of oxygen (as molecular water) and selected geologically and environmentally important ion species in natural and hot-pressed single and polyphase aggregates of common mineralogies over a range of temperatures, pressures, and coexisting fluid compositions. In addition, the connectivity of coexisting fluids in these aggregates is evaluated from the bulk diffusivity measurements. 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.

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 which are characterized using transmission (TEM) and scanning (SEM) electron microscopy.

Results: Interphase boundary diffusion rates of oxygen and potassium in fine-grained K-feldspar/quartz aggregates have been determined experimentally at 450°–700°C and 100 MPa (hydrothermal). The starting materials were hot-pressed and crystallized using equal weights of natural quartz fragments and orthoclase ($KAlSi_3O_8$) composition glass. Potassium and oxygen isotope profiles measured in the same samples are different, confirming a diffusional transport mechanism. Potassium diffusion in the K-feldspar/quartz aggregate has a greater activation energy than oxygen (218 vs 75 kJ/mole), and the Arrhenius relations cross at ~600°C. The $D'\delta$ values in the K-feldspar/quartz aggregates are about a factor of 4 greater than both oxygen and potassium $D'\delta$ values previously determined in monomineralic K-feldspar aggregates, and a factor of 20–40 greater than oxygen $D'\delta$ values in monomineralic quartz aggregates. The Arrhenius relations show the activation energies for both oxygen and potassium are similar for the K-feldspar/quartz and monomineralic K-feldspar aggregates, and significantly lower for oxygen in K-feldspar/quartz versus monomineralic quartz aggregates.

In addition, a series of experiments has been initiated to determine diffusional transport rates of oxygen and several important cations (K, Sr, and Ba) in a natural ultramylonite sample. The complex mineralogy of the ultramylonite sample greatly complicates the determination of diffusion rates; however, preliminary results indicate transport rates that are similar in magnitude to those obtained in hot-pressed K-feldspar/quartz aggregates. The ultramylonite has a well developed foliation and experiments are under way to determine the effect of the strong foliation on diffusional transport rates.

Also, studies continue on the role of non-hydrostatic stresses on fluid/feldspar interfacial energies. Aggregate pairs of hot-pressed albite and orthoclase compositions have been annealed at 900°C, 1.2 GPa, dry and with water added under hydrostatic and non-hydrostatic stress conditions. The sample microstructures have been characterized using transmission electron microscopy, and Na:K interdiffusion profiles have been measured using an ion microprobe and step-scan analysis. Results suggest that the equilibrium distribution of water in feldspar aggregates is greatly influenced by non-hydrostatic stresses.

GRANTEE: **CALIFORNIA INSTITUTE OF TECHNOLOGY**
Division of Geological and Planetary Sciences
Pasadena, California 91125

GRANT: **DE-FG03-93ER14311**

TITLE: **The Southern Sierra Nevada Continental Dynamics Project—Caltech Activities**

PERSON IN CHARGE: **Robert W. Clayton** (818-395-6909; Fax 818-564-0715;
E-mail clay@seismo.gps.caltech.edu)

Objectives: The main objective of this study is to determine whether the Southern Sierra Nevada Mountain Range is supported by a crustal root. A further objective is to deduce the relationship of this range to the adjoining Death Valley extensional province.

Project Description: To address these questions, two seismic profiles were executed. The first was a N–S profile running from Ridgecrest to Chafant Valley. The second was an E–W profile from Death Valley to Coalinga. The NPE shot of Sept 22, 1993, was recorded on the E–W receiver line. The data were analyzed by forward modeling with a staggered-grid finite-difference code.

Results: The first objective of the study was answered by the analysis of the data from a shot point in Owens Valley on the E–W profile, along with the recording of the NPE shot on the same line. Shot point 5 (Olancha, Owens Valley) showed that the PmP phase (P reflection from Moho) has nearly equal travel time when observed to the west (reflection points under the Sierras) or to the east (reflection points under Panamint Valley). The NPE recording also shows that there is no anomalous behavior of Pg (mid-crust phase) or Pn (Moho phase). These two observations indicate that there is no crustal root under the Southern Sierras. The waveforms produced by the finite-difference modeling confirm this interpretation.

The results have been submitted as a note to *Science* and a paper to *J. Geophysical Res.*

GRANTEE:	**CALIFORNIA INSTITUTE OF TECHNOLOGY** Division of Geological and Planetary Sciences Pasadena, California 91125
GRANT:	**DE-FG03-89ER13445**
TITLE:	**Infrared Spectroscopy and Hydrogen Isotope Geochemistry of Hydrous Silicate Glasses**
PERSONS IN CHARGE:	**S. Epstein** (818-356-6100; E-mail epstein@arms.gps.caltech.edu) and **E. Stolper** (818-356-6504; Fax 818-568-0935; E-mail ems@expet.gps.caltech.edu)

Objectives: The focus of this project is the combined application of the methodologies of experimental petrology, infrared spectroscopy, and stable isotope geochemistry to understanding the behavior of volatile components, particularly water and carbon dioxide, in natural and synthetic silicate melts and glasses.

Project Description: This project integrates (1) a laboratory component directed toward the development of analytical techniques and a solid understanding of the physical chemistry of volatile components in melts and glasses through carefully controlled experiments and syntheses, and (2) a field-oriented component in which these techniques and chemical principles are applied to specific petrological and volcanological problems. A key feature of this project is the combination of methodologies from stable isotope geochemistry with those from experimental petrology and mineralogy. A unique aspect of the project is the explicit focus on the roles played by different species of dissolved water and carbon dioxide in silicate melts and glasses (e.g., molecules of H_2O and hydroxyl groups; molecules of CO_2 and carbonate ion complexes). Many seemingly complex behaviors of volatiles in liquids, glasses, and magmas can be simply and quantitatively explained if the speciation is understood and taken into account.

Results: (1) We measured fractionation factors for oxygen between CO_2 and silica glass, rhyolitic glass/melt, and quartz. We are building the data base necessary for quantitative interpretation of the distributions of oxygen isotopes in nature. (2) We measured the fractionation of carbon isotopes between vapor and rhyolitic melt. Results indicate a fractionation of ~0‰, indicating solution of CO_2 molecules in the melt. (3) We determined kinetics of oxygen isotopic exchange between CO_2 and silica and rhyolitic glass/melt. Results suggest that isotopic exchange in glasses occurs by diffusion of H_2O and CO_2 molecules followed by exchange with the oxygen atoms of the glass structure. (4) We studied kinetics of reactions between water molecules and anhydrous silicate units to form hydroxyl groups in silicate glasses. Results can be used as a cooling rate indicator and geothermometer for volcanic glasses. (5) We measured C, O, and H isotopic compositions of natural apatites. Apatites are ubiquitous and have significant quantities of C, O, and H and thus are useful for thermometry and as tracers of petrogenesis. (6) We measured oxygen isotopes of olivine phenocrysts from the Hawaii Scientific Drilling Project corehole that penetrated ~300 m of lavas from Mauna Loa volcano and ~700 m of underlying lavas from Mauna Kea. Results show a jump in $\delta^{18}O$ from Mauna Kea to Mauna Loa and strong correlations with radiogenic isotope ratios. (7) We measured oxygen isotopes of olivine phenocrysts from EM1-rich basalts from Pitcairn Island. Results provide strong evidence against a simple sediment recycling origin for the EM1 component. (8) We simulated explosive volcanic eruptions by rapidly depressurizing CO_2-saturated water and using high-speed photography to follow bubble growth and motion, acceleration of the fluid, and "fragmentation" of the material.

GRANTEE: **CALIFORNIA INSTITUTE OF TECHNOLOGY**
Division of Geological and Planetary Sciences
Pasadena, California 91125

GRANT: **DE-FG03-88ER13851**

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

PERSON IN CHARGE: **G. J. Wasserburg** (818-395-6139; Fax 818-796-9823)

Project Description: We have studied the self-diffusion of Mg, Ca, Ba, Nd, Yb, Ti, Zr, and U in haplobasaltic ($Fo_{15}Di_{40}An_{45}$) melt, from 1350–1500°C. These measurements, including the first reported data for Yb, Ti, Zr, and U, provide an internally consistent set of self-diffusivities for elements covering a wide range in ionic radius and charge. Diffusion couples were formed by juxtaposing isotopically enriched and isotopically normal melts; isotopic concentrations, measured with an ion probe, show well-defined profiles, consistent with diffusion. Diffusion coefficients were determined to within ±15%, a significant improvement over most previous studies. Diffusion coefficients display a systematic decrease which is correlated with increasing ionic radius and increasing charge. The values, at 1400°C, range from 8.1×10^{-7} cm^2/s for Mg to 0.9×10^{-7} cm^2/s for U. This variation demonstrates that the Eyring relationship, which predicts identical diffusion coefficients for all species, provides an incomplete description of diffusion in silicate melts. The diffusion coefficients are negatively correlated with Z^2r. Although the significance of this relationship is unclear, it supports the interpretation that U^{6+} diffuses as a uranyl group. The total range in diffusion coefficients is relatively small and suggests that the actual diffusing species are very similar for all elements and that the cations may diffuse as constituents of larger complexes. The data follow an Arrhenius equation, with activation energies increasing with size and charge, from 170 kJ/m for Mg to 337 kJ/m for U. Activation energies are also correlated with the pre-exponential factors. The width of a boundary layer around a growing crystal is proportional to $D^{1/2}$. The coefficients measured in this study imply that trace element fractionation due to diffusion during crystal growth in basaltic compositions will be minimal.

^{232}Th and ^{230}Th of unfiltered and filtered seawater samples were measured along a depth profile of the Pacific Ocean using isotopic dilution and thermal ionization mass spectrometry. The ^{232}Th concentrations are constant from below 25 m down to over 2000 (45–60 × 10^6 atoms/cm^3) and then increase rapidly toward the bottom (119–360 × 10^8 atoms/cm^3 at 4000 m). The ^{230}Th concentration increases linearly with depth from 3×10^3 atoms/cm^3 at 25 m to 10×10^3 atoms/cm^3 at 4000 m. The reproducibility of replicate analyses and the regularity of the profiles demonstrate the reliability of the procedures. Some lack of reproducibility among different samples from the same depth has to be explained by intrinsic variability or by contamination during sample collection. Due to the very low ^{232}Th concentrations and relatively high ^{230}Th concentrations, the ^{230}Th/^{232}Th ratios can be as high as 1.6×10^{-3}. The ratio of the mount of Th on particles (size larger than 0.2 μm) to the amount of Th in solution is significantly higher for ^{232}Th (0.4) than for ^{230}Th (0.2). These data are interpreted with a model of particle transport, assuming local equilibrium between particles and seawater. The relatively high ^{230}Th concentrations and ^{230}Th/^{232}Th ratios measured at 25 m are consistent with a mixed layer of about 100 m. The linear increase of ^{230}Th with depth implies that the effect of eddy diffusion is negligible for over the Th-removal time scale. The depth profile is consistent with transport of ^{230}Th by reversible uptake on particles settling with a constant velocity. The ^{232}Th data are in-consistent with this model and they suggest that particles carrying ^{232}Th lose 70% of mass between the surface and 4000 m. This difference in the transport of ^{230}Th and ^{232}Th demonstrates the distinctive behavior of these isotopes during particle formation and subsequent remineralization and repackaging in the water column. Different speciation of ^{230}Th and ^{232}Th may be explained by their distinctive sources in the ocean (as ^{230}Th is produced in solution and ^{232}Th is carried by detrital material) and by their respective packaging mechanisms that are not known.

GRANTEE: **UNIVERSITY OF CALIFORNIA AT BERKELEY**
Department of Geology and Geophysics
Berkeley, California 94720

GRANT: **DE-FG03-85ER13419**

TITLE: **Advective–Diffusive/Dispersive Transport of Chemically Reacting Species in Hydrothermal Systems**

PERSON IN CHARGE: **Harold C. Helgeson** (510-642-1251; Fax 510-643-9980;
E-mail brogie@garnet.berkeley.edu)

Objectives: To achieve a better understanding of the effects of thermodynamics and chemical mass transfer on the occurrence, evolution, and development of energy resources in the crust of the Earth.

Project Description: The major scientific and technical issues of concern in this project are:

1. How reactive are organic molecules at elevated temperatures and pressures in sedimentary basins?
2. How prevalent are metastable equilibrium states involving these molecules and the minerals and waters in source rocks and reservoirs?
3. What is the role of oxygen fugacity relative to temperature and pressure in breaking down organic matter to hydrocarbons and the maturation of petroleum in source rocks?
4. What are the congruent and incongruent solubilities of detrital minerals in oil-field waters, and what diagenetic role do organic species in petroleum play at the oil–water interface in determining these solubilities and generating secondary porosity resulting from mineral dissolution?
5. What is the role of water and hyperthermobarophilic microbes in the generation and maturation of petroleum at depths in excess of ~3 km?

Results: During the past year, research efforts have been concerned primarily with generating equations of state group contribution algorithms for estimating the standard molal thermodynamic properties of solid and liquid high-molecular-weight compounds commonly found in kerogen and bitumen. According to conventional wisdom, oil generation from kerogen is caused by increasing temperature and time during progressive burial of source rocks in sedimentary basins. However, this paradigm has come into question in recent years with growing recognition of the likely dependence of kerogen degradation and the maturation of petroleum on the dramatic decrease in oxygen fugacity with increasing depth in these basins. This decrease favors incongruent melting of ether- and ester-bonded high-molecular-weight hydrocarbons in kerogen to form their liquid counterparts in bitumen, which may then react with increasing burial and further change in oxygen fugacity to form the lower-molecular-weight hydrocarbons that predominate in petroleum. To quantify this process requires both equations of state and values of the standard molal thermodynamic properties at 25°C and 1 bar of high-molecular-weight compounds such as ether- and ester-bonded n-alkanes, isoprenoids, steroids, hopanoids, and polynuclear aromatic hydrocarbons in kerogen, and their reduced counterparts in bitumen. Neither experimental values nor estimates of the standard molal thermodynamic properties of these compounds are currently available. As a consequence, a group contribution approach was used to estimate the properties at 25°C and 1 bar. The standard molal thermodynamic properties of these high-molecular-weight compounds at high temperature and pressure were then calculated from a group contribution algorithm which combines the Parameters From Group Contributions (PFGC) equation of state with the Maier–Kelley heat capacity power function.

GRANTEE: **UNIVERSITY OF CALIFORNIA AT DAVIS**
Department of Land, Air and Water Resources
and Department of Chemistry
Davis, California 95616

GRANT: **DE-FG03-92ER14307**

TITLE: **A New Method for Determining the Thermodynamic Properties of Carbonate Solid-Solution Minerals**

PERSONS IN CHARGE: **William H. Casey** (916-752-3211; Fax 916-752-1552;
E-mail whcasey@ucdavis.edu) and
Peter A. Rock (916-752-0940; Fax 916-752-899)

Objective: We are measuring thermodynamic properties for some carbonate solid-solution minerals that are important in soils and aquifers.

Project Description: Our new method is an electrochemical double cell without liquid junction. Such a cell for cadmium–carbonate minerals is (Rock et al., 1994, *Geochim. Cosmochim. Acta* **58**, 4281–4291):

$$\mathrm{Cd(Hg,\ 2\text{-}phase)|CdCO_3(s)|CaCO_3(s)|CaCl_2(aq)}$$
$$\mathrm{|Hg_2Cl_2(s)|Hg(l)}\ —$$

$$—\mathrm{Hg(l)|Hg_2Cl_2(s)|CaCl_2(aq),CdCl_2(aq)}$$
$$\mathrm{|Cd_xCa_{1\text{-}x}CO_3(s)|CdCO_3(s)|Cd(Hg,\ 2\text{-}phase)}$$

yielding a net cell reaction of:

$$(\mathrm{CaCO_3})^{\mathrm{calcite}} + (1\text{–}x)\ \mathrm{CdCl_2(aq)}$$
$$= (\mathrm{Ca_xCd_{1\text{-}x}CO_3})^{\mathrm{Cd\text{-}calcite}} + (1\text{–}x)\ \mathrm{CaCl_2(aq)}.$$

Values of $\Delta_f G^o$ for the solid solution relative to the endmembers are obtained from the cell voltage and known activities of the electrolytes. With these $\Delta_f G^o$ 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}) that we determined via high-temperature drop-solution calorimetry.

Results: Electrochemical studies of mixing in the $CaCO_3$–$CdCO_3$, $CaCO_3$–$SrCO_3$ and $CaCO_3$–$MnCO_3$ binary systems are essentially complete and the results prove the method suitability. Electrochemical cells were also constructed for studies of oxalate solids (Kubacki et al., *Geochim. Cosmochim. Acta*, submitted) and we have determined new values of $\Delta_f G^o$ for geochemically important end-member carbonate solids (Walling et al., 1995, *American Mineral.* **80**, 355–360).

The electrochemical method provides a means of estimating thermodynamic properties at the low temperatures that are characteristic of most soils and aquifers. At these conditions, acid-solution calorimetry is inaccurate for determining enthalpies of reaction because CO_2 degasses slowly from an aqueous solution. Solubility experiments are likewise difficult because secondary minerals typically precipitate in a dissolution experiment, thereby complicating interpretation of the data. Metastable equilibrium is much easier to achieve with the electrochemical cells that we employ because the voltage measurements do not dramatically perturb the system, unlike dissolution experiments where a significant fraction of the solid must be dissolved to receive information. Thermodynamic data are also derived from the electrochemical cell data directly, without a complicated model for solute speciation. Equilibrium in the cell can be demonstrated through: (1) Nernstian response of the potential to changes in solute activities; (2) the absence of hysteresis in voltage–current plots for the cell; and (3) the rapid and reversible response of the cell voltage to temperature cycling. The method is also demonstrably accurate; our estimated value of $\Delta_f G^o$ for otavite ($CdCO_3$) and cal cite ($CaCO_3$) are within 2 kJ•mol^{-1} of the NBS values reported in Wagman et al., 1982 (*J. Phys. Chem. Ref. Data* **11** [Supl. 2] 1–392).

In order to complement the electrochemical measurements, we are comparing the ΔG^{ex} values at 298 K with ΔH^{mix} values (also at 298 K) determined via high-temperature drop-solution calorimetry. The calorimetry is conducted using the laboratory of A. Navrotsky at Princeton University. Results are complete for $Ca_xSr_{1-x}CO_3$ solids (Fig. 1) and measurements are under way on the $Ca_xCd_{1-x}CO_3$ compositions.

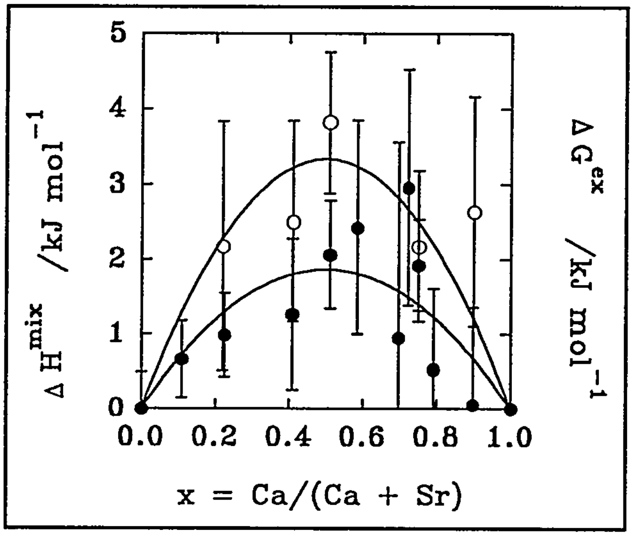


Fig. 1. The H^{mix} values at 298 K for mixing aragonite and strontianite to form $Ca_xSr_{1-x}CO_3$(s) solid-solutions (from Casey et al., *Environ. Sci. Tech.*, submitted) compared with the G^{ex} values (°) determined via the electrochemical-cell method (from Casey et al., in press, *Amer. J. Sci.*), also at 298 K. The dashed line corresponds to a fit of regular-solution model to the H^{mix} values (data at $x > 0.9$ are removed from the diagram and fit) and the solid line corresponds to a regular-solution fit to the G^{ex} values.

GRANTEE: **UNIVERSITY OF CALIFORNIA AT DAVIS**
Department of Geology
Davis, California 95616

GRANT: **DE-FG03-92ER14240**

TITLE: **Energetics of Melts from Thermal Diffusion Studies**

PERSON IN CHARGE: **C. E. Lesher** (916-752-9779; Fax 916-752-0951;
E-Mail lesher@.geology.ucdavis.edu)

Objectives: This research program characterizes mass transport by diffusion in geological fluids in response to thermal, solubility, and/or chemical gradients to obtain quantitative information on the thermodynamic and kinetic properties of multicomponent systems.

Project Description: Thermal diffusion is the phenomenon of chemical migration in response to heat flow along a thermal gradient. The details of this response are conditioned by the thermochemical properties and constitution of the substance. Silicate liquids undergo substantial thermal diffusion (Soret) differentiation, while the response in sulfide, carbonate, and aqueous fluids to an imposed temperature gradient is varied. The experimental observations of this differentiation are used to evaluate the form and quantitative values of solution parameters, and to quantify ordinary diffusion coefficients, heats of transport, and activation energies of multicomponent liquids. The diffusion, solution, and element partition coefficients determined for these geological fluids form a data base for understanding magmatic crystallization behavior and for evaluating geothermal, ore deposit, and nuclear waste isolation potentials. Thermal and isothermal diffusion experiments are conducted using the 1-atmosphere gas mixing apparatus, rapid-quench cold seal apparatus up to 0.3 GPa, piston cylinder device at pressures between 0.7–3.5 GPa, and a simplified multianvil device above 3.5 GPa. The electron and ion microprobes and the infrared spectrometer are used in the characterization of experimental run products.

Results: Current experimental capabilities include two 1-atm gas mixing furnaces, a rapid-quench cold seal apparatus using TZM and HZM vessels, three piston cylinder devices, and a Walker-style multianvil device driven by a 1000-ton Clifton press equipped with a computer-controlled hydraulic system. Automated pressure-regulation systems are now also available for the piston cylinder devices. Among the research activities of the last year we conducted thermal diffusion experiments at very high pressure on magmatic silicate liquids in an attempt to use the recovered heats of transport and chemical potentials as monitors of changing speciation with pressure. We continue to study the influence of water and carbonate species on the Soret diffusion properties of naturally occurring silicate liquids. We are expanding our study of network self diffusion to include highly polymerized melts, and we are continuing our quantitative treatment of chemical diffusion based on Darken's theory of ion mobility for Pb, U, and Th. We have also initiated a comprehensive study of thermal, self and chemical diffusion of multicomponent liquids of the system CaO–MgO–SiO_2. New collaborations with colleagues in material science are exploiting our capabilities for high-pressure generation to examine the sintering behavior of nano-alumina, nano-titanium, and amorphous silicon carbide at elevated T and P.

GRANTEE: **UNIVERSITY OF CALIFORNIA AT LOS ANGELES**

Department of Earth and Space Sciences
Los Angeles, California 90024

GRANT: **DE-FG-03-89ER14049**

TITLE: **K-Feldspar Thermochronometry**

PERSON IN CHARGE: **T. M. Harrison** (310-825-7970; Fax 310-825-4396;
E-mail tmh@argon.ess.ucla.edu)

Objectives: The ^{40}Ar/^{39}Ar method can furnish information about both the internal distribution of ^{40}Ar* and Ar diffusion parameters. The multi-diffusion domain model (MDD) has shown promise in explaining various effects seen in the laboratory and has been successfully applied to a variety of energy-related problems. The objective of this research is to develop K-feldspar ^{40}Ar/^{39}Ar thermochronometry into a robust tool for assessing upper-crustal thermal histories.

Project Description: In our formulation of the MDD model, the form of the Arrhenius plot and age spectrum are a function of the diffusion parameters for each discrete domain (activation energy, E, and frequency factor, D_o), the domain distribution parameters (domain size, ρ, and volume fraction, ϕ), and the thermal history. Since the diffusion parameters may be obtained directly from the Arrhenius plot and we have two independent measures of ρ and ϕ (the Arrhenius plot and age spectrum), we have sufficient information to obtain a solution for the thermal history. Both the underlying assumptions and general predictions of the theory can be tested through laboratory investigations, including diffusion experiments and direct imaging (using visible light, x-rays, and TEM methods), or through study of argon isotopic variations in natural K-feldspars.

Results: An early proposal to explain the relatively low argon retentivity in K-feldspars invoked perthite lamellar boundaries as paths of fast diffusion, effectively reducing the diffusive lengthscale for argon escape and lowering the closure temperature. This concept was criticized on the basis that these interfaces were usually coherent and thus could not behave as zones of rapid diffusion. To address this issue, we have utilized Ne isotopes as a probe of the diffusion behavior in and around perthite lamellae during laboratory step-heating. During the neutron irradiations needed to affect the ^{39}K(n,p)^{39}Ar reaction, nuclear reactions on Na produce all three neon. The nature of Ne loss from the sample can thus lead to insights into the role of perthite boundaries in facilitating diffusive transport and/or as a monitor of the lamellar annealing. Experiments were performed using both irradiated and unirradiated splits of albite glass and low-albite. In contrast to the glass samples, diffusivities yielded by the crystalline material exhibit non-linear Arrhenius arrays topologically identical to those obtained for Ar diffusion in K-rich alkali feldspar which we have attributed to the existence of discrete domains of Ar retentivity. The Bishop Tuff sanidine has a well-defined lamellar spacing of 155±6 nm and a high sodium content. All samples are characterized by enhanced Ne loss at low temperatures (non-linear Arrhenius arrays). We conclude that the large volume fraction of Ne released from these materials at low temperatures requires exsolution boundaries to be permeable to rare gas transport.

We have developed new approaches for automating K-feldspar thermal history modeling that greatly reduce operator bias. Code for both monotonic cooling and general thermal histories allowing reheating (based upon use of Chebyshev polynomials) produce best-fit solutions from generalized initial temperature-time histories. Through a variational process, the program is able to determine an optimum solution that fit the laboratory age spectrum to the desired accuracy. Under the constraint of monotonic cooling, any guess of an initial cooling history will produce essentially the same estimate of the best fit solution. When this constraint is relaxed, however, different solutions are obtained depending upon the initial guess. The present program produces a spectrum of solutions that fit the age spectrum at the desired accuracy by randomly introducing a variety of initial thermal histories. Contour plots of the probability density calculated from these solutions indicate the full range of T-t constraints afforded by the K-feldspar age and kinetic results. Because the approach is a variational process that calculates best fit cooling histories using the age spectrum, it is a significant improvement over Monte Carlo routines that simply calculate age spectra from random T-t histories.

GRANTEE:	**UNIVERSITY OF CALIFORNIA AT LOS ANGELES** Department of Earth and Space Sciences Los Angeles, California 90024-1567
GRANT:	**DE-FG03-91ER14222**
TITLE:	**Uranium, Thorium, Lead, and Oxygen Diffusion in Rock-Forming Minerals: Implications for Reactive Transport**
PERSONS IN CHARGE:	**K. D. McKeegan** (310-825-3580; Fax 310-825-2779; E-mail kdm@ess.ucla.edu) and **F. J. Ryerson** (Lawrence Livermore National Laboratory)

Objectives: The spatial distributions of isotopes of elements such as uranium, thorium, lead, and oxygen, observed on a microscale, can be utilized to constrain thermal histories of crustal rocks and the extent of their interactions with fluids. There are two requirements necessary for application of this idea to real geologic systems: first, microanalytical techniques must be employed to quantitatively measure the isotopic or elemental heterogeneities, and second, fundamental diffusion data must be experimentally determined in order to know the rates at which equilibrium between fluid (either melts or aqueous fluids) and host rocks can be approached as a function of various external conditions.

Project Description: The diffusion coefficients for uranium, thorium, lead, and oxygen will be determined in a number of different minerals under a variety of external conditions. The experimental diffusion runs are performed at the Lawrence Livermore National Laboratory and the analytical phase of the work is done at UCLA using the Cameca ims 1270 ion microprobe. Techniques for the *in situ* measurement of either experimentally induced or naturally occurring variations of isotopic and elemental concentrations are being developed for the UCLA ion microprobe.

Results: Most of our effort this past year has been dedicated toward continued development of the Cameca ims 1270 for measurements of isotopic and inter-element ratios on a ~10-mm spatial scale. A new instrument control system, based on a SPARC computer, has been installed and data acquisition and analysis software, written in LabVIEW, has been debugged. Along with our modified detector system, the new instrument control software has been important for improving precision and accuracy of isotope ratio measurements and depth-profiling capabilities. Techniques have been developed for the determination of U, Th, and Pb concentrations in monazite with better than 2% accuracy and for *in situ* measurements of O and C stable isotopic abundances in carbonates and silicates with permil precision.

Th–Pb age determinations on 15-mm spots of individual monazite grains from the Manaslu pluton have demonstrated that Pb inheritance can be widespread in leucogranite monazite. In several cases, complex microdistributions in age have been observed within an individual monazite grain. Further measurements at a finer spatial resolution (~1 mm) are being undertaken to determine if these heterogeneities can be interpreted as diffusion gradients that, with application of the appropriate diffusion law for Pb in monazite, can yield detailed thermochronological information. In collaboration with Daniel Farber, we have conducted experiments to measure Pb diffusion rates in monazite. The lead diffusion experiment was performed by immersing a polished sample of synthetic $PrPO_4$ monazite in PbS within a sealed SiO_2 glass capsule; the quenched PbS can be removed from the surface, which appears unaffected. Profiles consistent with the solution to Fick's Law for the imposed boundary conditions yield diffusion coefficients in the 10^{-20} m^2 s^{-1} range. We are currently performing experiments with gem-quality natural monazites.

Oxygen isotopic disequilibrium can be utilized as a tracer of the extent of fluid–rock interactions provided that spatially resolved isotopic data can be obtained and that the processes and rates of isotopic exchange quantified. We have developed an ion probe method for measurement of $^{18}O/^{16}O$ ratios in ~10-mm spots of insulating samples with a typical precision of ~1‰. So far this method has been applied to a study of carbonate cement formation from drill core samples obtained from petroleum reservoirs in the San Joaquin valley, CA. Ongoing calibration work for quartz, pyroxene, olivine, garnet, and feldspar will allow application of this technique to a broad range of problems. At the same time, we are engaged in a series of experiments to determine oxygen self-diffusion rates in garnet, olivine, and pyroxene under both anhydrous and hydrous conditions as a function of temperature and oxygen fugacity. The preservation of highly polished surfaces (necessary for the depth-profiling analyses) has proved to be a problem for some minerals during the experiments (especially under hydrous conditions) and is being addressed by varying P–T conditions, the characteristics of the reservoir, and fluid composition.

GRANTEE: **UNIVERSITY OF SOUTHERN CALIFORNIA**
Department of Earth Sciences
Los Angeles, California 90089-0740

GRANT: **DE-FGO3-87ER13807**

TITLE: **The Seismology of Geothermal Regimes**

PERSON IN CHARGE: **K. Aki** (213-740-5830; Fax 213-740-0011;
E-mail aki@coda.usc.edu)

Objectives: Development of effective interpretation theory for the analysis of seismic data collected in geothermal areas characterized by strongly heterogeneous subsurface structure and by seismic sources involving interactions among gas, liquid, and solid.

Project Description: Seismic data from active and passive experiments in geothermal areas are extremely complicated because of the strongly heterogeneous earth's structure and seismic sources involving interactions among gas, liquid, and solid. To develop effective interpretation theory for analyzing the data, our current objectives are the following. (1) Development of analysis methods for separately determining the scattering loss and the absorption loss in seismic attenuation as a function of frequency and application of them to various geothermal areas in the world. (2) Three-dimensional modeling of seismic source, path, and site effects on the observed spectra of seismic events in the active geothermal areas. (3) Exploration of effective inversion procedures for geometry and mechanical properties of subsurface structure using steady-state (frequency domain) data rather than conventional wave form (time domain) data. These problems are identified as targets of investigation with fruitful outcome in the near future.

Results: Taking advantage of the high-quality digital regional network data now available from the data center of the Southern California Earthquake Center, we were able to construct maps of coda Q^{-1} for southern California with unprecedented precision and resolution. The result is frequency-dependent and shows interesting correlation with other regional geophysical parameters. For example, for frequencies higher than about 5 Hz, a distinct high Q (low attenuation) region shows up along the Peninsular Range, where seismic velocity at a depth of 20 km is high, isostatic anomaly is high, and heat flow is low. For frequencies lower than about 5 Hz, the low Q zone appears to coincide with the zone of the steep gradient in the so-called "Palmdale uplift" revised recently. These results are in harmony with our working hypothesis that coda Q^{-1} at low frequency reflects the activity of creep fracture near the brittle–ductile transition region, while at high frequencies it reflects the physical state in the lower crust.

We found also that the Salton Trough, a major geothermal area in southern California, shows a puzzling feature that Q is high at low frequency, and low at high frequency, for which we do not yet have satisfactory explanation.

The Landers earthquake offered an excellent opportunity to continue our study of the seismic guided waves trapped in the fault zone. We found unequivocal evidence for the existence of the trapped modes and used them to delineate 3-D structures of the low-velocity, low Q wave guide.

We also found trapped modes generated by an explosive source in the fault zone and reflected back from the bottom of the fault zone, which agreed with the top of the lower ductile crust identified in a CALCRUST reflection section obtained near the Landers epicentral region.

GRANTEE:	**CARNEGIE INSTITUTION OF WASHINGTON** Geophysical Laboratory Washington, D.C. 20015-1305
GRANT:	**DE-FG02-93ER14400**
TITLE:	**Water–Rock Interaction in the Earth's Upper Mantle: Application of Combined Stable Isotope and Infrared Spectroscopic Analytical Techniques**
PERSONS IN CHARGE:	**D. R. Bell** (202-686-2410; E-mail dbell@gl.ciw.edu), **F. R. Boyd,** and **D. Rumble**

Objectives: To investigate the nature and extent of interactions between mantle rocks and hydrous melts or fluids by analysis of trace H and other elements and of stable isotope compositions of H and O in mantle minerals.

Project Description: Indications are that interactions between mantle rock and mobile hydrous phases play an important role in the Earth's global H cycle, and strongly influence internal geophysical and geochemical processes. These processes may leave a chemical and isotopic imprint of their operation in mantle rocks. Polarized single-crystal IR absorption spectroscopy is used to determine the OH content of minerals from mantle-derived xenoliths and stable isotope compositions are determined with the aid of both laser-fluorination (O) and conventional (H) extraction techniques. Mineral trace element concentrations are determined by electron- and ion-microprobe. Suites of rocks that reflect specific mantle processes, such as partial melting, crystal fractionation, and metasomatism, were selected to evaluate the importance of bulk composition, inter-phase partitioning, and mineral–fluid exchange in producing the observed variation of mantle OH, $^{18}O/^{16}O$, and D/H. Correlation patterns between OH, other trace elements, and stable isotope compositions in the minerals will be sought to define the role of fluids and fluid recycling in the mantle.

Results: In the past year, D. Rumble constructed a new laser microprobe for *in situ* O-isotope analysis. By using radiation in the UV range (248 nm), fluorination is achieved without the isotopic fractionation induced by heating and partial reaction on margins of laser-spots. Both UV and IR laser extraction systems yield satisfactory O-isotope results on standard materials and the major upper mantle minerals. Observations to date suggest little correlation between OH abundance and O-isotope composition in mantle minerals.

Analysis of OH concentrations in mantle olivines suggests a correlation with depth: deeper xenoliths, derived from kimberlites, are commonly higher in OH than spinel-facies peridotites from basalts. However, application of experimental calibrations of OH solubility in olivine indicates this may be an effect of petrologic environment, and not necessarily representative of the upper mantle in general. The H substitution mechanism in olivine appears not to be linked to other trace elements. Trace element studies of other mantle minerals indicate petrologic but not necessarily crystal chemical correlations between H and other elements.

A firmer basis for interpretation of H isotope data on mantle minerals was provided by a study of 17 megacryst amphiboles from Dish Hill, CA. These mantle samples, selected on petrographic, compositional, and volcanological criteria, revealed a generally uniform H content of 1.0 wt.% H_2O and δD_{SMOW} of $-46 \pm 7‰$, with only two strikingly deviant samples, in contrast with previous studies reporting substantial heterogeneity. This study provides a starting point for D/H investigations of fluid–wallrock interactions in mantle rocks from this region, and also for regional studies of the relationship between bulk D/H in mantle rocks and their tectonic environment.

GRANTEE:	**THE UNIVERSITY OF CHICAGO** Center for Advanced Radiation Sources Chicago, Illinois 60637
GRANT:	**DE-FG02-92ER14244**
TITLE:	**Synchrotron X-Ray Microprobe and Microspectroscopy: Technical Development for Advanced Photon Source Research and Low-Temperature Geochemistry Applications**
PERSON IN CHARGE:	**S. R. Sutton** (312-702-9930; Fax 312-702-5454; E-mail sutton@cars3.uchicago.edu)

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, and redox chemistry at the root-soil interface plant diseases. The goal is to extend this research at the Advanced Photon Source, the next generation of synchrotron radiation source at Argonne National Laboratory currently being commissioned.

Results: The main effort during the previous year concentrated on developing and applying methods based on x-ray absorption near-edge structure (XANES) to quantify and map oxidation state ratios in earth materials with microbeam resolution. Such information is crucial in understanding the toxicity, mobility, and containment of contaminating metals in the environment. The need for high spatial resolution is driven by the extreme heterogeneity, both in terms of concentration and speciation, of natural materials. The NSLS x-ray microprobe (XRM) is capable of (1) trace element analyses (≤1 ppm) with 5-micrometer spatial resolution and (2) x-ray absorption spectroscopy analyses with ≤100-micrometer spatial resolution and ≤100-ppm sensitivity. Work is continuing on developing and testing new microbeam production techniques including Kirkpatrick–Baez microfocusing mirrors and tapered capillaries. The K–B mirrors have produced x-ray beam sizes down to 2 microns with gains of about 1000 over pinhole-produced beams. Applications using the microprobe are conducted in large part as collaborations between University of Chicago personnel and other geochemists, environmental scientists, and agronomists. Examples of results of these research projects include: observations of ionic-size controlled differential incorporation of Co^{2+}, Zn^{2+}, and Ba^{2+} in calcite (R. Reeder et al., SUNY-Stony Brook), observation of iodine as I^- in water associated with illite (M. Fuhrmann, BNL), first speciation determination ($ZnCl_4^{2-}$) on a single fluid inclusion (R. Mayanovic, S. W. Missouri St., and A. Anderson, St. Francis Xavier Univ.), demonstration of trivalent Cr in CCA-treated wood (B. Illman, U. of Wisc.), time-resolved reduction of chromium in root/soil systems (T. Tokunaga, LBL), and preliminary studies of chemical heterogeneity in aerosol collections (J. Kelly, IIT). A new research thrust on microcrystallography of minerals containing metals of environmental and strategic importance was initiated.

GRANTEE: **THE UNIVERSITY OF CHICAGO**
Center for Advanced Radiation Sources
Chicago, Illinois 60637

GRANT: **DE-FG02-94ER14466**

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

PERSONS IN CHARGE: **S. R. Sutton** (312-702-9930; Fax 312-702-5454; E-mail sutton@cars3.uchicago.edu) and **M. L. Rivers** (312-702-2279; Fax 312-702-5454; E-mail rivers@cars3.uchicago.edu)

Objectives: GeoCARS 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 GeoCARS 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: Work has concentrated on beamline and optical design and the construction phase of the project is about to begin. The bending magnet beam will be split to allow simultaneous operation of two stations, a monochromatic (8–15 keV) side station and a multipurpose, white beam / monochromatic end station. The undulator beam line will have two white beam stations which may operate simultaneously using a double crystal monochromator (cryogenic Si) with a thin first crystal. In this mode, the upstream station will accept the monochromatized (4.5–22 keV) beam defected horizontally by a third (bendable) Ge crystal while the end station accepts the high-energy component (blue beam) transmitted by the first crystal. The need for small x-ray beams and broad spectral range have led us to base the focusing aspects of the optic design on grazing incidence mirrors. Both bending magnet and insertion device beam lines will have long (~1 m), bendable (demagnification < 11, E(cut-off) < 70 keV; beam sizes > tens of micrometers) mirrors. For smaller focal spots, small, dynamically bent Kirkpatrick–Baez mirrors (demagnification 100–400; E(cut-off) < 70 keV; beam sizes ~ 1 micrometer) will be used. A unique aspect of the insertion device beamline is the ability to deliver focused white beam to the sample through the incorporation of a power management pinhole in the first optics enclosure.

GRANTEE: **THE UNIVERSITY OF CHICAGO**
Department of the Geophysical Sciences
Chicago, Illinois 60637

GRANT: **DE-FG02-94ER144478**

TITLE: **Experiments and Models for Chemical Diffusion in Silicate Melts**

PERSON IN CHARGE: **Frank M. Richter** (312-702-8118; Fax 312-702-9505;
E-mail richter@dionheinz.uchicago.edu)

Objectives: To characterize and understand multicomponent chemical diffusion in silicate melts using laboratory experiments on molten $CaO–Al_2O_3–SiO_2$, $MgO–Al_2O_3–SiO_2$, and $MgO–CaO–Al_2O_3–SiO_2$ at 1500°C and 10 Kb.

Project Description: Chemical diffusion in molten silicates can be characterized by a diffusion matrix whose elements correspond to the set of linear coefficients relating the flux of each component to the chemical gradients of all the components present. Experimentally, the diffusion matrix is determined by inverting chemical interdiffusion profiles from diffusion couples run in different directions in composition space. The magnitude of off-diagonal elements of the diffusion matrix relative to the diagonal elements is a measure of the coupling between components during diffusion. Determining the diffusion matrix for silicate melts is only the first step in this project because while the diffusion matrix can accurately represent the diffusion process, it does not of itself give any understanding as to why silicate melts exhibit very strong diffusive coupling.

The second part of this project involves further experiments aimed at understanding the mechanisms responsible for coupling among diffusing components in a silicate melt. There are at least two sources of diffusive coupling. The first arises because diffusion is driven by chemical potential gradients and therefore in all but thermodynamically ideal systems the driving force for the diffusion of a given component will depend to some degree on compositional variations of the other components. The second form of coupling is a volume constraint that states that a mass flux of a given component into a fixed volume is only possible if an equivalent volume of the other components leaves that fixed volume. Thermodynamic coupling is addressed by experiments in which molten oxide mixtures are equilibrated with palladium metal and the concentration of the oxide components in Pd are used as a measure of their chemical activity in the melt. These experiments are used to determine the chemical activity–composition relations needed to calculate the diffusive coupling due to the non-ideality of molten silicates. Diffusive coupling arising from the volume constraint is addressed by constructing different models for how the constraint is apportioned among the different components. These models require knowledge of the molar volume of the components (taken from the literature) and the mobility (self diffusivity) of the cations and anions making up the melt. The mobility data is obtained from isochemical diffusion couples in which the two halves of the couple differ in the isotopic composition of the element whose mobility we seek to determine. Isotopic diffusion profiles for all elements including Al are analyzed using an ion probe. Understanding chemical diffusion in silicate melts involves constructing the diffusion matrix from the thermodynamic and mobility properties of the individual components and showing agreement between the constructed diffusion matrix and the one obtained by direct inversion of chemical diffusion data.

Results: (1) The complete diffusion matrix has been determined for $CaO–Al_2O_3–SiO_2$, and $MgO–Al_2O_3–SiO_2$ melts, and the results show very strong coupling among the components in that the off-diagonal terms are often larger than diagonal terms.

(2) Diffusion couples along certain compositional directions in both $CaO–Al_2O_3–SiO_2$ and $MgO–Al_2O_3–SiO_2$ are found to be unstable to double-diffusive convection even when the less dense melt is placed above the more dense composition. The conditions under which convection is seen in experiments is in excellent agreement with linear stability analysis. The demonstration of double-diffusive convection in $MgO–Al_2O_3–SiO_2$ melts explains why previous workers were unable to determine a diffusion matrix for this system, and more importantly, removes the concern expressed in the earlier work that chemical diffusion in silicate melts might not be representable in terms of a linear diffusion matrix.

(3) The self diffusion (mobility) coefficient for Ca, Al, Si, and O have been successfully determined over a broad range of compositions in molten $CaO–Al_2O_3–SiO_2$. The most striking result is that the mobility of the structural cations Si and Al is a linear function of degree of polymerization (as one might expect), but there is an abrupt break in the slope of the linear relationship at a particular composition, which is interpreted as a major and abrupt change in melt structure (a phase change?).

(4) A successful algorithm has been developed for calculating the elements of the chemical diffusion matrix for molten $CaO–Al_2O_3–SiO_2$ from the thermodynamic and kinetic properties of the individual components. The results show that thermodynamic coupling and the volume constraint are of comparable importance in promoting diffusive coupling among components of silicate melts.

GRANTEE: **UNIVERSITY OF COLORADO**
CIRES/Dept. of Geol. Sciences
Boulder, Colorado 80309-216

GRANT: **DE-FG03-94ER14419**

TITLE: **Seismic Absorption and Modulus Measurements in Porous Rocks Under Fluid and Gas Flow—Physical and Chemical Effects: A Laboratory Study**

PERSON IN CHARGE: **Hartmut Spetzler** (303-492-6715; Fax 303-492-1149;
E-mail spetzler@spot.colorado.edu)

Objective: The effect of fluids on the complex modulus of porous rocks is being investigated. The aim of the study is to provide a tool for monitoring changes in fluids near toxic and nuclear waste sites as well as aid in the detection and recovery of hydrocarbons.

Project Description: Fluids interact with rocks in various ways. Not only the physical properties of the rock matrix and of the fluid are important in the interaction, but also the chemical properties of both. To gain an understanding of the interaction three sets of experiments in decreasing complexity are being performed over a frequency range from 1×10^{-3} Hz to 100 Hz. The complex moduli of several partially saturated porous rocks have been measured. The results indicate a high sensitivity of the complex modulus to the chemical composition of the fluid and show a significant time dependence over at least 21 days. This complex behavior led to the design of experiments in which it is possible to isolate particular attenuation effects.

Results: Model cracks with aspect ratios of 0.01 consisting of wedges made from glass/quartz slides (25 mm × 75 mm × 1 mm) were tested with different fluids under static and dynamic conditions. Static tests gave good agreement with literature values for surface energies (surface tensions). The results from dynamic complex modulus measurements for fluids with viscosities much greater than that of water yield attenuation results which can be understood in terms of the fluids' viscosities. The crack stiffness at very low frequencies is too high to be explained by simple viscosity models. For fluids with viscosities in the range of water the behavior is very complex and cannot easily be explained in terms of such parameters as viscosity, surface energy, dielectric constant, etc. The behavior of the interface, the contact line where fluid solid and vapor meet, appears to dominate the attenuation.

The effect of the contact line force was measured while immersing or extracting a glass slide into or out of water or acetone. Significant hysteresis and force relaxation was observed for the water immersion, but not for the acetone immersion. Attenuation models for partially saturated rocks must consider the energy losses associated with the motion and the relaxation of the meniscus.

GRANTEE: **UNIVERSITY OF COLORADO**
Department of Geological Sciences
Boulder, Colorado 80309-250

GRANT: **DE-FG03-95ER14518**

TITLE: **Theoretical and Experimental Studies of Hydrological Properties of Rock Fractures During Active Deformation**

PERSONS IN CHARGE: **Shemin Ge** (303-492-8323; Fax 303-492-2606, E-mail ges@spot.colorado.edu), **Hartmut Spetzler,** and **Ivan Getting**

Objectives: 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. It has been recognized that the permeability within faults undergoes dynamic changes during active deformation from small-scale fracturing to large-scale thrust faulting. State of stress, fracture geometry, porosity, and geochemical reactions are some factors that can affect the permeability values. Considerable efforts have been expended on the mechanical properties of rock fractures under both laboratory and *in situ* conditions. Understanding of the hydrologic parameters and their roles during the hydromechanical processes, on the other hand, is still limited. Few experimental data and numerical models are available to describe the permeability evolution during active deformation of rocks and fractures. We are conducting a combined theoretical and experimental investigation on the hydraulic properties of rock fractures. The project consists of three components: (1) analytical study, (2) laboratory experiment, and (3) numerical modeling. In the analytical study, we plan to establish relations between hydraulic permeability and fracture parameters for a simple geometry under a kinematic shearing or compression process. The laboratory experiments will examine the interaction between fluid flow and fracture development. The numerical modeling will include modification of an existing code, implementation of new modules, calibration and verification, and prediction of permeability at larger scales. The analytical study will be performed during the first phase of the project. The laboratory experiments and numerical modeling will be integrated and intertwined during the entire project.

Results: This project was only recently initiated. Analytical study is currently under way and we will start to design the experiment in the fall of 1995.

GRANTEE: **UNIVERSITY OF COLORADO**
Cooperative Institute for Research in Environmental Sciences
and Department of Geological Sciences
Boulder, Colorado 80309

GRANT: **DE-FG03-95ER14499**

TITLE: **Interpretation of Geodetic Crustal Strains Using Massively Parallel Supercomputer Simulations of Nonlinear Dynamical Models**

PERSONS IN CHARGE: **John B. Rundle** (303-492-5642; Fax 303-492-1149;
E-mail rundle@cires.colorado.edu) and **W. Klein** (Boston Univ.)

Objectives: The underlying objective of this basic research is to understand the fundamental physical processes giving rise to the hazards and risks a variety of critical energy facilities face from several kinds of tectonic instabilities, notably earthquakes, volcanic eruptions, and landslides, in concert with the International Decade of Natural Disaster Reduction.

Project Description: A variety of nonlinear dynamical processes operate within the complex earth system, and are observed to display the signatures of many of the same phenomena as physical processes in other areas of physics, chemistry, and biology. In particular, scaling (fractal distributions), nonlinear thresholds and spatial interactions are all features possessed by these systems. Signatures of these processes include the appearance of scaling (geometric and dynamical fractal distributions), global and local self-organization, intermittancy (transitions from "laminar" to "turbulent" behavior), chaos, and the emergence of coherent space–time structures. The geodynamical effects observed in earthquake systems, particularly crustal straining, dynamical segmentation, and intermittent 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 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 Aperture Radar, and other field data.

Results: Although this research was only recently initiated, we have achieved major progress in understanding the origin of scaling in earthquake processes. In work accepted for publication in *Physical Review Letters,* we show that noise-driven earthquake fault systems develop a Boltzmann distribution in energy. We further show that the scaling distributions for the simulations can fall into one of two classes, involving fluctuations about either a symmetric or antisymmetric free energy well. Scaling exponents for the two classes can be readily computed from first principles, and have been verified in the simulations. The significance of this work lies in the demonstration that the scaling phenomena seen in this class of earthquake models is isomorphic to that seen in thermal and magnetic critical phenomena. We therefore predict that the nucleation phenomena for slip events (earthquakes) in the simulations will be similar and perhaps identical to that in thermal and magnetic systems. Discussions are under way on methods to test these predictions in field and laboratory data.

GRANTEE: **COLUMBIA UNIVERSITY**
Lamont–Doherty Earth Observatory
Palisades, New York 10964

GRANT: **DE-FG02-86ER13287**

TITLE: **Energetics of Silicate Melts from Thermal Diffusion Studies**

PERSONS IN CHARGE: **D. Walker** (914-365-8658; E-mail dwalker@ldeo.columbia.edu) and
M. C. Johnson (914-365-8712; Fax 914-365-8155;
E-mail krikitt@ldeo.columbia.edu)

Objectives: This research program characterizes mass transport by diffusion in geologic fluids in response to thermal, solubility, and/or chemical gradients to obtain quantitative information on the thermodynamic and kinetic properties of multicomponent systems. Equipment development for this research and many other community objectives is an integral part of the research.

Project Description: Thermal diffusion is the phenomenon of chemical migration in response to heat flow along a thermal gradient. The details of this response are conditioned by the thermochemical properties and constitution of the substance. Silicate liquids undergo substantial thermal diffusion (Soret differentiation), whereas the response in sulfide, carbonate, and aqueous fluids to an imposed temperature gradient is varied. The experimental observations of this differentiation are used to evaluate the form and quantitative values of solution parameters and to quantify ordinary diffusion coefficients, heats of transport, and activation energies of multicomponent liquids. The diffusion, solution, and element partition coefficients determined for these geological fluids form a data base for understanding magmatic crystallization behavior and for evaluating geothermal, ore deposit, and nuclear waste isolation potentials. Heating strategies for simultaneous high-pressure and high-temperature experiments as well as ambient pressure aqueous brines are developed.

Results: High-pressure and -temperature Soret diffusion experiments with carbonates, sulfides, and silicates were made possible through extensive technical advances in pressure media, gasketing configurations, and furnace materials for multianvil assemblies. Other multianvil labs will benefit from this development work. The development of new refractory semiconductors to fine-tune thermal structure has produced material which is robust against oxidation/reduction failure and will be of potential importance as fuel cell connector rod material. Experiments in brine/salt systems have demonstrated the potential utility of sulfate backfills in nuclear waste isolation applications. Pilot experiments at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory in the UK have demonstrated the feasibility of using epithermal neutron resonance pyrometry to calibrate the effect of pressure on thermocouple emf. In collaboration with colleagues at IBM, synthesis of novel precursors for high-temperature superconductors has been undertaken at high pressure.

GRANTEE:	**COLUMBIA UNIVERSITY** Lamont–Doherty Earth Observatory Palisades, New York 10964-8000
GRANT:	**DE-FG02-95ER14572**
TITLE:	**The Distribution in Space and Time of Wet Events in the Western North American Drylands**
PERSON IN CHARGE:	**Wallace S. Broecker** (914-365-8413; Fax 914-365-8155; E-mail broecker@ldeo.columbia.edu)

Objectives: The primary objective of this research is to map out spatial and temporal distribution of Heinrich (H2, H1) and Younger Dryas wet events that were recorded in 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 onset of varnish accumulation can be obtained from radiocarbon dates on subvarnish lichen remains 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 30°, from the south margin of the Cordillera ice sheet at north to the tropic areas of the central 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) AMS radiocarbon dating of subvarnish organic matter. Varnish from the latest Pleistocene glacial moraines (i.e., 25,000 to 10,000 years) and from fossil shorelines of paleolakes will be studied in greater detail to test if there is a temporal correlation among glacial advance, lake level fluctuation, and Heinrich wet events in the western North America. Altitudinal variation of the impacts of those wet events will also be investigated.

Results: Although this project has only recently been initiated, some preliminary results have been obtained. Varnish collected from the shorelines of Lake Lahontan in Nevada, Alkali Lake in Oregon, and from the fluvial erratic boulders of the Big Lost River in Idaho recorded Heinrich (H2, H1) and Younger Dryas wet events. Varnish collected from glacial moraines at the eastern flank of the Andes, South America and at the northern flank of the Tianshan Mountain, western China display the lamination patterns that are comparable to those in the Great Basin of the western U.S., with the surface layer (Holocene age) being Mn-poor and orange/yellow in color under a transmitted light microscope. Beneath this surface layer are a number of black layers (Mn-rich) that represent several wet periods during the late Pleistocene. Microprobe analyses indicate that chemical compositions of major and trace elements in the varnish are basically similar to those reported previously in the literature.

GRANTEE:	**UNIVERSITY OF CONNECTICUT** Department of Marine Sciences Groton, Connecticut 06340-6097
GRANT:	**DE-FG02-95ER14528**
TITLE:	**Rare Gas Studies of Fluids in the San Joaquin Basin: a Basin-Scale Test of Hydrogeological Process Models**
PERSONS IN CHARGE:	**Thomas Torgersen** (203-445-3441; Fax 203-445-3484) and **B. M. Kennedy** (Lawrence Berkeley National Laboratory)

Objectives: This research project will use isotopes of rare gases and their concentrations as *in situ* process tracers to investigate the source regions, release mechanisms, and time scales for fluid flow in the San Joaquin Basin. Specifically, this project will investigate the Elk Hills and Railroad Gap oil fields west of Bakersfield, CA. This project is joint with Lawrence Berkeley National Laboratory.

Project Description: The processes and timescales 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. Published studies on basin evolution and cementation history of the San Joaquin Basin suggest a simple (first cycle) sediment accumulation history and an episodic fluid flow history and significant cross-formation fluid flow from deeper in the system.

This project will use rare gas isotope measurements and chemical analysis of fluids obtained from oil wells and water wells in the San Joaquin Basin to (1) define endmember sources for these fluids and (2) use the dynamics of helium transport in the system to generate "helium model ages" (residence times). This study will provide first-order constraints on the parameterization of fluid flow controlling the evolution of gas/oil in this system. Such refinements provide a critical test of basin models and improvements in exploration/exploitation strategies.

Results: This project began in April 1995. Shallow-water samples were obtained (June, 1995) from the overlying Kern Fan deposits (Ca DWR) and a planning meeting was held with the operating contractors for the Elk Hills (Bechtel) and Railroad Gap (Chevron) fields. This meeting resulted in a refined list of suitable wells for sampling and background information on each individual well. Procedures and protocols for sampling and analysis of (1) aqueous, (2) oil, and (3) gas phases for major element chemistry, stable isotope composition, Sr isotope composition, rare gases, and possibly organic phase analysis have been refined and equipped for field sampling. Samples from Elk hills were collected in August 1995. Additional literature search and review has enabled the definition of the paleogeography within which source rocks were deposited, reservoir rocks were emplaced, and vertical and horizontal movement along the San Andreas provided driving forces for fluid flow within the system.

GRANTEE: **UNIVERSITY OF DELAWARE**
Department of Chemistry and Biochemistry
Newark, Delaware 19716

GRANT: **DE-FG02-89ER14080.A003**

TITLE: **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**

PERSONS IN CHARGE: **R. H. Wood** (302-831-2941; Fax 302-831-6335; E-mail rwood@brahms.udel.edu) and **Everett L. Shock** (Washington Univ.; 314-726-4258; Fax 314-935-7361; E-mail shock@zonvark.wustl.edu)

Objectives: The objective of this research is to measure heat capacities and volumes of key compounds of importance to predictions of geochemical phenomena at high temperatures and pressures. A second objective is to use the key compounds as a database together with simulations to develop empirical and theoretical methods for predicting a wide variety of other compounds.

Project Description: Measurements of volumes and heat capacities of a wide variety of organic electrolytes and nonelectrolytes at temperatures from 25 to 325°C will be made. This will allow the development of group additivity schemes to predict a very wide variety of organic species containing these functional groups. Previous measurements on H_2S, CO_2, CH_4, NH_3, and H_3BO_3 are being analyzed to find correlations which can predict other species. Molecular dynamics simulations of the chemical potential of aqueous methane, ethane, and propane at temperatures from 600 to 1200°C and water densities from 0 to 1 gm/cm^3 have been made. Revisions of the equations of state for aqueous ions and nonelectrolytes to allow better predictions of properties at high temperatures and pressures will be developed.

Results: The volumes capacities of aqueous solutions of 1- propanol, propanoic acid, pyridine, 1,4-butanediol, propylamine, adipic acid, succinic acid, propionamide, 1,6-hexanediol, 1,4-butanediamine, 1,6-hexanediamine, phenol, sodium acetate, propylamine hydrochloride, sodium propionate, and sodium benzenesulfonate measured previously at temperatures up to 250°C have been used to find functional group contributions. This allows reasonable predictions of 2o for any organic compound composed of the CH_3, CH_2, OH, COOH, $CONH_2$, NH_2, COO–, and NH_3^+ groups. Work is progressing on functional group contributions to heat capacity. Working with John O'Connell, a new equation of state for aqueous nonelectrolytes has been found which fits the experimental data on CO_2, CH_4, NH_3, H_2S, and H_3BO much better than the Shock and Helgeson equation with only two instead of five adjustable parameters. Theoretical reasons to question the high-temperature Stechenow coefficients of Helgeson and Oelkers have been found.

GRANTEE:	**UNIVERSITY OF SOUTH FLORIDA** Department of Marine Science St. Petersburg, Florida 33701
GRANT:	**DE-FG05-92ER14300**
TITLE:	**Clay Mineral Diagenesis in the Monterey Formation, California**
PERSONS IN CHARGE:	**J. S. Compton** and **W. M. Sackett** (813-893-9158; Fax 813-893-9189; E-mail Compton@marine.usf.edu)

Objectives: To study the progressive burial diagenesis and alteration of discrete vitreous volcanic ash beds to bentonite and metabentonite beds in order to determine the origin and mass balance of clay mineral reactions.

Project Description: Clay minerals are a significant constituent and are an important factor in silica, carbonate, and organic matter diagenesis of the Miocene Monterey Formation. Many of the clay minerals form as a result of progressive burial diagenesis and overlap with the burial depths associated with oil generation and migration. The mineral, elemental, and isotopic composition of Monterey rocks will be used in this study to (1) quantify the clay mineral reactions that occur in vitreous volcanic ash layers as they undergo increasing burial diagenesis (glass to bentonite to metabentonite), (2) test the hypothesis that the illitization of smectite is limited by the availability of K, and (3) determine the relation of clay mineral reactions to the maturation of organic matter. The results of this study will provide detailed analysis of the significance of clay minerals in the complex diagenesis of these hydrocarbon source and reservoir rocks.

Results: Regional variations in burial metamorphism of Monterey Formation rocks exposed in south-central coastal California allow comparison of equivalent aged volcanic layers from areas of low to increasingly higher diagenetic grade. Vitreous rhyolitic ash alters to smectitic clays below the transformation of biogenic silica (opal-A) to opal-CT and results in the loss of potassium, silica, sodium, rubidium and the REEs and an increase in aluminum, magnesium and water. The alteration appears to proceed by a dissolution/precipitation mechanism. Partial leaching of glass shards can result in an aluminum-rich, residual glass. Some bentonite layers are cemented by pyrite and marcasite while others are cemented by dolomite. Clinoptilolite is abundant in coarse-grained bentonite layers. Upon deeper burial to quartz-grade rocks, the smectite transforms primarily to kaolinite, because of the limited availability of potassium, as well as to illite and minor amounts of chlorite and ferroan dolomite. Significant amounts of ammonium illite can form from degradation of organic matter in these hydrocarbon source and reservoir rocks. The elemental and isotopic composition of separated zircon and apatite grains from volcanic layers are combined with the Sr isotopic composition of associated phosphorites and dolostones to increase the age resolution of the sections studied. Increased age resolution reveals that volcanism was episodic and corresponds in general with proposed variations in Neogene volcanic activity in the greater circum-Pacific region. Periods of increased volcanism may have contributed to increased nutrient supply and paleoproductivity.

GRANTEE: **GEORGIA INSTITUTE OF TECHNOLOGY**
School of Earth and Atmospheric Sciences
Atlanta, Georgia 30332-0340

GRANT: **DE-FOG5-95ER14517**

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

PERSON IN CHARGE: **P. M. Dove** (404-894-6043; Fax 404-853-0232;
E-mail dove@eas.gatech.edu)

Objectives: To understand surface geochemical controls on biomineralization that are currently limiting our ability to control carbonate precipitation and growth in natural and engineered earth systems. Our goal is to investigate the effect of amino acids on the *in situ* growth of calcite to determine the mechanisms by which these organic compounds modify rates and mechanisms of crystal growth.

Project Description: Calcium carbonate polymorphs comprise the most common family of biomaterials in natural systems. The soluble organic fraction associated with mineralizing molluscan shells plays a primary role in crystal formation and this fraction is distinguished by the near-ubiquitous presence of the amino acid, polyaspartate. Also, carbonates exposed to different polyamino acids exhibit a number of (macroscopic) growth habits. This suggests that systematic relationships between crystallization controls and surface interactions with the reactive groups of organic molecules must exist. These relationships are presently unknown.

This project combines *in situ* atomic force microscopic (AFM) investigations with kinetic measurements and surface chemical modeling to investigate the rates and mechanisms by which amino acids may modify the crystallization of calcium carbonate minerals. A suite of amino acids with different functional groups and stereochemistries will be investigated. The study uses oriented crystal fragments in characterized solutions to ascertain microscopic controls of amino acid pH saturation-state controls on carbonate growth processes.

Results: To begin this recently initiated project, we are conducting a series of experiments in a flow-through AFM study as controls to (1) quantify rates and patterns of growth in the absence of growth modifiers at characterized solution composition; (2) determine an appropriate saturation state for subsequent experiments including the amino acids. Observations by AFM at 30°C in additive-free solutions find that layer growth of calcite occurs by advancement of 3-Å straight steps along the $[\bar{4}41]$ and $[48\bar{1}]$ directions when saturation state (defined by ratio of IAP/K_{sp}) is <30. Rates of step advancement over the IAP/K_{sp} range over 4–15 are AFM-compatible. These findings provide a baseline for comparison with amino-acid-bearing experiments.

New observations of calcite growth in aspartic-acid bearing solutions at $IAP/K_{sp} \approx 4$ show that the advancement of 3-Å steps on the calcite surface is greatly modified by the presence of aspartic acid. The habit, spacing, and rate of step motion is affected and we are working to characterize the rates and mechanisms governing these differences. Aspartic-acid-bearing solutions also affect crystallographic controls on step retreat during dissolution.

An understanding of organic–mineral surface interactions 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 in the synthesis of lightweight mineral composites.

GRANTEE:	**UNIVERSITY OF HAWAII** Honolulu, Hawaii 96844
GRANT NUMBER:	**DE-FG03-95ER14525.A000**
PROJECT TITLE:	**Three-Dimensional Hydrogeology of Fault Zones**
PERSONS IN CHARGE:	**Steven Martel**; **Kevin Hestir** (801-797-2826; E-mail Hestir@sunfs.math.usu.edu) and **James P. Evans** (Utah State University); and **Jane C. S. Long** and **Janet Jacobsen** (Lawrence Berkeley National Laboratory)

Objectives: The project is designed to examine the three-dimensional hydrogeologic structure of fault zones by field mapping, mechanical modeling, and probabilistic modeling. The results of these efforts will be used in developing inverse techniques for determining fault zone hydrologic effects from well test data.

Project Description: We examine the three-dimensional permeability structure of faults in crystalline rocks and integrate these results into fluid flow models, will develop models which will represent the nucleation and growth of faults in three dimensions, and use these models in the development and testing of numerical models of fluid flow. This work will:

(1) Investigate the spatial distribution and permeability structure of small faults by documenting the geometry, the internal geohydraulic structure, the amount of slip, and the nature of hydrothermal deposits and alteration of faulted rocks.

(2) Develop a three-dimensional, numerical–mechanical technique to model fracture growth. The results of the model will be compared with the natural faults we investigate, and we will also conduct parameter studies to help predict how different states of stress and different material properties affect the distribution and linkage (i.e., organization) of permeable and impermeable features along faults.

(3) Develop stochastic models, based on field data and mechanical models, for fault development. These models will represent how permeable and impermeable features are likely to be organized. This work will form the foundation of a stochastic model which characterizes the hydrology of faults.

(4) Compare the long-term permeability structure of faults, as revealed by geologic evidence, with the short-term permeability structure revealed by well tests.

(5) Enhance how three-dimensional data and model results are portrayed pertaining to the geometry of faults and fracture flow systems in general.

This research integrates field work and deterministic and stochastic modeling to gain insight into how three-dimensional permeability 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: This project has only recently been initiated. Field work on well-exposed, small-displacement fault zones in the central Sierra Nevada mountains is currently under way. This work has documented the three-dimensional geometry of small faults, the internal structure of a fault zone with approximately 8–10 m of slip, and examined the hydrothermal alteration and evidence for the fluid flow history along and within the faults. Field work will continue through mid-August.

GRANTEE:	**INCORPORATED RESEARCH INSTITUTIONS FOR SEISMOLOGY (IRIS)** Arlington, Virginia 22209
GRANT:	**DE-FG05-95ER14545**
TITLE:	**Acquisition of Equipment for High-Resolution Seismic Imaging**
PERSONS IN CHARGE:	**David Simpson** and **James Fowler** (703-524-6222; Fax 703-527-7256)

Objectives: Purchase a high-resolution seismic reflection system to be used by the research community.

Project Description: The goal of this project is to purchase two portable 60-channel reflection recording systems which will provide instrumentation for very shallow to very deep seismic reflection investigations of the Earth's crust. The multi-channel instruments will complement the current PASSCAL inventory of REFTEK recorders and will greatly expand the amount of instrumentation available for active source seismic investigations carried out by university groups and government labs. DOE funding is for hardware costs only. As part of its NSF-funded core PASSCAL program, IRIS will service and maintain the equipment at its Stanford Instrument Center. In addition, IRIS will carry out the modification and developments necessary to fully integrate these instruments with the existing PASSCAL instruments in field operations and data analysis.

Results: This project has only just been initiated. An initial comparison of the types of systems available was made and bids received from the major manufacturers. The first 60-channel unit has been ordered along with:

- 90 high -frequency (40 -Hz) geophones.
- cdp cables for shallow reflection work.
- 75 strings of low-frequency (4.5-Hz) geophones.
- cdp cables for deep reflection profiling.
- A roll-along switch.

The equipment is scheduled for delivery in late fall of this year; the first experiments are planned for late December.

GRANTEE:	**INDIANA UNIVERSITY** Department of Chemistry Bloomington, Indiana 47405
GRANT:	**DE-FG02-91ER14175**
TITLE:	**Mechano-Chemical Self-Organization and Nonlinear Dynamics in Sedimentary Basins**
PERSON IN CHARGE:	**P. Ortoleva** (812-855-2717; Fax 812-855-8300; E-mail ortoleva@indiana.edu)

Objectives: A sedimentary basin is viewed as a nonequilibrium reaction–transport–mechanical system. As a result, phenomena such as reaction front fingering, stylolites, diagenetic bedding, and episodic fluid release from overpressured domains are put in the unified framework of instability and nonlinear dynamics and implications for petroleum are drawn.

Project Description: These phenomena are modeled and simulated numerically. Rate laws for stress-mediated reactions and the dependence of rock rheology, permeability, and dispersion on texture, mineralogy, and fracture parameters are set forth. A quantitative model is constructed based on equations of conservation of mass, force balance, and incremental stress rheology. The models are simulated numerically when small-scale features (such as stylolites, differentiated layering, or fractures) affect the basin-scale dynamics, and conversely, homogenization techniques are used to make the calculations practical. Parallel numerical algorithms are also developed and implemented. Emphasis is placed on basin simulations in three spatial dimensions.

Results: A basin simulator has been developed to test ideas on the nonlinear dynamics of a sedimentary basin. This is a unique "computational laboratory" due to its comprehensive inclusion of processes and its chemical generality.

Two- and three-dimensional basin simulators capturing fluid flow, aqueous chemistry, and mineral reactions (including pressure solution) have been developed. They are being used to predict reservoir quality and distribution within a basin and the role of nonlinear phenomena in fluid migration and trapping.

A numerical strategy for implementing our three-dimensional incremental stress model of basin deformation has been developed. Our model integrates poroelasticity, plasticity, pressure solution, and hydrofracturing. Rheological parameters have been calibrated using rock mechanics experiments and, for slow processes, geological data. Methods for handling complex sedimentation history and other geological constraint data in our model and 3-D graphical techniques for visualizing the results have been developed. Preliminary data sets from two basins have been obtained and will be used to model complex kilometer-scale basin nonlinear dynamics for comparison of predictions with real case studies.

GRANTEE: **JOHNS HOPKINS UNIVERSITY**
Department of Earth and Planetary Sciences
Baltimore, Maryland 21218

GRANT: **DE-FGO2-89ER14074**

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

PERSONS IN CHARGE: **D. R. Veblen** (410-516-8487; Fax 410-516-7933;
E-mail DVeblen@JHU.edu), and **E. S. Ilton** (Lehigh Univ.;
610-758-5834; Fax 610-758-3677; E-mail esi2@Lehigh.edu)

Objectives: This project will provide constraints on the physical and chemical conditions that control the rates of sorption and coupled sorption–reduction of environmentally sensitive elements to distinct crystallographic surfaces of silicate minerals in near-surface aqueous systems. XPS is being developed into a quantitative method for determining Fe(II)/Fe(III) in hydrous silicates.

Project Description: Cr^{6+}, Cr^{3+}, Se^{6+}, Cd(II) and Co(II) –bearing solutions will be reacted with ferrous silicates such as biotite, amphibole, and pyroxene. The surfaces and interior portions of the silicates will be examined with transmission electron microscopy (TEM), analytical electron microscopy (AEM), scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). These techniques will help to determine the oxidation state, form, and relative concentration of the sorbate. In a related project, HRTEM and AEM will be used to gain a greater understanding of the structure of silicate grain boundaries and the relationships between grain-boundary structure and transport properties. XPS is being calibrated to quantitatively determine Fe(III)/Fe(II) in the near surface of silicates. An outgrowth of this work is a project to develop XPS into a microbeam technique for determining Fe(III)/Fe(II) in minerals in thin sections. Such a method would replace unwieldy bulk analytical techniques and aid geoscientists in fields as diverse as petrology and environmental geochemistry.

Results: XPS of reacted biotite edges demonstrates strong solution and biotite compositional controls on the rate of $Cr(VI)_{aq}$ sorption–reduction. Increasing K^+_{aq} strongly inhibited the reaction rate. This result supports the hypothesis that electron transfer from biotite to sorbed species is dependent on the ejection of charge compensating cations, such as K, from biotite to solution. The reaction rate was appreciably enhanced in $I = 0.005$ relative to 0.001 M ($NaClO_4$) solutions. Further experiments are required to determine whether this is a general ionic strength effect or if high Na concentrations catalyze the reaction. Both high Fe/Mg and Fe(III)/Fe(II) in biotite increase reaction rate. These results may be explained by compositional controls on the conductivity of electrons in biotite. $Se(VI)_{aq}$ does not appear to be as reactive as $Cr(VI)_{aq}$.

XPS Fe(II)/Fe(III) analyses have been calibrated with a suite of well characterized pegmatitic biotites. *In situ* XPS analyses of Fe(II)/Fe(III) in biotites in metapelite thin sections show a positive correlation with bulk Mossbauer biotite analyses.

GRANTEE:	**LEHIGH UNIVERSITY** Department of Earth and Environmental Sciences Bethlehem, Pennsylvania 18015
GRANT:	**DE-FGO2-89ER145074**
TITLE:	**Reactions and Transport of Toxic Metals in Rock-Forming Silicates at 25°C**
PERSONS IN CHARGE:	**E. S. Ilton** (610-758-5834; Fax 610-758-3677; E-mail esi2@Lehigh.edu) and **D. R. Veblen** (Johns Hopkins Univ.; 410-516-8487; Fax 410-516-7933; E-mail DVeblen@JHU.edu)

Objectives: This project will provide constraints on the physical and chemical conditions that control the rates of sorption and coupled sorption–reduction of environmentally sensitive elements to distinct crystallographic surfaces of silicate minerals in near-surface aqueous systems. XPS is being developed into a quantitative method for determining Fe(II)/Fe(III) in hydrous silicates.

Project Description: Cr^{6+}, Cr^{3+}, Se^{6+}, Cd(II) and Co(II) –bearing solutions will be reacted with ferrous silicates such as biotite, amphibole, and pyroxene. The surfaces and interior portions of the silicates will be examined with transmission electron microscopy (TEM), analytical electron microscopy (AEM), scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). These techniques will help to determine the oxidation state, form, and relative concentration of the sorbate. In a related project, HRTEM and AEM will be used to gain a greater understanding of the structure of silicate grain boundaries and the relationships between grain-boundary structure and transport properties. XPS is being calibrated to quantitatively determine Fe(III)/Fe(II) in the near surface of silicates. An outgrowth of this work is a project to develop XPS into a microbeam technique for determining Fe(III)/Fe(II) in minerals in thin sections. Such a method would replace unwieldy bulk analytical techniques and aid geoscientists in fields as diverse as petrology and environmental geochemistry.

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XPS Fe(II)/Fe(III) analyses have been calibrated with a suite of well characterized pegmatitic biotites. *In situ* XPS analyses of Fe(II)/Fe(III) in biotites in metapelite thin sections show a positive correlation with bulk Mossbauer biotite analyses.

GRANTEE: **LEHIGH UNIVERSITY**
Department of Earth and Environmental Sciences
Bethlehem, Pennsylvania 18015

GRANT: **DE-FG02-93ER14373**

TITLE: **Surface and Solution-Interface Geochemistry of Lead Sulfide and Lead Selenide Minerals**

PERSONS IN CHARGE: **Carl O. Moses** (610-758-4907; Fax 610-758-3677;
E-mail com0@lehigh.edu) and
Eugene S. Ilton (610-758-5834; E-mail esi2@lehigh.edu)

Objectives: This project is an investigation of the aqueous reactivity of sulfide minerals and their selenide analogues (endmember and solid-solution compositions). The specific goal is a comprehensive and integrated understanding of reactivity based on fundamental high-vacuum surface chemistry and the rates of aqueous exchange and dissolution reactions. The present focus is on PbS and PbSe.

Project Description: Sulfide minerals play important roles in the distribution and mobility of metals, sulfur, and selenium in the hydrosphere. Their instability in oxic environments can make them a source of their components to the environment, while their stability in anoxic environments can make them a sink for such components. The research approach here integrates information from mass transfer experiments in aqueous solution with information from surface chemistry studies utilizing high-resolution x-ray photoelectron spectroscopy (XPS) and field-emission scanning electron microscopy. Research goals include characterizing surface stoichiometry, determining the depth of surface chemical alterations during gas- or solution-phase exposures, identifying changes in surface morphology during exposures, determining the scope of environmental controls on exchange and release rates, establishing reaction mechanisms for exchange and dissolution, and determining the range of mineral-solution interface properties that are environmentally relevant. The PbS–PbSe system was selected for this investigation because its crystal chemistry and electronic structure are well understood, the solid solution is complete and ideal, and mass transfer processes at their solution interfaces, which have implications for environmental quality, are incompletely understood.

Results: Evacuated-tube syntheses of pure PbS, pure PbSe, or intermediate PBS/PbSe compositions in the solid solution, using high-purity starting materials prepared in a controlled atmosphere, produce specimens with bulk lattice dimensions, determined by x-ray diffraction, that the are consistent with those predicted by stoichiometry.

The need for a pristine surface (no surface contamination of oxygen or carbon) for baseline reactivity studies has been met by evaporating a thin film (few hundred Â) of PbS onto a substrate of graphite or natural, single-crystal galena. Epitaxial growth of the film on single-crystal galena has been verified by x-ray photoelectron diffraction (XPD), so the thin-film surface is a pristine, single-crystal surface.

XPS examination of the pristine, single-crystal surface reveals a very small peak ~1 eV to the low-binding-energy side of the two main Pb 4f peaks. This feature is apparently under-coordinated Pb, which may be a non-stoichiometry (i.e., S-deficiency) defect. Alternatively, it may represent a true surface state; in the absence of contamination, Pb atoms at the PbS surface are in 5- rather than 6-coordination, leading to a small increase in the kinetic energy of photoelectrons. In either case, XPD measurements demonstrate that this feature is restricted to the surface (probably no deeper than 2 atomic layers). Furthermore, this material is an n-type semiconductor, owing to electron donation from the under-coordinated Pb, and its Fermi level is pinned to the bottom of the conduction band.

Controlled oxygen-exposure experiments show a loss of under-coordinated Pb in the earliest, most rapid stages of oxygen adsorption and a shift to p-type semiconduction as electrons accepted by oxygen leave holes at the top of the PbS valence band. The observed pinning shift in core-level peaks corresponds to the bulk PbS band gap (0.4 eV).

GRANTEE:	**UNIVERSITY OF MARYLAND** Department of Chemistry and Biochemistry College Park, Maryland 20742
GRANT:	**DE-FG02-94ER14467**
TITLE:	**Theoretical Studies of the Adsorption of Gold Complexes and Flotation Collectors Onto Sulfide Mineral Surfaces**
PERSON IN CHARGE:	**J. A. Tossell** (301-405-1868; Fax 301-314-9121; E-mail tossell@geo.umd.edu)

Objectives: This study utilizes computational quantum chemistry to study the structures, stabilities, and spectral properties of heavy metal sulfide species both in aqueous solution and adsorbed on mineral surfaces, and the interaction of flotation collector molecules with sulfide mineral surfaces.

Project Description: To understand the mechanism of formation of gold deposits one must understand both the dissolution and precipitation of gold sulfide minerals and the adsorption of gold-bearing species onto other mineral surfaces. To effectively concentrate gold deposits of low grade one must utilize sulfide-bearing flotation collector molecules which selectively bond to the surface of the gold minerals. In both cases a complete understanding requires knowledge of the structures and properties of both gold sulfide compounds and mineral surfaces in contact with water. Although both adsorption and flotation have been extensively studied experimentally, their microscopic mechanism is still poorly known. In this study we calculate the structures, energetics, and spectral properties of gold bisulfide, gold bichloride, and other complexes in aqueous solution and adsorbed on models for arsenic and antimony sulfide surfaces. The goal is to understand the preferential adsorption of gold complexes onto these surfaces in terms of the species formed. Another topic of study is the bonding of phosphorus oxysulfide collector molecules to gold and gold sulfide surfaces, with the goal of designing collector molecules with improved efficiencies.

Results: In the first year of the grant the main focus has been on calculating the structures, stabilities, and properties of various metal sulfide species in solution and of the arsenic and antimony sulfide minerals and their surface. First Au(I) and Au(III) species in solutions containing sulfide and chloride, such as $Au(SH)_2^{-1}$ and $AuCl_4^{-1}$, were studied. The calculations were tested by comparison with structural data from crystals and aqueous solutions and with available Raman and visible/UV spectra in solution. A parameterized form of the Born-Mayer approach was used to evaluate the solvent stabilization of the ionic species. The results support the presence of $Au(OH)(H_2O)$ in aqueous solution in the absence of chloride and sulfide, where the above formula gives the molecular composition of the central metal atom and its first coordination sphere. The $Au(SH)(OH)^{-1}$ complex is calculated to be stable at high pH, rather than the $Au_2S_2^{-2}$ species previously assumed. Calculated bond distances and vibrational frequencies for the $AuCl_x(OH)_{4-x}^{-1}$ series match well against EXAFS and Raman data and the replacement of Cl^- by OH^- is calculated to be exothermic. Trends in visible-UV energies are adequately reproduced but Au Mossbauer results seem erratic. Au(SH) forms a bond to the bridging S of a $Sb_2S(SH)_4$ surface model but bonds even more strongly to the terminal S of the hydrolyzed surface.

In collaboration with G. Helz (Univ. of Maryland) and D. J. Vaughan (Univ. of Manchester) structures and spectra have also been calculated for a number of As sulfide species in aqueous solution. New pH-dependent Raman spectra and solution EXAFS have been interpreted in terms of $AsS(SH)^{-1}$ and $AsS_2(SH)_2^{-1}$ species, rather than the oligomers often assumed.

The arsenic and antimony sulfides which can form molecular minerals, such as As_4S_3 (dimorphite) and As_4S_4 (realgar and pararealgar) have also been studied. Calculated structures and vibrational spectra are in good agreement with experiment, with the two different isomeric forms of the As_4S_4 molecule (present in realgar and pararealgar) calculated to differ in energy by almost 3 kcal/mol. In the low-energy triplet state of the realgar molecule, 2.2 eV above the ground singlet, an As–As bond is broken, facilitating a rearrangement to the pararealgar form.

GRANTEE: **MASSACHUSETTS INSTITUTE OF TECHNOLOGY**
Department of Earth, Atmospheric, and Planetary Sciences
Cambridge, Massachusetts 02139

GRANT: **DE-FG02-86-ER13636**

TITLE: ***In Situ* Permeability Determination Using Borehole and Seismic Logging Data**

PERSONS IN CHARGE: **M. Nafi Toksoz** (617-253-7852; Fax 617-253-6385; E-mail nafi@erl.mit.edu) and **C. H. Arthur Cheng** (617-253-7206; Fax 617-253-6385; E-mail cheng@erl.mit.edu)

Objective: The objective of this project is to identify, locate, and characterize *in situ* fractures using downhole and surface seismic methods. The goal is to estimate the permeability of these fractures from the way they interact with seismic waves.

Project Description: The purpose of this work is to study methods of determining *in situ* permeability or hydraulic conductivity of a fracture or fracture zone using full waveform and shear wave acoustic logging, vertical seismic profiling, and other downhole, cross-hole, and seismic imaging techniques. In addition, methods to determine the orientation and extent of natural and manmade fractures are studied. The behavior of full waveform and shear wave logs in a fractured medium is studied using numerical models, laboratory-scale model experiments, and actual field data. The method of locating a hydrofrac using micro-earthquake arrival time is being improved by relative and absolute location techniques. The aim is to characterize and image *in situ* fractures for the purpose of hydrocarbon production from naturally or artificially fractured reservoirs, nuclear waste disposal planning, and geothermal energy recovery.

Results: The major effort in the past year in the characterization of fractures from acoustic logging has been focused on shear wave logging using dipole sonic logging tools. In particular, the current and proposed techniques of determining the extent of shear wave anisotropy and the directions of the principal axes from cross-dipole logging data were investigated. Such anisotropy can be interpreted as caused by aligned fractures. These methods are usually borrowed from VSP applications for identifying shear wave splitting. However, since in dipole logging we are dealing with the flexural wave, which is highly dispersive; it is not clear that the VSP techniques are applicable. Using 3D finite-difference laboratory-scale models and actual field data, the behavior of flexural waves in azimuthally anisotropic media was studied. The different processing schemes used were examined by applying them to the synthetic and laboratory-scale model data. A tentative conclusion was reached that it is possible to estimate the direction of the principal axes of anisotropy, but it is not easy to accurately measure the amount of anisotropy. It is difficult to separate the two flexural waves, because of their dispersive nature and the likelihood that the later part of the wavetrain will be contaminated by the Stoneley wave. Thus the use of existing tools and processing algorithms to measure the amount of shear wave anisotropy is not well established.

Another part of our borehole acoustics effort is in the area of hydraulic fracture imaging. Continuing the work done by Lisa Block under this grant, relative location techniques were used by comparing microearthquakes of similar waveforms. These events were located more accurately, and this method also greatly decreases the uncertainty associated with the location. Using a subgroup of all the microearthquakes generated from the Los Alamos Hot Dry Rock Experiment at Fenton Hill, a fracture plane was clearly defined. Moreover, using the origin time associated with each event, the time history of the fracture process was obtained. The direction of the fracture is consistent with those obtained from fault-plane solutions and from waveform inversion. The time history of these microearthquakes will be extremely valuable in the evaluation of fracture models, especially in the presence of a local stress field. Data from another experiment conducted by ARCO, where the hydraulic fracturing is in a much softer sandstone, have also been examined. The initial results are that the hydraulic fracture appears to be more complex and not nearly as planar as the Fenton Hill data.

GRANTEE: **MASSACHUSETTS INSTITUTE OF TECHNOLOGY**
Department of Earth, Atmospheric, and Planetary Sciences
Cambridge, Massachusetts 02139

GRANT: **DE-FG02-94ER14431**

TITLE: **A High-Precision MT Study of the Mid and Lower Crustal San Andreas Fault Zone**

PERSONS IN CHARGE: **Theodore Madden** (617-253-6854; Fax 617-253-6385;
E-mail trm@halley.mit.edu) and **Randall Mackie**

Objectives: To study the variations in the electrical conductivity of the mid and lower crustal parts of the San Andreas Fault system in central California using magnetotelluric measurements.

Project Description: The relative and absolute weakness of the San Andreas Fault can be explained if the slip zone of the fault contains excess fluids with high fluid pressures relative to the rest of the fault zone and adjacent crust. Fluids in the fault zone have also been invoked to explain the behavior of the creeping section of the fault zone, and they may also play an important role in the earthquake cycle of the locked section of the fault. It has been suggested that any fluids in the fault zone may come from the lower crust, and if this is the case, then high-conductivity lower crustal channels created by the pore fluid paths should be resolvable using high-quality magnetotelluric measurements. This project will involve making magnetotelluric measurements across the Carizzo Plains section of the fault in the first year, and the Mojave section of the fault in the second year, and is associated with the San Andreas Deep Drilling Project.

Results: During the past year, very high-quality MT measurements were made along two profiles perpendicular to the San Andreas Fault in the Carizzo Plains area, going from the western side of the Caliente Range to the eastern side of the Temblors, just into the Great Valley. At each site along these profiles, EMI equipment was used to collect remote reference data, which spanned the frequency range 125–0.003Hz. At every other station, LIMS (Long-period Intelligent MT System) rented from the Canadian Geological Survey were installed. These instruments are designed to be in place for long periods of time (greater than 1 week), and they measure the MT fields from periods of 20s down to about 20,000–30,000s. The field strengths were very high during the field season, and the low cultural noise allowed for very good estimates of the MT impedances. An initial inversion of data along the southern profile is very interesting because it indicates that the crust to the east of the San Andreas is more resistive at a shallower depth than to the west, which is just opposite from what was expected for this area. Data from the northern profile are currently being reprocessed with robust processing routines and further detailed inversions for both profiles will be run. In the fall of 1995, these types of measurements will be repeated along the Mojave section of the San Andreas fault.

GRANTEE: **UNIVERSITY OF MIAMI**
Rosenstiel School of Marine and Atmospheric Science
Miami, Florida 33149-1098

GRANT: **DE-FG05-92ER14253**

TITLE: **Testing the Correlation Between Sequence Stratigraphy, Seismic Reflectors and Diagenetic Changes in Carbonates: Evaluation of Fluid Flow During Early and Late Diagenesis**

PERSONS IN CHARGE: **Gregor P. Eberli** (305-361-4678; Fax 305-361-4632;
E-mail geberli@rsmas.miami.edu),
Peter K. Swart, and **Jean Bahr** (University of Wisconsin)

Objectives: To assess and model fluid flow in carbonate platform margins, especially to evaluate how early diagenesis influences permeability and fluid pathways in the burial environment. In particular, test the hypothesis that early strata-bound diagenesis is related to variations in sea level and the resulting changing flow regimes.

Project Description: Two experiments are conducted to constrain the fluid flow within carbonate platforms. The first experiment relies on two core borings and a series of short cores from the western margin of Great Bahama Bank. The investigations consist of three parts: (1) assessment of fluid flow in the interstitial pore water chemistry of the piston and gravity cores, (2) evaluation of timing diagenesis and evolution of fluids through time by studying the different diagenetic stages of the core material, and (3) numerical modeling of fluid flow of Great Bahama Bank (in collaboration with Jean M. Bahr, University of Wisconsin).

A second experiment is designed to test our findings from the modern environment in an ancient system, in isolated Upper Devonian platforms (Miette and Ancient Wall) in Alberta, Canada. The main objectives of this study are (1) to evaluate diagenetic zones within the sequence stratigraphic framework with a special emphasis on diagenetic and physical properties changes associated with sequence boundaries, and (2) to investigate to what degree burial diagenesis obliterates early strata-bound diagenesis.

Results: Analysis of core borings from Great Bahama Bank has allowed characterization of a new diagenetic environment, the "marine burial environment." Marine burial diagenesis is characterized by alteration of metastable carbonate sediments to stable carbonate rocks in the absence of meteoric fluids but with fabrics that resemble those of meteoric diagenesis. Modeling and geochemical studies support these observations that suggest sea water flow into the bank. Marine burial diagenesis is also important for the petrophysical behavior, especially permeability, of carbonates. While intercrystalline and vuggy porosity have long been known to exert a major control on permeability, this study also documents the importance of the connected moldic porosity that forms during marine burial diagenesis. The correlation to seismic data confirms that sea-level-controlled changes in sediment composition and early diagenesis determine the petrophysical behavior of the rocks within the sequence stratigraphic framework. These findings from the modern are corroborated by the results from the Upper Devonian carbonate buildups of Canada, where a strong correlation between sequence architecture, TOC content, and the variation in dolomite content and early diagenesis can be documented. Petrophysical analyses of outcrop and cores will help quantify the influence of different stages of diagenesis on the rock properties.

GRANTEE:	**UNIVERSITY OF MICHIGAN** Department of Geological Sciences Ann Arbor, Michigan 48109-1063
GRANT:	**DE-FG02-94ER14412**
TITLE:	**Applications of ICP Magnetic Sector Multicollector Mass Spectrometry to Basic Energy Research**
PERSONS IN CHARGE:	**Alexander N. Halliday** (313-764-1435; Fax 313-763-4690; E-mail a.halliday@um.cc.umich.edu) and **Chris M. Hall**

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: Using the prototype ICP magnetic-sector multiple-collector mass spectrometer we have developed new techniques for the accurate isotope dilution measurement of In and Sn in basalts and sulfides. Whereas the overall distribution of In and Sn within the silicate earth is governed by lithophile affinity, In/Sn can be dramatically fractionated in sulfides. We have conducted a reconnaissance isotope dilution survey of In and Sn concentrations in sulfides and found that, in contrast to silicate rocks, In/Sn ratios in sphalerite and chalcopyrite commonly range between 1 and 50. We have made the first ^{115}In–^{115}Sn age measurements of sulfides using this technique. We have developed high-precision *in situ* isotopic measurements of Sr isotopic compositions using a Nd–YAG laser. Results for carbonates and feldspars are in excellent agreement with independently known values. These are the most precise *in situ* isotopic measurements of any kind made thus far. We have developed techniques for high-precision Hf and W isotopic measurements and used these to determine hydrothermal contributions to metalliferous sediments and the age of the Earth's core. We have developed new chemical separation and mass spectrometric methods for isotope dilution analyses of Pt and Pd. These techniques are now being applied to a variety of terrestrial materials. We have improved instrument sensitivity by a factor of 6 over the course of this year. Finally, the production version of the instrument is currently being commissioned at the University of Michigan.

GRANTEE: **UNIVERSITY OF MINNESOTA AT TWIN CITIES**
Department of Geology and Geophysics
Minneapolis, Minnesota 55455

GRANT: **DE-FG03-91ER14212**

TITLE: **Physical Modeling of Sedimentary Basins, Magma Mechanics, and Molecular Dynamics of Geological Solutions**

PERSON IN CHARGE: **D. A. Yuen** (612-624-1868 ; Fax 612 624-8861;
E-mail davey@krissy.msi.umn.edu)

Objectives: (1) Lithospheric dynamics; (2) Effects of phase transitions on lithospheric processes; (3) Viscoelastic relaxation processes; (4) Dynamical consequences of non-Newtonian rheology.

Project Description: This collaborative project with F. J. Spera at the University of California 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) Construction of new rheological apparatus and laboratory experiments on melts and magmatic suspensions; (2) Determination of the thermodynamical and transport properties of molten silicates by MD simulations; (3) Viscoelastic processes in the lithosphere; (4) Numerical modeling of magmatic underplating and the formation of granitic diapirs; (5) 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; (6) The dynamical influences of lithospheric phase transitions on the thermal–mechanical evolution of sedimentary basins; (7) The development of stress fields and criteria for faulting in the crust; and finally, (8) Numerical modeling of heat and solute transport driven by thermal and saline heterogeneities in geothermal systems.

Results: Together with UCSB we have studied the role played by compositional convection in promoting viscous heating under lithospheric conditions. The results have been reported in the Fall 1994 AGU meeting and we are in the process of writing up a manuscript. We list below the results for the Univ. Minnesota part of this project. Additional results are given in the summary of activities by the Univ. California team, led by F. J. Spera. We have accomplished a great deal in the past year on the effects of viscous heating in mantle plumes and their interaction with the lithosphere. Significant amounts of heat, considerably greater than mantle radioactivity, can be generated at the site of plume impingement at the base of the lithosphere. Toroidal motions near the surface are enhanced by viscous heating and form "river-like" structures, analogous to transform faults. Three publications have come out and have appeared in *Geophys. Res. Lett.* **22**, 477–480, 1995; *Geophys. Res. Lett.* **22**, 1277–1280; and *Science* **267**, 1150–1153, 1995. We have also studied the interplay between surface erosion and the dynamics of the underlying phase transitions in the lithosphere. We presented this work at the 1995 spring AGU meeting. This work will be written up shortly. We have also studied the sea-level variations in the Cretaceous , using wavelet analysis. This work was presented at the Fall 1994 AGU meeting and will be written up for publication. Two papers appeared respectively in *Geophysical Res. Lett.* **22**, 1549–1552, 1995, and *Earth Planetary Sci. Lett.* **129**, 249–260, 1995. They were on the subject matter of rheological transition in a composite non-Newtonian and Newtonian temperature-dependent rheology. Finally, we have a paper accepted in *Phys. Earth Planet Interior.* This paper dealt with the two-dimensional solution of the thermal-kinetic growth problem in metastable phase transitions.

GRANTEE: **NATIONAL ACADEMY OF SCIENCES/ NATIONAL RESEARCH COUNCIL**

Board on Earth Sciences and Resources
Washington, D.C. 20418

GRANT: **DE-FG05-89ER14061**

TITLE: **Board on Earth Sciences and Resources, Committee on Seismology, U.S. Geodynamics Committee**

PERSON IN CHARGE: **Craig M. Schiffries** (202-334-2744; Fax 202-334-1377; E-mail cschiffr@nas.edu)

Objectives: The Board on Earth Sciences and Resources coordinates the National Research Council's advice to the federal government on solid-earth science issues related to research, education, the environment, geologic hazards, resource utilization, and economic development.

Project Description: The Board provides information and advice to the government through committees of volunteer geoscientists drawn from academia, industry, and government. The primary purpose of these committees is to respond to requests from the Executive Branch, Congress, and federal agencies for information or advice on specific issues before the government. The committees also serve as a forum for discussions and exchange of information among government, university, and industry scientists and policy makers. The Board strives to provide accurate and timely advice that can be used for wise decision making by preparing reports and bringing scientists and policy makers together at workshops, symposia, and forums. The Board also coordinates activities of various U.S. National Committees, including those for the International Union of Geodesy and Geophysics, the International Union of Geological Sciences, the International Geographical Union, the International Union for Quaternary Research, and the US. National Committee for Rock Mechanics. The major committees of the Board and their areas of oversight include: Committee on Seismology (seismology related to research, hazards, and verification); U.S. Geodynamics Committee (solid-earth science issues, research and applications of geodetic data); Committee on Geophysical and Environmental Data (national and international data policies and services); Committee on Earth Resources (national energy and mineral resource issues); and Mapping Science Committee (spatial data handling and analysis issues).

Additional *ad hoc* committees and panels are formed to address topics that fall outside the purview of these committees. Current *ad hoc* activities include: "Seeing" into the Earth—Non-Invasive Characterization of the Shallow Subsurface for Environmental and Engineering Applications; Rediscovering Geography; and Research Programs of the U.S. Bureau of Mines.

Results: The Committee on Seismology issued two preliminary reports to assist U.S. negotiations in Geneva related to the comprehensive nuclear test ban treaty. The first is "Data Characteristics of Seismic Instrumentation Proposed for the International Seismological Monitoring System" (July 1994), and the second is "Data Access Issues for the Comprehensive Test Ban Treaty International Seismological Monitoring System" (December 1994). These reports are components of a larger study, "Seismological Research Requirements for a Comprehensive Test Ban Monitoring System," that will advise the Advanced Research Projects Agency. The committee also issued a letter report, "Technical Information Related to Seismic Monitoring" (June 1994), in response to a request from Congress. The committee is preparing two additional reports. One will review the opportunities and challenges for high-performance computing in seismology the other will review probabilistic earthquake-hazard estimates at nuclear power plant sites.

The U.S. Geodynamics Committee has established a panel to assess multidisciplinary research opportunities on the origin and evolution of sedimentary basins. This research will lead to a better understanding of important but poorly understood geodynamic processes such as sea level change, crustal uplift, and mantle convection, and it will improve the ability to predict the distribution and extent of hydrocarbon, water, and certain mineral resources. In the near future, the committee will establish a panel to assess the usefulness of secular gravity data to address dynamic Earth problems associated with geodynamics, natural hazards, and global change. At the request of the committee, a special session on Tectonics and Climate was held at the American Geophysical Union meeting in the spring of 1995. The committee has broadened its scope to include responsibilities of the Geodesy Committee, which has concluded its activities. The final reports of the Geodesy Committee are "Forum on NOAA's National Spatial Reference System" (1994), and "Airborne Geophysics and Precise Positioning: Scientific Issues and Future Directions" (May 1995).

The Committee on Geophysical and Environmental Data published a report, "On the Full and Open Exchange of Scientific Data" (March 1995). This fast-track report advised the United States to take all necessary actions to foster the principle of full and open exchange of scientific data in light of a proposal before the World Meteorological Organization Congress to impose restrictions on the exchange of data. The committee also published "Data Forum: A Review of an Implementation Plan for US. Global Change Data and Information" (1994), and "1993 Review of the World Data Center-A for Meteorology and the National Climatic Data Center" (1994). The committee is planning another forum to review the Global Change Data and Information System. In addition, two panels are being established under the aegis of the committee. The first will review the World Data Center-A for Glaciology/National Snow and Ice Data Center, and the second will set priorities for data needed to better understand sources and sinks of greenhouse gases. Finally, the committee is meeting to discuss data centers in the Internet era and the rise of virtual archives.

The Committee on Earth Resources is preparing a report based on the results of a workshop on the Implications of Sustainability and Sustainable Development for Mineral Resources. The committee has under consideration a study to investigate constraints on the availability of aggregate resources, and a study to evaluate the U.S. Geological Survey's Mineral Resource Surveys Program plan. At the request of the Office of Fossil Energy of the Department of Energy, the committee established an *ad hoc* panel to review the effectiveness of DOE's Reservoir Field Class Demonstration Program and to recommend improvements. The panel issued an interim report in less than four months, and a final report is in preparation.

The Mapping Science Committee is developing a number of short reports to help implement a more robust National Spatial Data Infrastructure (NSDI). The first two reports are "Promoting the NSDI Through Partnerships" (December 1994) and "A Data Foundation for the NSDI" (March 1995). In conjunction with the NRC's Marine Board, the committee also published "Charting a Course Into the Digital Era—Guidance for NOAA's Nautical Charting Mission." The committee is planning a forum to develop a vision for the NSDI in 2010–2015.

The Geophysics Study Committee has completed its activities with the publication of "Material Fluxes on the Surface of the Earth" (October 1994), and "Effects of Global Change on Life" (February 1995). Published as the final two volumes of the series *Studies in Geophysics*, these reports should serve as focal points for the organization of scientific activities in their respective multidisciplinary areas.

Other reports recently published by the Board on Earth Sciences and Resources include "Research Programs of the U.S. Bureau of Mines—First Assessment" (1994), and "Drilling and Excavation Technologies for the Future" (1994).

GRANTEE: **UNIVERSITY OF NEW MEXICO**
Department of Earth and Planetary Sciences
Albuquerque, New Mexico 87131-1116

GRANT: **DE-FG03-95ER14540**

TITLE: **The Crystal Chemistry and Structural Analysis of Uranium Oxide Hydrates**

PERSONS IN CHARGE: **Mark L. Miller** (505-277-9447; Fax 505-277-8843;
E-mail mlm@unm.edu) and **Rodney C. Ewing** (505-277-4163;
Fax 505-277-0090; E-mail rewing@unm.edu)

Objectives: To determine the crystal-chemical and crystal structural systematics of the corrosion products of uraninite and UO_2. These are commonly identified actinide phases in oxidizing environments, e.g., the corrosion of spent nuclear fuel.

Project Description: All known uranyl oxides are sheet structures, with the uranium occurring in a nearly hexagonal array within a sheet. The nearly linear uranyl groups are oriented approximately perpendicular to the sheet oxygens and hydroxyls which coordinate the uraniums.

The first phase of this project is the determination of the crystal structure of undetermined UOH phases and the development of a systematic quantitative description of the UOH phases. The structural descriptions will be used to create a crystal-structure-based (topologic) classification scheme for this group of structurally similar materials and to create a structural model for the estimation of thermodynamic quantities.

Results: In the first two months of this project, we have created a simple method of constructing all known UOH sheet topologies from three structural building blocks or "chains." The first of these structural units is a "chain" of alternating 5-coordinate uranyl groups and triangular vacancy sites. This unit is referred to as an "arrowhead" chain. The arrowhead chain occurs in all known UOH sheets, and it occurs with two senses, ñ, an upward-pointing chain (Fig. 1a) and ò, the downward-pointing equivalent chain (Fig. 1b). The second structural unit, the P chain, is a zigzag chain of 5-coordinate uranyl groups. The P chain is always flanked by arrowhead chains of the same sense, as shown in Fig. 1c. The final structural unit is a discontinuous "chain" of 4-coordinate uranyl groups. This "chain" is produced from ñò pair by shifting the individual arrowhead chains in the direction to which they "point" and away from the chain of opposite sense. This "rhombic shift" is diagrammed in Figs. 1d and e.

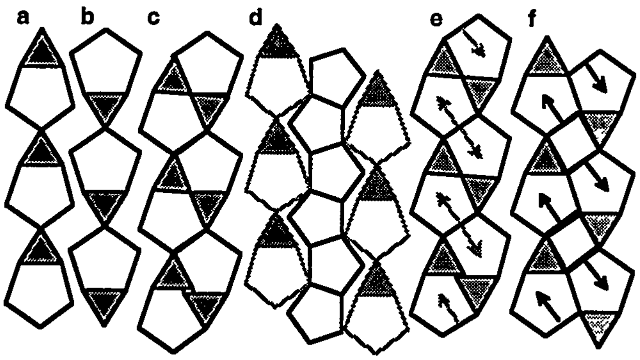

Fig 1. Structural units found in uranium oxide sheets:
(a) ñ, an upward-pointing arrowhead chain;
(b) ò, a downward-pointing arrowhead chain;
(c) an ñò pair showing "bow tie" vacancies;
(d) a P chain flanked by two ñ chains;
(e) the ñò pair in (c) prior to the application of the "rhombic shift";
(f) after shifting, the ñò pair becomes an ñ¯ò series which contains the discontinuous chain of 4-coordinate uranyl sites, indicated by the symbol ¯.

GRANTEE: **THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK**

Benjamin Levich Institute and Department of Physics
New York, New York 10031

GRANT: **DE-FG02-93-ER14327**

TITLE: **Stochastic Transport in Heterogeneous Flows and Media**

PERSON IN CHARGE: **Joel Koplik** (212-650-8162; Fax 212-650-6835;
E-mail koplik@sci.ccny.cuny.edu)

Objectives: We will obtain a description of the transport of passive tracer in flow through porous media with highly correlated strong disorder, relating measurable tracer characteristics to the geometry and statistical description of the reservoir.

Project Description: This research will seek a better understanding of fundamental physical laws that govern stochastic transport processes in heterogeneous media with macroscopically correlated disorder. For composites with "block" disorder, conventional macroscopic transport equations generally do not apply, and we will attempt to formulate the appropriate composition laws that permit a macroscopic description of transport in such systems. The superdiffusive motion of Brownian particles in a randomly stratified flow field will then be investigated. Steady-state and first-passage characteristics of this system appear to be controlled by exceptional fluctuations, leading to a multiplicity of basic time scales in the system. We plan theoretical and numerical studies to determine the appropriate macroscopic description. We will also explore the unusual transport properties of Brownian particles which are driven by prototypical random flow fields. Finally, we propose to examine the first-passage characteristics in source-sink flow, where the interplay between spatially varying convection and molecular diffusion is anticipated to yield unusual first-passage properties. We will extend these studies to fractured media, where fast transport in fractures competes in a subtle way with slow transport modes. These latter studies will be closely tied to ongoing experimental work.

Results: On source-sink flows, we are in the midst of extending our results for the (2-D) planar reservoir case to fully three-dimensional systems. For statistically homogeneous and isotropic systems, it appears that all of the features of the transit time distribution found in 2-D have direct 3-D counterparts. In particular, there is a regime of power-law decay temporal with an exponent determined by the multipole order of the distribution of sources and sinks, exponential regimes whose decay constant can be calculated from the flow field near stagnation points, and shoulders due to diffusive rebounding of tracer from the system boundaries. The effects of explicit heterogeneities and fractures are being studied now.

For stratified flow, we first examined in detail the first-passage characteristics of a two-layer system with adsorbing boundaries orthogonal to the flow direction, based on a lattice-generating function formalism. The first-passage probability distribution decays exponentially in time, with a decay constant that crosses over from quadratic in system length in the diffusive limit to linear in the convective limit. In semi-infinite systems the behavior is rather different, however, and long-time power-law tails are present in the first-passage probability. For a two-layer half-space problem with a single adsorbing boundary, as well as the infinitely layered case, extrapolation of exact enumeration results on finite systems and scaling arguments give a $t^{-5/4}$ decay law. In addition, we have obtained bounds on the first-passage probability using path-integral variational techniques, consistent with the results above.

GRANTEE: **STATE UNIVERSITY OF NEW YORK AT STONY BROOK**
Department of Applied Mathematics and Statistics
Stony Brook, New York 11794-3600

GRANT: **DE-FG02-92ER14261**

TITLE: **Three-Dimensional Imaging of Drill Core Samples using Synchrotron Computed Microtomography**

PERSON IN CHARGE: **W. B. Lindquist** (516-632-8361; Fax 516-632-8491;
E-mail lindquis@ams.sunysb.edu)

Objectives: The goal of this work is to investigate the utility of medial surface and medial axis transforms in characterizing the geometry of void and grain microstructure from three-dimensional microtomographic images of rock.

Project Description: High-resolution (1 to 5 micron), computed-microtomographic, 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 either medial surface (co-dimension one) or medial axis(co-dimension two) representations of the void (or grain) structure. The geometric properties of the medial surface/axis are then investigated statistically to develop predictive stochastic distributions characteristic of real, three-dimensional porous media geometry.

Results: During the past year, medial surface transforms for three samples—Berea sandstone, Danish chalk, and pack glass beads—have been completed. Distributions for the "erosion-layer volumes," the distribution of volumes of disconnected void spaces, and the geometric tortuosity of the medial surface have been obtained. The erosion-layer results suggest a one-parameter family of distribution functions that characterize the void structure in a large class of real rock types. The connectivity results suggest that the medial surface volumes associated with the smallest disconnected void spaces are distributed via a power-law relation with possible universal behavior. Finally, the tortuosity of shortest medial surface paths between parallel planes for the geological samples appears well described by a three-parameter gamma distribution. Currently, medial axis transform capabilities are being added.

GRANTEE: **STATE UNIVERSITY OF NEW YORK AT STONY BROOK**
Department of Earth and Space Sciences
Stony Brook, New York 11794-2100

GRANT: **DE-FG0294-ER14455**

TITLE: **Micromechanics of Failure in Brittle Geomaterials**

PERSONS IN CHARGE: **Teng-fong Wong** (516-632-8212; Fax 516-632-8240;
E-mail wong@seism1.ess.sunysb.edu) and
Joanne T. Fredrich (Sandia National Laboratories)

Objectives: The objectives of this project are 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 reservoir engineering, 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 compression and extension 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 processes 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) A technique for determining the three-dimensional pore structure was developed. Laser scanning confocal microscopy can be used to resolve sub-micron optical sections and the digital 2-D images can be analyzed using image analysis software to create 3-D reconstructions. As an application to analysis of transport properties, a quartz sandstone with a variable porosity which results from differing degrees of cementation during diagenesis was imaged; the reconstructions suggest that permeability evolution with porosity reduction is dramatically affected by a loss in connectivity with increasing cementation. Another application is the study of brittle failure processes, where the reconstructions reveal the complex pore geometry and micromechanical processes associated with increasing deviatoric compressive stresses. A paper describing this work appeared in *Science.* (2) Completion of triaxial compression experiments on five sandstones (with porosities ranging from 11% to 35%) and detailed characterization of the failure envelopes in both the brittle fracture and cataclastic flow regimes. The failure stresses have respectively positive and negative dependencies on effective pressure in the two different regimes. The yield stress in the cataclastic flow regime decreases with increasing porosity and grain size. A micromechanical model (incorporating the effects of normal loading and shear slip on the stress field and fracture mechanics of Hertzian contacts) captures the key attributes of the experimental observations. (3) Quantitative characterization of the damage accumulated in a porous sandstone in the brittle fracture and cataclastic flow regimes. (4) The microstructural observations underscore that cementation exerts significant control on brittle failure. The finite-element code ABACUS was used to analyze the stress field in the vicinity of triple junction (among the solid grain, cement, and pore space). Motivated by the microstructural observations and finite-element simulations, a model was developed to analyze how the presence of cement would inhibit the development of tensile stress concentration and microcracking.

GRANTEE: **RESEARCH FOUNDATION OF THE STATE UNIVERSITY OF NEW YORK**

(for and in conjunction with the State University of New York at Stony Brook)
Office of Research Services
Stony Brook, New York 11794-3366

GRANT: **DE-FG02-94ER14449**

TITLE: **High-Precision Radiometric Dating of Sedimentary Materials**

PERSONS IN CHARGE: **G. N. Hanson** (515-632-8210; Fax 516-632-8240;
E-mail ghanson@ccmail.sunysb.edu) and **W. J. Meyers**

Objectives: To develop field, petrographic, and geochemical criteria to allow high-precision U–Pb dating of calcretes or caliches enriched in uranium at paleo-exposure surfaces within rapidly deposited sequences of carbonate and clastic rocks

Project Description: The ultimate goal is to obtain radiometric ages with uncertainties of three million years or less for times of sedimentation. Such uncertainties would be much less than those for most epoch or period boundaries within the Paleozoic or early Mesozoic. U-enriched caliches will be selected from soils developed in rapidly deposited sequences. It is essential that the duration of soil development be less than the analytical uncertainties. We have begun our studies on caliches in the Mesozoic rocks of the Hartford Basin, Connecticut, and the upper Paleozoic rocks of the Sacramento Mountains, New Mexico. These studies should also lead to a better understanding of the geochemistry of paleosols, including the processes responsible for U-enrichment. They should also provide additional criteria for recognizing erosion surfaces.

Results: Studies during the last year have concentrated on resolving two major problems. One is recognizing pedogenic calcite from later calcite. The other is to develop analytical techniques that will allow the analysis of milligram-size samples of calcite with hundreds of ppb Pb and 1–10 ppm U. Petrographic and geochemical studies of caliche from the Hartford Basin show that there are at least three generations of calcite. The first, or earliest, generation is micritic. The second is blocky. Both have dull to dark cathodoluminescence and are associated with root related fabrics. The third generation is blocky calcite with bright cathodoluminescence. The first two generations have negative C and O isotope signatures consistent with development in a soil profile. The third generation is more likely burial or groundwater calcite. Fission track studies reveal that the first two generations have significantly higher U contents than the third. A number of approaches for the separation of U and Pb from calcite have been evaluated for recovery and element interference. Analytical data for 50-mg-size samples of soil calcite show that high-precision $^{238}U/^{206}Pb$ isochron ages consistent with their geologic age can be achieved.

GRANTEE: **NORTHWESTERN UNIVERSITY**
Department of Civil Engineering
Evanston, Illinois 60208-3109

GRANT: **DE-FG02-93ER14344**

TITLE: **Shear Strain Localization and Fracture Evolution in Rocks**

PERSON IN CHARGE: **J. W. Rudnicki** (708-491-3411; Fax 708-491-4011;
E-mail jwrudn@nwu.edu)

Objectives: To obtain an improved understanding of the occurrence, development, and evolution of zones of shear localization (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 is important. This project examines the applicability of a theory of localization that describes faulting as an instability of the constitutive description of homogeneous deformation. Because the predictions depend strongly on the constitutive parameters governing abrupt changes in the pattern of deformation, theoretical work is being done to develop a more realistic and elaborate constitutive model based on the growth and interaction of microcracks and resulting increase in overall compliance of the solid. This constitutive relation is calibrated by comparison with axisymmetric compression tests and then used to predict the response in more complex experiments (compression–torsion) with abrupt changes in the pattern of loading. Comparison of numerical studies with experiments addresses the effects of realistic geometries and boundary conditions.

Results: Abrupt changes in the pattern of deformation, such as occur in localization and in the combined compression-versus-torsion tests, cause unloading of open cracks in some orientations. Consequently, recent work (Jeyakumaran and Rudnicki, *GRL*, 1995) has examined in detail the unloading response predicted by a model in which opening and extension of tensile wing cracks is driven by sliding on an oblique crack with Coulomb friction. In contrast to previous analyses, the portions of the crack system that are open or closed and slipping or stuck are determined as part of the solution. Immediately upon unloading, the central portion of the planar crack is locked but there is closure of the open portions of the crack, causing a decrease in inelastic volume strain as observed in laboratory experiments. Reverse slip begins near the open portion of the crack and spreads toward the center. The rate of decrease of inelastic volume strain with axial stress remains small, causing an apparent "dead band" until the axial stress is sufficiently reduced to cause reverse slip on the entire crack. This apparent "dead band" is small because opening reduces the compressive normal stress on the planar crack. These calculations demonstrate that the behavior of this model is consistent with measurements of inelastic volume strain and acoustic velocity on laboratory rock specimens. This behavior is approximated in a phenomenological damage model by allowing cracks to close at fixed length upon initial unloading and then to decrease length linearly with the local stress intensity factor.

GRANTEE: **UNIVERSITY OF NOTRE DAME**
Department of Civil Engineering and Geological Sciences
Notre Dame, Indiana 46556-0767

GRANT: **DE-F602-93ER14391**

TITLE: **Energy Partitioning of Seismic Waves in Fractured Rocks**

PERSON IN CHARGE: **Laura J. Pyrak-Nolte** (219-631-8377; Fax 219-631-9236;
E-mail Pyrak-Nolte@nd.edu)

Objectives: The primary objectives of the proposed research are to investigate through numerical and laboratory investigations: (1) the partitioning of seismic energy between body waves, guided waves, and scattered waves produced by sources of finite size that are transmitted, reflected, and channeled along single and multiple fractures; (2) techniques for exciting these waves; (3) the effect of spatial variations in the mechanical properties along the fracture on seismic wave propagation; and (4) the effects of a finite fracture on seismic waves.

Project Description: Rock masses contain fractures and discontinuities on all length scales that affect the mechanical stability of a rock mass and the flow of fluids through a rock mass. A goal of site characterization for waste isolation or mineral exploration is to detect and characterize the hydraulic and mechanical properties of fractures using seismic techniques. Seismic data are often difficult to interpret because of wave conversions that occur at interfaces. Converted wave modes can arise when seismic waves are propagated through a fractured rock mass and these waves inhibit direct interpretation of the received signals. Because the existence of interface waves has not previously been taken into account in seismic data interpretation, it is important to understand how non-welded interfaces, such as fractures and joints, give rise to interface waves. In this research project, the partitioning of seismic wave energy into body waves and interface waves caused by fractures (non-welded contacts) is studied through laboratory experiments and numerical analysis.

Results: The specific results for the second year of this project include: (1) polarization-dependent precursors to failure before and during induced fracturing in rock were observed; (2) wavelet analysis was used to determine the dispersion of interface waves from which the stiffness of the fracture can be obtained; (3) compressional waves propagated along the fracture showed spectral shifts as stress on the fractures was changed. Through the analysis of energy partitioning, group velocity, and phase velocity, the growth of a fracture can be monitored using the observed precursors to failures, such as the shift in compressional wave energy to higher frequencies as the fracture is forming, or incipient interface waves that appear as a spectral shift of the shear-wave energy components to lower frequencies and lower velocities as the fracture is forming.

In the laboratory, interface waves have been generated by straddling the fracture with seismic transducers, which may not be possible in the field. Currently, a study of off-fracture generation and off-fracture receipt of interface waves is under investigation. Preliminary analysis indicates that interface waves can be generated from shear waves incident at the critical angle for shear-wave to compressional-wave conversion.

GRANTEE:	**OHIO STATE UNIVERSITY** Department of Industrial Welding and Systems Engineering Columbus, Ohio 43210
GRANT:	**DE-FG-0213749.A000**
TITLE:	**Investigation of Ultrasonic Wave Interactions With Fluid-Saturated Porous Rocks**
PERSONS IN CHARGE:	**L. Adler** (614-292-1974; Fax 614-292-1266, E-mail ladler@magnus.acs.ohio-state.edu) and **P. B. Nagy** (513-556-3353; Fax 513-556-5038, E-mail pnagy@uceng.uc.edu)

Objectives: The main objective of this research is the investigation of ultrasonic wave propagation in fluid-saturated porous materials. Our goal is to adapt the recently introduced surface and bulk inspection methods to characterization of the microscopic and macroscopic features of highly permeable (above 100 mD) porous rocks. This research should find applications in geophysical evaluation of fluid-bearing rocks, where parameters such as porosity, permeability, tortuosity, shape factor, inhomogeneity, saturation level, and internal impurity are difficult to measure by conventional techniques using low-frequency acoustic and other methods.

Project Description: In this research project, we have continued our investigation of ultrasonic wave propagation in fluid-filled porous materials. Our research effort was focused on two recently developed acoustic methods which are uniquely sensitive to the permeable nature of porous media. First, we continued to pursue our investigation of the slow surface mode and other experimental methods to characterize the pore structure via the stiffness of the capillary membrane produced by interfacial tension on the surface of a fluid-saturated rock. Second, we further developed our airborne slow wave technique towards the ultimate goal of ultrasonic evaluation of inhomogeneous pore structures in reservoir rocks.

Results: Our efforts are directed at two major areas of interest, namely pore structure characterization from the stiffness of capillary membranes and ultrasonic evaluation of inhomogeneous pore structures by slow wave imaging.

The surface stiffness of a fluid-saturated porous solid is defined as the ratio between a small change in capillary pressure and the average displacement of the boundary due to the resulting rise or fall of the fluid level in the pore channels. When the surface pores are structurally open, the surface stiffness is entirely due to the stiffness of the microscopic fluid membranes extended by capillary forces over the surface pores. Due to interfacial tension between the immiscible wetting fluid in the pores and the non-wetting fluid (air) above the surface, essentially closed-pore boundary conditions can prevail at the interface. Previously, we showed that the surface stiffness of a porous material containing cylindrical pores can be calculated simply as the surface tension of the saturating fluid divided by the static permeability of the porous solid. More recently, we proved that the same simple relationship can be generalized for the surface stiffness of fluid-saturated porous media containing parallel prismatic pore channels of any number, size, or shape. An immediate benefit of this result is the convenience of directly calculating the surface stiffness of fluid-saturated porous solids containing parallel prismatic pore channels from the static permeability, which is well known for a large number of geometries. Similar relationships for other regular formations, such as ordered spherical beads, are much more difficult to obtain. As the pore shape becomes more irregular in the axial direction the permeability is determined by the smallest cross-sections causing viscous friction while the surface stiffness depends more on the largest dimensions dominating the compliance of the surface membranes. Our experimental results indicate that the shape factor, which is calculated from the measured surface stiffness and static permeability, appears to be independent of pore size for self-similar specimens over more than one order of magnitude and it becomes less than one as the pore structure becomes more irregular and random. In light of our new analytical results, the decreasing shape factor is mainly caused by the axial irregularity of the pore channel, i.e., its changing cross section, rather than by its lateral irregularity, i.e., the particular shape of the cross section.

The propagation of slow compressional waves in air-saturated permeable solids was earlier studied by experimental means between 10 kHz and 500 kHz. Based on this method, a high-resolution slow wave imaging system was developed to study the inhomogeneous pore structure in permeable formations. Currently, the threshold sensitivity of our system is approximately 100 mD, making possible the characterization of typical petroleum reservoir rocks with spatial resolution of between 0.5 and 5 mm in the 50 kHz to 500 kHz frequency range. The degree of disorder in permeable solids is of crucial importance especially when the relative permeability is considered. It is expected that the slow wave imaging technique can complement such methods as laser scanning confocal microscopy and other high-resolution petrography for characterizing flow in porous rocks.

There are two major areas where the slow wave imaging technique requires further improvements. First, at the high inspection frequencies required to achieve desirable resolutions, acoustic scattering superimposes on and partially overshadows the viscous losses we would like to map. Second, because of the extremely high attenuation of the slow wave in natural rocks, we have to use very thin slices of 1–2 mm in thickness, that are not only fragile but also represent only a couple of grains instead of the optimum thickness of 10–20 times the average grain size. We have recently found that controlling the air pressure can solve, or at least significantly mitigate, both problems. Changing the pressure can be used to separate viscous losses from scattering ones since the sound velocity (which determines the scattering phenomenon) is independent of pressure while the kinematic viscosity (which determines the viscous losses) is inversely proportional to pressure. Because of this, slow wave images taken at different pressures but at the same frequency can be subtracted to obtain an image free of scattering interference. In addition, we can reduce the viscous losses so that imaging in thicker plates and less permeable materials can be achieved. When we place the imaging probe with the specimen in a pressure vessel kept at approximately 20 atm, viscous losses decrease by a factor of 4.5, producing a given attenuation in specimens of 20 times lower permeability or 4.5 times larger thickness, whichever is more needed to expand the feasibility of the method in a practical situation. It is expected that lowering the measuring range to 10 mD would be quite sufficient to expand the field of application of acoustic imaging for rocks of great practical importance and economic interest.

GRANTEE:	**UNIVERSITY OF OKLAHOMA** School of Geology and Geophysics Norman, Oklahoma 73019
GRANT:	**DE-FG05-913414209**
TITLE:	**A Study of Hydrocarbon Migration Events: Development and Application of New Methods for Constraining the Time of Migration and an Assessment of Rock–Fluid Interactions**
PERSONS IN CHARGE:	**R. D. Elmore** (405-325-3253; Fax 405-325-3140; E-mail delmore@geoadm.gcn.uoknor.edu) and **M. H. Engel**

Objectives: The objective of the research is to test and refine a paleomagnetic method for dating hydrocarbon migration and maturation of organic matter. The specific objectives include field tests of the dating method and laboratory simulation experiments to better constrain the mechanisms for the precipitation of authigenic magnetite under a variety of geologic conditions.

Project Description: Investigations of fluid migration are commonly hindered by a lack of temporal control. There is little doubt that the ability to constrain the time of oil migration would be of significant benefit for exploration. The paleomagnetic dating method is based on a genetic connection between hydrocarbons/organic matter and 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 tests of the method and laboratory simulation studies to constrain appropriate chemical and physical conditions for magnetite authigenesis.

Results: Along the southern margin of the Bristol Channel Basin, southwest England, a fault zone in Jurassic, organic-rich limestones was a major conduit for fluids. Migration of aqueous fluids as well as hydrocarbons through the fault zone is indicated by extensive calcite veins, some of which contain hydrocarbons. Paleomagnetic studies of hydrocarbon-bearing veins and nearby folded limestones indicate a chemical remanent magnetization (CRM) residing in magnetite that was acquired during deformation. A pole position suggests an early-middle Cretaceous age for development of folds and the veining. Geochemical studies indicate that radiogenic fluids precipitated the veins and also extensively altered the Jurassic limestones. Isotopic ($^{87}Sr/^{86}Sr$, $^{13}C/^{12}C$, $^{18}O/^{16}O$) as well as petrographic results demonstrate that the fluids were not confined exclusively to the major fault and fracture planes, and that microfractures provided important pathways for migration of the basinal fluids. Calcite veins impregnated with hydrocarbons in the Devonian Old Red Sandstone in Scotland contain a late Paleozoic CRM in magnetite. Non-degraded hydrocarbons in the calcite were generated from lacustrine, organic-rich lithologies in the Middle Old Red Sandstone. The CRM dates the time of oil migration and associated diagenesis in the calcite veins. The organic-rich lacustrine carbonates also contain a late Paleozoic CRM in magnetite that is related to *in situ* diagenesis (e.g., maturation) of organic matter in the unit.

The Belden Formation (Morrowan–Atokan) is an organic-rich limestone unit deposited in the Central Colorado Trough during the uplift of the Ancestral Rockies. Dark limestone samples contain a CRM that resides in magnetite that has partially replaced authigenic pyrite. The CRM is synfolding or prefolding and the time of remanence acquisition varies from Late Paleozoic to Cretaceous, depending on the sample locality. The age of the CRM acquisition is in agreement with the modeled time that the rocks entered the oil generation window. This suggests a chemical remagnetization mechanism related to diagenesis of organic matter. The geochemistry of late stage diagenetic replacement of pyrite by magnetite was investigated by laboratory experiments of pyrite dissolution and magnetite precipitation involving organically complexed ferric iron. The design of the experiments is based on the hypothesized geochemical conditions for *in situ* diagenesis in the Belden Formation. Aqueous solutions of ferric-ligand complexes and pyrite were heated (60°C) for 60 days in the absence of light and oxygen. Additional experiments with each ligand were performed both in the presence of bentonite and without ferric iron (ligand only). Raising the pH to ≥8.5 produced a green rust precipitate, and subsequent heating (90°C) resulted in the formation of magnetite. Ferric complexes of oxalate, salicylate, and acetylacetonate resulted in pyrite dissolution and magnetite formation. The activity of strongly reducing ligands (e.g., catechol) or unsaturated Fe(III)-exchange capacity (particularly in experiments with bentonite or with solutions of uncomplexed ligands) can result in an effective reduction of ferric iron concentration and prevent pyrite dissolution and/or the conversion of green rust to magnetite. The bentonite acted to adsorb dissolved species and also underwent direct dissolution, especially by the oxalate ligands. Although these reactions could occur at any depth, a continuing supply of molecular oxygen (more available in near surface settings) would result in the formation of hematite or the production of acidic sulfate conditions, whereas at greater depths (or restricted porosity) the redox gradation is halted at magnetite. The results of this study provide a likely geochemical mechanism for the replacement of pyrite by magnetite during the latter stages of diagenesis.

GRANTEE:	**OREGON STATE UNIVERSITY** College of Oceanic and Atmospheric Sciences Corvallis, Oregon 97331
GRANT:	**DE-FG06-92ER14277**
TITLE:	**Multi-Station Magnetotellurics**
PERSONS IN CHARGE:	**Gary D. Egbert** (503-737-2947; Fax 503-737-2064; E-mail egbert@oce.orst.edu) and **H. Frank Morrison** (University of California at Berkeley)

Objectives: The principal objective of this project is to develop and test new methods for collecting and processing remote reference magnetotelluric data in areas with significant cultural noise, with special emphasis on the "dead band" (approximately 0.1–10.0 Hz), where signal levels are low and noise levels are high.

Project Description: The project has three aspects: (1) In the first year, data were collected in a series of three-station MT arrays which span conditions from very noisy (just south of San Jose, CA) to very remote sites. Our emphasis was on collecting a large volume of dead-band data at a small number of sites. Multiple remote sites at varying distances, and in various combinations of noisy and quiet, were included to allow us to characterize spatial and temporal properties of signal and noise, and to test different approaches to remote reference data acquisition. (2) New approaches to remote reference data processing are being developed. We are adapting multivariate and robust statistical methods to the special problems of MT data processing in the dead band. (3) Using the multi-station MT (MSMT) data from our experiment, and other compilations of remote reference MT data, we are testing and comparing various strategies for collecting and processing remote reference MT data.

Results: Over the past year we have completed development of a prototype magnetotelluric "array" data processing package. This program (MULTMT) uses all simultaneously recorded data channels for computation of robust MT impedance estimates. MULTMT has been tested on a range of data sets, including wide-band MT data contaminated by severe cultural noise(the MSMT data, plus a series of two-station remote reference arrays south of the San Francisco Bay area), two continuous electric field (EMAP) profiles across the San Andreas fault (one with, and one without a reference site), and a series of 5–10-station long-period MT arrays.

In difficult circumstances (e.g., low signal in the dead band from 0.1–10 Hz; cultural noise) we have found that the multivariate approach offers significant advantages: signal-to-noise ratios are optimized by using all channels to define the signal, unusually noisy data segments ("outliers") in all data channels are easily cleaned up in an automatic fashion, and statistics diagnostic of coherent noise complications are available. For at least some sites in all of the test surveys we have achieved significant improvements in apparent resistivity and phase estimates with MULTMT, compared with those obtained with a more standard robust remote reference method.

GRANTEE:	**PRINCETON UNIVERSITY** Department of Geological and Geophysical Sciences Princeton, New Jersey 08544
GRANT:	**DE-FG02-85ER13437**
TITLE:	**Thermodynamics of Minerals Stable Near the Earth's Surface**
PERSON IN CHARGE:	**A. Navrotsky** (609-258-4674; Fax 609-258-1274; E-mail alex@weasel.princeton.edu)

Objectives: The goals of the project are to increase both the data base 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 minerals 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, and carbonate solid solutions are also studied.

Results: The energetics of nonstoichiometric (Ca-rich) dolomites has been published. The enthalpy of formation rises very steeply with excess Ca, from values of near –10 kJ/mol for $Ca/(Ca + Mg) = 0.50$ to zero or slightly positive values for $Ca/(Ca + Mg) = 0.57$. $(Fe,Mg)CO_3$ solid solutions show small positive heats of mixing and calorimetric study of $(Fe,Mg)\,Ca(CO_3)_2$ shows clearly that iron substitution destabilizes the ordered structure. Liang Chai defended his Ph.D. in July 1995.

Work on a series of amphiboles has been published, allowing estimates of the energetics of substitutions along the tremolite–tschermakite join.

Calorimetry of a series of synthetic faujasite zeolites having the substitution $Si^{4+} = Al^{3+} + Na^+$ shows that this substitution has a very similar energy to the corresponding reaction in silicate glasses along the SiO_2–$NaAlO_2$ join. If this relation holds generally, we have discovered a powerful tool for predicting the energetics of framework structures. Ivan Petrovic defended his Ph.D. thesis on zeolites in July 1995.

Natural Ca-zeolites in the laumontite–leonhardite–wairakite–yugawaralite family have been studied by calorimetry by Irina Kiseleva. The calorimetric data support reversed phase equilibria. The energetics of K, Na substitution for Ca in leonhardite have been determined.

On a two-oxygen basis, dehydrated Ca- leonhardite and anhydrous Na faujasite each have enthalpies only 10–15 kJ/mol higher than a mixture of dense framework silicates (feldspar plus quartz). This is comparable to the energy difference between pure silica zeolites and quartz studied earlier and also suggests systematics which can be used to predict zeolite thermochemistry. We are starting to study the energetics of hydration and ion exchange in a more systematic manner.

Work on Fe^{3+}, Al substitution in epidotes is complete and being prepared for publication. Eugene Smelik, the postdoctoral on this project, is moving on to an industrial job.

GRANTEE: **PURDUE UNIVERSITY**
Department of Earth and Atmospheric Sciences
West Lafayette, Indiana 47907

GRANT: **DE-FG02-93ER14365**

TITLE: **Rupturing and Ground Deformation During the 28 June 1992 Landers, California, Earthquake**

PERSON IN CHARGE: **Arvid M. Johnson**

Objectives: This project has the overall objective of understanding the form and significance of surface rupture produced by earthquakes. Specific objectives are to describe fracturing and other manifestations of broad belts of ground rupture during the Landers earthquake and to mechanically analyze the structures that form along the belts.

Project Description: Studies of the surface ruptures can lead to improved understanding of fault geometry and the very nature of faulting. During the summers of 1994 and 1995 we compiled our field and aerial photo maps for publication in U.S. Geological Survey Open-File reports. The maps of the Landers earthquake area show about 10 km of rupture zones along three faults at scales of 1:400 or more detailed, including rupture belts associated with growth of a tectonic ridge along the Emerson fault zone and rupture belts along the Kickapoo and Homestead Valley fault zones, so we have completed all the maps we started in 1992. The maps show a rift-like structure where the right-lateral Kickapoo and Homestead Valley faults join, the formation of en-echelon fault zones along the Kickapoo fault and a new duplex structure and several right- and left-steps that formed on the Homestead Valley fault zone. Perhaps our most interesting new results were obtained by photogrammetric surveying in combination with land surveying of the area of Tortoise Hill ridge, along the Emerson fault zone. The surveys allow, for the first time, the determination of differential vertical and horizontal displacements over a broad area near a growing ridge within a fault zone.

Results: In 1993/94 we completed mapping of fractures in the belt of shear zones (Johnson and others, 1994) north of the Tortoise Hill ridge and where the belt bifurcates and wraps around the ridge. The ridge is a topographic eminence, dome-shaped and measuring some 0.5 km by 1.5 km. In 1995 we used photogrammetry, precision land surveying, and leveling to determine deformations at different scales in the vicinity of the rupture zones and across the ridge. A network of control points was established during the 1970s by Southern California Edison Co. as part of their study of a proposed power plant. They surveyed x–y coordinates and leveled z-coordinates of a grid of benchmarks set every 1/4 mile extending from the tilted bedrock surface SW of the ridge, across the ridge and surface rupture of the Emerson fault zone, into the alluvial valley to the NE of the ridge. Forty-six bench marks with x–y–z were set as primary control and an additional 30 wing points were set for elevation control. We used much of our SCEC grant money to hire Southern California Edison Co. to resurvey and relevel the network, by repeating the sequence of measurements made in 1976. We use photogrammetry to survey a ladder of quadrilaterals across Tortoise Hill ridge. The purpose of both types of surveying was to determine changes in angles and changes in lengths of lines so that we could compute strains.

As a result of these surveys, we can describe the recent growth of a tectonic ridge; the ridge was pushed upward along bounding shear zones on the NE and SW about 1 m as about 3 m of right-lateral shift was accommodated across the Emerson fault zone during the Landers earthquake. This is a spectacular growth of a ridge during a single earthquake event.

Furthermore, we obtained a new insight into the origin of ridges along strike-slip fault zones. Tortoise Hill ridge is along a relatively straight segment of the Emerson fault zone, so it cannot be a result of a left-step or bend on a right-lateral fault zone (or vice versa), which is the current explanation for such phenomena. We suggest that Tortoise Hill ridge, like analogous ridges that occur in landslides (Fleming and Johnson, 1989), grew as a result of localized dilation of material within a belt of shear zones along the Emerson fault zone.

GPS and triangulation studies by Hudnut and others (1994) and Freymueller and others (1994) indicate that regional deformation over areas of several square km east and west of the Landers rupture is left-lateral shearing on the order of 10^{-5}. This deformation reflects elastic rebound. Our more detailed studies, closer to the Emerson fault zone, indicate that deformations are smaller than about 3×10^{-4} to within about 100 m of the belt of shear zones that bounds Tortoise Hill ridge on the SW. Within the belts and ridge, we photogrammetrically measure right-lateral deformations up to 10^{-2}. The deformations also show dilation normal to the long axis of the ridge. This peculiar deformation is consistent with a displacement vector for a control point in the center of the ridge which indicates that differential displacement was about 0.6 m at about 45° to the bounding belts of shear zones.

Measurements of differential vertical displacement indicate that ground more than 3 to 4 km SW, away from the ridge, change altitude insignificantly. The uplift gradually increases from there to the side of the ridge where the uplift is 0.2 m, but thereafter the uplift becomes highly localized and reaches a peak of about 1 m within the ridge. The pattern is an abrupt uplift of the ridge within the bounds of the surrounding belts of shear zones. The greatest growth of the ridge of 1 m is at the crest of an elliptically shaped domical area centered on the high ground of Tortoise Hill, but 0.3 m of uplift of anticlinal form continues at least 2 km SE of the ridge to another ridge to the SE. The large valley to the NE of the ridge was depressed at least 0.3 m during the earthquake, apparently because of a right stepover between the Emerson fault zone and the nearby Camp Rock fault zone.

We have published four papers and an open-file report on the research supported by DOE. Three manuscripts are in review as U.S.G.S. Open-File reports, to be published in shortened versions in journals later, and we plan at least three more. New technology purchased largely by funds from DOE has allowed us to compile and print large-format maps for Open-File reports, so we finally have the ability to preserve the highly detailed maps that characterize our research efforts. The results of this project have already exceeded our expectations.

GRANTEE: **RENSSELAER POLYTECHNIC INSTITUTE**
Department of Earth and Environmental Sciences
Troy, New York 12180-3590

GRANT: **FGO2-95ER144532**

TITLE: **Transport Phenomena in Fluid-Bearing Rocks**

PERSON IN CHARGE: **E. B. Watson** (518-276-6474; Fax 518-276-8627;
E-mail ellen@harold.geo.rpi.edu)

Objectives: The objectives of this project are twofold: (1) to develop and implement a new technique for measuring mineral solubilities and diffusivities of dissolved mineral components in supercritical fluids at pressures up to 3 GPa and temperatures up to 1200°C; and (2) to characterize the permeability of fluid-bearing rocks under conditions of mechanical equilibrium at lower-crustal to upper-mantle P–T conditions.

Project Description: The efficacy of fluid-assisted geochemical transport at depth in the Earth is controlled by a number of factors, including the solubilities of mineral components in the fluid of interest, the mobility of the fluid through the rock medium, and the diffusion characteristics of dissolved solutes. At the P–T conditions prevailing in the mid-to lower crust and in subduction zones, few data exist to constrain the overall process of chemical transport: information concerning, for example, mineral solubilities and diffusivities and rock permeability is almost non-existent at pressures in excess of ~1 GPa. Accordingly, the Rensselaer project involves the experimental measurement of some of these key parameters.

The first stage of this project involves the development of a special capsule for use in a piston-cylinder apparatus to measure mineral solubilities and component diffusivities in aqueous solutions at extreme P–T conditions. This capsule—called a differential solubility and diffusion cell (DSD cell)—is made of solid silver (Pt and Au being too costly!) and consists of two small chambers (~0.05–0.11 cm^3) connected by a thin capillary (0.5–1 mm dia.). By careful positioning of the cell in the thermal gradient of a piston-cylinder assembly, the chambers are maintained at slightly different temperatures. At the start of an experiment, crushed grains of the mineral of interest are placed in the "hot" (top) chamber, and both chambers and the capillary are filled with water. At run conditions, the temperature difference between the two chambers leads to dissolution of the mineral grains in the hot chamber (resulting in local saturation of mineral components in the fluid), diffusion of the dissolved mineral components through the capillary, and eventual precipitation in the cold chamber. Both numerical and "real" experiments show that the governing dissolution/precipitation kinetics are very fast, and lead to quick attainment of a steady state in which dissolution in the hot chamber is exactly balanced by precipitation in the cold chamber. The rate of the overall process is governed by diffusion of dissolved components through the narrow capillary. Once the steady state is reached, the total amount of material transported from the hot to the cold chamber in a given time depends upon the solubility difference (due to the temperature difference) and the diffusivity in the fluid. By executing two experiments at similar conditions but involving different capillary parameters, it is possible, in principle, to deduce both the solubility difference and the diffusivity of dissolved components. Absolute solubilities are then determined by anchoring the solubility difference data to a known value measured by conventional means.

The rock permeability measurements (not yet undertaken) are made by synthesizing porous "rocks" in the piston-cylinder apparatus. Mineral powders are loaded into a thick-walled capsule with the desired amount of the fluid of interest (H_2O, CO_2, and mixtures thereof) and annealed at high P–T conditions to produce a near-equilibrium microstructure that includes fluid-filled pores. The porous samples are then quenched and recovered from the high-pressure apparatus, and the permeability measurements made at near-atmospheric conditions—using air or argon—on specimens having a "quenched-in" porosity. It is hoped that this technique will circumvent the difficulty of performing permeability measurements at actual run conditions.

Results: The first year of this project focused upon that aspect considered to be the most challenging technically—i.e., the development and implementation of the DSD cell. Over 40 experiments have been made to date, in which several design incarnations of the cell were tested. The successful version has been used to measure the diffusivity of SiO_2 in H_2O at ~1 GPa and 530–880°C (SiO_2 solubility measurements have also been completed; these are in good agreement with published data). The diffusion data, summarized in Fig. 1, reveal extremely rapid transport of dissolved SiO_2 in supercritical water at the conditions investigated: at the high end of the temperature range, diffusion of aqueous SiO_2 approaches the rate of thermal diffusion in rocks.

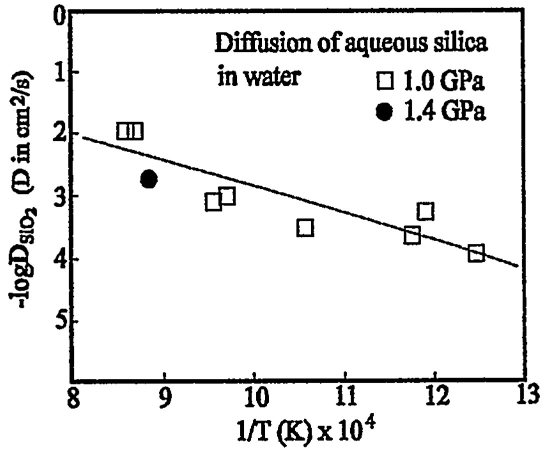

Fig. 1. Summary of measured diffusivities for dissolved SiO_2 in H_2O. Although the data are presented on an Arrhenius-type plot, it is not necessarily expected that $\log D_{SiO_2}$ be linear in 1/T. A significant pressure (H_2O density?) effect is suggested by the one result at 1.4 GPa.

GRANTEE:	**RICE UNIVERSITY** Geology and Geophysics Houston, Texas 77251-1892
GRANT:	**DE-FG05-92ER14295**
TITLE:	**Transition Metal Catalysis in the Generation of Petroleum and Natural Gas**
PERSON IN CHARGE:	**Frank D. Mango** (713-527-4880; Fax 713-258-5214)

Objective: It is proposed that the light hydrocarbons in petroleum, including natural gas, are formed catalytically through the condensation of hydrogen and n-alkenes in fine-grained carbonaceous sedimentary rocks. The transition metals are suggested as the catalytic agents. The objective of this research is to test this hypothesis and to explore the catalytic properties of transition metals under realistic geologic conditions.

Project Description: Various natural sources of transition metals including the asphaltene fraction of petroleum and source rocks are being analyzed for catalytic activity. Pure transition metal complexes, including 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 using FID detectors.

Results: A carbonaceous sedimentary rock moderately rich in transition metals has been found to be catalytically active in converting hydrogen and olefins into gas (Mango et al., *Nature* **368,** 535, 1994). The reaction proceeds under realistic earth conditions and the product is indistinguishable from natural gas in isotopic and molecular composition, marking the first time that natural gas has been generated in the laboratory. Various metal compounds in the pure state show the same levels of catalytic activity as sedimentary rocks and the products are identical. Nickel is particularly active among the early transition metals and is projected to remain catalytically robust at all stages of catagenesis. Nickel oxide promotes the formation of n-alkanes in addition to natural gas (NG), demonstrating the full scope of the hypothetical catalytic process:

$$\text{n-C}_x^{=} + H_2 \rightarrow \text{NG} + \text{n-C}_4 + \text{n-C}_5 + \ldots\ \text{n-C}_{x-1}$$

The composition of catalytic gas duplicates the entire range of natural gas, from so-called wet gas to dry gas (60 to 95+ wt% methane), 'while gas generated thermally is consistently depleted in methane (10 to 60 wt% methane). These results support the view that metal catalysis is probably a major pathway through which natural gas is formed in the earth.

GRANTEE: **STANFORD UNIVERSITY**
Department of Geological and Environmental Sciences
Stanford, California 94305-2115

GRANT: **DE-FG03-93ER14347.A000**

TITLE: **Cation Chemisorption at Oxide Surfaces and Oxide–Water Interfaces: X-Ray Spectroscopic Studies and Modeling**

PERSONS IN CHARGE: **G. E. Brown, Jr.,** and **G. A. Parks** (415-723-9168;
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Objectives: This project concerns chemical reactions between metal ions in aqueous solution and oxide surfaces representative of those found in the Earth's crust. These "sorption" reactions partition the metal between fluid and solid phases and must be understood at a molecular level to develop both quantitative understanding of the geochemistry of mineral surfaces and the macroscopic models required to predict the fate of contaminants in the environment. Our objectives are (1) to characterize sorption reactions by determining composition, molecular-scale structure, and bonding of the surface complexes produced using direct sorption measurements, synchrotron-based x-ray absorption fine structure (XAFS) spectroscopy, x-ray photoelectron spectroscopy (XPS), and UV/Vis/IR spectroscopy; (2) to investigate how these properties are affected by the solid surface and the composition of the aqueous solution; and (3) to develop molecular-level and macroscopic models of sorption processes.

Project Descriptions and Results: Three main thrusts and two supporting investigations are being investigated. The first two concern the structure of the host solid and its influence on the sorption complex(es). The third main thrust focuses on the influence of a simple organic complexing ligand on sorption of Cu(II) by oxides.

Sorption of cobalt(II) on Al_2O_3 *and* TiO_2*:* We are studying the sorption of Co(II) on Al_2O_3 and TiO_2 to resolve two issues in the sorption of cations onto oxides: (a) what specific surface site(s) (bridging or "atop" oxygen, kink sites, etc.) are involved in sorption; and (b) why large hydroxide-like clusters form at concentrations below those required for precipitation? To examine these problems, we have used XPS, powder XAFS, and single-crystal grazing-incidence XAFS spectroscopies.

To simplify characterization of sorption sites, XAFS data on Co adsorbed on several orientations of α-Al_2O_3 and TiO_2 (rutile) single crystals have been collected for comparison with similar data on powders. On both the (0001) and (01 I 2) faces of α-Al_2O_3, Co(II) adsorbs at edge-sharing tridentate sites, a local geometry similar to that of cobalt hydroxide. In contrast to samples prepared with powdered α-Al_2O_3 under the same solution conditions, polymeric complexes do not form to any significant extent. The Co(II)/TiO_2 data are still being interpreted, though preliminary inspection reveals intriguing differences among the various orientations.

Comparison of the apparent Co(II) sorption densities on powdered Al_2O_3 estimated by traditional solution concentration measurements and by XPS shows that at high uptake the sorbate forms clusters (>30Å in radius) while much of the surface is left uncovered. TEM studies have confirmed that, at all but the lowest Co(II) coverages, macroscopic precipitates (plates >100Å thick) of a material with structure similar to cobalt hydroxide have formed, in most cases under conditions where the solution was not supersaturated. Current efforts are directed toward understanding why this precipitation takes place, and towards distinguishing among various models that have been proposed for surface precipitation.

Sorption of lead(II) on Al and Fe oxides: Lead is a common and highly toxic anthropogenic contaminant of natural surface waters and aquifers. Sorption reactions of lead(II) onto Al and Fe oxides and oxyhydroxides are believed to be an important control on lead mobility in natural environments, in part due to the ubiquitous presence of these materials as reactive, high-surface-area colloids, minerals, and mineral coatings. In order to study these systems, we have collected spectra for lead(II) adsorbed on powders of Al and Fe oxide and hydroxide minerals, including γ- and α-Al_2O_3 (corundum), α-Fe_2O_3 (hematite), and α-FeOOH (goethite). α-Al_2O_3 and α-Fe_2O_3 are isostructural and allow us to probe the influence of the *chemical composition* of the oxide surface (i.e., Al vs. Fe in the substrate) on lead(II) sorption.

Collection of new data for lead sorption on γ-Al_2O_3 and α-FeOOH in the presence of Cl^-, and detailed, quantitative analysis of XAFS data in this and the corresponding chloride-free system have provided interesting insight into the role of a common complexing ligand on Pb(II) sorption. At low sorption density, in the absence of Cl^-, sorbed Pb(II) speciation is very similar on Al and Fe oxides and consists of monomeric complexes bound to the surface in a bidentate geometry, i.e., the Pb(II) coordination polyhedron shares two oxygens in an edge with the Al or Fe octahedron in the surface. Pb(II) in the surface complex is three-coordinated in a distorted trigonal pyramidal geometry, and the complex may have the composition $Pb(Al{\equiv}O)_2OH$ or $Pb(Fe{\equiv}O)_2OH$, where $Al{\equiv}O$ and $Fe{\equiv}O$ denote surface functional groups. At higher sorption density, however, surface speciation becomes highly dependent on the chemical composition of the substrate. On Al oxide surfaces, Pb(II) forms multinuclear oligomers with the proposed compositions $Pb_2(Al{\equiv}O)_3OH$ and $Pb_5(Al{\equiv}O)_6(OH)_3$. However, oligomeric species are not observed on the Fe oxides and hydroxides, indicating greater stability of monomeric complexes on the Fe (hydr)oxides than on the Al oxides. Preliminary analysis of XAFS data for Pb(II) sorbed on Al and Fe oxides in the presence of Cl^- suggests that Pb(II) adsorbs as $PbCl^+$ complexes at pH 5 and 6. But, between pH 6 and 7, the sorbed complexes appear to hydrolyze, becoming similar to the monomeric complexes observed in the absence of Cl^-.

Careful comparisons of XAFS spectra of Pb(II) and Co(II) sorbed on the (0001) and ($01\bar{1}2$) surfaces of single crystal α-Al_2O_3 have been made to help to elucidate the relative importance of the preferred coordination chemistry of the adion (e.g., coordination number, ionic radius) as a control on surface complex formation. Pb(II) has a much larger ionic radius than Co(II), tends to occur in distorted 3- to 5-coordinated polyhedra, and is a soft Lewis acid. Co(II) tends to occur in regular octahedral coordination and is a hard Lewis acid. Thus far, this study has revealed that Pb(II) adsorbs in a bidentate, inner-sphere mode on the α-Al_2O_3 ($01\bar{1}2$), but not on the (0001). In contrast, Co(II) adsorbs in inner-sphere mode on *both* orientations of α-Al_2O_3. These results can be interpreted in terms of differences in the types of binding sites available on the different crystal surfaces and lead to the tentative conclusion that only one surface site, present only on the ($01\bar{1}2$) surface, is reactive to Pb(II).

Copper(II) and 2,2'-bipyridine co-adsorption on oxide surfaces: We are interested in the co-adsorption of metal ions and organic ligands onto oxide surfaces in general and have chosen copper(II) and 2,2'-bipyridine (bipy) as the first system in our study. The study focuses on two fundamental questions: (i) how bipy affects the macroscopic uptake behavior and molecular-scale characteristics of sorption complexes formed on each oxide, and (ii) how and why uptake behavior and the characteristics of sorption complexes differ on different oxide surfaces.

Measurements of Cu and bipy uptake from solutions containing Cu and bipy at concentration ratios of 1:2 and 1:1 on amorphous silica (SiO_2), γ-Al_2O_3, and anatase (TiO_2); XAFS studies of the same systems; and infrared spectroscopic studies of the SiO_2 and γ-Al_2O_3 systems have been completed. For γ-Al_2O_3 and TiO_2, Cu sorption is inhibited by bipy, while for SiO_2 Cu sorption is enhanced. In the pH range 7–9, the molar ratio Cu:bipy in the sorption complex was found to be 1:2 on SiO_2 and 1:1 on both γ-Al_2O_3 and TiO_2 in the 1:2 aqueous solutions, and 1:1 on SiO_2 and <<1:1 on γ-Al_2O_3 in the 1:1 aqueous solutions. IR spectroscopy showed that all sorbed bipy was bound to Cu on SiO_2 and γ-Al_2O_3. Qualitatively, XAFS spectra of the γ-Al_2O_3 and TiO_2 sorption samples resemble the spectrum of the aqueous 1:1 complex, and the spectrum of the SiO_2 sorption sample resembles that of the aqueous 1:2 complex. Detailed analysis of these spectra suggests mononuclear sorption of Cu in all cases, and inner-sphere binding of Cu on γ-Al_2O_3 and TiO_2. There was no unambiguous evidence in the XAFS for or against inner-sphere binding on silica, so the mode of binding cannot yet be decided. Apparently adsorbates that inhibit Cu sorption bind copper quite differently than those that do not. On γ-Al_2O_3 and TiO_2 sorption displaces one bipy from the aqueous 1:2 complex and Cu is bound in inner-sphere mode, both observations suggesting relatively strong binding; yet, bipy inhibits sorption of Cu on these two oxides. On SiO_2 the 1:2 complex is not disrupted, suggesting weaker binding to the surface, yet in this system, bipy enhances Cu sorption. We are beginning multiple-scattering calculations to help interpret the XANES spectra, as well as EPR measurements, and diffuse reflectance UV/Vis spectroscopy in an effort to clarify this apparent discrepancy.

Molecular-scale modeling: We are continuing our efforts to constrain the geometries of metal ion surface complexes and the types of surface sites to which they bind using simple bonding concepts, including the effect of metal–oxygen bond covalences and Pauling bond valences on the redistribution of charge on surface functional groups. Using this approach, we have developed a model which correlates the log K for surface protonation and the partial charge of surface oxygens or hydroxides which is similar to other published models but with fewer assumptions. We are currently applying this model to the sorption of Pb(II) and Co(II) onto oxides and hydroxides.

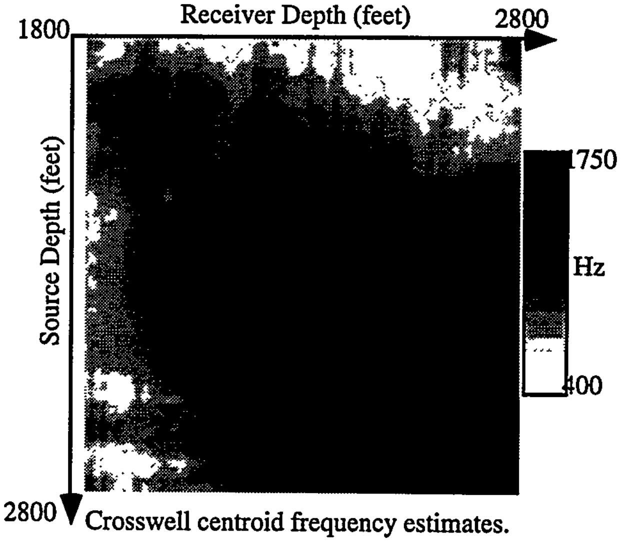
Macroscopic sorption modeling: Using a surface complexation, electrical triple layer sorption model in the chemical speciation codes HYDRAQL and FITEQL, we have found that the structural and compositional information derived from XAFS spectra are valuable constraints in selecting sorption reactions. A wide range of hypothetical sorption reactions is capable of simulating uptake data alone. In some systems, however, XAFS-derived 2nd-neighbor stoichiometry requires multinuclear surface complexes, and thus rules out strictly mononuclear models. Since models that omit multinuclear species predict significantly different concentration dependence in partitioning than do those that include them, the XAFS results are essential to robust macroscopic modeling.

GRANTEE:	**STANFORD UNIVERSITY** Geophysics Department Stanford, California 94305-2215
GRANT:	**DE-FG03-95ER14535.A000**
TITLE:	**Crosshole Seismic Attenuation Tomography and Attenuation Logging in Boreholes**
PERSON IN CHARGE:	**Jerry M. Harris** (415-723-0496; Fax 415-725-2032; E-mail harris@pangea.stanford.edu)

Objectives: The objectives of this research are to (1) develop methods for estimating attenuation from crosshole seismic and sonic log data; and (2) through the use of porous media models, apply the attenuation results, along with other data, to the interpretation of *in situ* reservoir properties, especially flow permeability.

Project Description: Attenuation imaging is possible using the frequency-shift dispersion method, where the downshift in the centroid frequency of a seismic wavelet is used as projection data in tomographic inversion. This is analogous to using travel time in velocity imaging. Frequency shift data are less sensitive to effects that severely contaminate amplitude data that might otherwise be used to estimate attenuation. If attenuation is caused by friction between pore fluids and the pore walls, then attenuation measurements offer potential of obtaining indirect and remote measurements of fluid permeability. The project incorporates forward modeling of seismic waves in viscoelastic media and Biot and BISQ poroelastic media. Methods for reliable and robust estimation of frequency-shift dispersion will be developed. Travel time tomography algorithms will be adapted to invert the frequency-shift data. And finally, the attenuation images will be interpreted, cooperatively with other data, for *in situ* permeability near and between boreholes. The project makes extensive use of synthetic modeling and real field data from the crosshole and sonic logging geometries.

Results: This project has only recently been initiated. Nevertheless, we have performed an analysis for frequency-shift dispersion in several crosshole field data sets and sonic logs. We found that the variations in the centroid frequency of kHz seismic waves correlated strongly with travel time variations and known lithologies (see crosshole example in figure), and therefore are useful for estimating *in situ* attenuation. In the example dataset shown, high centroid frequencies of more than 1700 Hz are observed through rock with lower attenuation (limestone), whereas less than 500 Hz can be observed over similar path lengths in rock with higher attenuation (e.g., shales).



Crosswell centroid frequency estimates.

GRANTEE: **STANFORD UNIVERSITY**
Geophysics Department
Stanford, California 94305-2215

GRANT: **DE-FG03-86ER13601.A004**

TITLE: **Porous Reservoir Rocks With Fluids: Acoustic and Reservoir Transport Properties**

PERSON IN CHARGE: **Amos Nur** (415-723-9526; Fax 415-723-1188;
E-mail nur@pangea.stanford.edu)

Objectives: The objectives of the research are (1) to relate seismic characteristics of hydrocarbon reservoirs and ground water aquifers to rock, soil, and pore-fluid properties; and (2) to apply the results to the design and interpretation of *in situ* seismic measurements to obtain subsurface flow description and monitoring. The research program involves laboratory measurements, theoretical modeling, and *in situ* field studies. It spans several projects.

Contact Laws for Cemented Grains

Project Description: (1) An analytical solution is obtained for contact stresses and macroscopic stress–strain laws in cemented granular media subject to large stress. The grains are elastic, the cement is elastic–plastic. (2) The solution for elastic grains and elastic cement is applied to model high-porosity weakly cemented reservoir rocks from the Oseberg field (North Sea).

Results: (1) The stress–strain laws obtained for the elastic–plastic cement case are close to the relations typically observed in clay-cemented sands. An initially isotropic aggregate becomes anisotropic (up to 10%) if the stress field is non-hydrostatic. (2) The velocities in the Oseberg samples can be accurately predicted by the cementation theory for both clean rocks (quartz cement) and rocks with clay (clay cement).

Squirt Flow in Partially Saturated Rocks

Project Description: A new analytical solution combines the pore-scale wave-induced squirt-flow mechanism and the large-scale squirt-flow mechanism (wave-induced flow between a fully saturated patch and the surrounding undersaturated rock). The solution allows for estimating frequencies at which a saturated patch becomes seismically visible.

Results: The theory is verified by earlier laboratory results. A saturated patch may be seismically undetectable at low frequencies but becomes seismically visible as the frequency increases. It is possible, by sweeping frequencies, to discriminate saturation heterogeneity from permanent lithologic heterogeneity. The technique can be applied to detecting large patches of contaminants, and undersaturated fringes above a water table.

The Effect of Fluid Distribution on Seismic Velocities

Project Description: Seismic velocities are linked to two types of liquid distribution in a partially saturated reservoir: (1) homogeneous distribution, and (2) patchy distribution. Saturation of each region in the reservoir is determined from the corresponding capillary pressure curve. At capillary equilibrium, a fully saturated patch may be located next to a partially saturated region.

Results: At capillary equilibrium, different lithologies in a reservoir have different saturations, depending on porosity and permeability. Heterogeneity in saturation has a large effect on the velocity–saturation relationship. Patchy saturation causes P-wave velocity to noticeably and almost continuously vary across the entire saturation range. The model uses lithologic information as input and can serve as a basis for inferring gas saturation from seismic. Given that the permeability distribution is a key factor in determining the saturation distribution, this may lead to a way of obtaining permeability information from the observed spatial variation in velocity data.

Frequency and Scale

Project Description: Seismic wave propagation in the earth's crust depends on the size of heterogeneous geological structures relative to wavelength. A laboratory study was conducted to investigate the impact of scale-dependent wave propagation in randomly layered media, as applied to sonic logs, surface seismic, and VSP.

Results: Neither ray nor effective medium theories can accurately predict travel time in a randomly layered medium. A simple approximate recipe is developed for predicting the scale-dependent travel times. It successively filters the medium using a running Bachus average and then uses ray theory. The recipe appears to accurately estimate the seismic arrival time in both the laboratory and the numerical experiments.

Seismic Monitoring of Oil Production

Project Description: The success of a monitoring project depends on the knowledge of compressibilities and densities of reservoir fluid mixtures at different temperatures and pressures. A laboratory setup is designed and built to acoustically measure these properties. The setup includes two reflectors and an ultrasonic transducer with double-burst train emission.

Results: Various oil–gas–brine mixtures can be placed in a small container and measured in the setup. Both temperature and pressure can span large intervals. The procedure is based on measuring acoustic velocity and reflectivity and thus is fast and reliable. Sample tests show that the precision of measuring velocity and density of a reservoir fluid exceeds 0.02 and 0.1%, respectively.

Seismic Detection of Residual Contaminants

Project Description: The key to effective characterization and treatment of contaminated sites is the ability to delineate the spread of contaminants in the shallow subsurface. Such mapping can be achieved by the methods of seismic reflection and refraction. The main factors that affect wave propagation in a contaminated region are fluid viscosity, compressibility, and density, the size of contaminated patches, and frequency. A field experiment was conducted to test the applicability of shallow seismic techniques to fluid detection.

Results: The experiment has been conducted on a sandy beach (Monterey Bay). The excursion of the water table due to tide was seismically monitored during 24 hours. The results show that standard geophones can be used to receive high-frequency signals. Partial (possibly patchy) fluid saturation was seismically visible above the water table. These results can be theoretically adjusted for contaminants whose viscosity is higher than that of water.

GRANTEE:	**STANFORD UNIVERSITY** Department of Geological and Environmental Sciences Stanford, California 94305-2115
GRANT:	**DE-FG03-93ER14366**
TITLE:	**Experimental Investigation of Kinetics and Rheology During Diagenesis**
PERSONS IN CHARGE:	**J. G. Liou** (415-723-2716; Fax 415-725-2199; E-mail liou@pangea.stanford.edu) and **B. R. Hacker** (415-725-0045; Fax 415-725-2199; E-mail hacker@pangea.stanford.edu)

Objectives: To determine the dehydration rate of laumontite and its effect on the frictional rheology of laumontite.

Project Description: Two processes of enormous economic consequence occur within the upper to middle crust: the formation, migration, entrapment, and degradation of hydrocarbons, and hazardous seismicity. Substantial scientific evidence suggests that both these processes are influenced by devolatilization reactions during diagenesis. However, surprisingly few laboratory studies have been conducted on materials actively undergoing low-grade metamorphism or diagenesis. Because of this, there exists no suitable basis for understanding the rates at which devolatilization occurs, and what effects this process has on deformation at shallow to moderate depths in the crust.

We are conducting a coordinated deformation and kinetic study of an important devolatilization reaction: the breakdown of laumontite. Laumontite is a common zeolite whose equilibrium phase relations and room-temperature frictional behavior are well understood. Besides serving as a model system for more complicated rocks, laumontite is an important mineral in its own right, particularly for hydrocarbon fields in sandstones and for fault zones in the crust. Hydrostatic experiments are being conducted to investigate (1) the kinetics and mechanism of laumontite dehydration, and triaxial deformation experiments will enable characterization of (2) the effect of differential stress on the reaction and (3) the effect of synkinematic dehydration on the mechanical behavior of rock. We anticipate results of significant import for hydrocarbon exploration and recovery and for understanding the strength and seismic potential of crustal fault zones.

Results: We have completed kinetic experiments in hydrothermal bombs on 20- and 200-µm laumontite powders at T = 350, 375, 400, and 425°C, and P_{H_2O} = 100 MPa. Reproducible, internally consistent data have been obtained for amounts of transformation ranging from 0 to 100%. At 350°C the reaction rate in the 200-µm material is intractably slow for experimentation, requiring 60 days for 50% transformation. Surprisingly, even at 425°C the 200-µm powder requires >200 hr to transform 100%.

The rate of transformation is accelerated in the 20-µm material by a factor of about 3, such that at 425°C complete reaction can be achieved in <72 hr. The activation enthalpy is approximately 150 kJ $mole^{-1}$.

We have completed nine friction experiments on laumontite powder at temperatures of 23°, 350°, and 400°C. Sliding rates have been varied between 0.01 and 1.0 µm/sec at a controlled H_2O pressure of 100 MPa and a fixed effective pressure of 100 MPa. All experiments so far are baseline measurements of the variations in laumontite friction with increasing temperature in the absence of transformation. At room temperature the strength of the laumontite gouge follows Byerlee's law, as expected, but at 350–425°C the coefficient of friction is the highest ever measured for a silicate, $\mu = 0.95 \rightarrow >1$. All samples strain harden, so the steady-state value may be higher. Pressure-stepping tests reveal that the strength is sensitive to confining pressure, suggesting that the deformation is dominantly brittle. This is confirmed by microscopic observation of the samples, which contain Riedel shears spaced 300–400 μm apart and made up of submicron-sized particles. Transmission-electron microscopy in progress is designed to reveal the deformation/transformation mechanism responsible for this unusual mechanical behavior.

GRANTEE: **STANFORD UNIVERSITY**
Department of Geological and Environmental Sciences
Stanford, California 94305-2115

GRANT: **DE-FG03-94ER14462**

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

PERSONS IN CHARGE: **D. D. Pollard** (415-723-4679; Fax 415-725-0979;
E-mail dpollard@pangea.stanford.edu) and **A. Aydin** (415-725-8708;
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Objectives: To describe and document the geometry of opening-mode fracture networks and clusters in sedimentary rock, to understand the mechanics of their development in relationship to faults and folds, and to develop a sound methodology for prediction of spatial variations of permeability in fractured aquifers and reservoirs using an integrated program of field mapping, laboratory simulation, and theoretical analysis.

Project Description: The principal elements of the project are: (1) to investigate the variations in orientation and distribution of fracture sets near normal faults and to characterize their geometric and fluid flow properties; (2) to investigate the mechanisms of fracture clustering and to construct conceptual and mechanical models for the impact of fracture clusters on the development of faults and folds in sedimentary rocks; (3) to design and carry out laboratory experiments using a brittle-coating technique to investigate the development of fracture networks in layered materials; (4) to design and carry out laboratory experiments on three-dimensional fracture propagation in blocks and rods of PMMA under mixed-mode loading to understand the relationships between loading and complex fracture geometries; and (5) to develop a computer code for predicting the connectivity and spatial density of fractures in a reservoir or aquifer using wellbore data.

Results: Field work during this period included detailed mapping of normal faults and joints at Arches National Park, Utah, in a region where fault-orthogonal joints are confined to blocks between sub-parallel normal faults. High angular relationships in map view between normal faults and joints are prominent near fault ends and at fault steps, where fault slip decreases.

At Valley of Fire State Park, Nevada, field work has documented how faults initiated from joint zones in sandstone and developed by discontinuous internal fragmentation along specific zones. Fragmentation loci apparently are related to slip on discrete fractures, echelon fault segment stepovers, intersections of existing discontinuities, and faulting-induced shear zones.

Results of fracture propagation experiments in PMMA blocks indicate how multiple fractures initiate and grow as a function of the ratio of mode I to mode III loading. A numerical code based on the boundary element method demonstrates how and where fractures cluster along layer interfaces in an elastic material. These results indicate where joints may localize near bedding-plane fault terminations within folded rock units.

Methods to predict the geometry of 2D and 3D joint networks in the subsurface from 1D borehole data on fracture orientation and spacing were developed based on the mechanics of fracture propagation and interaction. A computer code, PRED2/3D, was developed for use in petroleum and hydrogeological applications.

GRANTEE:	**STANFORD UNIVERSITY** Department of Geophysics Stanford, California 94305-2215
GRANT:	**DE-FG03-90ER14152**
TITLE:	**Induced Seismicity**
PERSON IN CHARGE:	**P. Segall** (415-725-7241; Fax 415-725-7344; E-mail segall@pangea.stanford.edu)

Objectives: The objective of this project is to develop a fundamental understanding of induced seismicity based on the mechanics of deformable porous media.

Project Description: The goal of this project is to develop a fundamental understanding of earthquakes triggered by energy development. The intent is to develop physical models that predict when seismicity is likely to occur, and to determine to what extent these earthquakes can be used to infer conditions within energy reservoirs. Early work focused on earthquakes induced by oil and gas extraction. Ongoing work has addressed earthquakes within geothermal fields, such as The Geysers in northern California, as well as the interactions of dilatancy, friction, and shear heating on the generation of earthquakes. The former has involved modeling thermo- and poro-elastic effects of geothermal production and water injection. Global Positioning System (GPS) receivers are used to measure deformation associated with geothermal activity, and these measurements along with seismic data are used to test and constrain thermo-mechanical models.

Results: Time series analysis shows that the rate of seismic activity at The Geysers is highly correlated (> 99% confidence) with both the rate of steam production, and liquid reinjection. Steam production and condensate injection are also highly correlated, so that statistical methods alone cannot discriminate between inducing mechanisms. Modeling reservoirs as ellipsoidal inclusions undergoing uniform decreases in temperature and pore-pressure allows for simple predictions of production-induced stress changes that are consistent with *in situ* hydraulic fracturing data. Estimates of average temperature decline at The Geysers, based on a reservoir-scale energy balance, demonstrate that thermo-elastic effects dominate over pore-pressure effects. Observations of surface subsidence and horizontal strain can help constrain the distribution of strains within the reservoir due to changes in temperature and pore-pressure. During the summer of 1994, 37 pre-existing sites were reoccupied with Global Positioning System (GPS) receivers. These data provide sub-centimeter horizontal precision and 1–2-cm vertical precision. Temperature changes due to injection of cold liquid into a fracture are computed assuming that convection within the rock parallel to the fracture walls can be neglected. For parameters typical of The Geysers the peak stresses close to the injector are greater than the hydraulic pressures expected at the bottom of the injector borehole. Thermoelastic stresses increase with high injectate fluxes, whereas hydraulic stresses increase with low permeabilities and hence low fluxes.

We have developed constitutive laws for dilatant fault gouges that include rate-dependent effects. Using these results together with laboratory-derived friction laws, we determine conditions under which dilatant faults can exhibit stick-slip instabilities. Under isothermal conditions, dilatancy is always stabilizing. However, for adiabatic fault zones a shear heating instability competes with frictional weakening to cause stick-slip. Our results suggest that frictional weakening is the dominant effect in initiating crustal earthquakes, although shear heating effects cannot be neglected.

GRANTEE: **STANFORD UNIVERSITY**

Department of Geophysics
Stanford, California 94305-2215

GRANT: **DE-FG03-94ER14430**

TITLE: **Scientific Drilling Into the San Andreas Fault Zone and Site Characterization Research and Coordination Efforts**

PERSON IN CHARGE: **Mark D. Zoback** (415-725-9295; Fax 415-725-7344)

Objectives: This project involves planning and coordination activities associated with a long-term proposal to conduct an integrated program of shallow geological and geophysical investigations and deep scientific drilling along the San Andreas fault. This work is being performed in close collaboration with co-Principal Investigators Steve Hickman (USGS–Menlo Park), Bill Ellsworth (USGS–Menlo Park), and Lee Younker (Lawrence Livermore National Laboratory).

Project Description: A deep (~10 km) scientific drilling experiment in the San Andreas fault zone would provide data essential to understanding the structure, composition, mechanical behavior, and physical state of an active, major plate-boundary fault. Toward this end, for the past 2-1/2 years we have been working with an international team of scientists and engineers in proposing a long-term, integrated program of surface-based geological and geophysical investigations and deep scientific drilling along the San Andreas fault system. To help answer fundamental questions concerning fault zone processes we propose coring inclined holes through the San Andreas fault to depths of 10 km and conducting extensive investigations in the holes and on the recovered materials. These investigations include laboratory measurements of the compositions, physical properties, and deformational behavior of exhumed gouges and pore fluids; measurements of pore pressure, stress, and fluid permeability directly within and adjacent to the fault zone; and studies of P- and S-wave seismic velocity, intrinsic attenuation, and anisotropy of the fault zone and gouge materials. The data from the deviated core holes will provide complete cross sections of the fault zone for compositional, microstructural, and rheological characterization of the fault over a wide depth range. Geophysical logging tools and cross-hole tomographic techniques would also be used to characterize variations in physical properties within and adjacent to the fault zone. Because of the likelihood of hole stability problems within the fault zone, we will conduct as many of the downhole experiments as possible after casing is cemented into the holes. In particular, we anticipate that fluid sampling and measurements of fluid pressure, permeability, and stress within the fault zone will be conducted through perforations in the cemented casing. Upon completion of drilling, seismometers and other instruments will be placed in the holes for long-term monitoring of earthquake locations and source parameters, seismic wave propagation, electromagnetic radiation, fluid pressure, fluid chemistry, temperature, and deformation.

Results: In FY 1994, progress has been made in the following areas: (1) Coordinate site selection studies and integrate data collected into a GIS database, (2) Convene second San Andreas conference, (3) Define engineering needs and establish linkages with private industry, (4) Represent the project to federal, state and local agencies, the public, and the press.

GRANTEE: **UNIVERSITY OF TENNESSEE**
Institute for Rare Isotope Measurements
Knoxville, Tennessee 37932

GRANT: **DE-FG05-95ER14497**

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

PERSONS IN CHARGE: **N. Thonnard** (615-974-8950; Fax 615-974-8289), **T. C. Labotka,** and **L. D. McKay**

Objectives: (1) To bring back into operation the proof-of-principle analytical methodology for ^{81}Kr and ^{85}Kr, (2) to identify performance limitations and implement improvements increasing reproducibility, accuracy, and throughput while reducing minimum sample size, and (3) to initiate research in the geosciences.

Project Description: The rare noble gas radioisotopes, ^{81}Kr and ^{85}Kr, having isotopic abundances and concentrations of $\sim 10^{-12}$ and 10^{-22} in modern water, could contribute in many ways to a better understanding of processes in the environment, including dating of polar ice and very old ground water, ocean circulation, and modern water flow patterns. Cosmogenic ^{81}Kr, with its 2.1×10^5 year half-life, should find applications in dating events in the 50,000 to 1,000,000-year time period, while anthropogenic ^{85}Kr with its 10.8-year half-life is useful in tracing events during the last 50 years. Neither isotope is accessible by accelerator mass spectrometry, although limited measurements of ^{85}Kr from ~200 liter water samples using decay counting have demonstrated its usefulness. The only ^{81}Kr measurements from natural samples to date are a handful of results from old groundwater and polar ice using the proof-of-principle laser-based system. The chemical inertness of the noble gases could in principle simplify interpretation of results. This new technique, when fully operational, should permit ^{85}Kr measurements using only 1 to ~5 liter samples and ^{81}Kr measurements from 10–20-liter samples. The technique presently consists of a multi-step process starting with (1) degassing of the sample, (2) separating Kr from the remainder of the gas, (3) a first isotopic enrichment reducing interfering isotopes by 10^5, (4) a second isotopic enrichment of 10^3, and (5) detecting the rare krypton isotope in a time-of-flight mass spectrometer utilizing resonance ionization. As there are only a few thousand analyte atoms in the sample, the sensitivity, element selectivity, and immunity to interferences of resonance ionization is required. A detection limit of ~100 ^{85}Kr atoms had been demonstrated earlier in the final mass spectrometer. Anticipated work required to make the system a practical analytical technique includes characterization of the efficiency, accuracy, and blank level of each step, stabilization and automation of operating parameters in steps (1), (2), and (3), complete redesign of step (4) and improvement to the laser and data acquisition systems in step (5). First research measurements using ^{85}Kr will be of hydrogeological samples from well-characterized systems permitting comparison to other measurements. As no other analytical technique exists for ^{81}Kr, first ^{81}Kr measurements will be from Arctic and Antarctic ice cores at depths having reliable ages, from very old aquifers, and from water in regions with intense underground radioactive sources to test for limits to underground production of ^{81}Kr.

Results: DOE funding for this project, co-sponsored by NSF, started in December of 1994. At this writing, the proof-of-principle equipment has been moved to the university and installation has been completed. Most components have been operated individually, while the design and implementation of upgrades is progressing.

GRANTEE: **TEXAS A&M UNIVERSITY**
Center for Tectonophysics
College Station, Texas 77843-3115

GRANT: **DE-FG05-87ER13711**

TITLE: **Mechanical Properties and Modeling of Seal-Forming Lithologies**

PERSONS IN CHARGE: **A. K. Kronenberg, J. E. Russell, and N. L. Carter** (409-845-0132; Fax 409-845-6780; E-mail akk8153@geopsun.tamu.edu)

Objectives: This research addresses the mechanical properties of two weak sedimentary lithologies, shale and rocksalt, that deform under gravitational and tectonic loads and examines the roles of these lithologies in the development of structural traps and unconventional oil and gas reservoirs.

Project Description: The shapes and physical properties of a wide range of structural traps and barriers to mobile hydrocarbons are governed by the mechanical properties of shale or those of salt and by the loading histories to which they have been subjected. Concurrent experimental and modeling studies are under way to determine the fracture and flow properties of these two lithologies, to determine physically based constitutive relationships that can be applied to geologically relevant conditions, and to make predictions concerning the development and timing of structural traps relative to known depositional histories. Triaxial compression experiments provide mechanical properties for shale and rocksalt over a wide range of conditions ($21° \leq T \leq 200°C$, $7 \leq P_e \leq 400$ MPa, $10^{-9} \leq \dot{\varepsilon} \leq 10^{-3}$ s^{-1}) and numerical modeling of salt diapirs with stratigraphic constraints on loading and ascent rates has extended predictions of mechanical response for rocksalt to strain rates of 10^{-15} s^{-1}.

Results: During this year, significant progress has been made toward characterizing both the mechanical and the transport properties of Wilcox shale saturated with NaCl brine and toward simulating the evolution of salt structures by modeling the deformation of rocksalt and overlying sediments with nonlinear rheologies determined experimentally.

The permeability of Wilcox shale has been determined by transient pulse methods as a function of flow direction relative to bedding, effective pressure, and inelastic triaxial deformation. Likewise, deformation experiments have been performed over a wide range of strain rates so as to examine possible effects of transient and spatially varying fluid pressures; however, all of the results suggest that pore fluids are essentially undrained over the time scales investigated and observed effects of strain rate appear to be intrinsic to illite-bearing shales. SEM investigations of deformed specimens have revealed the clay microstructures and fine-scale pores with limited connectivity that influence the mechanical and transport properties.

Modeling studies of salt tectonics now include examinations of such features and variables as multiple interfaces, allochthonous salt sheets, and sediment mechanical properties that closely approximate those determined experimentally for shale. Work is under way to examine different mechanisms of diapir nucleation and to determine whether the time scales required by these mechanisms correspond to geologic times available for the development of known structures. This work has received recognition by the U.S. National Committee on Rock Mechanics through the 1995 Award for the "Best Dissertation in Rock Mechanics" received by Ruben Mazariegos for his dissertation on "Mechanical Modeling of the Evolution of Salt Structures."

GRANTEE: **UNIVERSITY OF TEXAS**
Department of Geological Sciences
Austin, Texas 78712

GRANT: **DE-FG05-92ER14278**

TITLE: **Energy Flux and Hydrogeology of Thermal Anomalies in the Gulf of Mexico Sedimentary Basin—South Texas Example**

PERSON IN CHARGE: **John M. Sharp, Jr.** (512-471-5172; Fax 512-471-9425)

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

Project Description: To address the objectives, an extensive data base of fluid pressures, water chemistries, and formation temperatures was compiled into a geographic information system. Thermophysical properties were characterized by measuring mineralogy, porosity, bulk density, thermal conductivity, and radiogenic heat production of rock samples. Computer codes applicable to variable-density flow and heat transport were analyzed for utilization and codes were written to simulate heat conduction and free convection.

Results: The geothermal anomaly occurs from depths of 2 to at least 5.5 kilometers, has a half-wavelength of 100–150 kilometers, a depth amplitude of 2 kilometers, and a temperature amplitude of 50°C. Heat conduction does not appear to be a viable mechanism for producing the anomaly. The thermal anomaly is centered on the farthest basinward and deepest-seated of the Wilcox faults. Wilcox faults in south Texas are more linear and closer spaced than Wilcox faults to the north of the San Marcos Arch and are closer spaced than the basinward Frio faults. This results in a relatively well defined flow path and efficient heat advection. The present-day fluid pressure distribution appears amenable with the advective hypothesis, with a pressure halo evident along the fault zone. The fault-valve model is invoked for episodic ground-water flow. Fluid pressures in the area approach a limiting value of 0.85 times the lithostatic pressure at depths of 3–4 kilometers. This results in low differential stress that is a requirement for the initiation of hydraulic fracturing. Hydraulic fracturing in the prevailing extensional stress regime produces vertical fractures oriented parallel to regional strike and the thermal anomaly. The fluid flux (0.028 $m^3/m^2/yr$) required to reproduce the anomaly in numerical models appears to be geologically reasonable, especially for the pulsing hypothesis.

GRANTEE:	**UNIVERSITY OF TEXAS** Bureau of Economic Geology Austin, Texas 78713-8924
GRANT:	**DE-FG03-95ER14504**
TITLE:	**A Robust Economic Technique for Crosswell Seismic Profiling**
PERSON IN CHARGE:	**Bob A. Hardage** (512-471-1534; Fax 512-471-0140; E-mail hardageb@begv.beg.utexas.edu)

Objectives: This project will investigate techniques by which crosswell velocity tomograms can be constructed from seismic wavefields generated by a surface-positioned source and recorded by downhole sensors in two or more inline receiver wells, and will verify if this type of source–receiver geometry produces traveltime tomograms of sufficient accuracy to be used in reservoir characterization and monitoring.

Project Description: Crosswell velocity tomograms can be helpful in reservoir characterization and monitoring, yet crosswell applications cannot be attempted in highly attenuating rocks or between widely separated wells because of the limited energy output of present downhole seismic sources. In concept, crosswell data can be acquired in these no-data situations by using a robust surface-based energy source, and then measuring the traveltimes required for these surface-generated wavefields to travel between downhole sensors positioned at different depths in two inline receiver wells. If this combination of surface energy source and twin receiver wells allows ray paths to be recorded over an adequate angular aperture and also provides a traveltime accuracy that is adequate for velocity inversion, then crosswell applications can be implemented in reservoirs having almost any well spacing and any type of interwell lithology. The purposes of this research are to determine how to best record this type of crosswell data and then to verify if the data satisfy the numerical requirements for creating traveltime tomograms.

Results: Crosswell data were recorded between two receiver wells which penetrated low-velocity, weakly consolidated Pleistocene rocks in South Texas. The downhole sensors in each well were a 6-level hydrophone array having a 10-ft spacing between adjacent hydrophone elements. The surface energy source was a Bolt land air gun stationed at four offset positions; source points were inline with the two receiver wells. The downhole data were recorded at increments of 10 ft over a depth aperture of 1500–2500 ft in each well.

This work was done in an active oil field so that the typical background seismic noise of pumping wells, nearby workover activity, and continuous vehicular traffic associated with a producing reservoir would be superimposed on the downhole data. This environment was desired so a determination could be made if production activity has to be reduced in order to record crosswell data of adequate quality when using this type of source–receiver geometry. It is particularly important to know how these types of cultural noises affect free-hanging hydrophones, because a hydrophone array can be moved to a new downhole recording level quicker than can a wall-clamped receiver array, thus allowing crosswell data to be recorded in less time and at less cost.

Preliminary inspection of these data imply that they have sufficient signal-to-noise character to allow crosswell traveltimes to be determined. Data processing is now under way to verify if the traveltime data can be inverted to produce a stable tomogram.

GRANTEE:	**U.S. GEOLOGICAL SURVEY** Water Resources Division Menlo Park, California 94025
GRANT:	**DE-ASI03-93-ER14338**
TITLE:	**Causes of Abnormally High Fluid Pressure in the Uinta Basin, Utah**
PERSONS IN CHARGE:	**John D. Bredehoeft** (415-354-3382; Fax 415-354-3363; E-mail bjmcpher@usgs.gov) and **Brian J. McPherson**

Objectives: To understand oil migration patterns and the origin of high pore fluid pressures in the Uinta Basin, Utah.

Project Description: We developed a 3-dimensional, time-dependent model of the evolution of the Uinta basin, Utah, with the purpose of understanding the complicated basin system and its components, especially hydrocarbon generation, expulsion, migration, and associated high pore fluid pressures. The model couples (1) the structural/sedimentary development of the basin, (2) the thermal regime, and (3) the fluid regime including the multi-phase migration of oil. The numerical model is based on the TOUGH2 code, written at Lawrence Berkeley Laboratory initially for geothermal reservoir simulation but now widely used for multi-phase fluid-flow analysis. We modified the code to include a dynamic simulation of basin evolution including sedimentation, subsidence, uplift and accompanying erosion. The code simulates dynamic compaction in response to computed effective stress. Also simulated is *in situ* oil generation and multiphase migration that includes capillary effects.

Results: Our simulation of the Uinta basin reproduces the nearly lithostatic fluid pressures of the Altamont/Bluebell oil field. These pressures are shown to be consistent with ongoing oil generation in the area of Altamont. The simulation generates patterns of oil migration that are generally consistent with the distribution of oil fields in the Uinta basin. Oil moves from the deep Green River source beds toward Redwash and the Douglas Creek arch to the east, and southward toward the Sunnyside tar-sands and Book Cliffs. Model results indicate that most migration occurred prior to the start of a major episode of uplift and erosion 10 Mya. Oil migration is highly dependent on the basin's burial and thermal history, which, in turn, controls oil-generation rates and viscosity.

GRANTEE: **UNIVERSITY OF UTAH**
Department of Geology and Geophysics
Salt Lake City, Utah 84112

GRANT: **DE-FG03-93ER14313**

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

PERSON IN CHARGE: **Alan C. Tripp** (801-462-2112 or 801-581-4664; Fax 801-581-7065; E-mail actripp@mines.utah.edu)

Objectives: The project seeks to determine means of increasing the resolution of low-frequency electromagnetic techniques by means of *a priori* information and cooperative inversion.

Project Description: The research concentrates on three topics. The first goal is to improve local optimization by increasing the speed and versatility of the forward solution and by implementing novel methods of data conditioning and inversion regularization. The second goal is to investigate distributed global optimization for EM imaging using optimized forward code. The third goal is to lay a foundation for cooperative inversion of EM data with other data sets.

Results: The first goal of the project has been advanced this past year by further testing and refinement of a scheme for inverting DC resistivity data using a data weighting which optimally accounts for *a priori* model information, thus increasing the inversion resolution. This scheme has been generalized to the case of electromagnetic data. Further refinement of the technique in the electromagnetic case is being investigated.

The second and third goals of the project have been addressed in two ways in the past year. The first approach is to establish global bounds on the bulk complex conductivities of mixtures using various assumptions concerning the relative geometries, conductivities, or volume percentages of the components. These bounds can also be coupled to elastic property bounds. The existence of such *a priori* bounds means that a global optimization for composites can be directed to a specific region of parameter space. This approach is currently being illustrated with specific geophysical scenarios and proves to be very useful in assessing the relationship of information concerning geometries and properties to inversion solution uniqueness.

The second approach was to use the principles of cooperative game theory to formulate the cooperative inversion of electromagnetic and seismic data. As a proof of concept, a cooperative inversion of laboratory rock properties data was formulated using the Archie and the Wylie equations. Although conditions for Pareto optimality can be easily derived, the conditions did not prove useful in narrowing the range of possible porosities consistent with a simultaneous data set of electrical resistivities and seismic velocities. Consequently, this approach has been de-emphasized.

GRANTEE: **UNIVERSITY OF UTAH**
Earth Sciences and Resources Institute
Department of Civil and Environmental Engineering
Salt Lake City, Utah 84112

GRANT: **DE-FG02-90ER14133**

TITLE: **Assessing the Role of Active and Ancient Geothermal Processes in Oil-Reservoir Evolution in the Basin and Range Province**

PERSON IN CHARGE: **J. B. Hulen** (801-584-4446; Fax 801-584-445;
E-mail jhulen@esrilan.utah.edu)

Objective: The project objective remains a thorough test of the following hypothesis: Modern and fossil geothermal systems, by various means, have been instrumental in the generation, migration, and entrapment of oil in the Great Basin of the western United States.

Project Description: Eastern Nevada hosts numerous shallow and geothermally anomalous oil fields (for example, Blackburn and Grant Canyon/Bacon Flat) which share a surprisingly large number of essential attributes with many of the oil-bearing, Carlin-type, lowgrade disseminated gold deposits which occur in the same region, particularly those of the Alligator Ridge–Bald Mountain mining district in White Pine County. Is there a true genetic affiliation between these seemingly disparate natural resources, and are the Alligator Ridge orebodies three-dimensionally exposed analogues of the concealed, currently hot oil reservoirs? In seeking answers to these questions, we are focusing on the role of moderate-temperature geothermal systems in the generation, migration, and entrapment of oil, but in so doing we are also gaining valuable new insight into the mechanisms by which Carlin-type precious-metal deposits have formed. Our approach is multidisciplinary, involving techniques including, but not limited to: (l) detailed geologic mapping as well as logging of drill cuttings and cores, with emphasis on lithology, alteration, porosity characteristics, and vein mineralogy/paragenesis; (2) three-dimensional stratigraphic/structural analysis to allow reconstruction of fluid-flow paths used by both thermal waters and liquid hydrocarbons; (3) fluid-inclusion microthermometry; (4) whole-rock and vein-mineral geochemistry; (5) hydrogeochemistry of oil-field vs regional waters; (6) light-stable-isotope systematics of thermal waters and selected vein and alteration minerals.

Results: This past year, we have continued our evaluation of several oil-bearing gold deposits in the Great Basin as possible exposed analogues of the geothermally active oil reservoirs of Railroad and Pine Valleys in eastern Nevada. The work has once again focused in the southern Alligator Ridge mining district, about 80 km northwest of the town of Ely. Limited, related research was also completed at the hydrocarbon-rich Gold Point mine, at the eastern margin of Railroad Valley.

At the Gold Point mine, megascopically visible native gold is intimately associated with solid bitumen and oil in epithermal quartz veins hosted by stratiform jasperoid at the base of the Mississippian Chainman Shale, the Great Basin's premier hydrocarbon source rock. Reflectance of the bitumen, converted to an equivalent vitrinite reflectance, indicates that the substance, even though occurring in clearly epithermal quartz veins, is still within the favorable oil-generation "window." This finding is consistent with occurrence, in the gold-bearing quartz, of "live" oil fluid inclusions; the causative hydrothermal system was clearly transporting oil, and that oil had a direct influence in the precipitation of precious metal. The oxygen-isotopic signature of the quartz, coupled with primary fluid-inclusion entrapment temperatures (about 180°C), indicates that the oil-transporting, mineralizing hydrothermal fluid was dilute, meteoric in origin, and virtually identical in composition with the warm geothermal waters of the nearby Grant Canyon oil field. Other characteristics of the Gold Point occurrence, including alteration and vein mineralogy and whole-rock trace-element geochemistry, suggest that it is a slightly higher-temperature fossil analog of the deeply concealed Grant Canyon oil reservoir.

New Carlin-type, sediment-hosted precious-metal deposits being discovered and excavated in the southern Alligator Ridge district are all apparently similar to the Yankee deposit characterized earlier for this investigation—that is, they are oil-rich ("live" oil and fluid inclusion oil) and were deposited from dilute hydrothermal fluids at temperatures comparable to those now prevailing at Grant Canyon and Nevada's other geothermally active oil fields (about 120°C). Together with this finding, structural and stratigraphic analysis of the entire southern half of the district suggests that all these orebodies may have formed essentially simultaneously with a sizable concentration of anticlinally trapped liquid hydrocarbon—this Alligator Ridge oil reservoir may have exceeded in size fully half of Nevada's currently producing oil fields. Subtle decalcification fronts, oxygen-18 depletions, and trace element signatures help signal the presence of this oil reservoir and associated gold deposits at some distance from the higher-grade centers of mineralization. It is clear from our work that the Alligator Ridge oils were transported and entrapped in the same moderate-temperature geothermal system responsible for precious-metal mineralization. Pioneer Oil and Gas, of Midvale, UT, is at this writing spudding a deep oil well to penetrate deeply beneath the gold-ore horizon, in the hope that the now-extinct, oil-bearing geothermal system formed a second, deeper oil reservoir at Alligator Ridge still amenable to commercial production. The cuttings and well logs obtained from this well will be integrated into our broader Alligator Ridge geoscientific database to further refine the Great Basin geothermal/oil model outlined above.

A special session of the Rocky Mountain Section AAPG Annual Meeting in Reno in mid-July 1995 was convened to discuss the role of geothermics in general and geothermal systems in particular in the formation of hydrocarbon resources. A common theme of the presentations at this symposium was that under certain circumstances, active and fossil convective geothermal systems should be considered prime petroleum targets.

GRANTEE:	**UTAH STATE UNIVERSITY** Department of Geology Logan, Utah 84322-4505
GRANT:	**DE-FG03-95ER14526.A000**
TITLE:	**Three-Dimensional Hydrogeology of Fault Zones**
PERSONS IN CHARGE:	**Kevin Hestir** (801-797-2826; E-mail Hestir@sunfs.math.usu.edu) and **James P. Evans**; **Steven Martel** (University of Hawaii); and **Jane C. S. Long** and **Janet Jacobsen** (Lawrence Berkeley National Laboratory)

Objectives: The project is designed to examine the three-dimensional hydrogeologic structure of fault zones by field mapping, mechanical modeling, and probabilistic modeling. The results of these efforts will be used in developing inverse techniques for determining fault zone hydrologic affects from well test data.

Project Description: We examine the three-dimensional permeability structure of faults in crystalline rocks and integrate these results into fluid flow models, will develop models which will represent the nucleation and growth of faults in three dimensions, and use these models in the development and testing of numerical models of fluid flow. This work will:

(1) Investigate the spatial distribution and permeability structure of small faults by documenting the geometry, the internal geohydraulic structure, the amount of slip, and the nature of hydrothermal deposits and alteration of faulted rocks.

(2) Develop a three-dimensional, numerical-mechanical technique to model fracture growth. The results of the model will be compared to the natural faults we investigate, and we will also conduct parameter studies to help predict how different states of stress and different material properties affect the distribution and linkage (i.e., organization) of permeable and impermeable features along faults.

(3) Develop stochastic models, based on field data and mechanical models, for fault development. These models will represent how permeable and impermeable features are likely to be organized. This work will form the foundation of a stochastic model which characterizes the hydrology of faults.

(4) Compare the long-term permeability structure of faults, as revealed by geologic evidence, with the short-term permeability structure revealed by well tests.

(5) Enhance how three-dimensional data and model results are portrayed pertaining to the geometry of faults and fracture flow systems in general.

This research integrates field work and deterministic and stochastic modeling to gain insight into how three-dimensional permeability 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: This project has only recently been initiated. Field work on well-exposed, small-displacement fault zones in the central Sierra Nevada mountains is currently under way. This work has documented the three-dimensional geometry of small faults, the internal structure of a fault zone with approximately 8–10 m of slip, and examined the hydrothermal alteration and evidence for the fluid flow history along and within the faults. Fieldwork will continue through mid-August.

GRANTEE: **VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY**
Fluids Research Laboratory
Department of Geological Sciences
Blacksburg, Virginia 24061

GRANT: **DE-FG05-89ER14065**

TITLE: **Geochemical Studies of Fluid Systems**

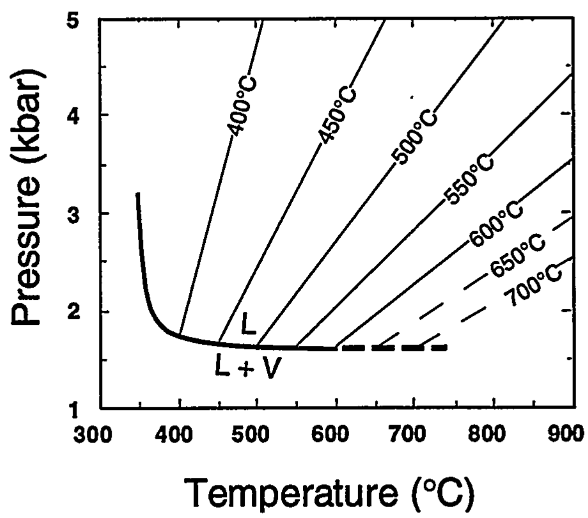
PERSON IN CHARGE: **R. J. Bodnar** (540-231-7455; Fax 540-231-3386;
E-mail bubbles@vt.edu)

Objectives: The objective of this project is to experimentally determine the pressure–volume–temperature–composition (PVTX) relationships of fluids encountered in crustal energy, resource, and waste-related environments over the complete range of appropriate PTX conditions. These data are used to develop equations of state to predict the volumetric properties of these fluids in crustal rocks.

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 empirical or theoretical equations of state to predict the thermodynamic properties of fluids over crustal PTX conditions, and provide information which may be used to interpret microthermometric results obtained from natural fluid inclusions. In this study the PVTX properties of aqueous solutions 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. Phase relations and P–T locations of isochores 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: The location of the liquid + vapor → liquid phase boundary and the P–T slopes of iso-Th lines were determined for a constant composition of 40±0.1 wt.% NaCl and 5±0.15 mol% CO_2 (both relative to H_2O) at high density. Synthetic fluid inclusions with this composition were formed in cold-seal pressure vessels at pressures of 2 and 4 kbar and temperatures between 350° and 700°C. The inclusions were analyzed on a gas-flow heating/cooling stage to determine the temperatures of halite dissolution $[T_m(H+L+V \rightarrow L+V)]$ and total homogenization $[T_h(L+V \rightarrow L)]$.

Addition of 40 wt.% NaCl to an aqueous solution containing 5 mol% CO_2 resulted in a significant shift of the liquid + vapor → liquid boundary toward higher pressures. The slopes of the iso-Th lines decrease from 29.5 bars/°C for $T_h(L+V \rightarrow L)$ of 400°C, to 6.4 bars/°C for $T_h(L+V \rightarrow L) = 600°C$ (see figure).



Addition of 5 mol% CO_2 to an aqueous solution containing 40 wt.% NaCl results in halite dissolution temperatures that are slightly higher (T_m(H+L+V→ L+V) ≈ 332°C) than the literature value of 323°C for the vapor-saturated liquidus of an H_2O – 40 wt% NaCl mixture. Extrapolation of this behavior to lower temperatures and pressures suggests that addition of CO_2 to brine-saturated solutions (as might be encountered in the Waste Isolation Pilot Plant environment after closure of the repository) will cause halite precipitation, leading to closure of fractures.

Calculated molar volumes for 40 wt.% NaCl + 5 mol% CO_2 solutions at 2 and 4 kbar show trends that are similar to those of other compositions in the ternary system H_2O–CO_2–NaCl at the same pressures and temperatures. In the P–T range of this study, all excess volumes are negative and lie between the values for the compositions H_2O – 5 mol% CO_2 and H_2O – 40 wt% NaCl.

GRANTEE: **UNIVERSITY OF WISCONSIN**
Department of Geology and Geophysics
Madison, Wisconsin 53706

GRANT: **DE-FG02-94ER14439**

TITLE: **Testing the Correlation Between Seismic Stratigraphy, Diagenesis and Physical Rock Properties: Evaluation of Fluid Flow During Early and Late Diagenesis**

PERSON IN CHARGE: **Jean M. Bahr** (608-262-5513; Fax 608-262-0693;
E-mail jmbahr@geology.wisc.edu)

Objectives: This project, being conducted in collaboration with G. Eberli and P. Swart of the University of Miami, is designed to test the conceptual models of diagenesis developed by those researchers with numerical modeling of fluid flow through the Great Bahama Bank.

Project Description: The finite difference code HST3D is being used to simulate fluid flow, heat transport, and solute transport through the Great Bahama Bank. Initial simulations are focused on a 2-D profile for which the major hydrologic units and properties were chosen based on available seismic and core data provided by the Miami collaborators. The model is being used to assess the sensitivity of flow patterns and flow rates to variations in hydraulic, thermal, and density gradients and boundary conditions. The numerical model will also be used to study the effects of sea level fluctuations and changes in permeability due to diagenesis. This will involve modification of the boundary conditions and permeability distribution to reflect conditions that are inferred to have existed during earlier diagenetic periods or as a result of sea level change.

Results: Simulations have been used to evaluate a combination of driving forces to generate large-scale fluid circulation in a heterogeneous bank. They have also been used to compare the significance of island recharge and head variations across the bank with temperature variations and geothermal flux along the lateral and basal boundaries as driving forces for fluid circulation. Temperature gradients and heat flow dominate head differences and island recharge as a driving force for large-scale circulation. For all simulations rapid flow occurs through Holocene carbonate in the upper 160 m of the bank. Large-scale Kohout convection occurs for contrasts in horizontal permeability of one order of magnitude or more between bank and straits deposits. Head differences of up to 0.6 m between the Straits of Florida and the Tongue of the Ocean do not produce cross-bank flow. Flow patterns below the Holocene carbonate are relatively insensitive to variations in island recharge rates. Vertical gradients in temperature along the steep edges of the bank are particularly sensitive to permeability magnitudes and contrasts within the bank, suggesting that temperature measurements in holes drilled in these areas may be particularly useful for constraining hydrologic properties of the bank.

GRANTEE:	**UNIVERSITY OF WISCONSIN** Department of Geology and Geophysics Madison, Wisconsin 53706
GRANT:	**DE-FG02-93ER14328**
TITLE:	**HRTEM Investigations of Interactions Between Minerals, Fluids, and Lithobionitc Communities During Natural Weathering**
PERSON IN CHARGE:	**Jillian F. Banfield** (608 262-0915; Fax 608 262-0693; E-mail jill@geology.wisc.edu)

Objective: To explore the hypothesis that reactions occurring at lichen–mineral interfaces are strongly impacted by biochemical processes and differ in their rates and products from inorganically mediated reactions. This system provides an ideal microcosm for modeling interactions between communities of microorganisms and minerals occurring in rhizospheres, soils, and the subsurface.

Project Description: Research involves naturally weathered samples of amphibole syenite from the Stettin Complex, near Wausau, Wisconsin. Rocks primarily consist of ferrohastingsite, ferriannite, perthitic feldspar, magnetite, and quartz. Most samples were collected from a lichen-colonized quarry. Knowledge of the age of quarrying allows us to constrain weathering rates. A variety of x-ray (diffraction, energy- and wavelength-dispersive analyses) and microscope-based techniques (light microscopy, high-resolution transmission electron microscopy, confocal laser scanning microscopy) were used to characterize intact lichen–mineral interfaces. The structures, microstructures, chemistries, and distributions of products were determined in order to compare biogeochemical and inorganic weathering. The conceptual framework for data analysis involved subdivision of the interface region to reflect the extent of biological influence: (1) photosynthetic, symbiotic zone with minimal mineral–organism interaction; (2) intimate contact between mineral surfaces and complex organic polymers; (3) biological impact restricted to dissolved organic species; (4) essentially inorganic geochemical environments.

Results: Crustose saxicolous lichens *Rhizocarpon grande* and *Porpidea albocaerulescens* colonize and penetrate mineral surfaces up to depths of 10 mm. Mineral fragments accumulated within the lower thallus are coated in extracellular mucopolysaccharides associated with bacteria, fungi, and endolithic algae. In this zone of intimate contact between lichens and minerals, biologically mediated weathering occurring within these extracellular gels involves a complex dissolution / selective transport / recrystallization process. Specialized microenvironments initially produce minute phyllosilicates from constituents derived from mineral surfaces. Reactions culminate in abundant 5–10-μm diameter polymer-bound aggregates of face-to-face oriented clay minerals with homogeneous compositions. Dissolution does not involve pervasive leaching. Amphibole surfaces along hyphae-filled cracks are highly corroded. Endolithic algal colonies occur in dissolution cavities along twin planes in otherwise essentially unaltered feldspars. The reactivity of organic compounds associated with these colonies is further illustrated by their capability to selectively adsorb Pb. In zone 3, non-isovolumetric, non-isochemical weathering of ferrohastingsite produces topotactically oriented Ca,K-smectite and goethite. At distance from the lichen–mineral interface, primary minerals are fresh. Thus, enhanced alteration in zone 3 may be attributed to the impact of dissolved organic compounds.

GRANTEE:	**UNIVERSITY OF WISCONSIN** Department of Geology and Geophysics Madison, Wisconsin 53706
GRANT:	**DE-FG02-93ER14389**
TITLE:	**Microanalysis of Stable Isotope Ratios in Geothermal Systems: Long Valley and Skye**
PERSON IN CHARGE:	**John W. Valley** (608-263-5659; Fax 608-262-0693; E-mail valley@geology.wisc.edu)

Objective: This project is developing and applying new geochemical techniques to decipher the complex effects of superimposed hydrothermal events in modern and fossil geothermal systems. At the Long Valley caldera, these results are providing insight into the nature of magma chambers at depth, the size of the modern geothermal resource, and the volcanic hazards.

Project Description: This study focuses on samples from the Long Valley Exploratory Well and related rocks from the Mt. Morrison roof pendant, and 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. This study is the first application of this technology to hydrothermally altered rocks. 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. The goals of this study will be enhanced by refining new techniques of ion microprobe and laser analysis of oxygen isotope ratio.

Results: Advances have been made improving the accuracy of laser probe analysis, and ion microprobe analysis is finally possible for silicate minerals. Ion probe analysis of quartz phenocrysts from hydrothermally altered Skye granites shows that some grains are isotopically homogeneous while others contain gradients in $\delta^{18}O$ of up to 13‰ over 400 microns between healed quartz in fractures and the surrounding quartz grain. The lowest $\delta^{18}O$ is in a micro-shear zone documenting hydrothermal flow that was heterogeneous, anisotropic and crack-controlled. At least five generations of quartz vein cut basement quartzites in LVEW drill core from beneath Long Valley. Combined ion probe and laser analysis demonstrates an early high-temperature origin for the earliest four, and only the latest generation involved meteoric water. In contrast, laser analyses of micro domaines in the overlying volcanic rocks in LVEW document an inverted thermal gradient resulting from vigorous, post-Bishop tuff hydrothermal convection.

GRANTEE: **UNIVERSITY OF WISCONSIN**
Department of Geology and Geophysics
Madison, Wisconsin 53706

GRANT: **DE-FG-02-91ER14194**

TITLE: **Poroelasticity of Rock**

PERSON IN CHARGE: **Herbert F. Wang** (608-262-5932; Fax 608-262-0693;
E-mail wang@geology.wisc.edu)

Objectives: The primary objective is to develop theory for, and obtain laboratory measurements of, poroelastic parameters to predict rock mass behavior under quasistatic conditions (Darcy flow).

Project Description: The main scientific issue is to understand the fluid response of a rock mass to stress, and vice versa. The quasistatic poroelastic constants are important for characterizing such coupled phenomena as subsidence due to large amounts of fluid extraction from reservoirs and fluid pressure response to the stress field generated by an earthquake.

The emphasis in this project year was to work with James Berryman at LLNL on development of a theory to treat the poroelastic response of a fractured, porous rock. The new theory can be applied in fractured reservoirs to geomechanics problems involving fluid flow.

Results: The constitutive equations for hydrostatic stress contain six independent coefficients, which relate the confining pressure, pore pressure in the matrix, and pore pressure in the fractures to the volumetric strain, the increment of fluid content in the matrix, and the increment of fluid content in the fractures. The coefficients occur in three categories, which correspond to the three original Biot coefficients—compressibility of the combined fracture–matrix system, two generalized poroelastic expansion coefficients, and three generalized storage coefficients.

The analysis contained two critical components. (1) When the fracture fluid pressure is set equal to that of the confining pressure, the matrix material is effectively isolated from the fracture behavior and three combinations of the dual-porosity coefficients can be determined from laboratory tests on core. (2) When the matrix fluid pressure is chosen to constrain it to behave rigidly, the fracture behavior is effectively isolated from that of the matrix, and a fourth combination is obtained from laboratory measurements of joint stiffness. A fifth condition is that the cross-storage coefficient is zero, which can be obtained from assuming that the solid grain bulk modulus for the matrix is the same as that for the fractured rock mass. This leads to the sixth equation that the overall compressibility is the volume average of the matrix compressibility and the fracture compressibility.

GRANTEE: **WOODS HOLE OCEANOGRAPHIC INSTITUTION**
Department of Geology and Geophysics
Woods Hole, Massachusetts 02543

GRANT: **DE-FG02-94ER14435**

TITLE: **Robust, Controlled-Leverage Magnetotelluric Data Analysis**

PERSON IN CHARGE: **A. D. Chave** (508-457-2000 Ext. 2833; Fax 508-457-2150;
E-mail alan@faraday.whoi.edu)

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, a 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 which 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 which 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 which 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 statistical formalism to allow multiple instead of single remote references has also been developed. 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, it is possible to robustify the projection operation, 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 solution formally reduces to the conventional remote reference one when only a single reference site is used. The multiple remote reference, robust, controlled-leverage algorithm with jackknife error estimates has been programmed and tested with a variety of data, and is undergoing further refinement. A manuscript describing these results is in preparation.

An X-windows graphical user interface to the robust controlled-leverage code is under parallel development. This interface greatly simplifies setting up and executing runs, and in particular facilitates viewing graphical output from a run.

A set of short-period (1–1000 s) magnetotelluric data from ten sites in the environs of the Nelson

Batholith in British Columbia has been re-examined for signs of electric and magnetic galvanic distortion after re-processing the original time series. While some sites are well explained by electric and magnetic field distortion, and few are explained solely by electric field distortion, many cannot be described by a galvanic model. A manuscript describing these results has been submitted for publication.

GRANTEE: **WOODS HOLE OCEANOGRAPHIC INSTITUTION**
Department of Marine Chemistry and Geochemistry
Woods Hole, Massachusetts 02543

GRANT: **DE-FG02-92ER14232**

TITLE: **Geochemical Incorporation of Sulfur into Organic Matter: Role of Sulfur in the Formation and Diagenesis of Macromolecular Organic Matter in Sediments**

PERSON IN CHARGE: **Timothy I. Eglinton** (508-289-2627; Fax 508-457-2164;
E-Mail teglinton@whoi.edu)

Objectives: The overall goal of this study is to improve our understanding of the role of sulfur in organic matter (OM) diagenesis. Three specific objectives are outlined: (1) development and evaluation of structural models quantitatively describing organically bound sulfur (OBS) in sediments; (2) application of these models for (a) assessment of sulfur incorporation into organic matter as a preservation (kerogen-formation) mechanism and (b) elucidation of diagenetic pathways for OBS.

Project Description: The experimental and theoretical approach is based on the premise that OBS can be represented as model structures that differ in S-linkage type (inter-molecular linkages vs intra-molecular bonds), as well as the number of linkages per molecule and the number of S atoms in each linkage. These models are pertinent for accurate prediction of organic carbon burial efficiency in sediments and delineation of temperature–time requirements for petroleum generation. X-ray absorption spectroscopy (XANES) is used for determination of S-speciation; chemical degradation experiments to provide information on linkage type, the sites of S-attachment, the number of linkages involved, and the molecular structures of the S-containing molecules; analytical pyrolysis to derive structural information and estimates on organic S content; S-isotopic measurements for information on the timing of diagenetic S incorporation. These analyses are performed on fractions isolated from sedimentary OM according to approximate molecular size and/or solubility. The Peru margin and Miocene Monterey Fm, CA, are the primary study areas because of their high sedimentary organic carbon and sulfur contents, and equivalence in terms of (paleo)depositional environment. A Monterey Fm sample was the subject of a series of isothermal laboratory heating experiments designed to simulate natural geologic maturation in the subsurface. Temperatures from 150 to 360°C (each 100 hr duration) were employed under closed vessel hydrous pyrolysis conditions. Gaseous, liquid, and solid products from these experiments were analyzed using the same analytical strategy described above.

Results: *Laboratory thermal alteration experiments (in conjunction with Dr. J. Seewald, WHOI):*

Several distinct thermal regimes were identified within which specific transformations in organic S occur: (i) even at the low temperatures (≤175°C) a significant decrease in the S/C ratio of the residual kerogen occurred and is attributed to elimination of H_2S; (ii) heating between 225 and 300°C resulted in maximum bitumen production and further preferential loss of S from the kerogen. This "low-temperature" bitumen was S-rich and contained abundant (poly)sulfide bonds; (iii) between 300 and 350°C peak generation of hydrocarbon-like products occurred, yielding bitumen and residual kerogen with lower S/C ratios. The highest-temperature experiments (350, 360°C) resulted in maximum gas yields (including H_2S), lower bitumen yields, and a sulfur-poor kerogen residue, in which the remaining sulfur was predominantly thiophenic. Based on XANES data and mass balance calculations, it seems likely that the S removed at low temperatures (<225 °C) is expelled from polysulfide bridges. At the slightly higher temperatures (≥250 °C), scission of –S–S– bonds in di- and polysulfide bridges, in addition to –C–S– bonds takes place, with the resulting generation of soluble products (bitumen). The bitumen is S-rich and comprised of large, polar products (asphaltenes, resins) which retain abundant sulfide bridges. At higher temperatures (>300° C) C–C and C–S bond scission reactions are likely to predominate, liberating hydrocarbon-like products typical of expelled petroleums, as well as driving these products toward lower molecular weights (i.e., gas generation).

Although the temperature regimes described only apply to laboratory heating experiments, the same progression in reactions likely takes place during maturation in sedimentary basins, albeit over different temperature intervals. Characterization of the proportions of S-linkages in kerogens will allow more accurate assessment of generation characteristics (in terms of timing of petroleum generation and petroleum composition) of potential source rocks.

Sulfur isotopic studies: Recently, emphasis has shifted to the measurement of sulfur isotopic composition ($\delta^{34}S$) of OBS to better define the mode and timing of S-addition to sedimentary organic matter (and hence predicts its distribution in sediments). $\delta^{34}S$ measurements conducted on bulk organic fractions (organic soluble "bitumens" and kerogens) from Peru margin and Miocene Monterey Fm sediment samples yielded ambiguous results with isotopic compositions apparently intermediate between the expected $\delta^{34}S$ values for pyrite and biogenic sulfur. Two novel approaches are being attempted to better define diagenetic organic sulfur isotopic signature: (i) $\delta^{34}S$ analyses on different molecular size fractions (isolated by gel permeation chromatography); (ii) measurement of sulfur isotopic composition of individual organic sulfur compounds isolated by preparative capillary gas chromatography (PCGC). To date, it has been established that PCGC isolation of >200 µg of individual target compounds is readily achieved with negligible contamination or isotopic fractionation. A suite of C_{20} isoprenoid thiophenes have been selected as initial target compounds since they have an unequivocally diagenetic origin. Work is in progress in conjunction with Dr. Brian Fry (Florida International Univ.) to develop a microscale sulfur isotopic measurement method.

Chemical degradation experiments: In conjunction with Drs. Schouten, Sinninghe Damste and de Leeuw (NIOZ, The Netherlands), samples of molecular size fractions previously isolated from a Monterey sediment (the same sample used for the artificial maturation experiments) were subjected to sulfur selective chemolysis using Nickel boride. Using this approach, released products which were bound by sulfur are labeled with deuterium atoms and readily identified. Our studies revealed that the extent of deuteration closely tracked the molecular size of the fraction. This observation lends very strong support to our hypothesis that the degree of sulfur bridging is strongly related to, and may even control, molecular size in sulfur-rich sedimentary organic matter. No such relationship could be established for a surficial Peru sample.

GRANTEE: **WOODS HOLE OCEANOGRAPHIC INSTITUTION**
Department of Marine Chemistry and Geochemistry
Woods Hole, Massachusetts 02543

GRANT: **DE-FG02-89ER13466**

TITLE: **Organic Geochemistry of Outer Continental Margins and Deep Water Sediments**

PERSON IN CHARGE: **J. K. Whelan** (508-457-2000, Ext 2819; Fax 508-457-2164; E-mail jwhelan@whoi.edu)

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: The geochemical research at Woods Hole is a portion of a larger university/industry consortium of researchers identified as the "Global Basins Research Network" (GBRN) and takes advantage of samples made available through drilling programs and research supported by industry and the DOE Fossil Energies Program. The GBRN is a distributed network of scientists working to understand the coupled physical and chemical processes that control fluid movement in sedimentary basins. These processes, which are currently poorly understood, are fundamental to oil and gas formation and migration, metal ore deposit formation, and hydrology and associated pollutant movements around basins. An overall thrust of our recent research has been on gas generation and migration, which are key to understanding oil migration.

Results: Current research is focused on the shelf edge and deep slope of the northern Gulf of Mexico, where it appears that gas solubilization of oil and pressure-dependent phase changes are causing pervasive oil and gas migration into reservoirs and to the seafloor at the present time. Work over the past several years has focused on Eugene Island Block 330 (EI-330) in the offshore Louisiana Gulf Coast, one of the world's most prolific Pleistocene oil and gas fields, with a total production greater than a billion barrels of oil since discovery in 1972. Estimated reserves in this field, composed of many discrete reservoirs, have declined much less than expected with increasing production. One possibility, supported by recent geophysical studies, is that some reservoirs are being replenished by current migration of oil and gas from greater depths. Key questions then arise regarding the cause, rate, and duration of the migration episode(s) as well as the origin of the migrating gas and oil. Recognition of superposition of currently active processes of generation and migration on processes of past geologic epochs provides an important new avenue in exploration and resource estimation. The concept of reservoir replenishment, perhaps with newly formed oil and gas from ancient sediments, is important in estimating the nation's oil and gas resources. Recent work suggests that these reservoir-replenishment processes may be even more pervasive to the south along the deeper-water continental slope than they are in EI-330.

Recent geochemical research at Woods Hole Oceanographic Institution supported by the BES/Geosciences Program has demonstrated that the oils in different reservoirs of the Eugene Island 330 field are related to one another and to a deeper source rock of Jurassic–Early Cretaceous age. However, wide variation in composition occurs due to subsequent migration–fractionation and biodegradation processes. Biomarker analyses together with oil and gas maturities provide a possible scenario for generation and migration of the EI-330 oils: oils were initially generated and trapped under salt. With further burial, this reservoir was carried down as a sealed system, causing retardation of oil destruction by buildup of gas pressure beneath evaporitic layers. More recently with further burial, oil cracking to gas caused pressure buildup and rapid upward migration of oil dissolved in methane through geopressure. Upward migration and release of pressure caused a fractionation with progressively lighter oil fractions filling progressively shallower reservoirs. Maturation data defines the current depth of this hypothetical deep reservoir as between 20,000 and 25,000 ft. The oil must have been generated at an earlier time because the Jurassic rocks, the probable oil source, currently lie at 30,000 ft or deeper under EI-330, assuming that migration is vertically upward.

Two very interesting questions have arisen from research this year: (1) What is the maximum depth to which oil can survive underneath EI-330? Hydrous pyrolysis results suggest that this depth may be highly dependent on the redox provided by the underlying minerals and inorganic fluids. (2) Assuming that rapid migration into these reservoirs is occurring, what is the mechanism? It is not clear at the present time that the predominant mechanism is or can be predominantly through faults.

Interpretations based on previous geophysical and geochemical observations as well as on new data gathered this year strongly support a dynamic, rather than a static, fluid injection model in some EI-330 reservoirs as well as throughout much of the broader slope area to the south. The short-term (years) time scale and continuous nature of oil and gas migration from depth in fields such as EI 330 suggests that treatment as a "steady state" rather than a fixed resource may be appropriate in these areas. Preliminary analysis suggests that similar phenomena may be taking place in other producing areas such as the North Sea, Niger Delta, Mahakam Delta in Indonesia, Trinidad Basin, Taiwan Basin, and (possibly) the Alaskan North Slope.

GRANTEE:	**YALE UNIVERSITY** Department of Geology and Geophysics New Haven, Connecticut 06520-8109
GRANT:	**DE-FG02-95ER14522**
TITLE:	**A Field Experiment on Plants and Weathering**
PERSON IN CHARGE:	**Robert A. Berner** (203-432-3183; Fax 203-432-3134; E-mail berner@milne.geology.yale.edu)

Objectives: A major control on atmospheric CO_2 over long geological time scales is the chemical weathering of silicate minerals, and an important factor in this weathering is the role played by higher plants. Our objective is to determine the quantitative effect of trees and other vascular plants in accelerating silicate weathering rate by performing controlled experiments under natural field conditions.

Project Description: Dissolved-element concentrations in throughfall and drain waters for small (60-m^2) vegetated and unvegetated plots are presently being determined as part of an ongoing ecological experiment at the Hubbard Brook Experimental Forest Station in New Hampshire. Three plots are being investigated: one that was planted with red pine in 1983, one planted with two species of grass. also in 1983. and a control containing only mosses and lichens and kept free of higher plants over the same period. All plots are lined with an impermeable plastic so that all water passing through the plots can be collected at an outlet pipe. By correcting for measured rain, snowmelt, and dry deposition inputs, as well as evapotranspiration (by normalizing to Cl), we can determine relative release rates of dissolved species in drainage from each plot. Flow rates are determined at the site and we are analyzing waters collected over the past 12 years, and now being collected weekly, for Na^+, K^+, Ca^{++}, Mg^{++}, SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-, F^-, H_4SiO_4, and pH. These water chemical results, when combined with data on storage in growing biomass and soil (from the results of other workers), will allow us eventually to obtain overall element release rates from primary minerals via chemical weathering.

Results: We have found a severalfold acceleration of the flux of all dissolved cations from the pine-covered plot relative to the plant-free control. The effect is greatest for Na. Uptake by the growing plants of K, Ca, and Mg causes their release in drainage waters to be less than that for Na, which is much less involved in biological cycling. Silica release rates are also distinctly elevated in the tree-covered plot. Similar results, but with a lesser accelerating effect, are found for the grass-covered plot. The fixation of CO_2 as HCO_3^- is accelerated under the trees but only in the spring during active plant growth. Sulfate and H^+ are enriched in drainage from the tree-covered plot at irregular intervals, probably due to enhanced trapping of sulfuric acid aerosols by pine needles. (One recent set of measurements showed that cloud condensate on the pine trees has a pH of 3.0–3.5.)

GRANTEE: **YALE UNIVERSITY**
Department of Geology and Geophysics
New Haven, Connecticut 06511

GRANT: **DE-FGO2-9OER14153**

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

PERSONS IN CHARGE: **A. C. Lasaga** (203-432-3114; Fax 203-432-3134) and **D. M. Rye**

Objectives: The objectives are to integrate new results and to develop new techniques along four directions: (1) experimental studies of water–rock reactions, (2) theoretical modeling of coupled fluid flow–chemical reactions, (3) geochemical field based studies of a lateritic bauxite deposit, and (4) stable isotopic variations on the regional scale, the vein scale, and the mineral-grain scale in several geologic settings.

Project Description: The main thrust of the theoretical modeling continues to be the further development of the differences between equilibrium, steady-state, and non-steady-state behavior of the chemical evolution of open fluid–rock systems. These differences have not been fully appreciated in previous models. The computer code developed in this project numerically treats multi-component, finite-rate reactions combined with advective and dispersive transport in one, two, and three dimensions and incorporates isotopic exchange and heat and mass transfer. Further development includes code that models flow along both fractures and porous media simultaneously. An important goal is to include a sophisticated algorithm that enables the code to track evolving reaction fronts efficiently without introduction of numerical dispersion.

We have developed microsampling techniques to be used in stable isotopic studies. The project is currently using these techniques to provide data sets that can be input into our models to determine the length and time scales relevant to fluid transport in a wide variety of geologic settings. These areas include: (1) the Wepawaug metamorphic schist, (2) the Irish base-metal ore system, (3) the Naxos metamorphic complex, (4) the Pijiguaos bauxite deposit, (5) and the Barrovian metamorphic complex in the Dalradian supergroup in Scotland.

We are conducting an integrated, field, experimental, and theoretical study of the Pijiguaos bauxite deposit in Venezuela.

The numerical codes we have developed are being tested in all of the isotopic study areas, and field areas as well in the Marysville contact aureole.

Extensive *ab initio* research and surface chemistry studies on the kinetics of water–rock reactions will be integrated with the numerical codes, isotopic measurements, and field studies.

Results: In the last year, we have made remarkable progress in our modeling of kinetically controlled quartz dissolution and precipitation in a two-dimensional heterogeneous permeable medium. This work vastly expands our view of the spatial and temporal complexity of crustal fluid evolution. Such developments are only possible with the computational efficiency we achieved with an implementation of a spectral transform technique for solving Darcy's law with significant spatial variations in permeability. This state-of-the-art technique, never applied before to spatially variable permeability or porous media flow, makes it possible to follow evolving flow characteristics with a time and spatial resolution not attainable before. Many aspects we find have been missed by previous investigators who looked for steady-state behavior, or who lacked the spatial resolution really required by the dynamics.

Features of the flow never visualized before include:

- Oscillatory thermal boundaries, leading to quartz

zonation down to the smallest observable scale.
- Arcuate zones of precipitation surrounding upwelling zones.
- Cold plumes plunging down through high-permeability zones, which normally carried upwelling flow.
- Saturation-state reversals in much of the domain.
- Channelization-enhancement mechanisms in high-permeability zones arising from advection.
- Fluid velocities which change by up to an order of magnitude over the course of an oscillatory cycle.
- Enhanced fluid disequilibrium in rapidly advecting high-permeability zones.
- Shifting locations of rapid flow zones due to dissolution and precipitation.
- Regions of undersaturated upwelling fluid moving down temperature, and regions of oversaturated downwelling fluid moving up temperature, both cases opposing the conventional wisdom based on equilibrium.

In fact, when there is significant departure from equilibrium, fluids can be moving in any direction, with any saturation state, and either up or down temperature. Long-term changes in the porosity and permeability show that regions of dissolution lead to faster flow velocities and greater undersaturation, whereas regions of precipitation gradually inhibit flow rates and the relative supersaturation. This "fully coupled" feedback, from chemistry, to flow, and back onto the chemistry, has been a goal of transport and reaction models of water–rock interaction. We are now poised to unravel the implications of this feedback, with special attention on the potential runaway dissolution regime.

Future work will address the influence of the presence of other minerals, and will include other reacting species. We are formulating a model for stable isotopic exchange between fluid and rock. This work, along with our field observations, will allow us to quantify time and spatial scales of fluid flow in a variety of geologic settings.

In the Wepawaug Schist, the application of the experimental data to the kinetics of isotopic exchange of water with quartz, and the model results has already shown that fluid flow was transient in cracks (now preserved as veins). Not only was the flow transient, the isotopic composition of the fluid oscillated between values that were isotopically lighter and heavier than the surrounding host rocks.

Oxygen isotopic zonation in garnets as well as isotopic, modal, and chemical profiles for individual minerals in wall rocks next to veins show that each fluid recorded in the veins infiltrated and reacted with the wall rocks. Garnets are isotopically zoned with the cores being isotopically lighter than the rims. Staurolite and kyanite throughout the profile formed late and are isotopically heavy. Quartz, biotite, and muscovite have intermediate isotopic compositions, and plagioclase is isotopically light. These results make it clear that we can no longer consider metamorphic rocks to be "closed or semi-closed" systems. Regional metamorphic rocks are, in many cases, metasomatic in origin. We can never go back to looking at whole rocks or single minerals, and we can never go back to looking at a single locality. However, the rocks do preserve some of the fluid flow history, and we can unravel that history.

Over the last two years, we have collaborated with the Central University of Venezuela and the Venezuelan bauxite mining company, Bauxilum, to obtain data on the huge lateritic bauxite deposit in the "Los Pijiguaos" region, located in the NW edge of the Guiana Shield. The available data from this bauxite deposit consist of chemical analyses of Al_2O_3, SiO_2, Fe_2O_3, TiO_2, and H_2O collected with a depth resolution of 1 m on a 100×100-m grid. The thickness of the total weathering profile (bauxite + saprolite) is on the order of 50 m. Each point is perfectly located in a three-dimensional network. These data allow us to see the changes in composition in three dimensions and correlate the changes to topography and to flow models of the infiltrating meteoric waters.

To characterize weathering properly we need accurate modal data as well as chemical data. This fact required us to develop an entirely new technique to obtain accurate modal analyses of samples that contained both gibbsite ($Al(OH)_3$) and kaolinite ($Al_2Si_2O_5(OH)_4$). Accurate modal analyses of many bauxite samples were obtained using standard image-analysis techniques on back-scattered electron (BSE) images on the electron microprobe/SEM system. As it was not possible to distinguish between gibbsite ($Al(OH)_3$) and kaolinite ($Al_2Si_2O_5(OH)_4$) using standard techniques, we developed a new technique involving digital image analysis of both BSE images and x-ray maps. The combination of the two types of images provided details of chemical and mineralogical composition at spatial resolution never before achieved.

The measured weathering profiles from the "Los Pijiguaos" region have an upper gibbsite-rich zone (the bauxite proper), underlain by a transition zone where both gibbsite and kaolinite are present, and a basal saprolite, with no gibbsite present. Relict quartz grains are present throughout the profiles.

Simulations, using our coupled reaction flow models, have shown that long time scales (several millions of years) are required to produce the observed weathering profiles, and that the presence of a transition zone with both gibbsite and kaolinite is only predicted if kinetic rate laws are used. The presence of relict quartz grains is also consistent with the slow dissolution rates of quartz, even in these long time scales.

The experimental work pioneered in our laboratories has produced several startling results on the kinetic rate laws of silicate–water reactions. Results from earlier experiments with gibbsite, kaolinite, and albite suggest that the variation of the rate with saturation state is much more complex than anticipated. The presence of a surface transition in the mechanism of dissolution leads to highly nonlinear variations of the rate with ΔG_R. Such surface effects have been tentatively identified as stemming from the energetic role of dislocation defects on the surface of minerals. A new full-rate law was proposed that explicitly incorporates the effect of ΔG_R, as well as that of temperature and catalysis or inhibition through the adsorption of H^+, OH^-, and other ions.

Recent experiments with smectite, anorthite, and the zeolites analcime and clinoptilolite have confirmed the non-trivial dependence of dissolution rate on ΔG_R. The effects of pH and Al inhibition are also being studied in more detail. The development of new column experiments (see below) constitutes an important step in conducting laboratory kinetics experiments that more closely reproduce natural systems. New *in situ* experiments are being developed for the direct observation of dissolving/precipitating minerals at room temperatures using the atomic force microscope and up to hydrothermal conditions using interferometric techniques.

Model simulations provided useful hints in how to recognize systematic trends in the results of gibbsite column dissolution experiments and separate far-from-equilibrium from close-to-equilibrium conditions. Experimental dissolution parameters (rate constant, pH effect) were then correctly determined. The excellent agreement between model and experimental results provided also a valuable link between the form of the rate law used to describe mineral dissolution and the experimental results. Similar approaches are being currently used in combination with experimental work related to the dissolution of kaolinite and the effect of oxalate in the dissolution of gibbsite.

The experimental data from our laboratory and others can account quite well for many of the observations in global chemical weathering. Not only can the experimental data predict the correct stability ordering of the minerals, but also quantitatively account for the time scales of global chemical weathering. In addition, the new experimental data can explain the variation of silica in rivers worldwide as a function of runoff, without the need of recourse to an equilibrium model. Finally, the residence times for transport of debris from high altitudes may be fast compared to the time required for chemical reaction. Such feedback between physical and chemical weathering can help formulate better the models for the geochemical cycles of CO_2.

Atomic force microscope studies of the surfaces of reacted kaolinite and muscovite have been successfully carried out and *in situ* studies are just beginning.

GRANTEE: **UNIVERSITY OF CALIFORNIA AT SANTA BARBARA**
Institute for Crustal Studies
Santa Barbara, California 93106

GRANT: **DE-FG03-91ER14211**

TITLE: **Physical Modeling of Sedimentary Basins, Magma Mechanics, and Molecular Dynamics of Geological Solutions**

PERSON IN CHARGE: **F. J. Spera** (805-893-2260; FAX 805-893-8649)
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Objectives:

(1) Construction of high viscosity rheometer and laboratory measurements on magma
(2) Determination by MD simulations of the structure and properties of aluminosilicate melts and glasses
(3) Numerical modeling of magmatic underplating and dynamics of granitic magma ascent
(4) Dynamics of thermohaline porous media convection

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) Construction of new rheological apparatus and laboratory measurements on melts and magmatic suspensions (2) Determination of the thermodynamical and transport properties of molten silicates by MD simulations (3) Three-dimensional modeling of salt diapirs including the effects of dehydration on salt rheology (4) Numerical modeling of magmatic underplating and the formation of granitic diapirs (5) 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 (6) The dynamical influences of lithospheric phase transitions on the thermal-mechanical evolution of sedimentary basins (7) The development of stress fields and criteria for faulting in the crust and finally (8) Numerical modeling of heat and solute transport driven by thermal and salinity heterogeneities in geothermal 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 simulations on melts in the system $NaAlSiO_4$-SiO_4 at 3 GPa and temperatures have been completed. Results have been published in *American Mineralogist.*

Design specifications of the high-temperature rheometer and work accomplished so far are given here. A split-tube vertical muffle furnace with MoSi heating elements capable of temperatures over 1600 degrees C will be employed, allowing great flexibility in experimental design. The split-shell furnace design will allow more precision in setting up the experiments prior to heating. A sample container and support for the experiments were designed and prototypes have been fabricated from 99.5% Al203 ceramic by Superior Technical Ceramics, St. Alban's, VT. A gear/DC servo-motor/tachometer system capable of achieving required output torques to 3 Nm and speeds ranging from 1 to 0.0001 rpm, using a two-stage reduction for the lowest speeds is available from MAXON Precision Motors USA, in Burlingame (San Francisco area), CA. Toque sensors of the required ranges are available from Transducer Techniques, in Temecula (San Diego area), CA. When final specifications for the furnace are decided upon, work will begin on the design and construction of the external supports and mountings. Numerical simulations accomplished to date include an analysis of the evolution of crustal anatexis by basaltic magma underplating and simulations of thermohaline convection in low-porosity porous media.

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GEOCHEMISTRY

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ON-SITE INSTITUTION	FY91	FY92	FY93	FY94	FY95
Argonne National Laboratory	385	440	540	533	655
Brookhaven National Laboratory	–	213	384	363	460
Idaho National Engr. Laboratory	–	35	50	121	119
Los Alamos National Laboratory	2518	2730	2622	1881	2241
Lawrence Berkeley National Laboratory	2109	2225	2340	2253	1897
Lawrence Livermore National Laboratory	2103	2288	2025	1743	1921
Oak Ridge National Laboratory	1097	1209	1041	1163	1140
Pacific Northwest Laboratory	735	780	975	664	665
Sandia National Laboratories	2167	2098	1987	1545	1345
Westinghouse Hanford Laboratory	44	46	45	0	0
Grand Junction Project Office	–	–	87	87	–
total, on-site	11158	12064	12096	10353	10442
total, off-site	5987	7114	7250	8477	7937
total, operating	17145	19178	19346	18830	18379
total, equipment	1110	1302	1270	1262	1141
Total, Geosciences	*18255*	*20480*	*20616*	*20092*	*19520*
OFF-SITE INSTITUTIONS					
U/Alaska (Lee)	145	125	151	–	49
U/Alaska (Eichelberger)*	–	149	120	112	–
Am. Geolog. Inst. (Davin)	–	–	–	36	40
Am. Muus. NY (Mathez)	–	49	39	37	72
Arizona St. (Buseck)	–	–	–	–	126
Arizona St. (Hervig)	–	–	–	62	86
Boston Univ (Klein)	–	–	–	–	71
Brown U (Yund)	71	141	146	302	–
Cal Tech (Clayton)	–	–	139	142	55
Cal Tech (Stolper)	87	90	150	153	123
Cal Tech (Wasserburg)	300	345	370	388	400
Calif, Univ of-Berk (Carmichael)	117	109	115	–	–
Calif, Univ of-Berk (Helgeson)	135	140	150	349	–
Calif, Univ of-Berk (Morrison)	–	68	–	–	–
Calif, Univ of-Davis (Lesher)	–	65	65	66	75
Calif, Univ of-Davis (Rock)	–	83	77	78	–
Calif, Univ of-LA (Harrison)	54	57	–	100	105
Calif, Univ of-LA (McKeegan)	64	–	40	85	–
Calif, Univ of-SB (Spera)	101	–	43	–	82

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Chicago, Univ of (Richter)	–	–	–	247	–
Chicago, Univ of (Rivers)	–	–	–	458	–
Chicago, Univ of (Smith/Sutton)	–	105	126	127	138
Colo, Univ of (Ge)	–	–	–	–	179
Colo, Univ of (Rundle)	–	–	–	–	109
Colo, Univ of (Smyth)	–	93	81	10	–
Colo, Univ of (Spetzler)	50	64	57	145	126
Colo Sch Mines (Larner)	200	–	–	97	–
Columbia Univ (Broecker)	–	–	–	–	131
Columbia Univ (Walker)	127	77	110	103	113
Conn., Univ of (Torgersen)	–	110	31	19	76
Delaware, Univ of (Wood)	67	176	–	90	108
DOSECC (Friedman)*	70	71	–	–	–
Florida, So. Univ of (Compton)	–	122	–	56	–
Florida St, Univ of (SCC)	–	–	99	214	–
Geophys. Lab, CIW (Bell)	–	–	92	89	92
Georgia Tech (Dove)	–	–	–	–	91
Hawaii, Univ of (Martel)	–	–	–	–	81
Headquarters Services	2	5	5	1	–
I.R.I.S. (Simpson)	–	–	–	–	211
Indiana, Univ of (Ortoleva)	80	85	63	–	100
Johns Hopkins Univ (Veblen)	135	134	138	–	156
JPL, IAU Coloq (Tobiska)	–	–	3	–	–
Lehigh Univ (Ilton)	–	–	–	–	44
Lehigh Univ (Moses)	–	–	223	–	–
Maryland, Univ of (Tossell)	–	–	–	35	–
Miami, Univ of (Eberli)	–	127	155	169	155
Michigan, Univ of (Halliday)	–	–	–	147	172
Min. Soc. Amer (Guthrie)	–	–	5	–	–
Minn., Univ of (Yuen)	102	–	47	–	82
MIT (Madden)	–	–	–	70	74
MIT (Toksoz)	485	372	342	374	367
NASA (Blankston)	–	–	–	100	–
NAS/NRC (Benson/Crowley)	–	–	–	10	–
NAS/NRC (Hart/Long/Burke)	200	–	100	–	–
NAS/NRC (Phillips)	–	–	–	121	–
NAS/NRC (Price)	–	–	–	100	100
Nevada, Univ of (Karlin)	–	48	–	–	–
New Mexico, Univ of (Crossey)	–	43	43	–	–
New Mexico, Univ of (Miller)	–	–	–	–	100
NY, City Univ of-CC (Koplik)	–	–	125	121	125

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NY, City Univ of-Q (C. Schreiber)	119	126	92	–	–
NY, State Univ of-SB (Hanson)	124	128	–	121	126
NY, State Univ of-SB (Lindquist)	–	21	22	22	33
NY, State Univ of-SB (Wong)	–	–	–	69	70
Northeastern Univ (Devaney)	–	–	145	–	–
Northwestern Univ (Rudnicki)	–	–	75	72	85
Notre Dame Univ (Pyrak-Nolte)	–	–	61	61	65
Ohio St. Univ (Adler)	56	59	62	161	–
Okla, Univ of (Elmore)	109	112	247	–	112
Oregon St. Univ (Egbert)	–	111	–	–	–
Penn St. Univ (Arthur)	–	129	134	–	–
Penn St. Univ (Brantley)	–	–	–	–	115
Princeton Univ (Navrotsky)	125	130	198	145	150
Purdue Univ (Fritz)	44	47	–	–	–
Purdue Univ (Johnson)	–	–	170	–	–
Rensselaer Polytech. Inst. (Watson)	–	–	–	144	140
Rice Univ (Mango)	–	127	100	97	136
Rust Geotech, Inc (Fukui)	–	–	–	–	87
San Diego St. Univ (Jiracek)	–	10	–	–	–
Santa Fe Inst (Rundle)	–	–	–	11	–
Calif, Univ of So. (Aki)*	160	160	160	155	–
Stanford Univ (Brown)	–	–	241	204	210
Stanford Univ (Ernst)	101	158	–	–	–
Stanford Univ (Harris)	–	–	–	–	115
Stanford Univ (Liou)	–	–	160	–	80
Stanford Univ (Nur)	–	176	–	173	185
Stanford Univ (Pollard)	183	159	–	210	224
Stanford Univ (Segall)	–	70	87	83	83
Stanford Univ (Zoback)	–	–	–	72	38
Tennessee, Univ of (Thonnard)	–	–	–	–	100
Texas, Univ of (Hardage)	–	–	–	–	170
Texas, Univ of-Aus (Land)	–	100	104	104	–
Texas, Univ of-Aus (Nelson)	–	–	–	5	–
Texas, Univ of-Aus (Sharp)	–	98	–	48	–
Texas, Univ of-Dallas (Mitterer)	112	114	0	0	–
Texas A&M Univ (Kronenberg)	143	149	155	156	167
Tulsa, Univ of (Barker)	84	205	–	–	–
USGS (Bredehoeft)	–	–	29	30	–
USGS (Dean)*	–	99	–	–	–
USGS (Kharaka)	–	18	–	–	–
USGS (Russ)	137	56	–	126	–

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Utah, Univ of (Hulen)	–	–	204	–	–
Utah, Univ of (Hulen)*	126	–	–	–	–
Utah, Univ of (Tripp)	–	–	57	59	64
Utah, Univ of (Wannamaker)	–	75	–	–	–
Utah St. (Kestir)	–	–	–	–	99
VPI & SU (Bodnar)	–	127	129	133	104
VPI & SU (Sinha)	74	63	28	–	–
Washington, Univ of (Booker)	–	101	104	247	–
Washington St. Univ-R (Reidel)	45	48	49	5	–
Wash Univ, St. Louis (Shock)	–	46	–	24	53
Wisconsin, Univ of (Bahr)	–	–	–	46	49
Wisconsin, Univ of (Banfield)	–	–	76	98	–
Wisconsin, Univ of (Haimson)	–	–	10	10	–
Wisconsin, Univ of (Valley)	–	–	144	142	149
Wisconsin, Univ of (Wang)	97	99	105	–	60
WHOI (Chave)	–	–	–	91	91
WHOI (Eglinton)	–	99	82	275	–
WHOI (Whelan)	197	199	180	180	191
Yale University (Berner)	–	–	–	–	78
Yale University (Lasaga)	91	113	385	–	207
Other	4	–	5	85	87
OFF-SITE TOTALS	5987	7114	7250	8477	7937