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Summaries of FY 91 Geosciences Research

November 1991

U.S. Department of Energy
Office of Energy Research
Division of Engineering & Geosciences

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Washington, D.C. 20585

MASTER

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 which 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 geology, petrology, geophysics, geochemistry, solar physics, solar-terrestrial relationships, aeronomy, seismology, and natural resource modeling and analysis, including their various subdivisions and interdisciplinary areas. All such research is related either directly or indirectly to the Department of Energy's long-range technological needs.

INTRODUCTION TO THE GEOSCIENCES RESEARCH PROGRAM OF THE OFFICE OF BASIC ENERGY SCIENCES

The Geosciences Research Program is directed by the Department of Energy's Office of Energy Research through its Office of Basic Energy Sciences. Research supported by this program is fundamental in nature and of long-term relevance to one or more energy technologies, national security, energy conservation, or the safety objectives of the Department of Energy. It is also concerned with the identification, extraction, and utilization of energy resources, as well as disposal of related wastes, in an environmentally acceptable way. The purpose of this program is to develop geoscience or geosciences-related information relevant to one or more of these Department of Energy objectives or to develop the broad, basic understanding of geoscientific materials and processes necessary for the attainment of long-term Department of Energy goals. In general, individual research efforts supported by this program may involve elements of several different energy objectives.

The Geosciences Research Program is divided into four broad categories:

- Geology, geophysics, and earth dynamics
- Geochemistry
- Energy resource recognition, evaluation, and utilization
- Solar, solar-terrestrial, and atmospheric interactions.

The following outline of these categories is intended to be illustrative rather than exhaustive, and will evolve with time. Individual research efforts at the Department of Energy Laboratories, academic institutions, research centers, and other Federal agencies supported by this program frequently have components in more than one of the categories or subcategories listed. It is also common that research activities involve a high level of collaboration between investigators at different institutions.

1. GEOLOGY, GEOPHYSICS, AND EARTH DYNAMICS

   A. ***Large-Scale Earth Movements***. Research related to the physical aspects of large-scale plate motion, mountain building, and regional scale uplift or subsidence.

   B. ***Evolution of Geologic Structures***. Research bearing on the history and development of geologic structures (e.g., folds, faults, landslides, and volcanoes) on a local or subregional 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.

   D. ***Rock Flow, Fracture, or Failure***. Research related to response of minerals, rocks, and rock units to natural or artificially induced stress, including the strain rates that range from those appropriate to drilling to viscoelastic response.

E. ***Underground Imaging***. Research related to imaging, especially the crust, to better characterize its layering, mineralogy and lithology, geometry, fracture density, porosity and fluid content, and composition, utilizing the methods of geophysics, particularly seismic and electromagnetic approaches.

2. GEOCHEMISTRY

A. ***Thermochemical Properties of Geologic Materials.*** Research related to thermodynamic and transport properties of natural geologic materials and their synthetic analogues. Emphasis is on generic rather than site-specific studies.

B. ***Static and dynamic Rock-Fluid Interactions.*** Research on energy and mass transport and on chemical, mineralogical, and textural consequences of interaction of natural fluids, or their synthetic analogues, with rocks and minerals.

C. ***Organic Geochemistry***. Research on naturally occurring carbonaceous and biologically derived substances of geologic importance, including the origin and development of coal, petroleum, and gas.

D. ***Geochemical Migration***. Research on geochemical migration in materials of the Earth's crust, emphasizing a generic rather than specific understanding, which may lead to predictive capability. These experimental and theoretical studies focus on chemical transport induced by pressure, temperature, and composition gradients within, between, and by a phase or phases.

3. ENERGY RESOURCE RECOGNITION, EVALUATION, AND UTILIZATION

A. ***Resource Definition and Utilization***. The principal goal of this research is to develop new and advanced techniques that are physically, chemically, and mathematically based, for energy and energy-related resource exploration, definition, and use.

B. ***Reservoir Dynamics and Modeling***. Research related to dynamic modeling of geothermal and hydrocarbon reservoirs in their natural and perturbed (by production, injection, or reinjection) states.

C. ***Properties and Dynamics of Magma***. Field, laboratory, experimental, and theoretical research bearing on the origin, migration, emplacement, and crystallization of natural silicate liquids or their synthetic analogue. It also includes basic studies relating to the extraction of heat energy from hot or molten rocks.

D. ***Information Compilation, Evaluation, and Dissemination***. These research activities are principally oriented toward evaluating existing geoscientific data to identify significant gaps, including the necessary compilation and dissemination activities.

E. ***Continental Scientific Drilling (CSD).*** Research on advanced technology and services as well as scientifically motivated projects concerned with utilizing shallow (0.3 km), intermediate (0.3 to 1 km), deep (1 to 10 km), and super-deep (>10 km) drill holes in the continental United States crust to obtain samples for detailed physical, chemical, mineralogical, petrologic, and hydrologic characterization and interpretation; correlating geophysical data with laboratory-determined properties; and using drill holes as experimental facilities for the study of crustal materials and processes. Research includes aspects of drilling technology development as a part of a multiagency (DOE, USGS, and National Science Foundation) program coordinated by an Interagency Coordinating Group under the aegis of the Interagency Accord on Continental Scientific Drilling.

4. SOLAR, SOLAR-TERRESTRIAL, AND ATMOSPHERIC INTERACTIONS

A. ***Magnetospheric Physics.*** Research directed toward developing a fundamental understanding of the interactions of the solar wind with the terrestrial magnetic field. Research related to 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 effects induced by solar radiation.

C. ***Solar Radiation and Solar Physics.*** Research on the solar constant, structure and dynamics of the sun, spectral distributions, and characteristics of solar radiation of the earth, including the long-term effects of solar radiation on the climate.

PART I

ON-SITE

CONTRACTOR:	**ARGONNE NATIONAL LABORATORY** Argonne, Illinois 60439
CONTRACT:	**109 ENG 38**
CATEGORY:	**Geology, Geophysics, and Earth Dynamics**
PERSON IN CHARGE:	**L. D. McGinnis**

A. Midcontinent Rift Structure beneath Lake Superior *(L. D. McGinnis [708-972-8722; FAX 708-972-7819; E-mail B35698@ANLEES.Bitnet])*

Research objectives of this program are (1) to determine structural and stratigraphic histories of basins associated with the Midcontinent Rift System using deep seismic reflection profiles over Lake Superior and outcrops on the perimeter of the lake, (2) to incorporate a scenario of midcontinent rifting into contemporary thoughts on the evolution of the North American craton, and (3) to evaluate the geologic setting of the rift relative to its potential for accumulation of hydrocarbons.

Early-stage rift processes, evidenced by the presence of deep planar reflectors, involved lava extrusion onto an erosional platform. The main rift stage that followed involved crustal extension, subsidence, and rapid lava extrusion (Keeweenawan) illustrated by fan-shaped reflectors that thicken toward the rift axis. A mixed volcaniclastic facies, characterized by intermittent, strong reflectors, separates the lava flows from overlying sediments that are transparent to elastic wave propagation. Post-volcanic sedimentary basins, including the recently named Marquette and Allouez basins in the western lake, reach 10 kilometers in thickness and are separated from each other along the rift axis by accommodation zones modified by late-stage compression. Compression brought to an end subsidence and sedimentary accumulations. During compression, the Keeweenawan-age volcanics behaved as a single thrust sheet, overriding a basal decollement between Animikie and pre-Portage Lake Volcanic units. The Isle Royale fault is recognized as the decollement in the west-central portion of the lake.

CATEGORY:	**Geochemistry**
PERSON IN CHARGE:	**N. C. Sturchio**

A. Hydrothermal System Evolution *(N. C. Sturchio [708-972-3986; FAX 708-972-6476; E-mail Sturchio@ANLCMT.CMT.ANL.GOV])*

The objective of this program is to achieve a better understanding of rock-water interactions and geochemical transport in shallow portions of the Earth's crust. Current emphasis is on studies of active hydrothermal systems, where we examine the sources of fluids and solutes, the mechanisms and rates of geochemical transport processes, and the relation of hydrothermal systems to larger-scale tectono-magmatic and climatic processes. These problems are addressed through field-based studies that include detailed chemical and isotopic analyses of the materials comprising natural hydrothermal systems. Such work is of basic importance to a wide variety of energy-related concerns involving mass transport in rock-water systems.

We continue to develop applications of uranium- and thorium-series measurements, and stable isotope ratio measurements (Li, B, C, N, O, S, and Sr), in our approach to the problems stated above. Field study areas include the silicic caldera systems of Yellowstone (Wyoming), Long Valley (California), and Valles (New Mexico), and several active andesitic volcanoes in Central America and the Colombian Andes.

We recently completed a study of the Ra isotope geochemistry of thermal waters at Yellowstone National Park. The concentration of ^{226}Ra in Yellowstone thermal waters ranges from < 0.2 to 25.7 dpm/kg. The ($^{228}Ra/^{226}Ra$) activity ratio ranges from 0.26 to 9.8, and that of ($^{224}Ra/^{228}Ra$) ranges from 0.73 to 2.1. Radium concentrations are inversely correlated with aquifer equilibration temperatures inferred from silica concentrations, whereas ($^{228}Ra/^{226}Ra$) and Ra/Ba ratios are dependent upon aquifer lithology. The dominant controls on dissolved Ra concentration appear to be barite solubility and zeolite-water ion exchange. Nuclear (α-recoil) effects are of secondary importance relative to chemical effects. Aquifer-to-surface travel times can be inferred from ($^{224}Ra/^{228}Ra$) variations, but the apparent strong control of Ra isotopes by temperature, water chemistry, and aquifer lithology limits other chronometric applications of Ra isotopes.

The history of hydrothermal discharge and glaciation in the northern Yellowstone area is being investigated through U-series age determinations of travertine deposits. High-precision mass spectrometric U-series measurements were made at Los Alamos National Laboratory in collaboration with M. T. Murrell. Episodes of travertine deposition occurred at ~ 400 ka, ~ 130 ka, ~ 55 ka, ~ 20 ka, and ~ 15 ka to present. The ages of the three most recent episodes, and the stratigraphic relations between the travertines and the glacial deposits (determined by K. L. Pierce of the U.S. Geological Survey), constrain the timing of the Pinedale glaciation in the area. Changes in the location of travertine-depositing springs with time in response to changing glacial conditions, and the compositional characteristics of the travertines (e.g., $^{87}Sr/^{86}Sr$), provide evidence regarding the subsurface permeability distribution and the continuity of the principal hydrothermal flow system in the area.

B. Isotopic Organic Geochemistry *(T. A. Abrajano [708-972-4261; FAX 708-972-6474; E-mail Abrajano@ANLCMT.CMT.ANL.GOV], A. J. Bakel, and B. D. Holt)*

This program aims to elucidate the process of organic matter alteration in sedimentary basins. The results will help define the limiting physical and chemical conditions for the formation, transport, and survival of hydrocarbon compounds in the Earth's crust.

A study aimed at reconstructing the depositional and post-depositional history of the early Proterozoic Animikie basin (Minnesota) through chemical and isotopic study of carbonates and kerogen has been completed. Correlations of $\delta^{13}C_{carbonate}$ with $\delta^{13}C_{organic}$ and with $\delta^{18}O_{carbonate}$ on a regional (basin-wide), local (within single drill core), and intrasample (between individual microbands) scale indicate inheritance of carbonate and organic isotopic compositions from geochemical processes at the time of deposition. Perturbations in total carbonate and total organic contents in sediments close to intrusions indicate only very localized thermal remobilization of organic and carbonate carbon.

A study aimed at understanding the complex isotope exchange history of water, carbonates, and organic matter around the thermal aureole of the Rapidan Sheet, Culpeper basin (Virginia), is in progress. Coupled ^{13}C and ^{18}O depletion in carbonates of the contact-metamorphosed Balls Bluff formation reflects the strong influence of external fluid infiltration on the isotope systematics. Carbon isotope exchange between organic and carbonate carbon is also suggested by the extremely depleted (< –8 per mil) $\delta^{13}C_{carbonate}$ values near the intrusion. Variation in $\delta^{13}C_{organic}$ values is consistent with preferential loss of ^{12}C-enriched low-molecular weight hydrocarbons during magmatic intrusion.

In the laboratory, we have investigated methods of determining the isotopic characteristics of different structural "domains" in kerogen. In contrast to extractable organic matter, kerogens are potentially more reliable recorders of the depositional and post-depositional history of indigenous organic material in sedimentary rocks. Stepped pyrolysis, stepped combustion, and chemical degradation techniques have been suggested by others for this purpose. Our work demonstrated that the stepped combustion technique employed routinely by geochemists studying sedimentary and meteoritic organic components results in partial decomposition and restructuring of structural moieties in kerogen.

Finally, much effort was devoted to setting up a new gas chromatograph/isotope ratio mass spectrometer (GC/IRMS) laboratory. The technique, which enables carbon isotopic analysis of chromatographically separated compounds, has been applied to analyses of saturated and aromatic compounds from numerous extracts and oil samples with a precision of better than 0.3 per mil.

CONTRACTOR:	**LAWRENCE BERKELEY LABORATORY** University of California Berkeley, California 94720
CONTRACT:	**DE-AC03-76SF00098**
CATEGORY:	**Geology, Geophysics, and Earth Dynamics**
PERSON IN CHARGE:	**T. V. McEvilly**

A. High Resolution Mapping of the Electrical Conductivity of the Ground Using Controlled-Source Electromagnetic (CSEM) Methods *(A. Becker, K. H. Lee [510-486-7468; FAX 510-486-5686; E-mail kiha@csem.lbl.gov], and H. F. Morrison [510-642-3804; FAX 510-642-3805], joint research with G. W. Hohmann, University of Utah)*

Studies continued in developing and refining numerical methods for imaging conductivity structures using low frequency electromagnetic (EM) fields. In our studies two CSEM tomographic techniques have been considered. The first approach is a direct adaptation of diffraction tomography to diffusive EM data called "diffusion tomography." One of the developments that took place in the past year involves an extension of the original, and impractical, line source formulation to the case of a vertical magnetic dipole in a borehole surrounded by radially symmetric inhomogeneities such as an expanding steam front. The other important development has been in the modification of the algorithm by replacing the original wavenumber-domain approach with the spatial-domain one. As a result we can achieve much better conductivity imaging using the higher-order Born approximations through iterations.

The second approach involves a transformation of diffusive EM fields into wave fields that satisfy a wave equation in fictitious time. The velocity of such a wave field is inversely proportional to the square root of conductivity. The idea is to use these wave fields to map conductivity distribution by directly applying imaging techniques such as transmission ray tomography. Our initial work suggested that a drawback to this approach was that more than four decades of high accuracy frequency domain data would be required. Recent work, however, shows that only two decades of time-domain data may be required to simulate meaningful wave fields. We need data to validate this approach, and for this purpose we are developing a new t-k numerical modeling algorithm.

Another objective of our work has been to critically evaluate the accuracy and resolution of a recently developed 3-D integral equation inversion scheme using high quality CSEM data. Although correct in estimating the geometry of the conductivity anomaly between bore holes, the information provided by the diffusion tomogram is essentially qualitative. To further refine the resolution, the output from the diffusion tomogram can be used as an initial guess for the least squares inversion. We have used the 3-D integral equation algorithm developed by the CEMI group of University of Utah for a conventional least squares inversion. We have successfully tested this concept using scale model data obtained from our Richmond Field Station.

B. Deep Electromagnetic Sounding *(H. F. Morrison and K. H. Lee [510-486-7468; FAX 510-486-5686; E-mail kiha@csem.lbl.gov])*

Deep electromagnetic (EM) sounding is a qualitative term used for EM mapping of electrical conductivity at depths in excess of 2–3 km. Controlled-source EM (CSEM) methods for these depths require high moment sources and sophisticated receivers and noise cancellation schemes to detect signals in the natural EM background. The magnetotelluric (MT) method uses the natural EM background, but the method has been thought to lack the resolution provided by CSEM. In the past year we have analyzed the vertical and horizontal resolution bounds that can be expected from properly sampled MT fields. In the process, we have also developed a remarkably effective direct imaging technique using a spatial transform of the surface fields.

This study is based on a linearization of the relationship, developed by Torres-Verdin and Bostick, between a perturbation in subsurface conductivity and the resulting perturbation in the surface electric and magnetic fields. Although this approach should only be valid for low contrasts in conductivity, we have found that the geometry of the fields is accurately determined, and this analysis is very well suited for basic studies of the resolving power of MT and for a simple imaging scheme. In addition, we have shown the power of spatial averaging in removing static effects. Also it has been shown in the analysis that in practice the maximum wavenumber that can be recovered from the subsurface resistivity distribution is inversely proportional to the Bostick depth of penetration at that particular sounding frequency. This analytic result has been demonstrated on numerically simulated data with and without electric static distortions.

Finally, we have developed an inversion scheme based on this linearized relationship. In this scheme 1-D inversions are carried out for each wavenumber and the results are inversely Fourier transformed to reconstruct the conductivity. This inversion procedure has been tested on numerically simulated data, and the results are remarkably good. In particular, it appears that this approximate wavenumber scheme will be an excellent first step in the application of a more rigorous nonlinear inversion using accurate finite difference or finite element forward solutions. We have applied this inversion scheme to a profile of MT stations taken at the Surprise Valley, California, geothermal area. This project, done in cooperation with Transpacific Geothermal, has been very helpful in understanding the deep conductivity structure.

C. Center for Computational Seismology (CCS) *(T. V. McEvilly and E. L. Majer [510-486-6709; FAX 510-486-5686; E-mail elmajer@lbl.gov])*

The establishment and continuing base level support of CCS has provided a facility that has aided not only BES programs but other DOE, government, and private industry cooperative ventures. CCS has now been built to the point where it can offer a wide variety of state-of-the-art software and hardware to carry out research at the highest level. During the last year research has focused on using active and passive sources for subsurface imaging on a variety of scales for a wide range of applications.

The CONVEX C-1/XP was replaced by a Solbourne 902 as a compute engine. This augments the Solbourne 602 file server, which was purchased during the last year. The Solbourne 902 is a dual processor (upgradeable to 8 processors) machine running a SUN Unix (UNIX is a Bell Labs trademark) operating system. The 902 is 25% faster than the 602, thus giving approximately 65 Mips of processing power at 12 Mflops for the dual processor machine. An additional 2 Gigabytes of disk space was added to bring the capacity to over 12 Gbytes. Currently there are over 60 routine users on CCS. One hundred six scientific publications have been produced with CCS report numbers. Interested people should contact E. Majer at LBL (elm@ccs.lbl.gov) for a list of these reports.

CCS has continued support of several different areas of seismology. The processing and interpretation of VSP data for fault delineation and fracture detection, CALCRUST, tomographic imaging, the analysis of natural source data for whole Earth imaging and detailed fault imaging, and several projects for the DOE nuclear waste program.

Some examples of CCS's role in seismic research are

1. Analysis of seismic data for CSDP and thermal regimes programs as well as other BES projects at LBL and other national laboratories (BES).
2. Development of seismic exploration and monitoring techniques for the geothermal industry (DOE geothermal and private industry).
3. Fracture detection research using VSP/tomographic techniques (DOE geothermal, waste isolation, and private industry).
4. Data processing for CALCRUST, a consortium of four universities using seismic reflection methods for intermediate and deep crustal structural analysis (NSF and private industry).

5. Computational support for software and hardware development of field systems for seismic monitoring (BES, DOE geothermal, waste isolation, private industry).

D. Microcrack Growth in Crystalline Rock *(L. R. Myer [510-486-6456; FAX 510-486-5686; E-mail myer@lbl.gov] and N. G. W. Cook)*

The purpose of this study is to develop a fundamental understanding of the growth of microcracks in brittle rock under compressive stress conditions. The results have broad applicability to any problems requiring knowledge of the effects of discontinuities on the mechanical properties of rock masses.

Previous theoretical work resulted in new crack models that were used to simulate the stress-strain behavior of brittle rock under triaxial compression. An experimental study aimed at obtaining quantitative data on microcrack growth under triaxial loading conditions was completed. As part of this study a Wood's metal casting technique was developed to preserve microstructures as they exist under load. Additional numerical studies have been carried out to investigate crack interaction in failing rock.

Recent emphasis has been on the effects of microstructure on the process of rock fracture associated with drilling. Laboratory indentation tests have been carried out, employing the Wood's metal casting technique to study the microstructure. Results have shown that, in porous rocks under high hydrostatic stress, the mechanism of fracture due to indentation associated with drilling is controlled by pore collapse and compaction of comminuted material.

This work has now been extended to investigate the influence of wetting and non-wetting fluids on the failure processes associated with indentation. Limestone samples were tested at elevated temperatures using sulfur, a wetting fluid, and Wood's metal, a non-wetting fluid, as pore fluids. Results showed that the force required for indentation was greater when the non-wetting fluid was used as the pore fluid. The interpretation is that the non-wetting fluid does penetrate the smallest apertures at the tip of cracks. As a result the crack tip is subjected to a confining pressure equal to the pore pressure in the liquid. This, in turn, inhibits crack growth and coalescence.

Detailed scanning electron microscope (SEM) studies were carried out to compare the fracture geometry beneath the indenter when wetting and non-wetting pore fluids were present. In the presence of the non-wetting fluid, the grains in the compacted region were more highly comminuted and shear bands originating at the cavity produced by the indenter were oriented at smaller angles with respect to vertical. In both cases, however, it was apparent that extensile crack growth and kinematic movement were key fundamental processes leading to the observed behavior.

E. Process Definition in Fractured Hydrocarbon Reservoirs *(L. R. Myer [510-486-6456; FAX 510-486-5686; E-mail myer@lbl.gov], N. G. W. Cook, J. C. S. Long, E. L. Majer, T. V. McEvilly, H. F. Morrison, and Y. W. Tsang)*

This program addresses the problems associated with detecting and determining the physical properties of fracture systems and relating these measurements to fluid transport in fractured hydrocarbon reservoirs. An integrated interdisciplinary approach has been adopted, involving laboratory studies of basic physical processes and properties of fractures, development of complementary seismic and electromagnetic methods for imaging of fractures and heterogeneities, numerical studies of flow in fracture networks of heterogeneous geometry, and hardware development for seismic imaging.

In the areas of fracture detection by geophysical methods, several goals have been accomplished. Complementary tomographic techniques have been developed for imaging of fractures using seismic and electromagnetic (EM) energy. A seismic diffraction tomography program has been developed and successfully applied to a data set from a small scale *in-situ* test. An electromagnetic diffusion tomography algorithm has also been developed with application to detection of planar fractures illuminated by a dipolar magnetic field. Both the diffraction tomography algorithm and the diffusion tomography algorithm used the Born approximation in the solution scheme. Work on imaging using EM techniques has continued with the investigation of a new approach, applicable to low frequencies, for modeling diffusion processes.

In this approach, diffusion processes are decomposed into a series of Fourier transforms that permit application of conventional seismic acoustic diffraction algorithms with back propagation.

In an activity complementing the seismic diffraction tomography development, a new approach to modeling wave propagation through fractured media is being studied. In this approach each fracture is represented by a zero-thickness interface with varying rheological properties. Seismic displacements and velocities are discontinuous across the interface. For a wave traveling through a rock containing a set of plane parallel fractures, this theory predicts a different variation in velocity with angle of incidence than would be predicted based on conventional effective moduli theory. The theory also predicts the existence of an interface wave, even if the material properties are the same on both sides of a fracture. Current work involves modeling of a data set from a crosshole survey in basalt containing pronounced structural anisotropy.

Laboratory measurements in support of the seismic theoretical studies have shown that the chemical interactions at the solid-liquid interface in a saturated fracture strongly affect, along with liquid viscosity and film thickness, the transmission of shear waves across the fracture. On-going laboratory seismic measurements on a schistose rock are providing both velocity and amplitude data for the study of shear wave birefringence.

In the study of methods for integrating geophysical data into hydrologic models, work has continued on application of conditional inverse methods. In these methods, geophysics is used to identify the major conductive elements in the rock mass. Then a model for the hydraulic properties is derived using simulated annealing. This technique was applied to a granitic rock mass in Sweden, where a significant amount of geophysical and well test data were available. Geophysical analysis yielded the location and orientation of seven major fracture zones. These zones became the base model for annealing, which was used to find a model that behaved like the pressure interference tests performed at the site. New capabilities were added to the annealing codes in order to be able to best utilize this type of data. For example, the code was modified to be able to co-invert several transient tests simultaneously. These methods have application to finding the connectivity of fracture systems in petroleum reservoirs, which is critical to secondary recovery operation.

Fundamental laboratory studies of fluid flow in single natural fractures have also been carried out. These studies revealed deviations from the "cubic law" over a wide range of apertures. It was found that departure from the cubic law could be quantitatively related to the tortuosity developed due to the roughness of the fracture surfaces. A new approach to analyzing tracer transport breakthrough data in highly heterogeneous fractured media has also been developed. The data are interpreted based on the conceptual model that flow is channelized in each single fracture in the medium. Data analysis affords the estimation of parameters such as mean aperture and the spatial correlation of the apertures of the flow channels important to fluid transport. A journal paper summarizing this new approach and its application to a set of field data is under review for publication in *Water Resources Research*.

Finally, work in hardware development for fracture characterization has centered on completion of a downhole swept frequency resonant shear wave source. Recent effort has resulted in completion of electronics for control and stabilization and a borehole clamping system. Final preparations are underway for field testing.

F. Coupled THM Processes in Petroleum Reservoirs *(C.-F. Tsang [510-486-5782; FAX 510-486-5686; E-mail chinfu@lbl.gov] and J. Noorishad)*

Various aspects of petroleum reservoir engineering, such as isothermal and nonisothermal hydraulic fracturing and permeability variations near injection and production wells, involve coupled thermal-hydraulic-mechanical (THM) processes. The computer code ROCMAS was developed to address these coupled phenomena. The aim of this project has been to improve the numerical solution approach used in the code and to enhance its modeling capability. In the area of computation, a major advance in the formulation of an efficient upstreaming method for the numerical solution of coupled transport problems has been achieved. With this technique the difficulties associated with sharp fronts, in convection dominated transport, can be dealt with. The studies resulted in a fundamental understanding of the nature of difficulties in solving hyperbolic equations. As a result, we are in the process of developing a criterion for more efficient space-time finite element solutions of these problems. In the area of code enhancements, we have accomplished an important step by implementing a solid elastoplastic material model in the ROCMAS code. The major part of the verification task of this new capability of the code has been completed.

G. Advanced Geoscience Research Concepts *(T. V. McEvilly [510-486-7347, FAX 510-486-5686; E-mail mcevilly@lbl.gov])*

This activity provides support to encourage development of new ideas in the geosciences. In this respect activities often encompass preliminary evaluation of the feasibility of performing contemplated research and scoping of experimental plans.

Development of the new STAR DENT graphics system for earth sciences applications had led to a new capability for display and manipulation of three-dimensional seismological data. This tool will greatly facilitate late analysis in many investigations of crustal processes.

A preliminary search for underground workings (mining and civil works) that would permit access for an underground Geosciences Research Facility (URF) was carried out. Site visits were conducted to three candidate openings: the Soudan mine, near Hibbing Minnesota, a fractured metamorphic greenstone; the CB and Logan Wash oil shale mines near Rifle, Colorado, both in fractured dolomitic marlstone; and the Collierville Adit in California, in quartz-mica schist. Results of these visits were presented at a meeting of the Underground Research Facility Working Group. The committee concluded that establishing a URF in an existing opening was feasible and recommended action aimed at gaining concurrence on the concept of a URF within the broad earth sciences community.

Finally, in a new effort, Sr isotopes in San Francisco Bay sediments are being used as a proxy for paleosalinity of the Bay. This, in turn, is then used as a measure of the Sacramento-San Joaquin river system. This project is being conducted to demonstrate the value of isotopic studies for addressing questions associated with global climate change. Preliminary measurements indicate that the method can be used to determine the cyclic nature of the river system discharge over the past 5000 years.

CATEGORY: **Geochemistry**

PERSON IN CHARGE: **T. V. McEvilly**

A. Thermodynamics of High-Temperatures Brines *(K. S. Pitzer [510-486-5456; FAX 510-642-8369; E-mail kspitzer@lbl.gov])*

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 certain geothermal and other natural resources and in fission-product waste disposal. Moreover, this information has a wide range of applicability, since similar solutions arise in many industrial processes and in high-pressure steam power plants.

The experimental program involves measuring heat capacities and heats of mixing or dilution of solutions at temperatures extending above 300°C and pressures to 1 kbar. The data base for the principal components of natural waters has now become adequate for the prediction of mineral solubilities up to 300°C in brines containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, OH^-, SO_4^{2-}, and H_2O. Contemplated research will extend this list to include Fe^{2+} and HS^-. Once the parameters are established for binary and common-ion ternary systems, no further parameters are needed for more complex brines and calculations are truly predictive.

The current theoretical program emphasizes CO_2 and the binary CO_2-H_2O. An empirical equation for

CO_2-H_2O was developed in connection with new volumetric measurements made at Virginia Polytechnic Institute for the range 400–700°C and 2–6 kbars. Current research is directed to a new general equation of state for CO_2 for the very broad range 218–1600 K and 0–40 kbars. This equation will then be generalized to the binary H_2O–CO_2 in a manner consistent with the statistical mechanics of multicomponent systems and connecting with an accurate equation of state for pure H_2O.

B. Studies of the Interactions between Mineral Surfaces and Ions in Solution *(D. L. Perry [510-486-4819; FAX 510-486-5401])*

This task encompasses fundamental studies to determine the basic surface chemistry of common minerals (both synthetic and natural) and the chemical reactions of metal ions with the mineral surfaces. The research encompasses (1) basic spectroscopy of natural minerals and their synthetic counterparts, (2) spectroscopic studies of metal ions that have been adsorbed onto the mineral surfaces, (3) syntheses and spectroscopy of model compounds that form in metal ion-mineral reactions, and (4) spectroscopy of organic compounds that have been chemisorbed onto minerals with metal ions associated with them.

X-ray photoelectron and Auger spectroscopic techniques have been used to study the surface of galena (PbS) and clausthalite (PbSe) and their reactions with silver and other metal ions in solution. These reactions, conducted at temperatures between 25 and 100°C in order to vary the kinetics and the extent of the reactions, are shown to vary greatly from the analogous reactions in which the reacting substrates are oxidized galena and clausthalite surfaces. The resulting surfaces are observed to be much less heterogeneous than the comparable reactions involving the oxidized surfaces. The air oxidation of PbSe, a species that is analogous and isostructural to PbS and also one that has been implicated in a number of environmental waste systems, also has been studied.

One example of a reaction system that gives dramatic results in this series is that of the solution interaction of aqueous silver(I) ions with the galena surface. Studies of that reaction surface using x-ray photoelectron and Auger spectroscopy indicate variable amounts of silver on the surface as a function of different sites. These studies also indicate the existence of segregated islands on the surface that are enriched in silver.

It is clear from these experimental data that the PbS and PbSe surfaces involved in interface reactions as described here cannot be satisfactorily described as a simple homogeneous surface available for dissolution or other subsequent reactions. Rather, the solid/solution interface reaction processes involving these surfaces can only be modeled as processes that must include a multiplicity of reactions involving chemical species such as silver(I), silver(0), lead(II), sulfur, and selenium. These (and related) reaction systems of metal ions will be studied further with respect to the reaction products, mechanisms, and kinetics. The experimental work described here with traditional x-ray photoelectron, Auger, and other types of spectroscopy is preparatory to studying these geochemical systems with the Advanced Light Source at Lawrence Berkeley Laboratory. Additionally, parallel research in these chemical systems of geologic materials is being continued using synchrotron radiation.

C. Chemical Transport in Natural Systems *(C. L. Carnahan [510-486-6770; FAX 510-486-5686; E-mail chalon@lbl.gov])*

This research involves theoretical and numerical studies of processes affecting the movement of chemically reactive solutes in groundwater flow systems. These studies are relevant to the understanding and quantitative description of a variety of energy-related phenomena including the production of geothermal energy, the formation of ore deposits, the chemical evolution of fluids in deep sedimentary basins, and the subsurface migration of toxic and radioactive wastes.

The theoretical studies focus on the development of conceptual and mathematical models based rigorously on physical, chemical, and thermodynamic principles. The models are the bases for computer programs that solve the coupled partial differential and nonlinear algebraic equations describing movement of dissolved reactive chemicals in geological media.

The computer program THCC, a simulator of migration of solutes participating in homogeneous and heterogeneous chemical reactions, has been modified to account for feedback from chemical reactions to fluid flow. The new program, THCVP, simulates changes of permeability (and, thus, fluid flow) caused by precipitation or dissolution of reactive solids. The THCVP program is a potentially useful tool for predicting mobilization (or immobilization) of chemicals as well as permeability changes in the subsurface produced by injection of reactive chemicals through boreholes or by mixing of waters having different chemical compositions. The effects of varying temperature on chemical reactions can be included in simulations with THCVP; this feature extends simulation capabilities to subsurface regimes influenced by variable temperature fields.

Extensive computations required by these investigations are made possible by OBES-supported access to supercomputers. Fundamental research carried out under this project has led to support by other DOE activities for applications to their particular interests.

D. Center for Isotope Geochemistry *(D. J. DePaolo [510-486-4975; FAX 510-486-5686; E-mail stborg@lbl.gov])*

The Center research combines 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. Current effort is concentrated on Sr, Ca, O, and Nd isotopic ratios and on problems of mass transport in fluid-rock systems, interpretation of past global climatic change, stratigraphy and structure of sedimentary basins, and crustal magmatic and tectonic processes.

Isotopic ratios can be useful indicators of subsurface hydrological parameters such as fluid residence times, fluid-rock reaction rates, and solute retardation factors and processes. 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. This approach is supplemented by systematic measurements of relatively simple natural systems and by the development of improved sampling and measuring techniques to enhance information return. Emphasis in development is on microsampling of geological materials and on high precision measurement of the small amounts of recovered material.

Isotopic measurements of natural waters and minerals precipitated from such waters are an important source of information on past Earth climatic and hydrological conditions. Such information is critical for all types of waste management and constitutes important baseline data for evaluating models of atmospheric processes. Our approach is to use mathematical models to understand how secondary processes affect climatic proxy indicators and to use the models to design measurement programs aimed at obtaining more reliable records. Our studies use continental groundwater and river water records as well as oceanic records.

Other efforts of the Center are aimed at geochemical techniques for dating and correlation of sedimentary rocks and for understanding the time scales and mechanisms of crustal processes such as extensional faulting, mountain building, and volcanism.

CATEGORY:	**Energy Resource Recognition, Evaluation, and Utilization**
PERSON IN CHARGE:	**T. V. McEvilly**

A. Hydrothermal Chemistry *(H. A. Wollenberg [510-486-5344; FAX 510-486-5686; E-mail mcevilly@lbl.gov])*

These activities are primarily associated with the Continental Scientific Drilling Program, where emphasis has been on the study of rock-fluid interactions in hydrothermal systems associated with calderas. Strong collaboration continues with colleagues at the Los Alamos National Laboratory and the USGS. Alteration mineralogy and isotope ratios in rock matrix and fracture linings are combined with chemistries and isotope ratios of downhole fluid samples and springs and with mineralogy of drill core and cuttings to determine the extent of rock-water interactions. Oxygen, hydrogen, carbon and strontium isotope ratios are used to trace the paths of hydrothermal fluids from precipitation in recharge areas through the hydrothermal systems to surface manifestations. Alteration mineral assemblages are used to reconstruct thermal regimes associated with earlier hydrothermal circulation. At Long Valley, California, isotope ratios in drill cores and surface outcrops, as well as in hydrothermal fluids and mixed meteoric-hydrothermal waters from surface springs, support the concept of contact of hydrothermal fluids with basement rocks, followed by upward flow of the fluids in the caldera's west moat and their subsequent eastward movement in the caldera fill. We are exploring opportunities with the geothermal industry to collaborate in deep drilling that would investigate the upflow zone of the caldera's hydrothermal system. Hydrothermal systems of the Valles and Long Valley calderas also provide settings for investigating mineral associations and mobility of uranium and thorium at elevated temperatures, under conditions analogous to those expected in tuffaceous rock encompassing a high-level radioactive waste repository.

B. Geophysical Measurements Facility *(T. V. McEvilly [510-486-7347; FAX 510-486-5686; E-mail mcevilly@lbl.gov] and H. F. Morrison)*

The Geophysical Measurements Facility (GMF) at LBL operates to facilitate the use of the large complement of field systems and equipment by researchers needing the particular measurements for their projects. The GMF support is used to maintain systems in field-ready condition and to instruct users in safe and technically proper equipment operation. Support comes from specific research projects for upgrading hardware and software, for fabricating new or modifying existing equipment, and for assistance in field deployments and operations. Examples during this reporting period are (1) operation and maintenance of microearthquake networks in use at The Geysers, Coso, and Parkfield; (2) operation and maintenance of the logging trucks and Vibroseis units used in several projects; (3) successful deployment of the downhole fluid sampler on ODP Leg 137 in a 165°C hydrothermal system on the Costa Rica Rise; and (4) hydrological and geophysical field studies at the Kesterson and Stillwater study areas. The GMF provides a test and development environment for the in-field seismic tomographic imaging system; operation of the aquifer test facility at the Richmond field station; crosshole tomography at the LLNL dynamic stripping remediation exercise; execution of a VSP and HE explosion source experiment for LLNL at NTS; field and technical support for the 10-company/DOE research in Texas on crosshole EM imaging; and assistance through equipment loans to various labs, universities, and Federal agencies needing modern field capabilities in geophysical measurements. GMF is a small but critical element in the LBL geoscience research effort.

CONTRACTOR:	**LAWRENCE LIVERMORE NATIONAL LABORATORY** University of California Livermore, California 94550
CONTRACT:	**W-7405-ENG-48**
CATEGORY:	**Geology, Geophysics, and Earth Dynamics**
PERSON IN CHARGE:	**F. J. Ryerson**

A. Rheology of Partially Molten Crustal Rocks *(F. J. Ryerson [510-422-6170; FAX 510-422-1002; E-mail ryerson@s91.es.llnl.gov], W. B. Durham, and B. P. Bonner)*

The diapiric rise of granite magma bodies through the lithosphere is an important process in controlling the distribution of heat-producing elements in the Earth's crust. Similarly, the post-emplacement fractionation processes within the crust control the subsequent chemical evolution of such magmas and the transfer of heat to the country rocks. The rates and efficiencies of these processes are difficult to evaluate owing to the paucity of data describing the rheological evolution of crustal lithologies throughout the melting interval. In this project we are developing the equipment and techniques required to measure the plastic deformation of crustal lithologies under conditions of crustal deformation. Current work concentrates on quartz-bearing aggregates both with and without the presence of alkali silicate partial melt. Similar experiments by previous workers have required relatively high confining pressures and temperatures in order to suppress brittle behavior. This is most likely due to the dominance of intracrystalline deformation mechanisms in samples with relatively large grain size. In order to enhance the contribution of grain boundary processes, we have focused a great deal of effort on the synthesis of monodisperse fine-grained aggregates. The sample powders are produced by spray drying components which are either totally in solution or in colloidal suspension. This process results in quartz aggregates with average grain sizes below 5 μm. Deformation experiments have now been performed on melt-free and melt-bearing aggregates at 1000°C and confining pressures of 2 MPa. Relative to the results of other workers, the greatest effect on sample strength appears to be associated with grain size; previous work on Heavitree quartzite deformed at 1000°C under "wet" conditions yields a differential stress of 700 MPa, although we have obtained differential stresses as low as 100 MPa in melt-free samples. The presence of melt at the 5 vol% level further decreases the differential stress but not nearly so dramatically. This may indicate that the weakening associated with the presence of a molten phase is due to stress concentration along the reduced volume of solid-solid grain junctions rather than to a change in deformation mechanism. The viscosities calculated from our experimental results are in good agreement with those obtained from models of granitic diapirism constrained by geochronologic data.

B. Diffusion in Silicate Materials *(F. J. Ryerson [510-422-6170; FAX 510-422-1002; E-mail Ryerson@s91.es.llnl.gov])*

Knowledge of the rates of diffusive transport in rock-forming minerals helps to constrain a multitude of geologic processes as well as providing information on the basic point defect chemistry of crystalline solids. For instance, diffusion parameters are required in the definition of closure temperatures for the various radiogenic clocks, thereby forming the basis for determining the thermal history of the Earth's crust. Similarly, isotopic exchange of oxygen between host rock minerals and hydrothermal solutions may be controlled by diffusive transport, and the thermal history of such interactions may eventually be elucidated through the analysis of oxygen isotopic diffusion profiles in the host minerals. The goal of this project is to determine the diffusion coefficients of various geochemically important elements in rock-forming minerals and melts and then to apply these data to a variety of geological problems. The project currently concentrates on the determination of diffusion coefficients of radiogenic isotopes in accessory minerals and oxygen diffusion in major rock-forming silicate and oxide phases. Previously, we have measured Pb and Sr diffusion in apatite and zircon between 900°C–600°C using a technique that combines ion implantation of the tracer followed by annealing and subsequent analysis of the diffusion profiles by Rutherford backscattering spectroscopy. Although the Pb and Sr data for apatite are in good agreement with those from previous high temperature measurements, the results of Pb diffusion in zircon were as much as 5 orders of magnitude greater than those obtained by geochemical inference, indicating the effects of radiation damage. To eliminate the possible effects of radiation damage on the diffusion coefficients determined for apatite, we have repeated the measurements by exchanging apatite with a powdered SrO reservoir. This method yields well-behaved chemical diffusion profiles, and the diffusion coefficients obtained are in excellent agreement with those obtained using the implantation technique. Taken together with our previous high temperature results, these new data comprise a single Arrhenius plot from 1200°C–600°C indicative of a single dominant diffusion mechanism in this temperature range. The extension of measurements to the lower temperature regime is important, as it eliminates the need to extrapolate the higher temperature data (which cover a relatively small range of 1/T) to crustal temperatures. For instance, when extrapolated to lower temperatures, Pb diffusion data for apatite obtained between 1000°C and 1200°C yield closure temperatures 100°C higher than those calculated from the lower temperature diffusion data for similar grain sizes and cooling rates. The determinations based upon the lower-temperature measurements are in closer agreement with closure temperatures based upon other isotopic systems.

C. **Electrical Conductivity, Temperature, and Radiative Transport in the Earth** *(A. G. Duba [510-422-7306; FAX 510-423-1057; E-mail duba @s61.es.llnl.gov] and B. J. Wanamaker, joint research with T. J. Shankland and L. M. Hirsch, LANL [E-mail SHANKLAND@ESSDP1])*

Both electrical and optical research efforts help determine temperature distributions in the crust and upper mantle. Electrical conductivity and thermoelectric effect in the mantle minerals olivine and pyroxene are being measured as a function of temperature, orientation, oxygen fugacity, and iron content. Ordinarily inference of upper mantle temperatures from electrical data is accomplished by inserting electrical conductivity (σ) measured in the field into the σ-T relationship. The intent of this work is to comprehend in detail the electrical conduction mechanisms in mantle-forming minerals so that mechanical, seismic, and electrical properties of the Earth's mantle may be understood to the point of predicting their values. A source of uncertainty derives from a compositional discrepancy: we have the most accurate and reproducible conductivities for mantle olivine by itself, but upper mantle rocks have other mineral phases, principally pyroxene, that lower the bulk Mg/Si stoichiometry from that of olivine. We have investigated the effect of buffered silica activity on conductivity of single olivine crystals by dusting samples with a layer of powdered pyroxene that acts as a silica reservoir. There is a measurable change, a decrease of log σ by 0.1 to 0.2 $\log_{10}$ units. Theoretical calculations of point defects support the conclusion that pyroxene activity produces a minimal effect by confirming the small change in majority carriers. These calculations are based on the mass-action equations governing equilibrium thermodynamic concentrations of point defects and on further constraints such as bulk charge neutrality and lattice site conservation. The major implication of this result is that the defect concentrations of the dominant charge carrier responsible for conduction in olivine in this temperature regime seem not to be grossly affected by the presence of pyroxene. Thus we believe that the minor effect of pyroxene can be treated as a perturbation when calculating temperature-depth relationships (electrogeotherms) for the mantle from olivine conductivity data. With this major uncertainty diminished we feel much more confident about using single crystal data from mantle-derived crystals to calculate conductivities, and mantle temperatures inferred from these conductivities are on a much firmer basis.

D. Attenuation and Dispersion in Partially Saturated Rocks *(J. G. Berryman [510-423-2905; FAX 510-422-1002; E-mail berryman@s123.es.llnl gov] and B. P. Bonner)*

The objective of this project is to combine theory and experiment to analyze attenuation and dispersion of waves in partially and fully saturated rocks over a broad range of frequencies. The techniques developed in this work will be applicable to many basic problems in energy recovery and will enable us to devise better methods of hydrocarbon and geothermal exploration and resource assessment and to improve remote sensing of groundwater flows for environmental applications. The results also are relevant to code calculations which simulate explosion induced high amplitude wave propagation and for the evaluation of seismic treaty verification issues.

Theories relating hydrological properties and wave propagation require independent measurements of the pore distribution and shape for the rocks of interest. We have applied high resolution acoustic reflection imaging to obtain grain scale images of sandstones, limestones, and oil shale that indicate porosity as well as other information, including relative acoustic impedance, texture, and the integrity of grain contacts. These laboratory results demonstrate that the resolution of acoustic methods can be increased to extract details of the physical properties useful for predicting the mobility of fluids underground.

Our theoretical efforts have led to a new fundamental result in the theory of wave propagation in saturated porous media, therefore extending our ability to determine pore fluid properties from measurements of the elastic properties, e.g., seismic velocities. Gassmann's equation shows how the elastic properties of a simple porous material depend on the compressibility of a saturating pore fluid. The simplification of Gassmann is embodied in the assumption that the porous elastic frame is composed of only one type of solid constituent. Since rocks generally contain multiple elastic constituents, Gassmann's result, although it is widely quoted and used, is nevertheless of somewhat limited practical value. Brown and Korringa have shown how to generalize Gassmann's result to porous frames with essentially arbitrary numbers of solid constituents, provided the pore size is much smaller than the length scale of variation of the solid constituents in the porous phases, and they found that only two new elastic parameters needed to be introduced. Although their result is quite general and provides a means of analyzing experimental data, it has not been possible (until now) to identify and compute the new parameters based on knowledge of the properties of the constituents except in the special case considered previously by Gassmann.

Berryman and Milton have derived exact results for the two parameters introduced by Brown and Korringa when the porous frame is composed of two distinct types of porous solid. It was also shown that additional results (such as rigorous bounds on the parameters) may be easily obtained by exploiting an analogy between the equations of thermoelasticity and those of poroelasticity. The method used to derive these results may also be used to find exact expressions for three-component composite porous materials when thermoelastic constants of the components and the composite are known. These exact results have been compared to single-scattering approximations for Biot's coefficients. The average T-matrix approximation, the coherent potential approximation, and the differential effective medium have all been shown to agree with Gassmann, with Brown and Korringa, and with the new results of Berryman and Milton. These formulas were also applied to the analysis of clayey sandstone.

E. Quantitative Image Analysis to Determine Rock Properties *(J. G. Berryman [510-423-2905; FAX 510-422-1002; E-mail berryman@s123.es.llnl gov] and S. C. Blair [510-422-6467; FAX 510-423-1057; E-mail blair@)s55.es.llnl.gov])*

The objective of this project is to use advanced image processing and analysis techniques to characterize the physical and mechanical properties of rocks. Important features of the topology of the pore space of rocks can be usefully quantified by analyzing digitized images of rock cross sections. One approach computes statistical correlation functions using modern image processing techniques, and we have successfully used these techniques to aid in prediction of the permeability of several different sandstones. During this year our work has focused on the study of relative permeability of sandstones and extension of our analysis to include the mechanical properties of rocks. This work is being pursued in collaboration with Professor Neville G.W. Cook at U.C. Berkeley.

In the study of relative permeability, we investigated two-phase flow in a sandstone. This was accomplished by first producing and analyzing images of a sample of Berea sandstone in which the pore space was segregated into regions occupied by wetting and nonwetting pore-casting phases. We then applied the Kozeny-Carman relation to the total pore space and the pore space occupied by each phase.

Our estimate of the overall permeability of the sample was within a factor of 2 of the measured permeability. Moreover, we found that the nonwetting fluid occupied the large, well-connected pores and that these pores controlled the permeability of the sample and had very low specific surface area. The pore space occupied by the wetting phase consisted of small isolated regions with high specific surface area. We also found that the nonwetting phase was imbibed at a saturation close to its percolation threshold and that, to estimate the relative permeability accurately for this phase, information on the tortuosity and/or percolation thresholds must be incorporated into the analysis. We developed analytical expressions which incorporate the percolation thresholds and also developed a simple but rigorous analytical expression relating the surface area of fluid/fluid interfaces to other surface areas considered in multiphase flow. Work also continues on measuring higher order correlation functions using image processing methods and applying them to the prediction of rock properties.

Our goal in the mechanical study is to develop a general methodology that can predict the mechanical behavior of rocks in the brittle field, based on properties of the rock microstructure and the rock mineral components. The mechanical behavior of rock in compression and at conditions appropriate to brittle behavior is known to be controlled by the growth and coalescence of microcracks. One method of analysis that can be used to study this process is "self-organized criticality," which is defined as the tendency of large interactive systems to evolve naturally toward a critical state in which a minor event can lead to catastrophe. Our approach is to use image processing as a method to study self-organized criticality in the mechanical behavior of rocks. Image processing provides methods to gain information on the microstructure and means of representing this information in a format that is directly useable by the computational methods of self-organized criticality.

In our analysis, rock is simulated as a collection of uniform cells. Initially the analysis is two dimensional, cells are square, and each cell contains a crack. The initial crack-length distribution is determined from image analysis of rock sections. Stress is applied to the simulated sample and cracks are allowed to grow based on a modified Coulomb criteria. If crack length in a cell reaches a predetermined length, the cell is said to "fail" and can no longer support stress. Clusters of failed cells and the cells bordering these clusters are identified and stress on the bordering cells is re-evaluated. Rock failure is predicted when the percolation threshold is reached; that is, when one cluster connects opposite sides of the sample. During this year we developed and tested algorithms that implement this methodology. Several simulations were completed using properties of Westerly granite and incorporating various levels of confining stress. Results were promising, as the simulated stress at failure was in good agreement with laboratory observations for this rock type.

F. Nonlinear Sources for Seismic Imaging: Rock Properties *(B. P. Bonner [510-422-7080; FAX 510-423-1057], joint research with T. J. Shankland [505-667-4907] and P. A. Johnson, LANL, and R. J. O'Connell, Harvard)*

This research is directed at developing a low frequency, directed source by nonlinear elastic wave mixing of two primary frequency waves. Directed sources would be ideal for probing rock masses using seismic tomography. A narrow, low frequency beam would improve examination of acoustic interfaces underground. Possible applications might include locating discontinuities associated with hydrocarbon reservoirs, burn fronts caused by *in-situ* processing, boundaries of ore bodies, and fluids migrating near waste repositories. A necessary first step toward optimization of the low frequency source is characterizing rocks to understand the effects of parameters such as pressure, excitation amplitude, porosity, and fluid saturation on the efficiency of nonlinear wave generation.

In order to optimize source performance, we have investigated nonlinear rock response with high precision ultrasonics and amplitude dependent attenuation at low frequencies. We have used our low frequency torsional oscillator to directly observe nonlinear behavior in Westerly and Sierra white granite samples containing single macroscopic fractures. Fractured rock masses are common in field situations. It has been our hypothesis that the strong elastic nonlinearity displayed by rocks results from large changes of elastic moduli with applied stress. By closing a single macrofracture with sufficient normal stress, we have unambiguously demonstrated that the elastic response of a fractured rock becomes highly nonlinear for strains above 5×10^{-6}. Westerly granite containing a macroscopic fracture also demonstrates harmonic generation. Transfer of energy to higher harmonics is another definitive indication of nonlinear behavior, as predicted by the theory of nonlinear vibrations.

We have measured amplitude dependent attenuation for Westerly granite progressively cycled to temperatures up to 300°C to quantify the effects of increases in microcrack density on nonlinear response. Both crack closure at low temperature and growth of new cracks above 150°C affect amplitude dependent attenuation at low frequencies. Independent measurements of crack density for thermally cycled Westerly granite from the literature enable us to correlate increases in amplitude dependent (and hence nonlinear response) attenuation with cracking.

Another objective is to study the feasibility of producing a collimated, low frequency source by nonlinear ultrasonic mixing of two high frequency signals; this is accomplished by conducting experiments in rocks with nonlinear response by using various source arrays to optimize generation and transmission of the nonlinear beam. The two primary signals are electronically summed and fed into the transducer so that the single transducer produces two overlapping waves propagating with separate frequencies. Their difference (low) frequency beam has the narrow width of the generating beams but can travel further because of lower attenuation. We have now verified in Berea sandstone one of the predictions that motivated our development of nonlinear sources. We used primary frequencies of 450 and 600 kHz on a large sample, and after 1.83 meters, the transmitted 150 kHz difference frequency was easily observed in the power spectrum, but the primaries were lost in noise. In addition, we have developed a sensitive, continuous wave phase method for measuring travel times in highly attenuating rock with this configuration. The method involves measurement of a dc level proportional to phase difference, in effect removing nearly all interfering high frequency noise from the data. The technique should be applicable to a variety of travel time measurements in strongly attenuating materials over long paths, including but not limited to rocks. Details of the method are given in LANL's companion report by Shankland et al.

G. Seismic Transmission Imaging *(G. Zandt [510-423-6835; FAX 510-422-1002; E-mail: zandt@s25.es.llnl.gov])*

The goals of this project are to develop enhanced resolution seismic transmission imaging (or reconstruction) methods and apply them to the study of complex structures and geological processes in the Earth's crust and uppermost mantle. Our immediate objectives are to improve existing travel-time tomography algorithms by including new travel-time codes and feasibility constraints, test new reconstruction techniques (including nonlinear optimization) with synthetic and existing data sets, and conduct preliminary field experiments to test new algorithms and approaches. Progress in each of these areas is summarized below.

Variational constraints based on physical principles can be used to stabilize nonlinear reconstruction schemes. In the case of seismic travel-time tomography, Fermat's principle of least travel time shows that a definite convex set of feasible slowness models exists for the fully nonlinear travel-time inversion problem. This observation led to methods for stabilizing existing algorithms and to new algorithms that use parallel search techniques to explore and classify models in the solution space. These ideas were used successfully to stabilize reconstructions of both real and synthetic data in examples where ray bending effects normally would cause the algorithms to diverge.

Currently, travel-time tomography still provides the highest resolution among transmission methods; hence a better understanding of its limitations and capabilities is useful. The most obvious way to improve resolution in travel-time tomography is to increase sampling density by using more stations and sources. We pushed the limits of our current in-house computing capabilities to obtain regional-scale seismic images for the northern California lithosphere. The broad concepts of the slab window model for the Mendocino Triple Junction were confirmed. The high velocity slab associated with the southern Juan de Fuca (Gorda) plate appears "broken" into two segments.

Using an efficient finite-difference method to calculate seismic travel times, we investigated the application of combinatorial optimization techniques in the solution of seismic travel-time tomography problems. Combinatorial optimization algorithms such as the Local Search or Simulated Annealing are typically used to solve problems containing large numbers of unknowns such as circuit-board design and communication network optimization. Such algorithms are computationally intensive owing to a "brute force" approach to the problem solution. We were encouraged by early results and believe that the robustness of these techniques in their search for global extrema and the simplicity with which we can implement constraints on the resulting models (through the cost function) could make them a valuable tool for the solution of seismological problems.

A long term goal is to incorporate waveform modeling into seismic imaging. A major impediment to this goal is accounting for scattering effects, including multiple reflections, P-to-S conversions, and body-wave to surface-wave conversions. In many geologically complex cases, scattering can be the limiting effect in the pursuit of higher resolution. We conducted a small-scale field experiment in Death Valley, California, with the goal of testing a new technique to confirm and characterize a mid-crustal bright spot reported on a COCORP reflection profile. The new method is based on characterizing the coda of the seismic phase that reflects off the base of the crust (PmP). Examination of relatively broad-band three-component seismograms recorded at 100–160 km along a profile through Death Valley shows the presence of a frequency dependent PmP-coda with significant converted shear energy, indicative of crustal models containing multiple, thin, low- and high-velocity layers in the mid-crust and consistent with the reflection "bright spot."

H. Modification of Fracture Transport *(W. B. Durham [510-422-7046; FAX 510-422-4198; E-mail durham@s38.es.llnl.gov] and B. P. Bonner)*

It is widely accepted that the movement of fluid through the crust is controlled not by the bulk permeability of the medium but by the network of joints (fractures) that pervade the medium. This project aims to understand the physics of fluid flow in individual fractures to better constrain models of flow in fracture networks. We emphasize a laboratory approach to validate new or existing suggested explanations (models) for the dependence of fracture permeability on factors such as surface roughness and normal force. Future plans are to study the time evolution of fracture hydrology as chemical changes (e.g., dissolution and precipitation) and physical changes (e.g., wear) occur.

We will use, with some modification, equipment that now exists in our laboratory to test fluid flow in specimens of fractured rock. Initially the rocks will be granites of low bulk permeability in which we introduce a single large fracture. The fracture and its behavior under pressure will be characterized as fully as possible, first by digitizing both rough surfaces that form the fracture and second by measuring the opening and closing of the fracture aperture under pressure. Simultaneous with the measurement of aperture change, we will measure water permeability through the fracture as a function of confining pressure. For large specimens we will use a pressure vessel with a maximum pressure capability of 200 MPa that can handle cylinders of rock up to 12 inches long by 6 inches in diameter. We have smaller vessels for smaller samples, and all vessels have been designed to allow fluids to be forced from one end of the sample to the other. The cornerstone of the project is a specialized profiling device built in our laboratory several years ago. This profilometer digitizes full surfaces, not simply two-dimensional traces of surfaces, and has sufficient accuracy in the plane of the fracture to allow the two pieces of the fracture, laid open under the digitizing head, to be reconstructed mathematically, providing a digital image of the three-dimensional joint space. A premise of the work is that joint permeability depends on the complex shape of the aperture and not, say, on a single parameter such as an average aperture. We hope, however, to demonstrate that most joints can be characterized with reasonably few parameters in predictive, analytical models (none of which currently exist) of fluid flow. The basis for this hope lies in the recent advances in the understanding of fractal geometry and the realization that joints in rocks are fractal. We have already developed the computational tools for turning digitized surfaces into a root-mean-square roughness and a fractal dimension.

I. Advanced Concepts (L. W. Younker [510-422-6472; FAX 510-422-4918; E-mail Younker@geo.lbl.gov])

This project provides support to encourage the development of new ideas and research directions in the earth sciences. New topics are selected each year based on scientific merit and relationship to the mission and interests of the Earth Sciences Department. Typically, the research is oriented toward developing capabilities that will be needed by Laboratory programs in the future. Seed money is also provided to assess the feasibility of a given research direction to scope out experimental or computational requirements. This year we have supported exploratory studies in the spectroscopy of organic complexes in aqueous solutions and in geodesy.

Using a new technique called cylindrical internal reflectance infrared spectroscopy we are exploring the possibility of making direct measurements of the complexation of aqueous metal-acetate complexes at elevated temperatures. This method promises the first opportunity to make direct observations of such complexes in water and offers to be a rapid method of determining high temperature thermodynamic data. We believe the technique will be broadly applicable in the study of aqueous organic chemistry.

Geodesy is the science of investigating the shape and dimensions of the Earth. Prior to the 1980s, most geodetic studies were confined to ground-based techniques; e.g., leveling, trilateration, triangulation. In the 1980s, extraterrestrial techniques, such as Very Long Baseline Interferometry (VLBI) and Satellite Laser Ranging (SLR) methods were developed, but utilization was limited by the expense of these techniques. Now the Global Positioning System (GPS) provides an accurate (~cm standard deviation), fast, and inexpensive technique to measure positions and motions on the ground.

We used advanced concepts funding to explore the feasibility of developing a geodesy initiative at LLNL. The initiative would involve two programs: (1) a crustal dynamics program, whose primary focus at first would be the construction of models for crustal instabilities and other processes that can be tested by the use of geodetic data, and (2) a global change program, in which a variety of activities will be undertaken in support of the analysis and interpretation of data bearing on global climate change. This work will establish a capability at LLNL in an expanding technological field with important potential applications in both defense and energy fields.

CATEGORY: Geochemistry

PERSON IN CHARGE: F. J. Ryerson

A. Thermodynamics, Kinetics, and Transport in Aqueous Electrolyte Solutions *(J. A. Rard [510-422-6872; FAX 510-422-4198] and D. G. Miller [510-422-8074])*

The purpose of this project is to measure the thermodynamic and transport data for aqueous electrolyte solutions that are relevant to geochemical brines, radioactive waste isolation, and diagenetic processes. To accomplish this we have been measuring osmotic and activity coefficients (isopiestic method), diffusion coefficients (Rayleigh and Gouy interferometry), densities (pycnometry), and solubilities (isopiestic method) for various binary and ternary solutions at 25°C. We have also been refining methods of analyzing such data and developing new estimation procedures.

This year we completed our experimental isopiestic study of aqueous $NaHSO_4 + H_2SO_4$ solutions, which extend from about 0.2 $mol{\cdot}kg^{-1}$ to supersaturated molalities, for seven different mole ratios. This is the first characterization of a ternary acidic sulfate solution over the entire composition range.

Equations for analyzing experimental diffusion data were further developed for ternary and quaternary systems where two or more eigenvalues of the diffusion matrix are equal. An invited paper on this subject was given at the 29th Canadian Metallurgy Conference. A complete analysis was given for 3-

component Gouy and Rayleigh and 4-component Rayleigh data. A second paper summarizing our diffusion measurements and the associated "diffusion Onsager coefficients" for the system NaCl - $MgCl_2$ - H_2O was also given at that meeting. The "almost equal" eigenvalue case has also been considered, both in terms of Taylor expansions and in terms of using one eigenvalue and the difference between the two as the associated least-square variables. In addition, the use of deviation functions of Rayleigh data has been considered as an analog to Gouy methods. Finally, conversion equations have been derived between "distinct diffusion coefficients" and the Onsager coefficients of irreversible thermodynamics, as well as the transformation of these quantities from one reference frame to other reference frames.

A detailed review article on the isopiestic method was written for the second edition of *Activity Coefficients in Electrolyte Solutions*. This review covers historical development, isopiestic standards, and errors and accuracy of the measurements. Also, the fourth of the five experimental papers on diffusion coefficients in NaCl - $MgCl_2$ - H_2O was published. This work is part of the international collaboration on this system.

B. Compositional Kinetic Model of Petroleum Formation *(A. K. Burnham [510-422-7304; FAX 510-422-3118], R. L. Braun, J. G. Reynolds, and J. J. Sweeney [510-422-4917; FAX 510-422-4918])*

The objective of this project is to derive and verify quantitative chemical kinetic models of petroleum generation and expulsion from its source rock. These models are to be incorporated into integrated basin analysis studies to increase the efficiency of oil and gas exploration and recovery. We are pursuing parallel tasks in oil generation kinetics, oil cracking kinetics, phase-equilibrium calculations, geochemical analysis, and geological modeling to achieve that objective. We test chemical kinetic models of varying complexity in an effort to outline the tradeoffs between simplicity and completeness, and we develop new geochemical analysis techniques to improve our ability to test the utility of these models.

We are exploring a variety of techniques to understand the similarities and differences well enough to have confidence in extrapolation to geologic times and temperatures. During the past year we expanded the data base for rapid, open-system pyrolysis using a commercial instrument called Pyromat that is designed to work with LLNL-developed kinetic analysis software. We also completed a kinetic study of the evolution of individual gas species by pyrolysis-mass spectrometry. We demonstrated that kinetics from these inert-gas-swept pyrolysis experiments agree well with hydrous pyrolysis experiments for the Posidonia and La Luna source rock. In particular, the kinetics of oil evolution in an inert gas seem to be very similar to describing the formation of an expelled oil phase in hydrous pyrolysis.

The computer code PMOD is a flexible model of oil and gas generation, rock compaction, and fluid expulsion designed to use the chemical reaction results described in the previous paragraph. Called PYROL JR in last year's summary, it is designed to be easily used by others and is intended to replace our previous code PYROL for most applications. In one mode, the code helps a user to construct a chemical reaction network that satisfies mass and elemental balance. The code computes the amounts of each chemical species as a function of time for a specified thermal and pressure (or depth) history. The reactor can be fixed volume or compacting, open, closed, or leaky. During the past year the code has evolved to the stage where it can address state-of-the-art questions relating to oil generation, cracking, and expulsion.

Most of the model verification activities are being conducted under related DOE Fossil Energy Projects, but there is a continuing need for new and better geochemical diagnostic methods to be sure that the reconstructed paleothermal histories are what we think they are and that the oils and bitumens come from where we think they come from. We have initiated an effort to measure the concentrations of ultra-trace metals (and ultimately, their organometallic form) in oils and bitumens by inductively coupled plasma mass spectrometry. Too little is known about these materials to make any specific predictions of how they may used for source and maturity indicators, but earlier work on trace metals is encouraging. So far, we have established a clean facility and associated procedures to minimize contamination, and we have modified the inlet and cooling systems of the instrument so that metals can be determined directly in organic media without plasma torch degradation. Preliminary analyses indicate the presence of many lanthanides and some actinides in the bitumens.

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

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

A. New Approaches to Underground Imaging, *(J. G. Berryman [510-423-2905, FAX: 510-422-1002; E-mail berryman@s123.es.llnl.gov] and W. D. Daily [510-422-8623, FAX: 510-422-3013])*

The goal of our underground imaging effort is development of data collection methods, data processing procedures, integrated data interpretation techniques, and enhanced means of data presentation in order to image and interpret physical characteristics of the Earth and underground fluids when present. Our work involves developing improved laboratory and field instrumentation, acquiring fundamental data on the properties of materials under varied conditions in the laboratory, and improving the overall image reconstruction and interpretation process. The results of this project benefit many DOE programs, including dynamic stripping of underground contaminants using electrical heating and imaging, enhanced oil recovery by steam flood, and basic research through imaging the detailed flow patterns of fluids in fractured rocks. Our work is now focused mainly on underground imaging using electrical methods, although there remain some important connections between this work and other work at this Laboratory on seismic imaging.

The main thrust of the project at present is toward the development of the imaging method called Electrical Impedance (or Resistance) Tomography (EIT/ERT). Electrical Impedance Tomography uses low frequency current input and voltage output to estimate resistivity distributions in the Earth. EIT has the advantage that signal attenuation is significantly lower than that in high-frequency electromagnetic tomography (developed earlier by this Laboratory); the disadvantage is that new, more sophisticated reconstruction methods must be developed to analyze the data, since the location of the electrical field lines depends on the resistivity distribution to be determined.

Work has continued on the new Electrical Impedance Tomography algorithms based on feasibility constraints—an idea which has been carried over from earlier work on seismic tomography. The new algorithm requires the measurement of power across the input current electrodes as well as the traditional voltage measurements across output electrodes. Simulations have shown that the additional data provide constraints, so that the reconstructed images are much less susceptible to noise in the voltage measurements. This premise has now been tested on experimental data, and the results are in agreement with the results of the simulations. In the past, our emphasis has been on circular and cross-borehole configurations, i.e., two-dimensional images. This year a code for analyzing three-dimensional EIT data and displaying the reconstructions has been written and is currently under evaluation.

Work is now completed on surface survey data, i.e., current is injected and voltage differences measured only on the surface of the Earth (assuming no boreholes are available). A field demonstration has shown that EIT can remotely detect and locate a leak in a lined hazardous waste storage pond. Numerical simulations have shown that EIT is also capable of imaging many types of underground targets of geophysical interest from cross-borehole measurements. Our reconstruction algorithms have been shown to be practical for underground imaging from just surface measurements. An automated data collection system was built and used for various field tests of EIT this year.

Work in the coming year will focus on applications of the new three-dimensional reconstruction code to real field data. An effort is also being made to disseminate the information now available on reconstruction methods using feasibility constraints. One set of general lecture notes on this topic has been completed. Another set that focuses exclusively on EIT reconstructions is currently being developed.

B. Katmai Resistivity Studies (P. W. Kasameyer [510-422-6487; FAX 510-422-4918; E-mail kasameyer1@llnl.gov or kasameyer@s69es.llnl.gov] and M. Wilt)

As part of the Continental Scientific Drilling Program, we participated in the geophysical expeditions to study the Novarupta area in the Valley of Ten Thousand Smokes, Alaska. The purpose of this work was to delineate subsurface electrical conductivity structures caused by groundwater depth variations, regions of intense alteration, and geologic structures.

The most interesting results came from the induction soundings. All soundings were interpreted to determine three-layer structures, and these structures were assembled into a three-dimensional model.

From this model, we make the following conclusions. (1) Very high near-surface resistivities (> 2000 ohm-m) were observed at all stations except those collected directly on areas of intense alteration. This resistive layer is presumed to represent the dry air-fall layers, varies in thickness from 25 to 125 m, and is draped over a relatively smooth, more-conductive base. (2) The base of the near-surface layer is a relatively smooth, westward dipping surface, with a local high under the Turtle. This could represent the water table or a change in lithology of the erupted material. (3) The geoelectrical section is underlain by a conductive "basement" which coincides with the outcropping Nak-Nak sedimentary rocks to the north. The top of the basement dips about 10 degrees to the south, and its appearance is suggested beneath the Turtle. The basement is not seen within about 500 m of Novarupta. These observations suggest that the basement is the pre-eruption surface and that it was reamed out to a diameter of hundreds of meters during the eruption. (4) Many complexities are seen between the near-surface resistive layer and the conductive basement. These will be studied in the future. In addition, we collected a 2–3 km long dipole survey line across a series of grabens suspected to be the northwestern boundary of the caldera. We found almost no structural change at the outermost graben but detected significant changes at the inner one. Careful modeling of this data is required before we can draw conclusions about the caldera boundary.

C. **CSD Review Group,** *(L. W. Younker [510-422-6472, FAX 510-422-4918; E-mail: Younker@geo.lbl.gov])*

The Long Range Plan for the DOE's sector of Continental Scientific Drilling (CSD) and the supporting activities of the DOE laboratories will benefit from the utilization of experts to review and assess the CSD drilling and research operations involving both DOE and non-DOE holes. These individuals will help to assure that the DOE effort is properly coordinated, both within the DOE and the other Participating Federal agencies. Appointment of the members of the Review Group and the provision of appropriate support services will be by one of the OBES Geoscience Program-supported DOE laboratories, currently LLNL, in consultation with the DOE Program Office. That laboratory will provide support facilities and meeting arrangements as well as operational assistance for the Group's activities. This responsibility for appointing and hosting the members of the Review Group will rotate on a 3-year schedule among the DOE laboratories most heavily involved in CSD activities. The laboratory will provide such reports to DOE as DOE may require.

Members of the CSD Review Group will render expert services to the laboratory and its designees in connection with the implementation of the long-range plan (5 year) for the CSD drilling and related research projects. This plan, approved by the Program Office, is intended to identify the key scientific issues and technological barriers to be addressed by the DOE program in continental scientific drilling and to describe the various aspects of a program necessary to address these issues. In their consultative capacity, members of the Review Group may be called upon to evaluate proposals for scientific and technical aspects of the drilling and related activities. A strong consideration of this evaluation will be the technical feasibility of carrying out the proposed work.

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CONTRACT:	**W-7405-ENG-36**
CATEGORY:	**Geology, Geophysics, and Earth Dynamics**
PERSON IN CHARGE:	**M. Fehler**

A. **Electrical Conductivity, Temperature, and Radiative Transport in the Earth** *(T. J. Shankland [505-667-4907; FAX 505-665-2971; E-mail SHANKLAND@ESSDP1.LANL.GOV] and L. M. Hirsch, joint research with A. G. Duba and B. J. Wanamaker, LLNL)*

Both electrical and optical research efforts help determine temperature distributions in the crust and upper mantle. Electrical conductivity and thermoelectric effect in the mantle minerals olivine and pyroxene are being measured as a function of temperature, orientation, oxygen fugacity (f_{O_2}), and iron content. Ordinarily inference of upper mantle temperatures from electrical data is accomplished by inserting electrical conductivity (σ) measured in the field into the σ-T relationship. The intent of this work is to comprehend in detail the electrical conduction mechanisms in mantle-forming minerals so that mechanical, seismic, and electrical properties of the Earth's mantle may be understood to the point of predicting their values. A source of uncertainty derives from a compositional discrepancy: we have the most accurate and reproducible conductivities for mantle olivine by itself, but upper mantle rocks have other mineral phases, principally pyroxene, that lower the bulk Mg/Si stoichiometry from that of olivine. We have investigated the effect of buffered silica activity on conductivity of single olivine crystals by dusting samples with a layer of powdered pyroxene that acts as a silica reservoir. There is a measurable change, a decrease of log σ by 0.1 to 0.2 $\log_{10}$ units. Supporting theoretical calculations of point defects support the conclusion that pyroxene activity produces minimal effect by confirming the small change in majority carriers. These calculations are based on the mass-action equations governing equilibrium thermodynamic concentrations of point defects and on further constraints such as bulk charge neutrality and lattice site conservation. The major implication of this result is that the defect concentrations of the dominant charge carrier responsible for conduction in olivine in this temperature regime seem not to be grossly affected by the presence of pyroxene. Thus, we believe that the minor effect of pyroxene can be treated as a perturbation when calculating temperature-depth relationships (electrogeotherms) for the mantle from olivine conductivity data. With this major uncertainty diminished we feel much more confident about using single crystal data from mantle-derived crystals to calculate conductivities, and mantle temperatures inferred from these conductivities are on a much firmer basis.

- Capabilities of "electrogeotherms" have been enhanced. Electrogeotherms are temperature (T) profiles in the Earth determined from electrical data by inserting electrical conductivity (σ) measured in the field into a σ-T relationship determined in the laboratory. Temperature is one of the governing properties related to seismic activity, geothermal resources, and volcanic hazards. By accounting for four of the major uncertainties in laboratory measurements of the mineral olivine—crystal anisotropy, contact with more silica-rich phases such as pyroxene, intercrystalline grain boundaries, and the thermodynamic activity of oxygen—we have enabled temperatures in the upper mantle to be better resolved.
- Buffer curve of oxygen activity is now available for entire mantle. Using recent data on Earth materials the thermodynamic activity of oxygen—the dominant element in the outer half of the

Earth—has been calculated up to the conditions of the core-mantle boundary at temperatures of 3000°C and 1.4 million atmospheres pressure. Knowing this aspect of silicate chemistry enables description of properties such as diffusivity, electrical conductivity, or viscosity that affect convection of the "solid" Earth.

B. Nonlinear Generation of Acoustic Beams *(P. A. Johnson [505-667-8936; FAX 505-667-8487; E-mail JOHNSON@SEISMO5.LANL.GOV], T. J. Shankland, and J. N. Albright)*

The intention is to take advantage of the strong nonlinear elasticity that exists in rocks to examine new classes of phenomena such as shifts of frequency content, crack-induced contributions to the equation of state, and interaction geometries. Such effects are intrinsic to generation of low frequency acoustic beams from the interaction of two high frequency beams in analogy to the case of nonlinear optics. We were pleased to observe that a representative reservoir rock, Berea sandstone, produced a stronger and cleaner nonlinear signal than did crystalline rocks studied earlier. For the first time we demonstrated that nonlinear interactions cause a change in spectral content as a strong elastic wave travels through a rock. In these experiments we corrected for station (receiver-transducer) effects by normalizing the signal from high intensity beams to low intensity beams. As a result, normalized primary signals in the center of the frequency distribution appeared steady as a function of distance from the source, but the nonlinearly generated difference signal at the low side of the distribution showed an initial relative increase in intensity with distance as the nonlinear interaction accumulated. Such behavior is utterly unlike that of the primary waves, which simply fall off exponentially with distance as they are absorbed. Such a result could profoundly affect estimation of seismic and explosive source magnitudes because extrapolation of the low frequency wings of the band gives a misleadingly high result at zero distance. The measurements will be used in the theoretical calculations as means of understanding and defining conditions for nonlinear wave generation. These are key effects in other applications, for instance, monitoring fluid migration within or outside a reservoir or repository.

- Shifts in frequency are observed that may affect estimation of earthquake magnitude.

C. Nonlinear Sources for Seismic Imaging *(T. J. Shankland [505-667-4907; FAX 505-665-2971; E-mail SHANKLAND@ESSDP1.LANL.GOV] and P. A. Johnson, joint research with B. P. Bonner, LLNL, and R. J. O'Connell, Harvard)*

This research is aimed at developing directed sources that can be used to probe rock volumes using seismic tomographic techniques. Such probes are needed to identify reservoir characteristics and search for interfaces underground, e.g., burn fronts or boundaries of ore bodies. One research objective is to study the feasibility of producing a collimated, low frequency source by nonlinear ultrasonic mixing of two high frequency signals; this is accomplished by conducting nonlinear experiments in rocks using various source arrays to optimize generation and transmission of the nonlinear beam. The two primary signals are electronically summed and fed into the transducer so that the single transducer produces two overlapping waves propagating with separate frequencies. Their difference (low) frequency beam has the narrow width of the generating beams, but it can travel farther because of lower attenuation. We have now found a result that was one of the predictions that led to our development of nonlinear sources from the beginning. We used primary frequencies of 450 and 600 kHz on a large sample, and after 1.83 m the transmitted 150 kHz difference frequency stood out clearly in an FFT spectrum while the primaries were lost in the noise. In addition, with this configuration we developed a sensitive, continuous wave (cw) phase method for measuring travel times of waves across the sample. To perform the measurement, a secondary source signal created in an electronic multiplier is input to a second multiplier, where it combines with the secondary source signal created in the rock. As one primary frequency is swept, the phase difference between the electronically and physically produced waves creates an interference signal whose frequency is inversely proportional to travel time across the sample. We can also modulate an electronic primary frequency against a primary wave passing through the rock to obtain travel time using only a single multiplier (a traveling-wave analogue to the standing-wave resonance method commonly employed in ultrasonics). This travel time is obtained independently of those from the secondary source wave. By using both primary and secondary waves, we have measured travel times for short and long propagation path lengths using the primary and secondary wavetrains, respectively. An added benefit of the cw method is low-noise data collection capability, because we record only the phase difference signals that are effectively narrow-band filtered. Other research aims are to study the transition from linear to nonlinear elasticity using high precision ultrasonics and low frequency attenuation observations in rock and to develop a theory describing effects of crack density, fluid content, and anisotropy on nonlinear interactions with the intent of optimizing conditions for testing the nonlinear source. In order to quantify the effects of increases in microcrack density on nonlinear response, we measured amplitude-dependent attenuation for Westerly granite progressively cycled to temperatures up to 300°C. We find that both crack closure at low temperature and growth of new cracks above 150°C affect amplitude-dependent attenuation at low frequencies. Independent measurements of crack density for thermally cycled Westerly granite from the literature enable us to correlate increases in attenuation with cracking. We are extending low frequency measurements on Westerly granite containing a macroscopic fracture to further investigate energy transfer in the frequency domain, as predicted by the theory of nonlinear vibrations. By closing the single macro-fracture with normal stress, we can vary the strength of the nonlinearity and systematically study its characteristics.

- Predicted low frequency difference beam is observed to propagate farther in rocks than the primaries generated. Using nonlinear elasticity to mix two primary acoustic beams to create a collimated beam at their difference frequency, we have verified the predictions that led to our development of nonlinear sources from the beginning. We used primary frequencies of 450 and 600 kHz on a large sample, and after 1.83 m the transmitted 150 kHz difference frequency stood out clearly in an FFT spectrum while the primaries were lost in the noise.
- Seismic travel time method has been developed. We developed a sensitive, continuous wave (cw) phase method for measuring travel times of waves across a rock body by electronically mixing the generating signal with that from waves traveling across the rock. Observing travel times and their changes in time is one method of monitoring waste repositories for fluid loss or locating interfaces such as those in petroleum reservoirs and mines.

D. Imaging of Reservoirs and Fracture Systems Using Microearthquakes Induced by Hydraulic Injections

(M. Fehler [505-667-1925; FAX 505-667-8487; E-mail FEHLER @SEISMO5.LANL.GOV] and L. House)

Although hydraulic fracturing is commonly used to improve the performance of both oil and gas and geothermal reservoirs, the effects of the fracturing are often only poorly known. Active seismic methods such as vertical seismic profiling (VSP) can be used to probe the fracture system, but they are expensive and provide information mainly near the wells used. Microearthquakes induced by the fracturing are located throughout the fractured volume and are considerably more energetic sources of seismic waves, particularly shear waves, than the sources used by the active seismic methods. Because the presence of fluid paths in rock affects shear (S) waves more than compressional (P) waves, shear waves are a particularly sensitive way to probe fracture systems created by hydraulic fracturing. Thus, data from induced microearthquakes can provide a much more detailed view of the structure of the fractured rock volume than any other data.

Arrival times of both the P and S seismic waves provide information about seismic velocities in the fractured rock as well as about the microearthquake locations. These arrival times can be inverted to simultaneously relocate the microearthquakes and obtain a three-dimensional seismic velocity structure of the fractured rock. The velocity structure, often termed a "tomogram," from one hydraulic fracture experiment has provided a more comprehensive view of the effects of the fracturing than has been heretofore available. Those portions of the tomograms with seismic velocities lower than the intact rock velocities should correspond to rock volumes that have a significant proportion of fluid-filled fractures. In addition to arrival times, the waveforms from the induced microearthquakes can contain very detailed information about some parts of the rock structure in and near the fractured volume. Of particular interest are the portions of the waveforms after the direct P and S arrivals (termed the coda). Distinct arrivals in the coda result from prominent scatterers. In an otherwise fairly uniform rock, newly created fluid-filled fractures will provide some of the most prominent scatterers in the vicinity of the fractured rock volume. Locating these scatterers may also locate some of the best fluid paths in the fractured volume. These analysis methods have the potential for defining the internal structure of hydraulically fractured rock with considerably greater detail than was previously available.

- A method to determine the three-dimensional structure of a hydrofractured reservoir from microearthquakes induced by fluid injections has been developed and tested.
- An array method to find the seismic velocities in a small region containing a cluster of microearthquakes without using time-consuming ray tracing methods has been implemented and applied to field data from a hydrofracturing operation.

E. Two- and Three-Dimensional Magnetotelluric Inversion *(B. J. Travis [505-667-1254; FAX 505-665-3687; E-mail BJT@CANOPUS.LANL.GOV], joint research with A. D. Chave, AT&T Bell Laboratories)*

The goal of this research project has been the development of highly efficient, user-friendly numerical/computational models to solve a variety of 2-D and 3-D forward and inverse problems in geophysical electromagnetic sensing. Natural source and controlled source frequency domain models have been created using moving finite element methodology. These computational tools are being used to estimate the resolution of subsurface structure that one could expect from analysis of seafloor measurements over mid-ocean ridges. This project ends this fiscal year; a comprehensive paper is being prepared on the algorithm, and a separate paper is in preparation on the applications to CSEM mid-ocean ridge analysis. The software, including front-end finite element grid generator and the moving node forward EM solver, will be available to interested parties upon request in late summer.

F. Jemex Imaging and Tomography Experiment (JITEX) *(M. Fehler [505-667-1925; FAX 505-667-8487; E-mail FEHLER@SEISMO5.LANL.GOV] and W. S. Baldridge)*

The objective of this study is to construct a model of the crust and upper mantle beneath the Valles caldera that incorporates data from as many geophysical and geological disciplines as possible. A majority of the effort will involve collecting and interpreting seismic data to be used in imaging the subsurface structure beneath the caldera. We will test models for the geometry of the caldera structure and fill, the 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. We expect this work to lead to a fundamental new understanding of the origin, evolution, and modern thermal regime of a major intraplate magmatic system.

The Jemez volcanic field and Valles caldera are important targets for a major geophysical field experiment because (1) the caldera is the world-known textbook example of an ash-flow center and type site for recognition of magmatic resurgence; (2) the deposits are geologically young, structurally relatively simple, and relatively small, thus manageable for detailed imaging experiments; (3) its major structural elements (topographic caldera wall, resurgent dome, and keystone graben) and structural boundary (ring fault as reflected by an arcuate collar of postcollapse lava domes) are especially well defined; and (4) abundant geologic and geophysical framework data are available, including substantial "ground-truth" drillhole data.

We are currently developing a suite of models for the subsurface structure of the Valles caldera using available geophysical and geochemical results. Our objective is to use these physical models in a forward modeling scheme to determine an optimal configuration for a seismic experiment whose goal is to find the most appropriate model for the subsurface structure of the volcanic field. We thus hope to configure our seismic experiment to allow the most unambiguous choice to be made from among the suite of hypothetical models.

G. **Advanced Concepts** (C. W. Myers [505-667-3644; FAX 505-667-3494] and R. W. Charles [505-667-4985; FAX 505-665-5688; E-mail 081948@INCDP3.LANL.GOV])

Three limited term projects are underway in 1991:

1) Measuring Erosion Rates in Arid Regions Using ^{3}He *(J. Poths)*

This activity explores the possibility of determining surface exposure ages using cosmogenic noble gases. Cosmic rays penetrate to a few meters depth in the Earth's surface, producing among other cosmogenic nuclides ^{3}He and ^{21}Ne. The build-up of these stable noble gases allows the "age" of a surface to be estimated. We are determining the concentration of cosmogenic noble gases in samples of Bandelier tuff, Los Alamos area, to estimate erosion rates. Results to date suggest that on mesa surfaces, erosion is occurring at a rate of 1–2 cm/ka. A study of samples over a broader area and other effects (i.e., depth dependence) is underway. This technique shows promise for extension to other questions of interest in geosciences, such as dating climate related events that created stable surfaces (landslides, glaciation), unraveling the origin of desert pavement, and attaching a time scale to the evolution of a recent volcanic field.

2) Stable Isotopically Labeled Organic Tracers for Geological Processes *(D. R. Janecky, W. Spall, P. R. Dixon, and G. K. Bayhurst)*

Tracer experiments are essential to characterize accurately and efficiently flow paths and coupled chemical reactions in the subsurface. We are examining potential for use of multicomponent organic tracer families in broad application to geothermal, fossil energy, environmental, and basic geoscience questions. In conjunction with the USGS and the National Park Service, we used a suite of organic tracers in the Mammoth Hot Spring area of Yellowstone National Park in order to determine flow paths in this complex reservoir system. The compounds used were acetic acid, benzoic acid, phenol, analine, t-butyl alcohol, and glycine. Tracers were detected at all sampling locations to more than 1.25 km from the points of injection. Not only flow paths but basic rock-fluid interactions have been determined, such as weak acid interactions with the travertine substrate.

3) Volcanic Gas and Tritium Studies *(F. E. Goff)*

Collection and analysis of gases and steam condensates from Mount St. Helens (Washington) and Pu O (Kilauea, Hawaii) volcanoes has been undertaken to determine the contribution of magmatic volatiles to the new St. Helens hydrothermal system and to attempt to characterize the tritium content of magmatic water. The latter objective stems from the hypothesis of S. Jones (Brigham Young University) that cold nuclear fusion in the Earth should cause anomalous tritium to be emitted from volcanoes. The field and analytical work at Mount St. Helens is complete, but we are still waiting for analytical results for Pu O samples.

CATEGORY: **Geochemistry**

PERSON IN CHARGE: **D. Janecky**

A. **Uranium-Series Disequilibrium Measurements in Geologic Systems Using Mass Spectrometry** *(M. T. Murrell [505-667-4299; FAX 505-665-5688; E-mail 099691@INCDP3.LANL.GOV], A. M. Volpe, S. J. Goldstein, B. L. Fearey, J. A. Olivares, D. R. Janecky, R. E. Perrin, joint research with N. C. Sturchio, ANL, and R. W. Williams, UCSC)*

The goal of this project is to develop and then apply mass spectrometric techniques for measurements of the uranium decay series in young (< 500 ka) geologic samples. The approach we have taken at LANL is unique in that we have simultaneously developed mass spectrometric methods for all the long-lived ($t_{1/2}$ > 100 a) members of the uranium decay series. We are able to routinely measure ^{238}U-

^{234}U-^{230}Th-^{226}Ra, ^{235}U-^{231}Pa, and ^{232}Th-^{228}Ra using mass spectrometry with improvements of 10 to 100 times for sample size, precision, and/or counting times over that which is typically obtained by decay counting techniques. This research has provided an improved capability for geochronology—one that we are using to answer basic questions in geochemistry and geology as well as having practical applications to geologic hazard risk assessment and paleoclimate.

Previously, we evaluated the U-Th disequilibrium technique for both geochronological and petrogenetic studies of mid ocean ridge basalts (MORB). More recently, barium, ^{226}Ra, and ^{231}Pa have also been measured in many of these same basalts. Large ^{226}Ra excesses (up to 2.5 times relative to ^{230}Th) and ^{231}Pa excesses (up to 3 times relative to ^{235}U) are found in the youngest samples. Age differences for MORB younger than 8 ka were resolved using ^{226}Ra-^{230}Th disequilibria and Ba/Th variations. Such ages obtained for basalts from distinct ridge segments are found to agree with relative locations across ridges and Th-U model ages. The ^{231}Pa data we have obtained are the first of this kind for MORB. U-Pa dates obtained by assuming constant initial disequilibrium on eruption are in excellent agreement with the U-Th ages and the ^{226}Ra ages. In general, our results obtained using mass spectrometry demonstrate that it is possible to clearly resolve age differences with precise U-series data. Our ability to obtain such information for spreading centers is vital to our effort to understand the processes that create oceanic crust.

Recent volcanic activity at Mt. Shasta, California, has also been examined using U-series disequilibrium techniques. These results provide the first demonstration that the degree of ^{230}Th-^{226}Ra fractionation among minerals with relatively high Ba/Th ratios, such as plagioclase and hornblende, can be used to provide ages of very young (5–10 ka) volcanic rocks. Through these data, we are gaining insights into the processes responsible for the generation, mixing, storage, and eruption of magma. High precision U-series age measurements for thermal-spring travertine deposits have been used to study glaciation and hydrothermal systems at Yellowstone. These data show that the elevation of travertine deposition at Yellowstone has responded to climate-controlled changes in meteoric recharge rates and water table elevation. We have been able to bracket the age of Pinedale glaciation by travertine ages of 53.6, 46.3 ka and 22.1, 18.6 ka, and we have also determined that travertine deposition has been continuous at Mammoth Hot Springs and Bear Creek since 9.8 ka. Such information is important for paleoclimate studies being conducted in the Yellowstone region.

- A joint collaboration between ANL and LANL produced the first high precision U-series age measurements of glaciation and hydrothermal systems at Yellowstone.
- A joint collaboration between UCSC and LANL produced the first dates of eruption using measurements of ^{235}U-^{231}Pa disequilibrium in ocean basalts.
- Unique ^{226}Ra-^{230}Th disequilibrium data were obtained by mass spectrometry for rocks and minerals separates from Mt. Shasta.

B. Thermodynamic Properties of Aqueous Solutions at High Temperatures and Pressures *(P. S. Z. Rogers [505-667-1765; FAX 505-665-3403; E-mail 084120@INCDP3. LANL.GOV])*

Knowledge of the thermodynamic properties of electrolyte solutions at high temperatures is important in studies of geothermal systems, hydrothermal alteration processes, and element transport in deep brines such as those that have been encountered in the Continental Scientific Drilling Program (CSDP). Properties to at least 473 K for carbonates, hydroxy species, and organic complexes are especially needed to model cementation, mineral diagenesis, and element transport in sedimentary basin evolution. The purpose of this investigation is to determine the activity coefficients of geochemically important ionic species in aqueous solutions over a wide range of composition and temperature.

An automated, flow calorimeter has been constructed to measure the heat capacities of concentrated, electrolyte solutions to 673 K and 40 MPa. The heat capacity data can be integrated to yield enthalpy and total free energy information by using literature data available at room temperature to evaluate the integration constants. The total free energies can be used directly in calculations of mineral/solution equilibria. If the data can be extrapolated to infinite dilution (this is proving to be a serious problem for electrolytes other than the 1–1 charge type at temperatures above 500 K), calculation of standard state properties and activity coefficients is possible. These can then be treated using Pitzer's equations to provide a compact model for mixed electrolyte solutions at high temperatures.

Heat capacity data have been obtained for the systems $NaCl$-Na_2SO_4-H_2O, $NaOH$-H_2O, and Na_2CO_3-$NaHCO_3$-$NaCl$-H_2O to 40 MPa and 598 K and sodium acetate to 40 MPa and 473 K. Heat capacities for NaOH have been combined with high quality enthalpy of dilution measurements by J. M. Simonson (ORNL) to provide standard state values. These are also of interest because they can be used to fix the standard state values for HCl(aq) through the reaction to form NaCl and H_2O. Heat capacities for $NaHCO_3$-Na_2CO_3-H_2O are being combined with enthalpy data from ORNL to provide a complete thermodynamic model for this system.

- Heat capacities for Na_2CO_3-$NaHCO_3$-H_2O have been measured to high temperatures and pressures. The heat capacity data can be integrated as a function of temperature to provide enthalpy and free energy data for this system.

C. Dynamics of Rock Varnish Formation *(R. Raymond, Jr. [505-667-4580; FAX 505-665-3285; E-mail 085602@ESSDP2.LANL.GOV], C. D. Harrington, S. L. Reneau, and D. L. Bish)*

Rock varnish is a microns-thick coating, composed primarily of manganese and iron oxides and clay minerals, that is ubiquitous on exposed rock surfaces in arid and semi-arid regions. Rock varnish contains distinct micro-stratigraphic layers that record environmental changes during the period of varnish formation, and these layers have the potential to provide an improved understanding of paleoenvironmental changes in desert regions. However, the effects that relationships between varnish mineralogies, varnish elemental contents, varnish diagenesis, and the mechanism of varnish formation have on elemental and mineralogic attributes used in paleoclimatic studies are not yet understood.

We are using a combination of optical microscopy, electron microanalysis, x-ray diffraction, x-ray fluorescence, infra-red spectroscopy, and chemical analysis to evaluate the mineralogic and elemental compositions of rock varnish as a function of local geology, geochemical environments, and varnish source environments. The objectives of this research are (1) to isolate the major environmental variables responsible for variations in rock varnish chemistry and morphology; (2) to use rock varnish micro-stratigraphy to understand the nature of environmental changes in different parts of the southwest deserts; (3) to use variations in rock varnish micro-stratigraphy to map out the extent of specific environmental changes, such as changes in rainfall patterns associated with changes in regional atmospheric patterns; and (4) to document the climatic conditions present at the times of formation of major landscape features.

The research has the potential to expand knowledge of the paleoenvironmental history of deserts and thus allow a better understanding of possible environmental changes associated with global climatic changes. Such knowledge will make it possible to decipher more accurately the timing of erosional, depositional and tectonic events for semi-arid and arid regions not only in the southwestern United States but in other strategic regions of the world. Understanding of such timing will be of significant value to enhanced resolution of young mantle/crust interactions, improved seismic risk evaluations, and improved characterization of sites for nuclear power plants and toxic and nuclear waste disposal.

D. Geochemistry of Technetium *(N. C. Schroeder [505-667-0967; FAX 505-665-5568; E-mail 098491@INCDP3.LANL.GOV], J. Fabryka-Martin, M. Attrep, Jr., R. D. Aguilar, D. B. Curtis, R. E. Perrin, F. Roensch, and D. J. Rokop)*

The objective of this research is to study the geochemistries of long-lived radionuclides, ^{99}Tc, ^{239}Pu, and ^{129}I, in uraniferous rocks. Specifically, our program is (1) to measure concentrations of these radionuclides in different geochemical environments; (2) to compare measured concentrations with those predicted for closed or static systems; and (3) to interpret measured concentrations in terms of retention by the source rock, migration in groundwater, or retardation down gradient of the source rock.

We have continued to improve our ability to model ^{239}Pu production rates in unaltered and unweathered uranium deposits using a Monte Carlo

Neutron Transport Code to model neutron-induced reactions. Our initial model predicted higher plutonium concentrations than the measured values. Refinements to the model, which take into account the moisture and heavy rare earth content in the ore body and the lower uranium concentration in the surrounding host rock, have increased the model's sensitivity. The refined model now shows that measured plutonium concentrations fall into the range of uncertainty of the predictions. Thus we are gaining greater confidence in our conclusion that plutonium is being retained by unaltered uranium ores.

In the last year we have made some progress in measuring ^{99}Tc/U atom ratios in uranium ores. The results are slightly higher than what is expected from production due to spontaneous fission, 1.6×10^{-12}, and therefore probably includes a contribution of ^{99}Tc from neutron-induced fission of ^{235}U.

Our improved modeling capability is also being used to predict ^{99}Tc production rates in other types of deposits such as molybdenite. The model predicts that ^{99}Tc production from neutron capture reactions by ^{98}Mo should be approximately of the same level of importance as that from spontaneous fission of ^{238}U. However, the model also indicates that the ^{99}Tc content of molybdenite will vary considerably due to the non-uniform distribution of key elements controlling the neutron production rate and the neutron flux, especially U, Th, F, and H or water content. Measured values for separated molybdenite agree quite well with the calculated value.

- The agreement between measured and predicted plutonium concentrations in uranium ores is improving due to a refined radionuclide production rate model.

E. Rock-Water Interactions and Element Migration *(D. R. Janecky [505-665-0253; FAX 505-667-2964; E-mail 098106@INCDP3.LANL.GOV], R. W. Charles [505-667-4985; FAX 505-665-3403; E-mail 081948@INCDP3.LANL.GOV], P. S. Z. Rogers, P. R. Dixon, G. K. Bayhurst, and J. Musgrave)*

The emphasis of this project is integration of studies of chemical interactions between rocks and fluids in hydrothermal systems applicable to environments of general interest for the discovery and recovery of energy, whether geothermal or fossil. Present efforts include laboratory experiments, computational modeling, field studies, and application of unique analytical facilities.

The major focus at this time is characterizing processes in geothermal systems in volcanic terranes and sedimented basins. Samples from Valles caldera drill core are being analyzed to determine element redistribution on bulk to microscopic scales. Nuclear microprobe analyses of individual minerals in selected samples is providing unique insights into which major minerals contain minor and trace elements (< 1 wt% concentrations) and how different assemblages of minerals change the distribution of these elements. Our high temperature down-hole fluid sampler is being used to collect solutions that can be compared to the analytical results and phase equilibria calculations. Experimental systems are being applied to saline brine reactions and rock-water reaction processes at conditions near critical. Saline brine experiments are providing a high quality data set to test and enhance computational models and characterization of reaction path processes analogous to natural systems. Development is ongoing of analytical and experimental approaches to use solutions spiked with ^{29}Si or ^{30}Si to quantify dissolution and precipitation processes for systems close to equilibrium. The results of these experiments and models are also compared to other well-studied geothermal systems. Other modeling efforts involve developing approaches and methodology to explicitly integrate sensitivity analysis and spatial/temporal heterogeneity into large geochemical models and data bases.

F. A Search for Evidence of Large Comet or Asteroid Impacts at Extinction Boundaries *(C. J. Orth [505-667-4785; FAX 505-665-4955; E-mail 063844@INCDP3.LANL.GOV] and M. Attrep, Jr.)*

The objectives of this work are to search for geochemical evidence of large-body impacts and/or massive volcanism across the numerous extinction boundaries in the fossil record, to examine the environmental consequences of local releases of ultra-high amounts of energy (impacts), to develop the field of chemostratigraphy and establish geochemical time markers in the geologic column, and to gather trace-element migration data that will provide information of value for nuclear waste storage considerations.

Instrumental neutron activation analysis and radiochemical methods are used to measure abundances for more than 40 elements, including the platinum group with emphasis on iridium (Ir). This work has involved collaborations with more than 80 geoscientists from around the globe.

The major focus is on the 93-Ma late Cenomanian extinction of marine animals. Two closely spaced Ir abundance anomalies coincide stratigraphically with the extinction interval. Also present with the Ir in anomalously high concentrations are Sc, Ti, V, Cr, Mn, Co, Ni, Au, and Pt. The elemental abundance patterns are similar to those of mid-Atlantic Ridge basalts and of hot-spot volcanism, but not of meteorites. Work to date on sections in North and South America, in Europe, and on DSDP cores from the Atlantic, Pacific, and Indian Ocean basins suggest that the source area was in the proto-Caribbean. The source itself might have been a center of intense spreading or merely upwelling of deep, mineral-rich water during the great Cenomanian-Turonian eustatic rise.

Measurements are also directed at the other biological crisis horizons in the fossil record from the Cretaceous-Tertiary (K-T) boundary back to the 570-Ma Precambrian-Cambrian transition. Work on the K-T event is currently concerned with providing evidence for a single impact versus multiple impacts and information about the target rocks (impact site(s)). Considerable emphasis is placed on the major extinctions at the Permian-Triassic, Late Devonian Frasnian-Famennian, and Ordovician-Silurian boundaries, and on the poorly established Precambrian-Cambrian transition. Work on the K-T, Late Cenomanian, Mississippian-Pennsylvanian, and Devonian-Mississippian elemental abundance anomalies has provided chemostratigraphic markers that can be used to stratigraphically correlate these horizons over great distances.

- The two Late Cenomanian iridium abundance anomalies discovered in western North American marine sequences have been observed at a site near Chaparral, Colombia.
- Similar elemental abundance patterns in the two visibly distinct K-T boundary clays in North America suggest a single impact.

G. Direct Speciation of Metal Ions by Optical Spectroscopies *(C. D. Tait [505-667-3965; FAX 505-665-3403; E-mail 103104@INCDP3.LANL.GOV] and D. R. Janecky)*

Optical spectroscopies, including UV/Vis electronic absorption, Raman scattering, and infrared absorption spectroscopies, are being used to directly determine the speciation of metal ions under systematically different environments. Improved characterization of chemical speciation in aqueous fluids is required to further understand geochemical processes involving solutions in oil field, environmental, and geothermal systems.

One current focus is on organic/halide ligand competition for dissolved metals, especially from the platinum group elements (PGEs). Initial palladium(II) chloride speciation experiments that studied variations in chloride concentration, pH, and temperature have been completed, and these now provide the background for the current competition studies with organics such as acetate, oxalate, and phthalate. The organics are remarkably good complexers, especially the oxalate. For example, some complexation at neutral pH values by 0.001 M sodium oxalate (up to 0.005 M oxalate has been recorded in natural systems) is noted even in the presence of 0.560 M NaCl (~ sea water salinity). This predilection for organic base ligands, along with the increased pH ranges for palladium(II) solubility in the presence of organic bases, as noted by Prof. S.A. Wood's group at McGill University, argue for the possibility of palladium-organic complex transport in surficial environments. Hence this work suggests that organics need to be considered along with conventional inorganic ligands such as chlorides and sulfides in the transport of metals in low to moderate temperature systems.

Another current interest continues to be organic acid complexation/interaction with silicates and aluminum silicates, with important implications for mineral dissolution, groundwater and geothermal transport and precipitation, and fossil fuel/reservoir interactions. Despite a previous report of direct silicon complexation by oxalate (as a silicon ester), we have found only free oxalate in solution as determined by infrared absorption and NMR spectroscopies. Therefore, some other mechanism besides direct complexation must be found to explain the increased silicon weathering in the presence of organics. Aluminum, on the other hand, is complexed by oxalate, and the IR signature of this complexation has been found. In fact, oxalate is able to solubilize aluminum from a slurry of aluminum oxide at neutral pH values. We are currently exploring the temperature dependence of this complex with IR and Raman spectroscopies.

- Palladium(II) chloride speciation studies with respect to systematic changes in pH, chloride concentration, and temperature were completed, showing significant speciation in natural systems.
- Using Pd-Cl background information listed above, ligand competition studies between chloride and organic bases for palladium showed strong formation constants for the organic bases, suggesting a role for organics in trace metal transport in low to moderate temperature systems.
- Careful infrared and NMR studies disproved previously claimed silicon oxalate complexation (as a silicon ester). Another mechanism for increased silicon dissolution in organics must be found. Because of the ubiquitous nature of silicon rock matrices, silicon dissolution has implications for permeabilities of fossil fuel reservoirs (and hence the efficiency of enhanced oil recovery (EOR) methods) and waste containment sites.
- Aluminum oxalate complexes can be formed by stirring a neutral pH slurry of aluminum oxide and oxalate. Temperature dependence is being explored. As with silicon, aluminum oxides are important components in rock matrices, and aluminum dissolution also has rock permeability implications.
- External collaborations continue with Phil Bennett (University of Texas, Austin) on organic interaction/complexation with silicon and aluminum and were initiated with Scott Wood (McGill University, Montreal) on organic complexation with palladium.

H. Alfred O. Nier Symposium on Inorganic Mass Spectrometry *(D. J. Rokop [505-667-5166; FAX 505-665-5688; E-mail 089038@INCDP3.LANL.GOV])*

The symposium was held at Tamarron resort near Durango, CO, May 7-9, 1991. The event was in honor of Dr. Nier's many contributions to mass spectrometry and to honor his 80th birthday. Many of the top mass spectrometrists in the world were present, a total of 106 attendees. These individuals presented a broad spectrum of topics in mass spectrometry and isotopic studies. This was an attempt to duplicate a conference organized by Hipple at NBS in 1958. The list of speakers reads like a Who's Who of mass spectrometry for many years. A proceedings volume is in preparation. Plans are to make this a triennial meeting.

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

PERSON IN CHARGE: **G. Heiken**

A. Core Hole VC-2B: Scientific Drilling to Investigate Caldera Processes, Hydrothermal Dynamics, and Mineralization, Sulphur Springs Geothermal System, Valles Caldera Magma-Hydrothermal System, New Mexico *(J. N. Gardner [505-667-1799; FAX 505-665-3285; E-mail GARDNER@ESSXRF.LANL.GOV] and F. E. Goff, joint research with J. B. Hulen, University of Utah Research Institute)*

Research core hole VC-2B, the third in the Department of Energy's Continental Scientific Drilling Program efforts in the Valles caldera, was continuously cored to 1.762 km on the western flank of the caldera's resurgent dome in 1988. Bottom hole temperature is about 295°C within Precambrian (1.5 Ga) quartz monzonite, deep within the liquid-dominated portions of the Sulphur Springs hydrothermal system. VC-2B is the deepest, hottest, continuously cored hole in North America. In concert with the 528-m deep companion hole, VC-2A, the objectives of this project are to investigate the structure, stratigraphy, ore mineralization, thermal history, and evolution of the Sulphur Springs geothermal system. The project is jointly managed by Los Alamos, University of Utah Research Institute, and Sandia National Laboratories.

Work in VC-2B by our team for 1990 consisted of the following efforts:

1. Continued acquisition of data on major element, trace element, and gold plus 17 pathfinder element variations in the core.
2. Continued acquisition of δD, $\delta^{13}C$, and $\delta^{18}O$ data on whole rock silicate and carbonate rocks and on vein calcite, quartz, and illite in the core.
3. Completion of 18 K-Ar dates on illite fractions from the core.
4. Initiation of a study on chemistry, isotopic composition, and fluid inclusion history of hydrothermal epidote in the core.
5. Completion of a study on volcaniclastic sedimentary interbeds between the tuff units of the core.
6. Completion of five *in-situ* sampling experiments using three high-temperature, slim-hole, downhole samplers.
7. Successful plugging of the bottom (open-hole) section of the well at depths below 1650 m. Successful perforation of the solid liner at five horizons in the upper part of the hole.
8. Successful stimulation of the five perforated horizons and completion of an initial three-day flow test.
9. Completion of chemical and isotopic analyses on all fluid (water and gas) samples collected during items 6 and 8.
10. Organization of two half-day oral sessions and one poster session at Fall 1990 AGU meeting (San Francisco) on caldera processes, with emphasis on Valles caldera research.

The VC-2B science team currently consists of about 100 researchers, representing universities, industry, and government agencies from the U.S. and six other countries. The work of these researchers is not reflected in the tasks described above. Some work mentioned in this summary has been done in collaboration with the Isotope and Nuclear Chemistry Division of Los Alamos, University of Utah Research Institute, Sandia National Laboratories, Lawrence Berkeley Laboratory, and/or U.S. Geological Survey.

- We believe that the most important highlight has been to drill into an active member of Earth's largest class of volcanoes (calderas) and to extract core and fluid samples that provide insight into the formation of geothermal resources and ore deposits.

B. Operation of a Sample Management System for the CSDP *(S. J. Goff [505-667-7200; FAX 505-665-3285; E-mail 087845@ESSDP1.LANL.GOV], joint research with R. Dayvault, UNC, Grand Junction)*

The Curation Office, managed from Los Alamos, operates the DOE Core and Sample Repository at Grand Junction, Colorado. This facility is designed to provide the scientific community with access to geologic samples from CSDP core holes. The core repository occupies about 7200 square feet of space in Building 7 at the DOE Grand Junction Project Office. In addition to the core-storage area, the repository contains office space for the curator, a receptionist, and visiting scientists, as well as rooms housing specialized sample preparation equipment. Core can be viewed in a large enclosed and heated area, which is equipped with sample tables designed for laying out 1000 feet of core. Equipment includes a 24-slab saw, a trim saw, a drill press, and a core splitter. Also available for scientists are binocular and petrographic microscopes. The repository presently contains 43,700 feet of drill core from various CSDP and related projects. The Curation Office has published Curatorial Policy Guidelines and Procedures for the Continental Scientific Drilling Program, field curation manuals, core logs, and newsletters. It is also the responsibility of the Curation Office to provide on-site curatorial supervision to assist principal investigators on curation policy and procedures during drilling.

C. Plug and Abandonment of CSDP Core Hole VC-1 (F. E. Goff [505-667-8060; FAX 505-665-3285; E-Mail @ESSXRF.LANL.GOV] and S. J. Goff)

VC-1, the first Continental Scientific Drilling Program core hole in the Valles caldera, New Mexico, was drilled and completed during August–September 1984. This project was very successful, resulting in publication of 23 abstracts, 19 journal papers, 10 reports, and 2 theses using data and samples from the well. All planning, permitting, contracting, drilling, logging, and science activities were managed and coordinated at Los Alamos (F. E. Goff, principal investigator). At the time of drilling, Los Alamos negotiated a 5-year permit with the U.S. Forest Service to use the hole for scientific purposes. All scientific activities are now completed, and the Forest Service required plugging and abandonment. This activity was completed according to the guidelines of the USGS Geothermal Resource Operations Order No. 1, and the hole was plugged in a manner that prevents subsurface interzonal migration of fluids and surface leakage. Abandonment required a cement plug to be set in the NQ rods to 1750 ft. In addition, we cut off the wellhead, removed miscellaneous hardware, and restored the site.

CATEGORY: **Solar, Solar-Terrestrial, and Atmospheric Interactions**

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

The objective of this program is to carry out theoretical and experimental research on the plasma physics of the solar wind and the Earth's magnetosphere and ionosphere. Since the solar wind and magnetospheric plasmas are the media through which solar-generated disturbances propagate and in which solar wind convection energy is stored and subsequently released to the auroral ionosphere, these studies help us understand the coupling of solar variations to the near-Earth environment. This research supports the Department of Energy's missions in fusion energy research and space-based defense activities, as well as its ongoing solar-terrestrial research program.

A. Energy Transport in Space Plasma (S. P. Gary [505-667-3807; FAX 505-665-3332; E-mail 082438@ESSDP1.LANL.GOV])

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. We use particle distribution functions observed by Los Alamos plasma instruments on scientific satellites as well as computer simulations developed at Los Alamos to carry out fundamental studies of plasma instabilities and associated transport in and near the solar wind, the Earth's bow shock, and the terrestrial magnetosphere.

Our most important accomplishment of 1990 has been our further description of the solar wind's interaction with newly created ions in the distant environment of comets. Our computer simulations have yielded analytic scalings that describe how wave-particle interactions cause pitch-angle scattering of cometary ions. In particular, our results predict a two-fold increase in the pitch-angle scattering of cometary water-group ions as the solar wind velocity/magnetic field angle changes from parallel to perpendicular, in qualitative agreement with observations at comet Halley. Our simulations also predict that this scattering rate should increase as the square root of the ion creation rate, a result that we hope will soon be subject to experimental study.

- Computer simulations show agreement with plasma observations near Halley's comet.
- Three-dimensional computer model of the Earth's magnetotail provides new insight into solar-terrestrial coupling.
- Exceptionally strong solar activity in 1989 and 1990 monitored by Los Alamos energetic particle sensors at geosynchronous orbit.

B. The Solar Wind–Magnetospheric Interaction (J. Birn [505-667-9232; FAX 505-665-3332; E-mail BIRN@ESSDP1.LANL.GOV] and E. W. Hones, Jr., 505-667-4727)

The interaction of the solar wind with the magnetosphere is that of a fast flowing, highly conducting plasma with a stationary magnetic field, i.e., it is completely analogous to the action of a magnetohydrodynamic (MHD) electric generator (although much more complex) and is thus electrodynamical in nature. The purpose of this research is to extend the understanding of this complex magnetoelectrical plasma system by examining its global structure and dynamics through correlative studies of data from multiple sites within and near the magnetosphere (including the Earth itself as well as scientific satellites) and by the development and use of theoretical and computational models of the structure and dynamics of the magnetosphere.

Our most important achievements in 1990 were made in extending our magnetohydrodynamic simulations of magnetotail dynamics to include effects of field-aligned currents in the near tail and the coupling with the ionosphere. These simulations studied the evolution of a current circuit consisting of deviated current from the tail, through the ionosphere, and back into the tail ("substorm current wedge") and showed that its development is an integral part of the large-scale instability of the tail that also leads to plasmoid formation and ejection through magnetic reconnection. Another significant achievement was the extension of our quasi-equilibrium magnetotail theory to include the effects of magnetic field-aligned plasma flow.

C. Energetic Particle Acceleration *(G. D. Reeves [505-665-3877; FAX 505-665-3332; E-mail 105277@ESSDP1.LANL.GOV])*

The primary effort of this research involves the analysis of energetic particle data from Los Alamos spacecraft in the Earth's magnetosphere. Energetic, here, means electrons and ions with energies above the bulk thermal plasma population (tens of keV) to energies dominated by cosmic ray particles (hundreds of MeV). The goal of this research is to understand the radiation environment in the magnetosphere (and particularly at geosynchronous orbit) as well as to investigate the acceleration mechanisms and transport processes that produce that environment.

Our major research effort during 1990 involved investigation of the injection of energetic particles into the geosynchronous region of the Earth's magnetosphere during substorms. Using a computer code to model the motion of electrons and ions of various energies in the Earth's magnetic field, we have analyzed data from several spacecraft to determine the longitudinal extent of the substorm injection region. We were able to precisely determine the time of injection onset even from data collected remotely from the injection region by carefully analyzing the properties of particles which have drifted to the spacecraft. This technique has been used in studies of the magnetosphere using data from Los Alamos spacecraft alone as well as with data from additional spacecraft.

D. Radiation from Space and Astrophysical Plasmas *(G. R. Gisler [505-667-1375; FAX 505-665-3332; E-mail 090091@ESSDP1.LANL.GOV])*

The goal of this research is to understand how relativistic charged particles originate in both astrophysical and Solar System plasmas and how these energetic particles couple with background thermal plasma and electromagnetic radiation. Our most important accomplishment of 1990 came from the study of particle heating in computer simulations of diamagnetic plasma expansions. We found that entropy generated during the free expansion of plasma along the magnetic field lines is returned to the diamagnetic cavity and results in the heating of the trapped plasma to temperatures well above the initial adiabat. This heating occurs first for the ions and is later shared with the electrons. In addition, some acceleration of particles of both species into a suprathermal tail is observed; we believe this is due to second-order Fermi acceleration in the strong fluctuation fields at the edge of the cavity. This research has applicability to diamagnetic cavities in the interstellar medium produced by supernovae or hot stars, to cavities of unknown origin naturally occurring in the solar wind, and to cavities in magnetospheric plasmas produced by artificial injection experiments such as AMPTE and CRRES.

- Computer simulations show agreement with plasma observations near Halley's comet.
- Three-dimensional computer model of the Earth's magnetotail provides new insight into solar-terrestrial coupling.
- Exceptionally strong solar activity in 1989 and 1990 monitored by Los Alamos energetic particle sensors at geosynchronous orbit.

CONTRACTOR:	**OAK RIDGE NATIONAL LABORATORY** Martin Marietta Energy Systems, Inc. Oak Ridge, Tennessee 37831
CONTRACT:	**DE-AC05-84OR21400**
CATEGORY:	**Geology, Geophysics, and Earth Dynamics**
PERSON IN CHARGE:	**R. T. Williams**

A. Coupled Acoustic Seismic Imaging and Geochemical Studies of Magmatic Processes *(R. T. Williams [615-974-2366; FAX 615-974-2368; E-mail utx@ornl.gov], M. T. Naney, A. J. Witten, and G. K. Jacobs)*

This project combines seismic and electrical imaging with geochemistry to investigate the spatial configuration and thermal, physical, and chemical properties of magmatic and hydrothermal systems. It is coordinated with the production of a man-made magma body in a test of *in-situ* vitrification (ISV) for the stabilization of waste sites. There are two main objectives for the research. (1) Produce an experimental seismic data set for a well-defined object that simulates magmatic and hydrothermal features in the Earth. Melts produced in previous ISV tests have been excellent approximations to geologic-scale features, but have not been as completely characterized in terms of temperature, petrology, geochemistry, and physical properties. (2) Test candidate seismic imaging algorithms by comparing the images produced by various algorithms with the known object. The intent is to produce a method for recovering the velocity and Q structure of the simulated magma that can be used to image magmatic or hydrothermal systems in the Earth's crust. Insight gained from this research will also be useful for modeling heat and volatile transport associated with the emplacement of crustal magma bodies.

A trench is constructed to simulate a waste disposal trench, melted by electrical resistance heating, and allowed to cool to a partially crystallized, vitreous body. The maximum size of the melt is reached after ~80 hours of heating. The cooled body is core drilled to determine its shape and to obtain samples for geochemical studies. Seismic data are obtained along two profiles using three-component geophones in boreholes and on the surface and hydrophones in boreholes. Electrical resistivity data are obtained from an array of electrodes in six boreholes around the melt. Temperature data from an array of thermocouples and pyrometers are used to infer the physical state of the system (crystalline, crystals + liquid, liquid) during periods of both heating and cooling. Gas and particulate samples are obtained to continuously monitor changes in composition during the course of the experiment. This complement of sensors and samples will provide data needed to analyze heat and volatile fluxes associated with the controlled generation of the melt body.

Generation of the ISV melt was begun on May 12. The collection and analysis of geophysical and geochemical data are now underway.

CATEGORY:	**Geochemistry**
PERSON IN CHARGE:	**R. E. Mesmer** (615-574-6903; FAX 615-576-2912; E-mail rem@ornl.gov)

A. Complexation of Metal Ions by Organic Acid Anions in Aqueous Solutions *(J. L. S. Bell [615-576-4600; FAX 615-576-2912], D. A. Palmer, D. J. Wesolowski, and S. E. Drummond, joint research with T. H. Giordano, New Mexico State University)*

The goal of this research has been to determine formation constants for metal/carboxylate complexes likely to play an important role in diagenesis, mineral alteration, and porosity changes in geothermal and sedimentary basin brines at relevant conditions of temperature and ionic strength. Work to date has focused on acetate, the most abundant soluble organic acid encountered in natural waters at depth. Potentiometric titrations and mineral solubilities have been used to measure formation constants for acetate complexes with iron, zinc, and aluminum at ionic strengths to 5 molal and at temperatures to 295°C, 295°C, and 150°C, respectively. Our most recent results from titration of $AlCl_3$ with acetate buffer solutions indicate that acetate forms a strong complex with aluminum (for example, at 100°C and an ionic strength of 1.0 molal, the molal formation constant for the monoacetate complex of aluminum is approximately $10^{2.8}$), which has important implications for the enhancement of porosity in lithofacies associated with petroleum and petroleum brines.

B. Aluminum Geochemistry in Brines at Elevated Temperatures *(D. J. Wesolowski [615-574-6903; FAX 615-576-2912] and D. A. Palmer)*

Over a wide range of pH, temperature, and brine composition, the aqueous speciation of aluminum is dominated by $Al(OH)_4^-$ in basic solutions and by Al^{3+} and its complexes with organic and inorganic ligands in acidic solutions. In order to determine precisely the free energies and enthalpies of these important ions, as well as their activity coefficients in natural brines, we have completed extensive studies of the solubility of gibbsite, $Al(OH)_3$, in the system Na-H-Al-Cl from 30 to 70°C and in the system Na-K-Cl-OH-$Al(OH)_4$ from 5 to 80°C. From these results and available literature data, we have developed quantitative functions for the molal formation constants of the reactions $Al(OH)_3 + 3H^+ \leftrightarrows Al^{3+} + 3H_2O$ and $Al(OH)_3 + OH^- \leftrightarrows Al(OH)_4^-$ using the Pitzer ion interaction model. These equations, valid in the 0–100°C range and at all salinities commonly encountered in basinal brines and geothermal systems, allow quantitative calculation of the thermodynamic properties of Al^{3+} and $Al(OH)_4^-$ and the activity coefficient ratios $\gamma Al^{3+}/\gamma(H^+)^3$ and $\gamma Al(OH)_4^-/\gamma OH^-$, in addition to the Pitzer parameters for $AlCl_3$, $NaAl(OH)_4$, and $KAl(OH)_4$. The Pitzer parameters are now available for input into computer codes such as EQ3/EQ6, which facilitate modeling of water/rock interactions associated with diagenesis and mineral alteration. This effort has been enhanced by related research funded by the Division of Geothermal Technology Development at ORNL.

C. Dissociation Constants of Important Natural Acids in Hydrothermal Brines *(D. J. Wesolowski [615-574-6903; FAX 615-576-2912] and D. A. Palmer, joint research with R. M. Kettler, University of Nebraska, and A. G. Dickson, Scripps Institute of Oceanography)*

Soluble organic and inorganic acids play a dominant role in metal transport and mineral transformation reactions by buffering the pH of natural waters and providing anionic ligands for metal complexation. Potentiometric titrations using our hydrogen electrode concentration cell allow quantitative determination of dissociation constants for acids stable or sufficiently metastable with respect to hydrogen at temperatures to 295°C over a wide range of brine compositions. This technique has been employed to measure the first and second dissociation constants of oxalic acid, $H_2C_2O_4$, in 0–5 molal NaCl brines to 175°C. This simplest difunctional carboxylic acid is common in groundwaters and has been reported in significant concentrations in oilfield brines. Because oxalate is known to form strong complexes with doubly and triply charged ions (Fe^{2+}, Ca^{2+}, Al^{3+}, etc.) at room temperature, we suspect that, if formed in significant quantities during kerogen maturation, it may play an important role in secondary porosity development and primary oil migration in sedimentary basins. In addition to this work, we have completed and published a detailed study of the dissociation constants of bisulfate, HSO_4^-, in 0–5 molal NaCl brines in the 25–250°C range. Support for the latter study was supplemented by the Division of Geothermal Technology Development.

D. Solubility of Carbonates in Hydrothermal Solutions *(D. R. Cole [615-574-5473; FAX 615-576-2912] and D. J. Wesolowski)*

As a continuation of our studies of the co-solubility of calcite and dolomite, we have conducted solubility experiments in the system $CaCO_3$-H_2O-CO_2. The objectives of these gold-bag rocking autoclave experiments are to (1) establish an independent set of equilibrium constants for calcite solubility as a function of temperature and pressure and (2) help validate the attainment of equilibrium in the co-solubility study, particularly because dolomite is so sluggish to react. We have measured calcite solubility at temperatures of 30, 50, 150, and 200°C and pressures of 300, 800, and 1300 bars and at 100 and 250°C at 300 bars. The CO_2 concentrations in these experiments were very similar to those used in the co-solubility work, hence the good agreement of the new calcite solubilities with those from the co-solubility studies confirm the earlier work. By ramping up and down pressure at constant temperature, we have reversed the calcite-only experiments to within approximately 10%. At 300 bars, values of log K for the reaction $CaCO_3 + H_2O + CO_2 \leftrightharpoons Ca^{2+} + 2HCO_3^-$ of –3.69, –4.00, –4.81, –6.01, –7.10, and –8.49 have been obtained at 30, 50, 100, 150, 200, and 250°C, respectively. An increase in pressure results in an increase in the calcite solubility. For example, at 150°C, log K changes from –6.01 at 300 bars to –4.97 at 1300 bars, which indicates that pressure changes in sedimentary basins may play an important role in porosity development and fluid migration.

E. Mechanisms and Rates of Stable Isotope Exchange in Mineral-Fluid Systems *(D. R. Cole [615-574-5473; FAX 615-576-2912], joint research with T. E. Burch and A. C. Lasaga, Yale University)*

Experiments have been conducted to evaluate how fluid composition and pressure influences the nature and rates of stable isotope exchange. In the system calcite-H_2O-NaCl (300–600°C, 0.5 to 2 kbars), SEM observations clearly show an increase in the intensity of dissolution and recrystallization with increasing NaCl concentration. Additionally, there is a pronounced increase in the F values (degree of exchange, 1.0 = 100% equilibration) with increasing temperature, salinity, and pressure. At 400°C and 1 kbar, for example, F values increase from 0.13 at 0.1 m to 0.36 at 4 m NaCl. F values of 0.30, 0.36, and 0.54 were obtained at 500°C, 0 m NaCl at pressures of 0.55, 1, and 2 kbars, respectively. Arrhenius relations for this system yield activation energies ranging from 15.1 to 18.9 kcal mol^{-1} for 0 m and 4 m NaCl, respectively, consistent with other isotope exchange systems where surface reactions dominate. The nature of isotope exchange in the system calcite-H_2O-CO_2 (300–700°C, 1 kbar, % X_{CO_2} = 0, 2, 4, 6, 11, 18, 100) differs considerably with calcite-H_2O-NaCl exchange. SEM evidence indicates there is no wholesale grain growth, only very minor grain rounding. Consequently, we have treated the data with a diffusion model. Diffusion coefficients for $^{13}C/^{12}C$ at 700°C, 1 kbar are in general agreement with those determined by SIMS techniques. In addition, we observe a profound decrease in ^{13}C diffusivities with increasing X_{CO_2} (10^{-15} cm^2/sec at $X_{CO_2} = 0.02$ to 10^{-16} cm^2/sec at $X_{CO_2} = 1$, at 700°C, 1 kbar). Our analysis of the data has shown that the recrystallization of calcite is suppressed to such an extent with the addition of CO_2 to the system that diffusion alone can account for the observed isotope exchange.

F. Paleoclimate Controls on Stable Oxygen and Carbon Isotopes in Fossil Soils *(D. R. Cole [615-574-5473; FAX 615-576-2912], joint research with G. Mack and T. H. Giordano, New Mexico State University)*

Stable oxygen and carbon isotopes have been used to quantify the paleoclimatic record of late Pliocene (3.2 mya) to middle Pleistocene (0.8 mya) paleosols from south-central New Mexico. Stage II and III caliches, dated by paleomagnetic techniques, exhibit ranges in $\delta^{18}O$ (PDB) and $\delta^{13}C$ (PDB) of –9.6 to –5.5 per mil and –5.5 to –2.4 per mil, respectively. Both the oxygen and carbon isotopes display an overall trend of enrichment with decreasing age. Calculations suggest that precipitation in equilibrium with the caliche increased in $\delta^{18}O$ (VSMOW) from –8.5 to –4.5 per mil, reflecting a warming trend in the mean annual temperature from 8 to 18°C over a 2.4 my interval. The long-term warming trend was punctuated by several episodes of less pronounced warming and cooling on the scale of 10^5 years associated with climatic changes accompanying continental glaciation. Similar trends in $\delta^{18}O$ and $\delta^{13}C$ data from paleosols in East Africa suggest that Plio-Pleistocene warming may have been global in scale.

G. The Rb-Sr Systematics of Brine Inclusions in Evaporites from the Gulf of Mexico Sedimentary Basin *(J. Horita [615-576-2750, FAX 615-576-5235] and L. S. Land, joint research with R. A. Eustice, University of Texas at Austin)*

Evaporite deposits are an important component in many sedimentary basins, affecting significantly their hydrogeology and hydrochemistry. The stability of evaporite deposits over a geologic time scale has also been a critical issue in conjunction with possible sites of nuclear waste repositories. At present, however, the mechanisms and magnitudes of interaction between evaporite deposits and subsurface basinal waters are poorly understood. In order to evaluate the "open" vs. "closed" nature of evaporite deposits in sedimentary basins, we initiated a study of Rb-Sr systematics of brine inclusions in evaporites from the Gulf of Mexico basin, which is the largest U.S. reservoir of oil and hydrocarbons, because Sr isotopes are one of the best indicators for the origin of salts and diagenetic processes. Many $^{87}Sr/^{86}Sr$ ratios of evaporite minerals from the Gulf of Mexico basin appear to be radiogenic compared to those of coeval Jurassic seawater, even after taking the contribution of ^{87}Rb decay into account. These data suggest that Rb was lost from the evaporites and/or that radiogenic Sr was incorporated into them as a result of large-scale evaporite-water interactions after the deposition. There might have been a significant contribution of nonmarine Sr. Our study of brine inclusions in the evaporite minerals combined with other geochemical data will give a clearer picture of the history of evaporite-water interactions in the basin.

H. Hydrothermal Stability of Organic Acids *(J. L. S. Bell [615-576-4600; FAX 615-576-2912], D. A. Palmer, and S. E. Drummond, joint research with R. M. Kettler, University of Nebraska)*

Acetic acid is the most abundant carboxylic acid found in sedimentary basin waters and, as such, may play an important role in processes such as the formation and or destruction of porosity, the primary migration of natural gas, and the deposition of sediment-related ore deposits. The ability of acetic acid to participate in the above processes depends in part on its hydrothermal stability. Earlier experiments showed that the decomposition of acetic acid and its anion acetate are effectively catalyzed by various mineral surfaces but that, in the absence of these minerals, the acid may be expected to persist for geologically meaningful lengths of time. Our recent work demonstrates that the pH of the solution also has a profound effect on the rate of acetic acid/acetate decomposition. The decomposition rates for buffer mixtures of acetic acid and sodium acetate were found to be much faster than the rates for solutions containing either acetic acid or acetate alone. We have developed a working model for the decomposition mechanisms in the case of acetic acid/acetate buffer mixtures, which suggests that the decomposition rate remains high until the acetic acid/acetate buffer capacity of the solution is exceeded, i.e., either acetic acid or acetate is entirely consumed, after which the rate decreases to a rate similar to that expected for the remaining species.

Redox equilibria involving carboxylic acids have been suggested as a possible control of oxygen fugacity in sedimentary basins. Preliminary experiments have been performed in order to measure the rates of reaction involving acetic and propionic acid: $2CH_3CH_2COOH + O_2 \leftrightarrows 3CH_3COOH$ and $3CH_3COOH + 2H_2 \leftrightarrows 2CH_3CH_2COOH + 2H_2O$. Experiments were conducted at 275°C for periods of 2 months in which (a) 1 molal acetic acid solutions were exposed to 1000 psi hydrogen gas pressure and (b) 1 molal propionic acid solutions were exposed to 800 psi of oxygen gas pressure, both in the presence of various catalysts (stainless steel, quartz, montmorillonite, magnetite, pyrite, and titanium. In the acetic acid + H_2 experiments, no change in total acetate or any additional new species was observed by ion chromatographic analysis. However, the propionic acid solutions exposed to oxygen gas exhibited quantitative conversion to acetic acid in the presence of stainless steel. Therefore, it is possible that redox equilibria among carboxylates may be achieved in geologically relevant time frames, but reversal of the propionate → acetate reaction has not been demonstrated.

I. Crustal Stability of C-O-H Fluids *(J. G. Blencoe [615-574-7041; FAX 615-576-2912; E-mail jgb@blencoe.chem.ornl.gov], D. B. Joyce, and J. C. Seitz)*

A series of reconnaissance runs was conducted to establish the precision and accuracy of data obtained from a vibrating-tube densimeter designed to measure the pressure-volume-temperature (PVT) properties of C-O-H gases and gas mixtures. The runs were performed at 500–1000 bars, 50–400°C, using H_2O, Ar, N_2, and He as standards and CO_2 as a nominal "unknown" C-O-H gas. An isobaric, isothermal, staged flow-through method was employed to obtain the PVT data. Data obtained from the four standards indicate a precisely linear relationship between density (ρ) and tube response. CO_2 densities calculated from least-squares fit calibration equations relating density to vibrational frequency are in good agreement with corresponding values calculated from the equations of state published by Holloway and by Bottinga and Richet. Precisions ultimately achieved during experimentation were P, ±0.1 bar; T, ±0.01°C; and ρ, ±0.0001 g/cm^3. Conservative estimates of accuracy are P, ±2.0 bars; T, ±0.2°C; and ρ, ±0.0015 g/cm^3. In addition to the vibrating-tube studies, experiments will be performed to investigate the equilibrium speciation and activity-composition relations of C-O-H gas mixtures at high pressures and temperatures. In preparation for these experiments, two new types of $Ag_{25}Pd_{75}$ membranes were designed for use in our hydrogen service internally heated pressure vessel (IHPV), one designed for simple rugged operation in sensing H_2 fugacity only, and the other, with a much larger surface area, intended to measure and control H_2 fugacity. Both designs appear to work well.

J. Experimental and Thermodynamic Investigations of Synthetic, Hydrous Feldspar Melts *(J. G. Blencoe [615-574-7041; FAX 615-576-5235; E-mail jgb@blencoe.chem.ornl.gov])*

Published thermodynamic models for $NaAlSi_3O_8$-H_2O (ab-w) melts are based on various thermodynamic, phase-equilibrium, and spectroscopic data for the $NaAlSi_3O_8$ and $NaAlSi_3O_8$-H_2O systems. Significantly, however, there is no single thermodynamic model that is completely consistent with all of the high quality experimental and analytical data for these systems.

To further investigate the thermodynamic mixing properties of ab-w melts, two methods were developed for calculating γ^L_{ab} and γ^L_w at any set of PT conditions defined by the stable coexistence of analbite (Ab), hydrous albite melt (L), and H_2O-rich vapor (V). Calculations were performed for 1.0 kbar, 883°C; 2.5 kbars, 800°C; 5.0 kbars, 748°C; and 8.0 kbars, 712°C. For each set of PT conditions, the input data for calculations were (1) the enthalpy and entropy of fusion of Ab at 1 bar; (2) the volume of fusion of Ab; (3) the temperature of the reaction Ab + V = L; (4) a value for X^L_w in L(Ab,V); and (5) a value for X^V_w in V(Ab,L). These data are necessary and sufficient to evaluate the mixing parameters of the two-parameter Margules and three-parameter Redlich-Kister formulations. These formulations yield calculated values of γ^L_{ab}, γ^L_w, a^L_{ab}, a^L_w, G^{ex} and G^{mix} for ab-w melts. Key results of the calculations are that, with increasing X^L_w from $X^L_w = 0.0$, γ^L_w increases from <1.0 to >1.0 and, concomitantly, G^{ex} decreases sharply (becomes strongly negative), levels off, and ultimately increases to near 0.0 at the vapor saturation surface. These results uphold the H_2O dissolution model for silicate melts advanced by Stolper and coworkers, the key elements of which are that (1) hydroxyl groups are the dominant hydrous species at very low total water contents; (2) molecular water predominates at high total water contents; and (3) once total dissolved water exceeds a few weight percent, essentially all additional water dissolves in molecular form.

K. Investigations of the Crystal Chemistries and Thermodynamics of Rock-Forming Crystalline Solutions *(J. G. Blencoe [615-574-7041; FAX 615-576-5235; E-mail jgb@blencoe.chem.ornl.gov])*

X-ray diffraction data were obtained for $NaAlSiO_4$-$KAlSiO_4$ (ne-ks) nephelines and kalsilites synthesized at 2 kbars, 800°C; and for ne-ks nephelines crystallized at 5 kbars, 800°C. These data indicate that (1) diffraction maxima for ne-ks nephelines and kalsilites vary linearly with mole fraction $KAlSiO_4(X_{ks})$ and (2) for ne-ks nephelines, there are breaks in the slopes of 2θ versus X_{ks} in the range $0.25 < X_{ks} \simeq 0.30$. It was concluded that determinative equations based on the (201), (210), and (311) reflections of nepheline and the (002), (102), (111), and (112) reflections of kalsilite are the most suitable for calculating X_{ks}. "Average X-ray compositions" for ne-ks nephelines and kalsilites calculated from these determinative equations appear to be accurate to ±3.0 and ±1.5 mole percent $KAlSiO_4$, respectively.

Multivariate, second-order regression equations were developed to quantify the effects of Na* [= 100 Na/(Na + K)] and Fm[= $\Sigma(Fe_T + Mg + Mn)$] on the a, b, 1/2 c sin β and V cell parameters of muscovite (143 specimens) and paragonite (22 specimens). Na* substitutions occur on the XII sites of these micas, and it was assumed that all Fm substitutions occur on the VI sites. It was found that Na* substitution has large effects on 1/2 c sin β and V but only small effects on a and b. Fm substitution is largely restricted to muscovite and causes the a and b dimensions to increase. However, increases in the a and b dimensions of the octahedral sheet necessitate rotations in the adjacent tetrahedral sheet, which has the effect of causing 1/2 c sin β to decrease. Thus the net effect of Fm substitution on V is a small increase. Regression equations for unit-cell volume indicate positive excess volumes for Na-bearing muscovites but approximately zero or slightly negative excess volumes for K-bearing paragonites.

Analysis of compositional data for natural, quasi-binary paragonite-muscovite pairs suggests that the "natural" binary paragonite-muscovite solvus is not as asymmetric toward paragonite as previously believed. The compositional data for high-temperature muscovites (estimated final equilibration temperatures > 500°C), taken as a whole, indicate that the maximum degree of *stable* paragonite dissolution is approximately 30 mole percent, nearly 10 mole percent less than previously believed. It is concluded that all natural muscovites with paragonite contents > 30 mole percent were metastable at the time of their formation. Additionally, a sizable number of natural muscovites with paragonite contents between 25 and 30 mole percent are interpreted to have metastably high Na contents.

L. Stable Isotope Systematics during Burial Diagenesis in the Alberta Deep Basin: An Ion Microprobe Study *(D. R. Cole [615-574-5473; FAX 615-576-2912], W. Christie, T. Rosseel, and L. Riciputi, joint research with H. Machel, Univ. Alberta)*

The principal objective of this new project is to use stable isotopes coupled with detailed mineralogy, fluid inclusion studies, and trace element distributions to quantify the chemical mass transfer processes influencing porosity and permeability during diagenesis of clastic and carbonate rocks in the Alberta Basin. The first stage of this work has involved the development of analytical techniques for isotope and trace element analysis using our 4f Cameca ion microprobe. By analyzing doubly charged ions of odd isotopic species, we have established linear standardization curves for the REE (Lu, Nd, Sm, Eu, Gd, Dy, Yb, Lu) over 2.5 orders of magnitude in concentration (2 to 500 ppm). Reproducibility on a particular day is better than ±5%, and absolute precision over periods of several weeks is ±10% without any correction for drift. We have also demonstrated the capability of analyzing REE concentrations of less than 1 ppm in mineral matrices (augite, garnet) for spot sizes of 20–50 microns. Our analytical techniques for oxygen isotopes show great promise, particularly for conductive samples. Precisions of ±1 per mil ($^{18}O/^{16}O$) have been achieved for magnetites using beam sizes of 20 microns.

M. Salt Effects on Oxygen and Hydrogen Isotope Fractionation between Water Vapor and Brines

(J. Horita [615-576-2750; FAX 615-576-5235], D. J. Wesolowski, and D. R. Cole)

Saline natural waters with wide ranges of chemical composition and temperature are encountered in groundwaters, sedimentary basins, crystalline rocks, and hydrothermal systems. It has long been known that isotope activity ratios of salt solutions differ from their isotope concentration ratios (D/H, $^{18}O/^{16}O$), but this effect has not been quantified, especially at elevated temperatures. In order to determine oxygen and hydrogen isotope fractionation factors between vapor and liquid water, and the effects of dissolved salts on the activity/composition relationships, a series of vapor-liquid water equilibration experiments were carried out for pure water and for NaCl and KCl solutions at 50, 70, and 100°C. For pure water, values of $10^3 \ln \alpha_{l-v}$ were 55.7 and 42.3 for δD, and 7.51 and 6.34 for $\delta^{18}O$ at 50 and 70°C, respectively. These results are in excellent agreement with those of Majoube. Vapor-liquid water equilibrations of NaCl and KCl solutions were carried out at the same experimental conditions as for pure water. δD values of water vapor in equilibrium with NaCl solutions were consistently higher than those in equilibrium with pure water with the same isotopic composition. The effect is linear with the molality of the NaCl solutions and decreases with temperature; ca. 2 per mil/molal (0–6 molal) at 50°C and 1.5 per mil/molal (0–4 molal) at 70°C. Dissolved NaCl has no effect on $\delta^{18}O$ values within analytical error. The effects of 0–3 molal KCl solutions at 50 and 70°C were the same as that of NaCl solutions for both δD and $\delta^{18}O$ values. Our results agree well with those at similar temperatures by Truesdell and by Kakiuchi, who employed CO_2- and H_2-liquid water equilibration techniques, respectively. Preliminary NaCl solution-vapor equilibrations at 100°C suggest a possible deviation from a simple linear salt effect vs. molality trend, consistent with the unpublished results of Kazahaya.

N. Advanced Concepts *(D. J . Wesolowski [615-574-6903; FAX 615-576-2912], D. R. Cole, and D. A. Palmer)*

Development of a stabilized-zirconia flowing emf cell for potentiometric measurements on aqueous solutions to 450°C and 1 kbar continued during this period. This device will enable the measurement of acid and base dissociation constants and the stability constants of metal ion complexes with hydroxide and weak acid and base salts (e.g., acetate, sulfate, carbonate) at temperatures and pressures relevant to deep sedimentary basins and magma/hydrothermal systems. The furnace and pressure-temperature control system have been constructed, and the cell design is being formulated with engineering input from Coors Technical Ceramics Co.

CONTRACTOR:	**PACIFIC NORTHWEST LABORATORY** Battelle Memorial Institute Richland, Washington 99352
CONTRACT:	**DE-AC06-76RLO 1830**
CATEGORY:	**Energy Resource Recognition, Evaluation, and Utilization**
PERSON IN CHARGE:	**E. W. Kleckner**

A. Remote Sensing: Geoscience Data Analysis and Integration *(H. P. Foote [509-376-8418] and G. E. Wukelic)*

This research emphasizes the development of advanced interactive techniques for processing, analyzing, and displaying combinations of remote sensing and geosciences data. Both data types are becoming more abundant and more relevant to DOE's responsibilities in resource discovery, energy development, environmental restoration, global environmental change, and national security. Previously developed techniques have been effectively applied in a variety of earth science, environmental, and national security programs.

Large multidimensional geophysical and geologic data sets are now becoming commonplace. Examples include three-dimensional seismic reflection data, computer tomography, and output from three-dimensional simulation models. These data sets may contain from 10^6 to 10^8 data values, and thus are of the same order of size as multispectral satellite data sets.

The recent California Loma Prieta earthquake and aftershock history is a good example of this type of data set. It consists of several thousand hypocenter locations with time of occurrence and magnitude. We have used a workstation, coupled to a video disk system, to record a computer-generated moving display of this data set. The video display allows a viewer to assimilate quickly the principal spatial and temporal features of the aftershock history. The video sequence may be recorded for later review, comparison, or distribution to other investigators. We have produced computer simulated flyovers by combining digital topographic data with satellite imagery and digitized geologic maps. These video sequences have been produced for the Valles caldera, New Mexico; for Yucca Mountain, Nevada; and for the Nevada Nuclear test sites.

In the past year we have developed an interactive change detection program that allows a user to quickly register and compare a sequence of images for natural or man-made changes. The program incorporates an image correlation algorithm developed earlier for correlation of stereo imagery. We have successfully tested this program with a time sequence of nine SPOT satellite images.

In the area of satellite data analysis, we are continuing to improve our capability to digitally correlate stereo imagery for the automatic measurement of parallax and for the production of gridded elevation data sets. We are currently working with a SPOT satellite stereo pair for Long Valley, California. Our goal in this analysis is to improve the accuracy of the correlation process for a wide range of surface-cover types and, in particular, to determine the characteristics of satellite data needed to achieve a prescribed level of elevation error.

B. Remote Geologic Analysis *(M. G. Foley [509-376-8635; FAX 509-376-5368; E-mail mg_foley@pnl.gov (Internet)] and P. G. Heasler)*

We are developing an automated pattern-recognition system for spatial analysis and synthesis of digital topographic, geologic, seismic, and geophysical data. Our emphasis is on identifying the imprints on topography of the underlying structures that enhance and channel migration of fluids in fracture-controlled flow systems in low-permeability crustal rocks. Our development objectives for this Remote Geologic Analysis system are (1) semi-automatically and quantitatively determine from pattern-recognition and spatial analyses of topographic and geomorphic features (e.g., valleys, drainage networks and divides, scarps, dip slopes, and terraces) the three-dimensional orientations of deeper-seated structures manifested at the Earth's surface by warping or propagation of fracture systems through intervening overburden rocks, (2) correlate them with planar or curvilinear features found in seismic hypocenter data, and (3) provide three-dimensional interpretations and visualizations of crustal fractures and stresses, potential fluid-migration pathways (e.g., for hydrocarbons, geothermal fluids, or natural gas), and spatial relations with features identified from other remotely sensed data such as gravity and aeromagnetic anomalies, seismic profiles, active and passive imagery, lithologic isopachs, groundwater potentiometric surfaces, and hydrogeochemical contour maps. Because our analyses depend on digital topographic and geologic-contact surfaces, we are also studying the noise and error structures of digital models of topography and subsurface geology and the way in which those errors are propagated through our analyses.

The Remote Geologic Analysis system is currently operational for a limited suite of pattern-recognition approaches, and we are testing its utility for exploration for natural gas in tight shales and gas sands in cooperation with DOE's Morgantown Energy Technology Center. We think that it will also be a critical component of the characterization of sites for disposal of DOE's hazardous and radioactive wastes and that it has potential for application to spatial aggregation of watershed models in support of Global Change studies.

CATEGORY: **Solar, Solar-Terrestrial, and Atmospheric Interactions**

PERSON IN CHARGE: **E. W. Kleckner**

This program is centered on aeronomy and space physics in the upper atmosphere, while in the lower atmosphere it is concerned with the processes of radiative transfer. Specifically, the aeronomy program is concerned with processes at the boundaries between the plasmasphere-magnetosphere and the ionosphere-stratosphere regions. While significant advances have been made in our understanding of these regions during the past two decades, there are still outstanding questions as to energy coupling mechanisms at the interfaces. Our understanding of the physics of these zones is particularly important when attempting to arrive at definitive solar-terrestrial cause and effect relationships.

A multi-year database of direct and diffuse multi-spectral solar radiation measurements forms a baseline for much of the insolation research program. Our research has two goals: to measure the spectral characteristics of scattered and direct sunlight under various atmospheric conditions and to create models of the effects of clouds and trace species in the troposphere and lower stratosphere on incoming solar radiation. These natural or man-made trace species include aerosols and gases.

A. DOE Aeronomy/Insolation Studies *(E. W. Kleckner [509-376-8425; FAX 509-376-5368; E-mail ew_kleckner@pnl.gov (Internet)], D. W. Slater, and N. R. Larson)*

We study mid- and high-latitude auroral and ionospheric phenomena to investigate solar-terrestrial relations involving wide-ranging and complex interactions. A major goal of the aeronomy program is to investigate the coupling of the ionospheric, plasmaspheric, and magnetospheric regions, primarily through the use of optical remote sensing. We have, since 1978, used a network of automatic photometers to acquire synoptic observations of the aurora and airglow above the North American continent. To extend our observations, we have recently designed new imaging systems based on the Charge Coupled Device (CCD) technology. All data acquired in this program are available to outside researchers.

We completed a statistical study of Stable Auroral Red (SAR) arc occurrence rates covering an entire solar activity cycle. We found that there are at least two long-term variations in SAR arc emission intensities: solar cycle and seasonal. This led to extensive collaborations with researchers from the University of Michigan and involved the integration of ground-based remote sensing, satellite *in-situ* measurements, and a modeling effort to explain these variations. Our results indicate that the observed seasonal variation of SAR arc properties can be explained by differences in the neutral atmospheric and ionospheric compositions rather than by changes in the magnetospheric heat source. The longer term variations of these properties tied to the solar cycle period require significant changes of magnetospheric heat influx to explain the PNL observations. We have attributed this variation of the energy source to compositional changes of the magnetospheric plasma surrounding the Earth.

A CCD intensified imager, designed and built at PNL, is in operation recording auroral and airglow emissions from the nighttime sky. Our design includes an all-sky imaging lens, filtering and intensification sections, with a cooled CCD detector. We have also completed the design and construction of a second-generation (non-intensified) CCD camera system. This allows improved dynamic range and spectral sensitivity. A critical requirement of this design is operation with extremely low instrumental noise; the system has met design criteria and is operating with combined thermal and readout noise of approximately 6 electrons/pixel. Both CCD systems have been used for studies of naturally occurring light emissions from the upper atmosphere as well as active experiments in space (chemical releases).

Energy sources and energy policy affect the deposition of man-made aerosols in the atmosphere. Natural sources, such as volcanic eruptions, also release significant quantities of aerosols to the troposphere as well as the stratosphere. By studying the natural aerosol releases, we can arrive at an understanding of the major processes operating, the range and limits of natural variability, and we can create models that allow a predictive capability of the effects of these aerosols within the atmosphere. Our studies of these phenomena, reported over the past few years, have identified both a seasonal and a long-term component to the stratospheric aerosol burden following equatorial region volcanic eruptions. Our multistation data set allows us to look at the meridional transport of these aerosols between the equatorial and arctic regions.

Ground based measurements of atmospheric aerosols and trace gases are now being made with the family of Rotating Shadowband Radiometers and Photometers (RSRs) developed at PNL. Our most advanced operating model, the Multiple Detector RSR, employs seven filtered detectors to make multiple wavelength measurements of direct, diffuse, and total solar irradiance. These three radiation components can be used to determine the cloudiness, dominant cloud types, and turbidity of the atmosphere at any site. These parameters have an important influence on atmospheric radiation balance and constitute a vital input to computer model studies of climate variation. Atmospheric turbidity, or visibility, is especially important in environmentally sensitive or pollution-prone areas.

A linear array CCD Rotating Shadowband Photometer that will provide much greater spectral resolution for solar radiation measurements is under construction. Spectra of direct solar radiation, and diffuse and total sky radiation, are focused on a 256 element CCD detector to provide 0.6 nanometer (nm) resolution at 350 nm wavelength and 12 nm resolution at 1050 nm. Each CCD element provides a separate measurement of the irradiance in a specific wavelength band, enabling the monitoring of the molecular absorption bands of a number of important trace gases, such as ozone and water vapor.

CONTRACTOR:	**SANDIA NATIONAL LABORATORIES** Albuquerque, New Mexico 87185
CONTRACT:	**DE-AC04-76DP00789**
CATEGORY:	**Geology, Geophysics, and Earth Dynamics**
PERSON IN CHARGE:	**R. K. Traeger** (505-844-2155; FAX 505-844-7354)

A. Acoustic Emissions and Damage in Geomaterials *(D. J. Holcomb [505-844-2157; FAX 505-844-7354])*

The Kaiser effect method is the only method currently proposed for determining *in-situ* stress independent of material properties. In addition, the method does not require an empirical model to bridge the gap between what was measured and the desired quantity. If the method is workable, it should find widespread use in the oil industry and geotechnical engineering. It would be applicable to any situation where core could be retrieved, without depth limitations.

Work focused on applying the information that has been accumulated on 2-D damage surfaces. Two tasks were undertaken. First, the existing mathematical model for damage development in rock was revised. Second, the Kaiser effect method developed for studying damage was applied to determining *in-situ* stress.

In what was initially thought to be a minor correction, the microcrack damage model, which has been the main theoretical tool for investigating damage surfaces, was revised. A mean-stress term describing crack growth suppression was replaced by a normal-traction term. Investigation showed that the change eliminated an instability in the predicted form of the damage surfaces and improved the fit of the deformations calculated using the model. Using the revised damage model, the problem of calculating the *in-situ* stress from the damage surface measured using core samples was investigated. A proof was developed that the existing method, based on the Kaiser effect measured in uniaxial compression testing, is generally incorrect. A new method was developed that in principle can determine the *in-situ* deviatoric stress tensor.

B. Anelastic Strain Recovery Method of *In-Situ* Stress Determination *(L. W. Teufel [505-844-8680; FAX 505-844-7354])*

Definition and understanding of *in-situ* stresses is needed in many energy related processes, including petroleum reservoir dynamics and production, waste repository stability, horizontal drilling strategies, and underground testing. Anelastic strain measurement techniques, analyses, and interpretation are being developed in this research program. Portions of this research have been successfully transferred to industry and are in use. Continuing research is developing understanding of the strain relaxation process needed for the applied modeling done in other DOE programs and by industry.

In order to interpret *in-situ* stress measurements, perform core and log analyses, and conduct many other laboratory and computational studies of rock, it is necessary to invoke an effective stress law for the material and process. This law gives the relationship between confining stress and pore pressure on specific stress-sensitive properties of the rock. Some rocks may exhibit complicated pressure and stress dependencies because of relaxation microcracks and unconnected porosity. A consequence of this behavior is that the effective stress law may not be linear.

We have made laboratory measurements of volumetric strain and permeability as a function of confining stress to 70 MPa and of pore pressure to 50 MPa for different sedimentary rock types. A powerful statistical technique known as the response surface method has been used to analyze the laboratory data and to determine if the effective stress law is linear. The results of the laboratory study show that the effective stress laws for permeability and deformation vary with stress and pore pressure, depend upon the material, and do not agree with theory.

C. Transport Properties of Fractures *(S. R. Brown [505-846-0965; FAX 505-844-7354])*

This research focuses on the physics of transport of fluid and electric current through fractures in rock and the scale dependence of related properties. This work should prove useful to many energy programs involving fractured rock — including fractured oil/gas reservoirs, geothermal reservoirs, and waste isolation and remediation sites.

Two new computer codes were developed to allow further numerical simulations concerning the effect of anisotropic roughness and the relationship of transport properties to normal stress across the fracture. One code is a self-affine fractal surface generator, which creates realistic fractures with various degrees of anisotropic roughness, shear offset, and mismatch of the opposing surfaces. The other code is for elastic contact of rough surfaces. These codes have been used recently (1) to show that the effect of surface roughness anisotropy on fluid, electric current, and solute transport in fractures is an extremely important consideration in the interpretation of field and lab experiments and (2) to develop a scaling law for elastic normal stiffness of fractures.

Work has begun to evaluate the potential use of an electrokinetic effect (electric currents induced by fluid flow) for the study of groundwater motion in fractured and other heterogeneous media. A bench-scale experiment has been done to demonstrate that the effect is measurable. Additional experiments are planned to demonstrate the method in a two-dimensional tabular sample with fractures.

D. Reservoir Characterization: Reef-Type Reservoir *(G. J. Elbring [505-844-4904; FAX 505-844-7354] and H. C. Hardee [505-844-2257])*

Better characterization of oil and gas reservoirs can be accomplished through the use of combined compressional (P), vertically polarized shear (SV), and horizontally polarized shear (SH) wave data sets. In conjunction with Roger Turpening of MIT, a reef-type reservoir will be imaged with directly generated crosshole data sets of each of the above wave types. Downhole P-wave sources are commercially available, but Sandia is responsible for the development of the shear-wave sources. Upgrades to the existing Sandia downhole SV source have been made to increase the output at higher frequencies through better valves, oscillator pistons, and clamping mechanisms. A gas supply system has been developed and tested that allows virtually unlimited downhole operation with rapid cycling of the seismic sweeps. The SV version will be ready for field operation in July 1991. The SH version of the source will be ready the following year. A new processing method for treating the resonant sweep pilot signal is under development. The integrated crosshole P, SV, and SH data sets should provide not only better spatial resolution as compared with surface seismic methods but will also provide greater information on the properties of the reservoir itself.

E. Borehole Geophysical Techniques *(S. Ballard [505-844-6984; FAX 505-844-7534] and M. E. Thompson)*

The objective of this project is to gain understanding and document performance characteristics of the In Situ Permeable Flow Sensor, a new device for measuring groundwater flow velocities in saturated, permeable geologic materials. The flow sensor has many applications, particularly in monitoring flow in environmentally interesting areas such as sites undergoing waste remediation. Because the flow sensor is still being developed, understanding of its expected performance under differing conditions is not complete. Two approaches are being used in the analysis: numerical modeling of the device's behavior using finite element techniques and actual physical testing of the flow sensor using a large laboratory tank. Work this year has focused on numerical simulation of the sensor using the FIDAP finite element code (licensed to SNL by Fluid Dynamics International, Inc.). The code calculates the temperature field surrounding the instrument under varying flow conditions by solving the coupled equations for flow in a porous medium and the energy equation (including convective effects). Successful characterization of the flow sensor's performance will enable both optimal deployment of the instruments and precise calculation of the flow velocities.

F. Advanced Concepts *(R. K. Traeger [505-844-2155; FAX 505-844-7354])*

Exploratory research is performed in several geoscience areas with the purpose of exploring new concepts or developing new ideas that may lead to future proposals and research programs.

1) Calculation of Flow and Diffusion via Lattice Gas Automata *(H. W. Stockman [505-846-1371; FAX 505-844-7354])*

Lattice gas automata (LGA) are being used to model pore- and fracture-scale processes for transport of solutes, colloids, and emulsions through geologic media. The project goals are (1) to develop viable LGA models and test the models against finite element calculations and analytical solutions wherever possible and (2) use the LGA models to assess dependence of bulk properties (that might be measured in a laboratory or field experiment) on fundamental or microscopic properties of the solvents, solute, and porous medium. Bulk quantities include "retardation" (determined via breakthrough curves for contaminant transport) and relative permeability; fundamental properties include surface reaction rates, fluid diffusion coefficients, colloid birth/death rates, medium geometry (pore structure and fracture roughness), and the viscosity ratio of coexisting immiscible fluids. Unique aspects of the research include the development of rules to yield zero-surface-tension colloids, the characterization of the colloid populations, development of LGA solids with built-in Langmuir isotherms for adsorption, and the design of algorithms to yield realistic colloid-wall interactions. This work can be applied to the transport of actinide colloids in waste repositories or to the uptake of chlorinated hydrocarbons in soils and fractured rocks.

2) 1992 U.S. Symposium on Rock Mechanics *(W. R. Wawersik [505-844-4342; FAX 505-844-7354])*

The U.S. Symposium on Rock Mechanics is an annual meeting to promote the synthesis of diverse rock mechanics activities in professional societies, academia, industry, and government. The 1992 meeting, in Santa Fe, New Mexico, will be organized and hosted by Lawrence Berkeley Laboratory, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, and Sandia National Laboratories. BES support for this meeting is directed at evaluating the state of the art through special lectures, short courses, and workshops. An interlaboratory organizing committee was established and the symposium program defined. In addition, commitments were obtained by scientific leaders to present lectures and participate in developing sessions. Examples include a lecture by D.D. Pollard, Stanford University, on the evolution of fractures and fracture systems and other discussions including fractals, with demonstrated and potential applications, nonlinear dynamic systems, constitutive modeling and strain localization, geostatistics and reliability, modeling of fractured reservoirs, and induced seismicity. Meeting announcements have been completed and mailed, and all meeting facilities have been reserved. The 1992 rock mechanics symposium and workshops are coordinated with the regional conference of the International Society for Rock Mechanics, Fractured and Jointed Rock Masses, to take place at Lake Tahoe, California, during the week preceding the rock mechanics symposium. The coordination between the two meetings is expected to maximize the international attendance at the rock mechanics conference in Santa Fe.

3) ZOGS: A New Transient Electromagnetic Sounding Technique *(G. A. Newman [505-844-8158; FAX 505-844-7354])*

ZOGS (zero offset grounded source sounding) is a new concept in transient electromagnetic (TEM) sounding. The transmitter is a grounded bipole 1 to 2 km in length; the horizontal magnetic field is measured midway along the transmitter wire after the current is shut off. ZOGS enables mapping of electrical conductivity structure to depths of several kilometers, while minimizing the effects of lateral changes in conductivity, providing better focusing than loop-source TEM soundings, and enabling superior resolution to both in-loop TEM and magnetotelluric soundings due to induced vertical current flow in the Earth. Accurate mapping of geoelectric properties to these depths can provide critical information relating to the geologic structure and properties (e.g., hydrology) of the mapped areas. Current efforts are focused on theoretical investigations of the technique, including assessment of the depth resolution, and the effect of 3-D statics arising from shallow depths on the interpretation of the deeper geoelectric structure.

CATEGORY: **Geochemistry**

PERSON IN CHARGE: **R. K. Traeger** (505-844-2155; FAX 505-844-7354)

A. Magmatic Volatiles *(H. R. Westrich [505-846-9613; FAX 505-844-7352] and J. C. Eichelberger)*

The bulk of this year's work included bulk and microprobe (ion and electron) analyses of matrix glasses and melt inclusions for samples collected from Katmai and Redoubt volcanoes, Alaska. The samples from Katmai were studied in conjunction with the on-going CSDP program and included the three basic magma types of the 1912 eruption. These analytical and experimental studies will permit a better understanding of the role of volatiles upon magmatic processes in shallow volcanic environments. Analyses were made from samples of the 1989-90 Redoubt, Alaska, eruption, in collaboration with researchers from the USGS.

Experimental work has centered on bubble resorption and growth in rhyolite magmas at low pressures in order to simulate the development of vesiculated and dense rhyolite volcanic eruptive products. Most tests were made with aphyric tephra samples, and has led to a refinement of our permeable foam model for the eruption of small-volume rhyolite magmas. In addition, our D/H tracer tests are the first *in-situ* demonstration of the relationship between fluid permeability and porosity in a hydrous rhyolite magma.

B. Diagenetic Processes *(H. R. Westrich [505-846-9613; FAX 505-844-7352], W. H. Casey, and B. Bunker)*

This year we have completed measurements of the dissolution kinetics of plagioclase feldspars at 25°C in aqueous solutions (pH 2 and 3) as a function of composition (An_{00}-An_{93}). We have begun examining the low temperature dissolution kinetics of beryllate compounds. These minerals, which include phenacite (Be_2SiO_4), chrysoberyl ($BeAl_2O_4$), and beryl ($Be_3Al_2Si_6O_{18}$), are unique compounds for the study of dissolution processes because the coordination chemistry for Be, Al, or Si does not change. Gem-quality crystals have been obtained for single-crystal dissolution tests and post-reaction surface characterization by ERD and RBS ion beam techniques. Preliminary results for beryl indicate no SiO_2 repolymerization on the surface after reaction in solutions at pH 2.

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

PERSON IN CHARGE: **R. K. Traeger** (505-844-2155; FAX 505-844-7354)

A. Katmai Research Drilling Project *(J. C. Eichelberger [505-844-5929; FAX 505-844-7354])*

The Katmai Project is part of the national Continental Scientific Drilling Program, which seeks to understand fundamental processes of crustal evolution through three-dimensional investigation of the continental crust. The 1912 eruption near Mt. Katmai on the Alaska Peninsula was the outstanding volcanic event of this century in the United States, and indeed in the world. The eruption is ideally suited to investigation of explosive volcanism, because it is relatively simple, both in terms of geologic setting and chronology of the event itself. Objectives of the project are to improve models for explosive eruptions, to determine the source and mechanisms of metals transport in fumaroles of the 1912 ignimbrite, and to establish the rates and mechanisms of ongoing cooling of the system. The project was selected for implementation based upon peer- and panel-reviews by the U.S. Department of Energy, National Science Foundation, and the U.S. Geological Survey and a panel review (as to suitability of the site) by the National Academy of Sciences. The approximately 40 scientists involved in the project come from numerous universities, the USGS, and several DOE laboratories. About half of this group was active during the surface phase of the project. The main surface effort took place in 1989-90, when a coordinated suite of geophysical surveys defined a 2-km-diameter vent for the eruption, buried beneath its own ejecta at the head of the Valley of Ten Thousand Smokes. This work also provided evidence of a huge magma body still present beneath the region. A search for this chamber is being planned for 1992. The project plan calls for drilling into the 1912 vent over a two-year period, beginning in 1993 or 1994 (dependent upon timing of completion of the National Environmental Policy Act process). Two holes will provide a complete cross section of the vent and sample its still-cooling feeder to a depth of 1.2 km. The main activity at present is the writing of an Environmental Impact Statement under the management of the Alaska Region Office of the National Park Service. If the project goes to completion, it will provide an unprecedented view of the processes and structures that give rise to explosive eruptions as well as new insights into the processes of ore formation and hydrothermal circulation.

B. Geoscience Research Drilling Office (GRDO) *(P. J. Lysne [505-844-7333; FAX 505-844-3952], A. Sattler, D. Blankenship, and R. Jacobson)*

The GRDO supports geoscience research scientists who require drilling and other field operations to investigate processes in the Earth's crust. Support generally starts during conception of research that requires drilling; provides the drilling, instrumentation, and other required engineering and field logistics; and concludes when the research well is abandoned.

Katmai Drilling Project. In support of the research led by J. C. Eichelberger (SNL) in the Valley of Ten Thousand Smokes, Alaska, GRDO has published an Operations Plan. Generation of this detailed plan required interaction with numerous local, State, and Federal permitting agencies, as well as many drilling and support groups working in Alaska. The Plan is serving as the basis for developing the environmental Impact Statement, which is being done by the U.S. Park Service. Details and costs of drilling, logging, and other operations continue to be refined as goals and needs become clearer.

VC-2B. In support of research led by Jamie Gardner (LANL) and Jeff Hulen (University of Utah Research Institute), the research well previously completed in the Valles Grande, New Mexico, was logged by GRDO and perforated at five zones to provide fluid samples. The temperature at the bottom perforation was 280°C, which exceeds capabilities of commercial systems. GRDO modified the commercial tools to allow successful perforations at these conditions.

Fluid Sampling. Fluid sampling tools from LANL and LBL were used to obtain fluid samples for F. E. Goff (LANL). Anomalously large quantities of fluid obtained led to analyses indicating sampler failure mechanisms. Design changes were recommended.

ES&H. The environmental, safety, and health issues increasingly influence field operations. A training class on ES&H issues in drilling operations was held to train staff for upcoming operations.

Ocean Drilling Program. GRDO maintains strong interactions with the developments in the ODP through participation in the Down Hole Measurements Panel and continuous discussion with their drilling engineers.

C. Southern Basin and Range Transect (SOBART) *(D. J. Borns [505-844-7333; FAX 505-844-7354])*

A complex interaction of deformation and magmatism accommodates extension of the crust as in the Basin and Range. This interaction influences fluid flow, volcanism, and mineralization in the region, impacting future groundwater resources and the location for a high level nuclear waste repository.

An interdisciplinary and inter-institutional project (SOBART) has been proposed to understand the process occurring in an area from the Panamint Valley and Death Valley, across the Walker Lane belt, through to the northwestern part of the Las Vegas shear zone. A workshop in ding 70 geoscientists from universities, national laboratories, government, and industry began to outline the research program and to define the fundamental issues of continental extension.

A science plan is in publication that describes the results of the workshop and subsequent discussions. This science plan plus continued discussions will provide a basis for agencies to assess their interest in SOBART and for researchers to develop individual proposals.

D. Seismicity Induced by Hydrocarbon Production *(D. F. McTigue [505-846-0578; FAX 505-846-0295; E-mail DFM[illegible]@SANDIA.GOV] joint research with P. Segall, Stanford University)*

Seismicity that correlates with extraction of hydrocarbons is observed at numerous localities throughout the world, posing a potential safety hazard, as well as a threat to production. The goal of this research program is to gain a fundamental understanding of this induced seismicity. The phenomenon is somewhat unexpected, because fluid extraction causes a decrease in pore pressure and a corresponding increase in the magnitude of the effective confining stress, which stabilizes rock against frictional failure. A possible mechanism for the phenomenon has been identified in the elastic coupling of contracting reservoir rocks with their surroundings; the model is generally consistent with the locations and focal mechanisms of observed events. The current research program involves reduction and analysis of independently obtained field data, development of analytical and numerical models for the poroelastic stresses generated by fluid extraction, and comparison of the observations and simulations. Available data include accurate earthquake locations, as well as well-log, gas production, reservoir-pressure, and leveling records for a producing field at Lacq, France, obtained through collaboration with J. R. Grasso (University of Grenoble). The analytical model study seeks solutions for poroelastic deformation in axisymmetric geometries. Numerical simulations are also being developed to address more realistic, complex geometries and nonlinear material behavior. The model will be validated by comparisons of measured and predicted reservoir pressure changes and ground-surface displacements. Finally, the modeled stress changes will be compared with observed seismic hypocenter locations and focal mechanisms for consistency.

PART II

OFF-SITE

GRANTEE:	**UNIVERSITY OF ALASKA** Geophysical Institute Fairbanks, Alaska 99775-0800
GRANT:	**DE-FG06-86ER13530**
TITLE:	**Magnetic Field Annihilation in the Magnetosphere and Its Applications**
PERSON IN CHARGE:	**L. C. Lee and S.-I. Akasofu** (907-474-7410; FAX 907-474-7290; E-mail fred::lclee (Span) or fflcl@alaska (Bitnet))

In our project, we have carried out theoretical and simulation studies of the basic plasma processes associated with magnetic reconnection at the dayside magnetopause and the nightside magnetotail, which are important in the solar wind-magnetosphere interaction transferring energy, mass, and momentum from the solar wind into the Earth's magnetosphere. The aurora seen in the sky is one manifestation of this solar wind-magnetosphere interaction. The results obtained in our present study are also applicable to the magnetic reconnection processes in thermonuclear fusion devices, solar flares, and other astrophysical plasmas.

In our 2-dimensional global MHD simulations, the global magnetic Reynolds number (R_m), the critical current density (J_c) for the resistivity enhancement, and the solar wind Alfv'en Mach number (M_{Asw}) are found to be the most important parameters in determining the reconnection patterns at the dayside magnetopause. The classic quasi-steady and the bursty single X line reconnections tend to occur when R_m is small (< 100), whereas the impulsive multiple X line reconnection takes place when R_m is large (> 200). A current-dependent resistivity and a large R_m lead to various multiple X line reconnection patterns at the dayside magnetopause, and a large M_{Asw} results in magnetic reconnection in the high latitude region.

Magnetospheric plasmas are so dilute that they become collision free. Magnetic reconnection in the collisionless magnetospheric plasmas is studied on the basis of $2^1/_2$-dimensional particle simulations. Particle acceleration in the reconnection process results in a power law energy spectrum of $f(E) \sim E^{-4}$ for energetic ions and electrons, where E is the particle energy. Field-aligned particle heat fluxes and intense plasma waves associated with the collisionless magnetic reconnection process are also observed. Typical power spectra of fluctuating magnetic and electric fields are found to be $P_B \sim f^{-3.8}$ and $P_E \sim f^{-1.8}$, respectively, where f is the wave frequency.

Our 1-dimensional hybrid simulations of slow shocks with a subsonic upstream incident speed show that there is a critical intermediate Mach number (M_c) above which there exists a large-amplitude rotational wave train in the downstream region. M_c depends on the shock normal angle and the upstream plasma beta. Based on the simulation results, we proposed an ion heating mechanism of slow shocks, which is associated with the chaotic motion of particles in the downstream rotational wave field. Our study indicates that the nonlinear interaction between the particles and the downstream wave field may result in the chaotic motion of particles and the damping of waves. The criteria obtained from our theory for the occurrence of highly chaotic particle motion are found to be consistent with our simulation results of slow shocks.

It is found in the 2-dimensional MHD simulations that in the presence of a normal diffusion flux and the mass transport at the magnetopause, the Kelvin-Helmholtz instability may lead to the formation of vortex flow and density structures in the low-latitude boundary layer. It is also found that when the ionospheric effects are included, the ionospheric conductivity provides a dissipation, which may lead to the decay of the vortices formed in the low-latitude boundary layer. Several enhanced conductivity regions which are associated with the boundary layer vortices and the upward field-aligned current filaments can be formed along the post-noon auroral oval. These enhanced conductivity regions may account for the bright auroral spots observed in dayside auroras.

GRANTEE:	**UNIVERSITY OF ARIZONA** Department of Physics Tucson, Arizona 85721
GRANT:	**DE-FG02-89ER13670**
TITLE:	**Solar Variability Observed through Changes in Solar Figure and Diameter**
PERSON IN CHARGE:	**H. A. Hill** (602-621-6782; FAX 602-621-4721; E-mail poglesby@sclera.physics.arizona.edu)

The objective of this program is to utilize accurate measurements of the time-varying solar shape, diameter, and limb darkening function as an indirect diagnostic of temporal changes in the solar luminosity. These observations can preferentially reveal fundamental changes in global photospheric structure by eliminating the effects of solar active regions which affect full disk radiometer measurements. This approach is a valuable complement to the total irradiance measurements made from space. The observations consist of intensity profiles of the solar limb made by continuously scanning the outermost approximately 32 arcseconds of the Sun at various solar latitudes. Limb-darkening observations at the extreme solar limb have the advantage of sampling a wide range of photospheric depths while maintaining a relatively short horizontal range across the Sun. The deleterious effects of atmospheric seeing associated with this approach are overcome with the use of the FFTD (Finite Fourier Transform Definition) of the solar edge. This definition can be used to derive a differential radius, which is a quantity characterizing the solar limb darkening.

The observational thrust of the SCLERA program has produced continued success. In 1990, data for 16 days were obtained between May 15 and June 28 and an additional 20 days between September 13 and December 6. Observations in 1991 began April 4 and are currently underway. Also during 1990, the spatial coverage of the limb has been augmented. Observations now consist of 36 separate limb locations, which will allow the delineation of differing limb-darkening functions at various latitudes.

Data obtained in 1973, 1979, 1981, 1983, 1984, and 1986–1990 have been analyzed for the more fundamental changes in the limb-darkening function as reflected in differential radius observations. The results of observations made during solar cycle 21 indicate that from 1973 to 1983 the differential radius increased significantly, an increase which may be important for understanding the change in total irradiance measured by the ACRIM and ERB radiometers that is not explained by sunspot and facular phenomena. Further, the residual luminosity change implied by the magnitude of the change in differential radius over the decade beginning in 1973 is great enough to have possible consequences for the Earth's climate. Since 1983 the limb-darkening function has shown no significant change aside from small season-to-season variations. That the solar limb darkening remained relatively unchanged following a period of significant change shows that there are phenomena relevant to the solar energy output that are not connected to the cycle of solar activity.

Using these intensity observations of the solar limb and the FFTD, a measurement of the solar diameter can be obtained. Data analysis to permit comparison of these diameter measurements from 1988 to the present is proceeding. In conjunction with the differential radius, the diameter measurements supplement our knowledge of the outermost several arcseconds of the solar limb, where there is evidence that the largest intensity perturbations are occurring.

Further evidence of long period gravity-mode oscillations was found in the analysis of 1986 and 1987 differential radius observations. Also, work was continued on the evidence of mode coupling of the intermediate-degree gravity modes. The long-period gravity modes may be relevant to understanding luminosity variations because of the long lifetime of these modes.

GRANTEE:	**UNIVERSITY OF ARIZONA** Department of Geological Sciences Gould-Simpson Bldg. Tucson, Arizona 85721
GRANT:	**DE-FG02-90ER14115**
TITLE:	**Electrochemical Determination of the Gibbs Free Energies of Rock-Forming Minerals**
PERSON IN CHARGE:	**L. M. Anovitz** (602-621-4618; FAX 602-621-2672; E-mail Anovitz@arizrvax (Bitnet))

This project involves measurement of thermodynamic data for rock-forming minerals using an electrochemical approach. Gibbs energies will be measured directly for several phases on the joins diopside-hedenbergite and enstatite-ferrosilite using redox equilibria and solid-state electrolytes. Measurement of these data as a function of temperature will strongly constrain both the standard state Gibbs free energies and entropies of these phases. The Fe/Mg ordering state of the orthopyroxenes being measured will also be examined as a function of composition and temperature to further constrain our understanding of the effects of submicroscopic properties on the activity composition relations of this join. The relative accuracy of electrochemical measurements and the fact that this technique is the only one currently available which directly measures the Gibbs energy of a phase as a function of temperature makes data obtained in this manner ideal for many types of geochemical calculations. These phases commonly occur in a wide variety of igneous and metamorphic rocks, and high quality thermodynamic data for them are essential to understanding the conditions under which these rock types form.

Work this year has concentrated on synthesis of pyroxenes, construction of necessary equipment, and completion of a re-evaluation of mixing properties on the join diopside-enstatite, necessary if the binary data collected in these experiments are to be combined into a ternary model for Ca-Fe-Mg pyroxenes. Orthopyroxene glasses have been synthesized across the enstatite-ferrosilite join, although as expected high-iron glasses crystallize olivine and quartz. Crucibles pressed from 5 mil Mo foil have proven an inexpensive alternative to Pt for making reduced iron glasses in a gas-mixing furnace. As with graphite, however, small amounts of Mo metal are occasionally found in the glass. The amount varies from run to run, and we are currently exploring methods of minimizing this contamination. The glasses formed in these runs commonly form pyroxene quench crystals, which may then be reground and rerun at subsolidus temperatures to homogenize their compositions. Work on this synthesis is under way.

Re-examination of the diopside-enstatite join was necessary because currently available models for this join predict that end-member diopside is metastable with regard to a subcalcic diopside and wollastonite. A model in which this is no longer the case has been completed which suggests that activity-composition relations for ordered intermediate phases such as diopside are strongly model dependent. A manuscript describing this work is in submission. Direct measurements of the activities of such materials are needed in order to constrain possible models. Using the electrochemical technique, cobalt-diopside appears to be an ideal candidate for such a test, and synthesis of these materials is also under way.

GRANTEE:	**ARIZONA STATE UNIVERSITY** Department of Geology Tempe, Arizona 85287
GRANT:	**DE-FG02-91ER14218**
TITLE:	**Organic/Inorganic Interactions of Nitrogen in Oilfields** **Part I. Geochemistry**
PERSON IN CHARGE:	**L. B. Williams** (602-965-3480; FAX 602-965-8102)

This project is a collaborative effort with R. E. Ferrell (Louisiana State University). Our initial investigation of fixed-NH_4 anomalies as a tool for hydrocarbon exploration has shown that fixed-NH_4 concentrations in a diagenetic environment may be used to indicate levels of hydrocarbon maturation within a source rock and to trace paths of hydrocarbon migration. We developed a model suggesting that N released from hydrocarbons during maturation and migration is incorporated in authigenic clay minerals as NH_4^+. Anomalously high levels of NH_4-substitution can therefore indicate paths of migration. The suggested exploration tool may be applicable to basins hosting the majority of known hydrocarbon accumulations and therefore deserves to be tested thoroughly. A detailed investigation, which includes mapping fixed-NH_4 anomalies across an oilfield, could assist greatly in siting productive well locations and in establishing areas containing bypassed oil.

We plan to field-test the model and to improve our understanding of NH_4-fixation. Fordoche field, a multi-reservoir oil field in Louisiana, has been identified as an ideal case study for the determination of fixed-NH_4 as a tool for mapping hydrocarbon migration paths. The field offers variable depth reservoirs (from 11,000 to 16,000 ft) representing temperatures from 60 to 150°C, so temperature effects on fixed-NH_4 can be tested. Other areas are also being considered for field-wide studies.

GRANTEE:	**BROWN UNIVERSITY** Department of Geological Sciences Providence, Rhode Island 02912
GRANT:	**DE-FG02-90ER14144**
TITLE:	**Grain Boundary Transport and Related Processes in Natural Fine-Grained Aggregates**
PERSON IN CHARGE:	**R. A. Yund and J. R. Farver** (401-863-1931; FAX 401-863-2058; E-mail ray@brownvm.bitnet)

The nature of grain boundaries in rocks and the rate of transport along these boundaries are important questions for many applications, including the migration of chemical components in nuclear repositories and of hydrocarbons in geological environments. This study is the first to directly measure grain boundary diffusion rates in rocks and to determine how the rates vary with rock composition and microstructure, as well as temperature and pressure.

The starting materials include both natural and experimentally sintered fine-grained aggregates of quartz and feldspar, which have been characterized using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Samples of these materials are used to determine the rate of transport of stable isotopes of oxygen and to select geologically and environmentally important cations.

The analytical procedure involves using the ion microprobe (SIMS) and either a depth-profiling technique previously developed for determining volume diffusion rates in these same minerals or a step-scanning technique previously developed for determining oxygen diffusion along macroperthite lamellar boundaries. By collecting data from an area much larger than the grain size of the sample, diffusion along many individual boundaries is averaged to yield a representative value for grain boundary diffusion in the sample. The fine grain size also ensures a strong analytical signal and eliminates thermal cracking of the samples. Using numerical and graphical solutions appropriate to the boundary conditions employed, the product of the grain boundary diffusion coefficient (D') and the effective grain boundary width (δ) are calculated from the SIMS profiling data. The value of $D'\delta$ is independent of the grain size, geometry of the grains, and grain boundary tortuosity.

In addition to temperature, pressure, and sample composition, the effect of fluid composition on transport rates is being investigated. Different fluid compositions produce different equilibrium microstructures; some produce a "wetted" structure with interconnected pores and channels, whereas others produce a "non-wetted" structure with isolated fluid pores. A separate series of experiments has been done to establish the equilibrium microstructure for quartz and feldspar aggregates in the presence of different geologically important fluids, ranging from pure CO_2 to various dilute electrolyte solutions. Samples with different equilibrium microstructures, as characterized in TEM, were then used to determine grain boundary transport rates.

By determining the grain boundary diffusion rates of both oxygen and select cations in natural and experimentally sintered aggregates with geologically important mineralogies over a wide range of temperature, pressure, and fluid composition, the results provide a much better understanding of grain boundary transport in geological materials under natural conditions and allow estimation of diffusion rates in rocks for which the grain boundary microstructure is known.

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**
PERSON IN CHARGE:	**S. Epstein** (818-356-6100) and **E. Stolper** (818-356-6504; FAX 818-568-0935; E-mail ems@expet.gps.caltech.edu)

The focus of this project is the combined application of infrared spectroscopy and stable isotope geochemistry to the study of hydrogen-bearing species dissolved in silicate melts and glasses. We are conducting laboratory experiments aimed at determining the fractionation of D and H between melt species (OH and H_2O) and hydrous vapor and the diffusivities of these species in glasses and melts. Knowledge of these parameters is critical to understanding the behavior of hydrogen isotopes during igneous processes and hydrothermal processes. These results also could be valuable in applications of glass technology to development of nuclear waste disposal strategies.

We have measured the partitioning of hydrogen isotopes between water vapor and silicate melts and glasses at temperatures of 550–850°C and pressures of 2–2000 bars. Our results make it possible to use hydrogen isotope data to model the degassing of high-level silicic magmatic centers of the sort being considered as geothermal resources. For example, the large vapor-melt fractionation factor we have determined suggests that rhyolitic domes (e.g., those found in the Mono craters and Inyo craters systems in California) evolved by open-system degassing of water-rich magmas.

Diffusive transport of water in silicate liquids and glasses plays an important role in many phenomena of interest in the geological and materials sciences. For example, the rate of water diffusion in silicate liquids controls the growth of bubbles in ascending magmas and influences the degree to which magmas can dehydrate on ascent and the availability of compressed vapor in bubbles to power explosive volcanic eruptions. Hydration and dehydration of silicate glasses in geological and man-made environments are also limited by water diffusion and relate to issues such as the chemical stability of glasses, the mechanical strength of glass fibers, the kinetics of SiO_2 film growth on Si substrates, water-rock reactions leading to ore deposition, and obsidian hydration dating of young volcanic rocks. We have shown that in volcanic glasses, the diffusivity of water molecules is much greater than that of hydroxyl groups. The uniqueness of our approach stems from our ability to measure the concentration profiles of these separate species, which allows us to treat the problem in terms of two diffusing, reacting species and to obtain diffusivities for both molecular water and hydroxyl groups.

We have used our results on volcanic glasses as a basis for understanding the "self-diffusion" of oxygen in silicate minerals and glasses. In particular, it is well known that the diffusion of oxygen is significantly enhanced under hydrothermal conditions. We have developed the theory needed to understand the connection between the diffusivity of water and oxygen and have shown that diffusion of molecular water in nominally anhydrous minerals and melts is likely the control on measured self-diffusion coefficients of oxygen.

We have extended our study of stable isotope fractionation factors between vapor and silicates to the fractionation of oxygen isotopes between CO_2 vapor and silicate minerals and glasses. We have shown the feasibility of measuring fractionation factors precisely by equilibrating small amounts of vapor with large amounts of silicate, followed by mass spectrometric analysis of the vapor. These data are critical to the interpretation of observed variations in stable isotope ratios in nature and are complementary to our studies of the fractionation and mobility of hydrogen isotopes in silicates.

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 Processes Using Actinide Elements**

PERSON IN CHARGE: **G. J. Wasserburg** (818-356-6439; FAX 818-568-0935)

Water dehydration experiments on rhyolitic glasses have been carried out at 400–550°C in a N_2 atmosphere. Concentration profiles of both H_2O molecules and OH groups were measured by Fourier transform infrared spectroscopy, and diffusion coefficients were calculated for both species as a function of water content. The diffusion of total water is described by considering the diffusion of both H_2O molecules and OH groups and the reaction between them. The diffusion coefficient of OH is found to be negligible compared to that of H_2O ($D_{OH} < D_{H_2O}$); H_2O is the dominant diffusing species even at water concentrations as low as 0.2 wt%. It is shown that molecular H_2O is the dominant diffusing species at very low to high water concentrations. D_{H_2O} is constant to within a factor of 2 for water contents of 0.2 – 1.7 wt%; the activation energy is ~103 kJ/mol. This study indicates that the total diffusion coefficient is a function of the diffusion coefficients and relative proportions of all species. An understanding of the role of speciation in diffusion further helps to relate the diffusion coefficients of apparently unrelated components, e.g., ^{18}O and H_2O. These results show that the presence of H_2O even at levels of 1–10 ppm will govern the mobility of O in silicates. It follows that virtually all of the measurements of D_O already available in the literature are really measurements of D_{H_2O} and water content in the silicate. A theoretical analysis of the nonlinear diffusion equations has been carried out. It is shown that for dehydration processes, the square of the concentration is proportional to $X/\sqrt{\tau}$. This provides a direct relationship between the weight loss of water and time.

A detailed study of the ^{238}U-^{234}U-^{230}Th in aragonite, dolomite, and groundwaters from Pleistocene coral-reef terraces in Barbados was performed to evaluate the behavior of U-Th during water-rock interaction in carbonate systems. Well-preserved aragonitic fossil corals gave ^{230}Th ages of 219 ± 3 and 224 ± 6 ky. This enhanced resolution over alpha-counting techniques provides an extension of the age range over which climatic models for sea level change can be tested. The elevated and variable $\delta^{234}U(T)$ values in corals relative to modern seawater are indicative of open system behavior. The high $^{230}Th/^{238}U$ activity ratios and $^{232}Th/^{238}U$ ratios for dolomite and the low $^{230}Th/^{238}U$ activity ratio for modern groundwaters reflect the enhanced mobility of U relative to Th during water-rock interaction. The results demonstrate major U-Th isotope distinctions between Pleistocene aragonitic corals, secondary dolomites, modern groundwaters, and seawater. The absence of ^{234}U enrichments in groundwaters in marine carbonate terraces shows that these waters cannot be the source of diagenetic fluids causing elevated $\delta^{234}U$ in fossil corals.

We have developed a negative thermal ionization mass spectrometric (NTIMS) technique that produces intense ion beams of negatively charged oxides of Os, Re, and Ir in a conventional thermal ionization mass spectrometer. Os isotope ratios have been determined by NTIMS with a precision of better than ±2‰ for 4 ng Os and ±5‰ for 70 pg Os. The ionization efficiency for Os is 2–6%, corresponding to a detection limit below 10^{-14} g. The ionization efficiency is more than 200 times higher than achieved by ion probe analysis and more than 4×10^4 times higher than achieved by laser resonance ionization mass spectrometry. The NTIMS technique will permit ^{187}Re-^{187}Os chronometry to be widely applied to terrestrial and extraterrestrial materials with a precision and sensitivity not previously attainable and without the need for highly specialized analytical equipment.

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:	**H. C. Helgeson** (510-642-1251; FAX 510-643-9980; E-mail oelkers@violet.berkeley.edu)

The goal of this project is to achieve a better understanding of chemical mass transport attending fluid flow and water-rock interaction in geochemical processes. The overall focus of the research has been on development of comprehensive mass transfer models together with calculation of the thermochemical properties of minerals and the thermodynamic and transport properties of aqueous species as functions of temperature, pressure, and composition. During the past year, research efforts have been primarily concerned with solute speciation and mineral solubilities in supercritical hydrothermal solutions.

The thermodynamic behavior of supercritical aqueous alkali metal halide solutions plays a significant role in various industrial and natural processes, including corrosion of metals, mineral solubilities, solvent extraction, crystal growth, and the formation of hydrothermal ore deposits. The properties of electrolytes in aqueous solution change dramatically with increasing temperature owing to the large decrease in the dielectric constant of H_2O from ~ 80 at low temperatures to < 15 at supercritical temperatures and pressures. Experimental investigation of the behavior of electrolytes in low dielectric constant solvents indicates that supercritical electrolyte solutions are dominated by a complete suite of higher order complexes ranging from single ions in dilute solutions to large mega complexes at the high concentrations typical of many hydrothermal processes. To assess the role of polyatomic clusters in these solutions, stepwise dissociation constants for triple, quadruple, quintuple, and sextuple complexes of 16 1:1 electrolytes were generated from the results of molecular dynamical calculations reported by Gillan using dissociation constants for ion pairs taken from Oelkers and Helgeson. Species distribution calculations generated from these dissociation constants and activity coefficients for charged and neutral aqueous species indicate that single ions and neutral ion pairs predominate only at dilute (< 0.5 m) electrolyte concentrations. Polyatomic clusters consisting of three or more atoms predominate at higher concentrations.

A speciation model was developed during the past year to predict mineral solubilities in the system K_2O-Na_2O-Al_2O_3-SiO_2-H_2O-HCl at temperatures from 300° to 700°C and pressures from 500 to 5000 bars. The model takes account of the Hückel and Setchénow equations and the law of mass action for the formation of ion pairs and triple, quadruple, quintuple, and sextuple clusters. Calculations carried out with provisions for these species afford close approximation of experimentally determined values of m_{KCl}/m_{HCl} and m_{NaCl}/m_{HCl} in aqueous solutions coexisting with K-feldspar + muscovite + quartz, K-feldspar + andalusite + quartz, albite + paragonite + quartz, and other mineral assemblages reported by Hemley, Shade, Montoya and Hemley, and Sverjensky et al. at temperatures to 700°C, pressures to 5 kb, and electrolyte concentrations to 5 molal.

GRANTEE: UNIVERSITY OF CALIFORNIA AT BERKELEY
Department of Physics
Berkeley, California 94720

GRANT: DE-FG03-87ER13667

TITLE: **Isotopic Studies of Noble Gases in Terrestrial Samples and in Natural Nucleosynthesis**

PERSON IN CHARGE: **J. H. Reynolds** (510-642-4863; 642-2260; FAX 510-643-8497; E-mail reynolds@garnet.berkeley.edu)

Our objective is to use noble gases to provide a unique perspective on the many and complex processes influencing compositions and evolution of crustal fluids. Recent interests are hypotheses put forward by J. Oliver (Cornell University) and others suggesting that in many cases the distribution of economic deposits in sedimentary basins is related to the injection of fertile fluids deep into the basins during tectonic collisions along continental margins. Our analyses of CH_4-rich natural gases from Alberta, Texas, and New Mexico have repeatedly encountered anomalous contents of ^3He relative to ^4He as expected for U-Th radioactive decay in typical crustal rocks. The utility of ^3He as a tracer for crustal input of mantle volatiles via magmatic activity is well documented. However, all the aforementioned reservoirs are in sedimentary basins which have not experienced any significant tectonomagmatic activity during the last ~ 200 my. Preliminary studies of core samples from cap, reservoir, and source rocks appear to rule out potential "exotic" ^3He sources such as radiogenic production in Li-enriched environments, cosmogenic production, or cosmic dust. Aside from a lack of recent magmatism, a feature common to the sedimentary basins studied is that all are located on the continental side of orogenic belts, implying that the mantle ^3He may have been injected deep into these basins, perhaps along with ore-bearing fluids, in a manner similar to that hypothesized by Oliver. The occurrence and magnitude of excess ^3He in sedimentary basins may eventually be a sensitive tracer for identifying the origin and distribution of orogenic fluids within stable cratons and their relationship to the economic deposits contained therein.

In fluid inclusions we have observed noble gas nuclides in granites produced by natural neutrons. In the case of the Stripa granite, for which counting rates in a BF3 counter have been published, measurements can be compared with calculations taking into account both thermal and epithermal neutrons. We are attempting to determine the extent to which fast neutrons are important, a relatively unexplored field. Preliminary indications are that fluids included in granites contain too much neutron-produced noble gas for the reactions to have occurred *in situ* so that such nuclides may also prove to be a tracer for geological fluids.

We submitted a third paper on noble gases in diamonds, concentrating on observed effects of ^4He, ^3He, and fission xenon implantation from nuclear processes in adjacent material in the matrix rock. The effect is quite evident in diamonds from an ancient lamproite pipe in Western Australia. Formulae were derived for various cases where the particle sources are inhomogeneously distributed in the matrix.

GRANTEE:	**UNIVERSITY OF CALIFORNIA AT BERKELEY** Department of Geology and Geophysics
GRANT:	**DE-FG03-91ER14200**
TITLE:	**Experimental Measurement of Thermal Conductivity in Silicate Liquids**
PERSON IN CHARGE:	**I. S. E. Carmichael** (510-642-2577; FAX 510-643-9980)

Quantitative understanding of both the evolution of silicate melts within the Earth and the industrial formation of silicate glasses require knowledge of the thermodynamic and transport properties of these liquids. Now that the thermodynamic properties of silicate melts have been largely measured, we have shifted focus to the poorly known transport properties. Of the transport properties (chemical diffusion, viscosity, electrical conductivity, and thermal conductivity), the thermal conductivity (λ) is the least constrained. Despite the paucity of data on λ, the need for those data are far reaching. The thermal conductivity arises in calculations wherever silicates melt or crystallize including *in-situ* fusion of rock, the industrial formation of glass, and in the Earth, where λ is necessary for the understanding of processes ranging in scale from the cooling of large magma reservoirs beneath volcanoes to crystal growth kinetics. We are in the early stages of a project to measure this parameter experimentally in silicate melts as a function of temperature and composition. Our goal is to measure λ on a range of simple silicate compositions from temperatures ranging from their liquidi to 1600°C and use these data to calibrate an empirical expression for predicting λ as a function of temperature and composition. The model can be tested by comparison with measurements on several natural lavas.

In the early months of this project, we have assembled the necessary data acquisition facilities and tested them with a simulated apparatus on the bench. We have also begun work on fabrication of the high temperature cell.

GRANTEE: UNIVERSITY OF CALIFORNIA AT LOS ANGELES
Department of Earth and Space Sciences
Los Angeles, California 90024

GRANT: DE-FG03-89ER14049

TITLE: **K-Feldspar Thermochronology**

PERSON IN CHARGE: **T. M. Harrison** (213-825-7970; FAX 213-825-2779)

Work over the past year has shown that many, and perhaps most, alkali feldspars contain diffusion domains with activation energies that may vary by as much as 8 kcal/mol. An extraordinary consequence of even relatively small variations in activation energy between domains is that the shape of an $^{40}Ar/^{39}Ar$ age spectrum can change dramatically by varying the laboratory heating schedule. We find that Arrhenius and $\log(r/r_0)$ plots have the potential to reveal even small differences in activation energy (~ 2 kcal/mol) between domains, at least in cases where the domains are well separated in size. Variations in activation energy of ~ 5 kcal/mol can result in differences in calculated closure temperature of up to 30°C from that obtained assuming equal activation energies for all domains.

Results of TEM and light microscopy on heated and unheated samples of the K-feldspar sample in which the domain structure was first recognized (MH-10) reveal that three classes of substructure are present: (1) cross-hatched extinction is common, and there is almost no albite/pericline twinning, only tweed microstructure; (2) 5–10 vol% of this K-feldspar consists of turbid zones with complex twin and tweed structures at the sub-micron scale and numerous dislocation and strain features; (3) about 20% of the K-feldspar consists of 0.01 x 0.2-1 µm albite exsolution lamellae. The network of fractured/turbid zones divides the sample into blocks of approximately 50 µm, and the separation between albite exsolution lamellae produces K-feldspar domains on the order of 0.1 µm. Independent crushing and diffusion experiments suggest the scale of the largest domain is on the order of tens of microns, whereas the smallest domain size is inferred to be ~ 0.1 µm. Although this apparent agreement appears promising, we still have no candidate for the intermediate diffusion domain.

We have performed $^{40}Ar/^{39}Ar$ age spectrum experiments on K-feldspar separated from Proterozoic quartz monzonite taken from a depth of 1.76 km down the VC-2B drill hole, Valles caldera, north-central New Mexico. Our results reveal a classic diffusion domain structure but virtually no recent degassing of radiogenic argon, despite the present temperature of 295°C. These results suggest that near peak temperatures in the Sulphur Springs hydrothermal system have only been achieved over the past 10,000 years. This result is similar to our earlier finding from the Hot-Dry-Rock site but contrasts with our previous result from Baca 12, which indicates a much longer duration of heating.

GRANTEE:	**UNIVERSITY OF CALIFORNIA AT LOS ANGELES** Department of Earth and Space Sciences Los Angeles, California 90024
GRANT:	**DE-FG03-91ER14222**
TITLE:	**Oxygen and Cation Diffusion in Oxide Minerals**
PERSON IN CHARGE:	**K. D. McKeegan** (213-825-3580; FAX 213-825-2779)

This project concerns the experimental determination of diffusion coefficients for a number of important rock-forming minerals under a variety of external conditions. The data support efforts to constrain the physical properties of minerals as a function of chemical environment, e.g., the variation in plastic deformation rates as a function of oxygen fugacity and in thermochronometry of crustal rocks and meteoritic materials; specific attention is paid to isolating the relationships between point defect chemistry and diffusive transport. Work is proceeding in the following areas: (1) the role of f_{O_2} and silica activity on the diffusion of oxygen in olivine; (2) the role of f_{O_2} and silica activity on the diffusion of silicon in olivine; (3) determination of activation volumes for oxygen, silicon, and magnesium diffusion in olivine; (4) oxygen diffusion in diopside, spinel, hibonite, and melilite solid solutions; and (5) lead diffusion in monazite.

GRANTEE:	**UNIVERSITY OF CALIFORNIA AT RIVERSIDE** Institute of Geophysics and Planetary Physics Riverside, California 92521
GRANT:	**DE-FG03-89ER14088**
TITLE:	**Volatiles in Hydrothermal Fluids: A Mass Spectrometric Study of Fluid Inclusions from Active Geothermal Systems**
PERSON IN CHARGE:	**M. A. McKibben** (714-787-3444; FAX 714-787-4324)

Fluid inclusions provide fundamental information on the thermal and chemical history of rocks and fluids in a variety of energy-related environments. In particular, analytical data on the gas contents of inclusion fluids in authigenic minerals allow estimation of fluid pressure and chemistry during water-rock interaction. These parameters are crucial in modeling mass transport and deposition in hydrothermal systems.

Active geothermal systems offer unique opportunities to calibrate and test analytical techniques for fluid inclusion chemistry, because the temperature, pressure, and composition of coexisting fluids are known. Thus comparative studies between fluid inclusion mass spectrometric data and modern fluid chemistry in active systems can play an important role in validating fluid inclusion analytical techniques.

We have constructed a system based upon quadrupole mass spectrometry for the analysis of fluid inclusion gas contents. The spectrometer is interfaced to a PC for data acquisition and analysis. The system vacuum is generated and maintained by a roughing pump, a turbomolecular pump, and an ion pumping system. System vacuums are routinely maintained in the 10^{-8} Torr range. Recent addition of a pulse counter has increased the sensitivity of the instrument by two orders of magnitude.

The metal parts of the system are temperature controlled in two zones, the sample section and the spectrometer section. The temperatures are nominally set at 120°C to minimize adsorption problems that occur during analysis. The gas sample is introduced into the spectrometric section by a stainless steel precision leak valve.

The inclusions are opened by mechanical decrepitation. This involves a custom built crushing chamber, which has provisions for entrapment of dust from the filter assembly by helium to minimize contamination, and small, modular design to minimize surface area and ease of operation. Current efforts are to add a laser ablation system for decrepitating individual fluid inclusions.

The system is calibrated using gas mixtures of known composition. We are analyzing fluid inclusions from several active geothermal systems whose fluid chemistry is well known, including Valles caldera in New Mexico, Salton Sea and Coso Hot Springs in California, and Cerro Prieto in Mexico. Comparison of results with the calibration gases indicates what instrumental corrections need to be made for gas adsorption and reaction before the technique is applied to fluid inclusions whose chemistry is unknown.

GRANTEE:	**UNIVERSITY OF CALIFORNIA AT SANTA BARBARA** Institute for Crustal Studies Santa Barbara, California 93106
GRANT:	**DE-FG03-89ER14050**
TITLE:	**Experimental Investigations of Magma Rheology and Numerical Simulations of Caldera Collapse and Magma Withdrawal**
PERSON IN CHARGE:	**F. J. Spera** (805-893-2260; FAX 805-893-8649)

This is a collaborative study with David A. Yuen at the University of Minnesota. Research carried out at UCSB includes high-temperature experimental rheometry and numerical simulations of magma withdrawal. A fluid dynamical model based on solution of the conservation equations for mass, momentum, and species has been applied to the withdrawal of magma from magma bodies that are strongly zoned with respect to composition. Dimensional, scaling, and numerical experiments provide insights into the interpretation of commonly observed correlations between stratigraphic height and composition. Natural eruptions span the dynamic range from the viscous regime to the inertial regime. For central vent eruptions from flat-roofed, layered magma bodies, eruptive intensity varies as σ^{-1}, $\sigma^{-3/5}$ and $\sigma^{-1/2}$, where σ is the super-hydrostatic (effective) pressure, $\sigma = p' + \tau_b$. Effective pressures needed to drive an eruption are proportional to $\dot{M}$, $\dot{M}^{5/3}$, and $\dot{M}^2$ in the viscous, sub-inertial, and inertial regimes, respectively. Typical driving pressures are around 10^3 Pa in the viscous and sub-inertial regimes and roughly 10^6 Pa in the ultraplinian regime, where $\dot{M}$ can be as large as 10^9 kg/s. Tidal stresses, maximum values of which are on the order of 10^4 Pa, are sufficient to drive eruptions in the viscous or sub-inertial regime. The time interval during which upper layer magma is a significant component of the eruptive products (t_{ss}) depends on the thickness of the upper layer, the effective pressure, and the viscosity contrast. When the layers have different viscosities, t_{ss} is proportional to $\eta_r^{0.46}$, where η_r is the relative viscosity of the layers. Simulations of central vent and ring fracture eruptions from flat-roofed and sloped-roof magma bodies with layered compositional profiles show that compositional gaps in ignimbrites may be artifacts of the withdrawal process.

The rheological behavior of dilute emulsions of GeO_2 containing from 0.8 to 5.5 vol% air bubbles has been measured experimentally between 1100 and 1175°C at 1 kPa at shear rates between 0.05 and 7 s^{-1}. At constant bubble volume fraction, the rheological behavior of the emulsions is modeled by a power-law constitutive relation. The power-law emulsions are pseudoplastic (shear-thinning), having a flow index of 0.87 to 0.93. Bubble deformation is promoted by shear and opposed by surface tension. Two dimensionless parameters governing bubble deformation are the capillary number $Ca \equiv \dot{\gamma}\eta_m r_b/\sigma$ and viscosity ratio $\lambda \equiv \eta_b/\eta_m$ determined from melt viscosity η_m, bubble viscosity η_b, bubble radius r_b, shear rate $\dot{\gamma}$, and vapor-melt interfacial tension σ. The capillary number is a measure of the relative importance of shear and interfacial stresses. Low-λ bubbles may attain very elongate stable shapes, and high shear rates are required before fragmentation occurs at a critical capillary number $Ca_{crit,f}$. Bubble fragmentation has consequences for observed bubble size distributions both in post-experimental counts and in nature. Bubble fragmentation by the fracture mechanism is unlikely (or at least not dominant) in most natural magmatic flows. Instead a sub-critical instability known as tip-streaming can occur at a much lower capillary number, $Ca_{crit,ts} = 0.56$. This mechanism produces much smaller daughter bubbles than that of fracture but is more relevant to magmatic flows. Normal stress differences amounting to several percent of the total shear stress can be produced at shear rates of less than 10 s^{-1}. In rotating rod rheometry, this leads to rod-climbing behavior (Weissenberg effect).

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 Aqueous Solutions**
PERSON IN CHARGE:	**F. J. Spera** (805-893-2260; FAX 805-893-8649)

This is a collaborative project with D. A. Yuen (University of Minnesota) to conduct numerical modeling of three problems of relevance to the geoscience mission of the DOE. The three areas include (1) thermo-mechanical modeling of sedimentary basins, including porous media convection; (2) molecular dynamical investigation of the physical and chemical properties of aqueous solutions in the temperature and pressure regime characteristic of continental lithosphere; and (3) magma dynamics with emphasis on magma withdrawal and caldera resurgence. The detailed work plan includes (1) the dynamical influences of lithospheric phase transitions on the thermal-mechanical evolution of sedimentary basins; (2) the coupling between mantle convection and, in particular, mantle plumes on the thermal regime and subsidence history of rift-related sedimentary basins; (3) numerical modeling of heat and solute transport driven by thermal and salinity gradients in a fractured and/or granular porous medium as commonly encountered in sedimentary basins undergoing diagenesis and lithification; (4) the thermodynamic and electrostatic properties of water determined by state-of-the-art molecular dynamics (MD) methods, taking into account effects such as oxygen polarization and molecular dissociation in order to account for the dielectrical properties of water at conditions characteristic of the crust and lower lithosphere; (5) the dynamics of magma removal from large crustal reservoirs for magma treated as a Bingham plastic fluid; and (6) the dynamics of the resurgence of volcanic calderas in continental regions.

GRANTEE: UNIVERSITY OF COLORADO
Department of Geological Sciences/CIRES (Cooperative Institute for Research in Environmental Sciences)
Boulder, Colorado 80309-0216

GRANT: DE-FG02-87ER13804

TITLE: **Seismic Absorption in Fluid Filled Porous Rocks as a Function of Seismic Frequencies, Pressure, and Temperature**

PERSON IN CHARGE: **H. Spetzler** (303-492-6715; FAX 303-492-1149; E-mail SPETZLER_H@CUBLDR.COLORADO.EDU (Bitnet))

We are engaged in the development of an apparatus for measuring seismic attenuation (Q^{-1}) in partially fluid saturated sedimentary rocks. The motivation for this research comes from the desire to better understand the effects of fluid and gas interactions in rocks. Practical results from this research should enhance the interpretation of seismic data in terms of the fluid saturation of rocks as well as the characteristic of the fluid and thus aid in the monitoring of waste sites and the detection of hydrocarbons. Based on the experience of earlier investigators and to be able to make measurements under crustal conditions, our Q apparatus has the following important features:

1. Longitudinal and shear Q values will be measured on a sample without removing it from the apparatus.
2. Frequencies will be in the seismic range. We anticipate making measurements from 0.01 to 100 Hz.
3. Amplitudes will be smaller than 10^{-6} to assure Q values independent of amplitude.
4. The samples will be jacketed and measured under confining pressure to avoid the interaction between the fluid and the sample-atmosphere interface (Biot-Gardner effect).
5. Three measurement stations will be used to determine each value of stress and each value of strain. This is necessary to assure pure mode deformation. Without knowledge of the purity of the mode of deformation, meaningful Q measurements cannot be made.
6. Control of pure mode deformation is accomplished with two sets of three deformation transducers.

GRANTEE:	**COLORADO SCHOOL OF MINES** Golden, Colorado 80401
GRANT:	**DE-FG02-89ER14079**
TITLE:	**Computational Methods for Improving the Resolution of Subsurface Seismic Images**
PERSON IN CHARGE:	**K. L. Larner** (303-273-3428; FAX 303-273-3478; E-mail klarner@Mines.Colorado.edu), **D. Hale, N. Bleistein, and J. Cohen**

Toward the goal of enhancing subsurface images of the Earth, we are investigating two important problems in computational seismology. Both problems lie in the accurate and computationally efficient representation of seismic wavefields.

The first one is to develop new methods for representing subsurface geologic models in a computer. These new methods must be capable of representing complex geologic structures, such as overhanging salt diapirs and inhomogeneous reservoirs, while facilitating the accurate and efficient computation of seismic wavefields. To this end, we have developed and refined an interactive algorithm that characterizes geologic structure as a *Delauney mesh*, an optimum triangulation of a medium based on supplied node points along with constraints that contain an *adjacency topology* of the model that enables all triangles to be aware of and communicate with their neighbors. Ray tracing of seismic waves through the mesh of triangles is then particularly efficient because ray paths know which triangle they are entering when they leave a previous one, and, with the chosen characterization of velocity structure, ray paths are simply parabolas within each triangle. With this ray tracing, we have implemented the method of Gaussian beams for efficient, interactive generation of synthetic seismograms on an IBM RS/6000 advanced workstation. Current work is aimed at extending the method to three dimensions, wherein the triangles become tetrahedra, and making the model generation and modification more fully interactive.

The second problem is to develop and make use of accurate and computationally efficient descriptions of seismic waves that travel more or less horizontally through a geologically layered subsurface. The problem is significant both in cross-hole experiments used to delineate known oil and gas reservoirs, for which horizontally propagating seismic waves are the rule rather than the exception, and in surface-seismic imaging of steep flanks of salt domes. We have developed a new approach to doing migration for media in which velocity does not vary laterally. With care taken to minimize grid dispersion, this approach, which operates in the time-wavenumber domain, is capable of accurately imaging reflections from interfaces with dip at and beyond 90 degrees, such as happens for overhanging salt domes. Other investigations in this second problem area include (1) a reformulation of the Cagniard-de Hoop method for analysis of wave propagation in stratified media that makes the method more tractable and straightforward than in the past and (2) analysis of the sizable error in reflection amplitude of reflections from steep interfaces due to simplifying assumptions about geometrical spreading corrections that are typically made in practice.

GRANTEE: COLUMBIA UNIVERSITY
Lamont-Doherty Geological Observatory
Palisades, New York 10964

GRANT: DE-FG02-88ER13221

TITLE: **Seismology and Tectonics of the Eastern Aleutian Arc**

PERSON IN CHARGE: **G. Abers** (914-359-2900; FAX 914-359-5215; E-mail abers@lamont.ldgo.columbia.edu) and **K. Jacob**

Physical processes associated with plate convergence and subduction are investigated at the Alaska Aleutian arc-trench system. In the Shumagin Islands we study a 300-km-long arc segment with data from a digital seismic network with 10–15 remote stations linked by telemetry and one central broad-band station. This segment is a seismic gap with an inferred high probability for a large earthquake during the next two decades. In the Gulf of Alaska, the eastern Bering Sea, and elsewhere in the Alaska-Aleutian region, we study the occurrence and source parameters of earthquakes and assess their role in active tectonics by combining seismic results with other geological and geophysical information. Research applications concern the seismic, volcanic, and tsunami hazard to oil lease-sale areas. Detailed studies of the tectonics of the Shumagin region help to understand the plumbing system and geothermal resource potential of the volcanic arc and the thermal and tectonic histories of basins with petroleum potential. Other topics concern engineering seismology, earthquake prediction, and assessment of seismic/volcanic risk to future energy projects in this active tectonic region. The following topics are investigated:

Arrival times from earthquakes recorded by the Shumagin network are used to constrain the three-dimensional structure of the fore-arc by joint inversion for structure and hypocenters. An exact ray-tracing technique is employed in the inversion, with velocities allowed to vary smoothly in three dimensions; this approach eliminates potentially incorrect results due to approximate raypaths. Results from these inversions are compared with gravity measurements to better understand the nature of heterogeneous structure in subduction zones. Of particular interest are low velocities associated with the volcanic arc and high velocities that correlate with large-scale features in subduction-zone gravity fields. These results constrain the mass distribution above the downgoing plate and allow better determination of the forces active at subduction zones.

Large earthquakes in the Gulf of Alaska region are studied, e.g., in the St. Elias region, near the transition from a transform to a subduction plate boundary, particularly the causes of the $M_W = 7.3$ earthquake in 1979. The mainshock source mechanism and depth have been analyzed by studying long-period surface waves and teleseismic body waves, and mechanisms for several other nearby earthquakes have been determined. Aftershock locations have been assessed. These observations have allowed us to better constrain the kinematics of this plate "corner" and assess the mechanism by which terranes are emplaced.

A strong (M_S 6.8) earthquake occurred in February 1991 on the margin of the Bering Shelf several hundred km north of the Aleutian arc. This is the first significant recorded earthquake in this region, although historical reports suggest that much larger earthquakes occurred nearby in the 19th century. We are analyzing the mechanism and location of this earthquake in order to test the possibility that it occurred on one of the large, apparently young structures that bound basins and canyons near the Bering Shelf edge. These basins are believed to have significant petroleum potential and have been proposed as sites for future off-shore oil lease sales. Analysis of the February 1991 event will help us better understand the seismic risks associated with construction of oil exploration and production facilities in Bering Shelf basins, as well as better understand the geological setting of these basins.

GRANTEE:	**COLUMBIA UNIVERSITY** Lamont-Doherty Geological Observatory Palisades, New York 10964
GRANT:	**DE-FG02-86ER13287**
TITLE:	**Energetics of Silicate Melts from Thermal Diffusion Studies**
PERSON IN CHARGE:	**D. Walker and C. E. Lesher** (914-359-2900; FAX 914-365-3183))

A detailed characterization of silicate liquids is required for a predictive understanding of the evolution of natural magmas within the Earth's crust. A magma's crystallization behavior and interaction with its surroundings determine, among other things, the potential for geothermal energy extraction and the formation of ore deposits. The thermodynamic evolution of magmatic systems depends not only upon the thermochemical details of the solidification products but also on the thermochemical properties of the initial magmatic liquids. These properties are more poorly known for the liquids than for the solids. It is the purpose of this project to aid in the characterization of the thermodynamic properties of silicate liquids by a novel experimental approach, thermal diffusion studies.

Thermal diffusion is the phenomenon of chemical migration in response to a thermal gradient. In a substance with more than one component, chemical heterogeneity can develop in an initially homogeneous substance as a result of a diffusional mass flow consequent on heat flow. The details of this response are conditioned by the thermochemical properties and constitution of the substance. We have experimentally demonstrated that silicate liquids do undergo substantial thermal diffusion differentiation and that observations of this differentiation provide the data necessary to evaluate the form and quantitative values of silicate liquid solution parameters. This information supplements calorimetric and phase equilibrium data on silicate liquids. Techniques have been developed to extract ordinary diffusion coefficients, heats of transport, and energies of mixing from experimental T-X thermal diffusion profiles of multicomponent silicate liquids. Immiscibility relations in the system Fe_2SiO_4(Fa)-$KAlSi_2O_6$(Lc)-SiO_2(Qt) have been successfully retrieved solely on the basis of thermal diffusion results using a ternary asymmetric regular solution model. A similar approach is being used to quantify solution behavior of naturally occurring silicate and sulfide magmas.

Recent application of thermal diffusion studies to magmatic and aqueous systems involving coexistence of crystals with a multicomponent fluid has shown that there is a substantial potential for inducing chemical migration, even in the absence of convection. Laboratory observations of cumulate maturation under the influence of thermal diffusion have been applied to postcumulus evolution of magma bodies and the formation of cyclic evaporite deposits.

GRANTEE:	**UNIVERSITY OF DELAWARE** Department of Chemistry and Biochemistry Newark, Delaware 19716
GRANT:	**DE-FG02-89ER14080**
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**
PERSON IN CHARGE:	**R. H. Wood** (302-451-2941; FAX 302-451-6335; E-mail CQD00050@UDELVM (Bitnet))

Measurements of the apparent molar heat capacity of aqueous solutions of H_2S, CO_2, and CH_4 are being made at twelve temperatures from 25°C to 450°C and at pressures near 350 bars. Measurements of the apparent molar volume of aqueous solutions of H_2S, CO_2, and CH_4, are being made at the same twelve temperatures and at two different pressures. These measurements will accurately define the equilibrium properties of aqueous solutions of these gases at temperatures up to 450°C and pressures to 350 bars. The solutes are crucial reactants or products in (1) the dissolution and precipitation of sulfide minerals, (2) the dissolution and precipitation of carbonate minerals, and (3) the formation of natural gas products. An accurate knowledge of their thermodynamic properties will permit a much better understanding of the driving forces for these processes. The measurements will double the amount of information available on volumes and heat capacities of aqueous nonelectrolytes at high temperatures.

At the present time volumetric measurements on aqueous H_2S, CO_2, and CH_4 have been completed at the following temperatures and pressures: CH_4 at 280 and 350 bars and 25 to 380°C; CO_2 and H_2S at 200 and 350 bars and 25 to 380°C.

Theoretical models capable of representing these data and extrapolating them to higher temperatures and pressures are being investigated. Correlations and theoretical models that will allow the estimation of the properties of other nonelectrolytes of geochemical interest are also being investigated.

GRANTEE:	**UNIVERSITY OF HOUSTON** Houston Petroleum Research Center Houston, Texas 77204-4231
GRANT:	**DE-FG05-89ER14058**
TITLE:	**Crosshole Geotomography in a Partially Depleted Reservoir**
PERSON IN CHARGE:	**J. A. McDonald** (713-749-7336; FAX 713-749-4169; E-mail west76@archie.agl.uh.edu)

Continuing research is directed at improving techniques to increase the resolution of the seismic method. Increased emphasis on oil recovery methods mandates the need for better ways to describe the oil reservoir. Conventional surface seismic methods provide vertical resolution of geological and geophysical parameters on the order of 100 ft. Vertical seismic profiling (VSP) techniques are valuable for determining parameters near the borehole but also suffer the limitation of seismic sources confined to the Earth's surface. Geotomography takes advantage of positioning the seismic source in a borehole, thus bypassing surface attenuation effects. Spatial resolution on the order of 10 ft or less is possible using this method.

The Seventy-Six West Field in Duval county, south Texas, is a state-owned reservoir which will have only produced an estimated 38% of oil in place on abandonment. A research program in conjunction with the Bureau of Economic Geology (BEG) of the state of Texas and the Southwest Research Institute (SwRI) is directed at producing high resolution tomograms from this field. To date, four cross-well tomography experiments have been completed in Seventy-Six West. In addition to cross-well data, inverse VSP data were recorded from surface receivers at the same well locations.

Experimental results show that seismic energy over 1000 Hz can be successfully transmitted between wells with up to 600 ft spacing. In a poorly consolidated environment such as Seventy-Six West, these frequencies can provide resolution to the order of 10 ft. An airgun tool provides a high energy, low frequency signal not considered optimum for high resolution purposes. A piezoelectric bender responding to a programmed input can provide the desired high frequencies to successfully image interwell space. Processing of a complete, tomographic data set is currently in progress.

The capability to produce high resolution images or tomograms of interwell geology will provide valuable information that will directly influence the location of new wells that are drilled. Optimal placement of new wells will increase the total recoverable reserves expected from the field.

GRANTEE: INDIANA UNIVERSITY
Biogeochemical Laboratories
Departments of Geological Sciences and of Chemistry
Bloomington, Indiana 47405

GRANT: **DE-FG02-88ER13978**

TITLE: **Organic Geochemical and Tectonic Evolution of the Midcontinent Rift System: Organic Geochemistry and Micropaleontology**

PERSON IN CHARGE: **J. M. Hayes** (812-855-5610; FAX 812-855-7961; E-mail biogeo@ucs.indiana.edu), **L. M. Pratt, and A. H. Knoll**

If we are to improve our ability to locate and evaluate deposits of fossil fuels, we must first improve our understanding of (i) the biological sources of and the deposition of organic matter in sedimentary environments and (ii) the post-depositional processing of organic matter in sedimentary strata. This work is aimed at these goals in the context of the late Precambrian. Sediments of this age are of particular interest. In North America, they have received relatively little attention from commercial prospectors in spite of the fact that petroleum and natural gas deposits of substantial economic significance occur in late Precambrian strata in Oman, Siberia, and, possibly, Australia. Though many are rich in organic carbon and derive from an interval in which unicellular forms of marine life were flourishing, they predate the development of complex life forms and of most land-based plants and animals. The time-temperature conditions associated with the maturation and preservation of late Precambrian fossil-fuel deposits represent the low-temperature, long-time extreme in any systematic examination of conditions required for the development of significant quantities of mobil hydrocarbons.

As a means of probing those and related points of interest, we are combining four lines of inquiry: (i) molecular organic geochemistry, the quantitative analysis and structural identification of sedimentary organic compounds, particularly the various "biomarkers" found to carry useful information in the study of younger sedimentary deposits; (ii) isotopic geochemistry, in this case the study of natural variations in the abundances of the stable isotopes of carbon, nitrogen, and sulfur; (iii) sedimentary geochemistry, particularly systematic investigations of relationships between the concentrations of carbon and of sulfur; and (iv) paleontological study of organic microfossils associated with deposits of organic matter. Together, these investigations provide a rather complete view of the production, preservation, and maturation of sedimentary organic material.

A thorough study of materials from the North American Midcontinent Rift System, involving the study of the sedimentology and microfossils, as well the geochemical indicators, is just being completed. For purposes of comparison, geochemical characteristics of materials from late Precambrian deposits in Oman and Siberia, as well as from modern environments with apparently similar biological communities, are being studied. Results of these investigations will have general significance as demonstrations of new lines of organic-geochemical and isotopic-geochemical investigation and as indications of the state of biological and environmental evolution in the late Precambrian and will have specific significance as indications of the relative importance of the Midcontinent Rift as a zone of interest for petroleum exploration.

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@iubacs (Bitnet))

A sedimentary basin evolves in time by a variety of coupled reaction, transport, and mechanical processes. As a result of these couplings this "diagenetic transformation" may lead to the development of submeter- to kilometer-scale patterns of mineralization, permeability, and porosity and to the temporally periodic or chaotic migration of fluids at depth. The analysis of the basin from the viewpoint of nonlinear dynamical systems is leading to the understanding of a number of heretofore unexplained phenomena and the discovery of new phenomena involving the spontaneous development of spatial and temporal periodicities and more complex patterns. Analysis of these phenomena can play an important role in understanding the migration and trapping of petroleum and the genesis of quality reservoir rock. In this regard the development of quantitative models of these phenomena can have important future applications for petroleum engineering and exploration.

Our approach is to develop mathematical reaction-transport-mechanical models that describe the participating processes (grain growth/dissolution and, in particular, pressure solution, pore fluids, solute reactions and transport, fluid flow, fracturing, and other rock deformation). The models are simulated numerically and, in some cases, solved analytically. In this way we are able to describe compaction, unstable compaction (e.g., stylolitization) as well as regular and irregular episodic fluid migration from overpressurized, kilometer-scale domains. A central goal of the development of the quantitative models is to predict the characteristics and range of existence of these phenomena as grain size, shape, mineralization, geothermal gradient, and tectonic history vary. The studies involve an integration of notions and methods of physical chemistry, geochemistry, rock mechanics, and applied mathematics.

GRANTEE:	**INTERNATIONAL BASEMENT TECTONICS ASSOCIATION, INC.** Montana Bureau of Mines and Geology Butte, Montana 59701
GRANT:	**DE-FG02-91ER14201**
TITLE:	**Characterization and Comparison of Precambrian through Mesozoic Plate Margins**
PERSON IN CHARGE:	**M. J. Bartholomew** (406-496-4177)

International conferences are useful for focusing attention onto key scientific areas and for the timely dissemination of information. This particular conference, the 8th Conference on Basement Tectonics, held in August 1988, had the unifying theme to examine all aspects of ancient continental margins and terrane boundaries and to compare younger (Mesozoic) ones, about which more is known, with older (Paleozoic and Precambrian) ones. The tectonothermics of continent-continent collisions and continental accretion is important to the understanding of metallogeny and the formation of hydrocarbon resources.

The conference attracted approximately 110 participants to hear 87 invited and volunteered oral and poster presentations. Out of 57 manuscripts received and reviewed, 51 were selected by the editors of the Proceedings volume. Camera-ready copy is being finished, and a Proceedings volume of some 710 pages will be published as a single hardcover book by Kluwer Academic Publishers.

GRANTEE:	**THE JOHNS HOPKINS UNIVERSITY** Department of Earth and Planetary Sciences 34th and Charles Streets Baltimore, Maryland 21218
GRANT:	**DE-FG02-89ER14074**
TITLE:	**HRTEM/AEM Study of Trace Metal Behavior, Sheet Silicate Reactions, and Fluid/Solid Mass Balances in Porphyry Copper Hydrothermal Systems**
PERSON IN CHARGE:	**D. R. Veblen** (301-338-8487; FAX 301-338-7933) and **E. S. Ilton**

Many geochemical processes are controlled by reactions between metal-bearing aqueous fluids and silicate minerals in rocks and soils. An understanding of the crystal chemistry of such reactions is fundamental to such practical problems as the mobilization and demobilization of toxic metals in soils, the evolution of hydrothermal systems, and the formation of metallic ore deposits.

We have been using high-resolution and analytical transmission electron microscopy (HRTEM and AEM) to study the crystal chemistry of anomalously Cu-rich biotites in porphyry copper systems and to study Cu absorption by biotite in the laboratory, at room temperatures and pressures. The characterization of solid run products in previous absorption studies typically has been performed using techniques such as powder X-ray diffraction. Instead, we are using the combination of HRTEM and AEM to directly determine the structural mode of incorporation of Cu in biotite. This approach better constrains the precise reactions by which minerals such as mica can demobilize metals from aqueous solutions. HRTEM and AEM of high-Cu regions in biotite from porphyry Cu deposits show that there are at least three distinct structural modes of copper enrichment: (1) formation of discrete precipitates of metallic (native) copper in the interlayer regions; (2) formation of Cu-enriched goethite and chrysocolla within the mica; and (3) formation of Cu-rich expanded interlayers, presumably with vermiculite-like copper interlayer complexes. Biotite, however, is a suitable microenvironment for native Cu even where native Cu is not stable in the surrounding bulk rock. Of fundamental importance is the observation that features (1)–(3) are restricted to oxidized ore. Moreover, we were able to duplicate features (1) and (3) in the absorption experiments. These results indicate that high-Cu biotites probably do not form during the magmatic or main-stage hydrothermal phases of porphyry Cu evolution (as previously thought). Instead, they apparently form during weathering of copper sulfide-bearing rocks.

We are now using HRTEM and AEM to study Cu-enriched vein assemblages (smectites, kaolinite, chrysocolla, and goethite) and Cu-enriched alteration assemblages in feldspars from a suite of core samples from the oxidized portion of the Cyprus Casa Grande porphyry Cu deposit, Arizona. Moreover, we are investigating the kinetics of Cu absorption by biotite in low temperature and low pressure experiments.

Whereas there has been much work on the absorption and adsorption of metals by clay minerals (and to some extent micas), our results emphasize the general importance of using TEM/AEM methods for directly observing the interlayer regions of micas and clays that have been reacted with metal-bearing solutions. It is important to note that the interlayer region can provide a microenvironment for precipitates that are unstable with respect to the bulk solution. The TEM data from our studies specifically show how base metals migrate and are demobilized during supergene ore-forming processes, but other benefits include increasing our understanding of the chemical processes involved in acid mine drainage and *in-situ* mining, suggesting more judicious use of biotite as a pathfinder to Cu ore deposits and furthering our general understanding of trace metal mobility and fixation under low-temperature conditions in soils and rocks.

GRANTEE:	**LOUISIANA STATE UNIVERSITY** Department of Geology and Geophysics/Basin Research Institute Baton Rouge, Louisiana 70803-4101
GRANT:	**DE-FG05-87ER13748**
TITLE:	**Ammonium Silicate Diagenesis and Its Influence on the Interpretation of Fixed-Ammonium Anomalies as an Exploration Tool**
PERSON IN CHARGE:	**R. E. Ferrell** (504-388-5306; FAX 504-388-2303) and **L. B. Williams** (now at Arizona State University; 602-965-3480; FAX 602-965-8102)

This research focuses on the organic/inorganic interactions of nitrogen in hydrocarbon producing environments. The main objective is to understand the evolution of nitrogen from hydrocarbons and the incorporation of organogenic-N into silicates, particularly clay minerals, during diagenesis. Nitrogen in the form of ammonium (NH_4^+) substitutes for K^+ in diagenetic minerals, and this so-called "fixed-NH_4" can be an indicator of hydrocarbon maturity and migration pathways. This research primarily examines the field relationships of fixed-NH_4 anomalies within hydrocarbon producing environments. Experimental NH_4-fixation at low temperatures is a second aspect of the project, intended to determine some of the physico-chemical conditions optimal for NH_4-fixation in various clay minerals.

More than 250 samples have been analyzed from reservoirs in the Gulf Coast, Colorado, and California in order to determine the influence of different types of organic matter and geologic environments on fixed-NH_4 concentrations. Although concentrations of fixed-NH_4 are largely dependent on the degree of diagenetic illite formation (or other K^+-bearing mineral), the level of NH_4^+ substitution within the host mineral can indicate organic maturity or the presence of migrated crude oils at the time of mineral formation. Fixed-NH_4 concentrations are low where diagenetic mineral formation is minimal, where subsurface conditions are oxidizing, and where bacterial activity reduces the NH_4^+ concentrations in brines. However, the formation of significant quantities of NH_4-illite in typical hydrocarbon reservoirs suggests that the NH_4/K ratio in oilfield brines is generally high and is reflected in the diagenetic minerals.

The analysis of NH_4-substitution within a basin could lead to an understanding of the mode of entrapment of hydrocarbons and could aid in enhanced oil recovery by indicating which sandstones acted as important migration conduits. The completion of this research will lead to a better understanding of the nitrogen cycle in terms of organic/silicate interactions in hydrocarbon-producing basins and may lead to the formulation of an improved technique for evaluating organic maturity levels in source rocks and for tracing hydrocarbon migration paths through heterogeneous reservoirs. Ideally it will lead to increased success rates in the exploration and recovery of liquid and gaseous hydrocarbons.

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**

PERSON IN CHARGE: **M. N. Toksöz** (617-253-7852; FAX 617-253-6385; E-mail nafi@erl.mit.edu), **and C. H. A. Cheng** (617-253-7206; FAX 617-253-6385; E-mail cheng@erl.mit.edu)

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 acoustic logging (FWAL), vertical seismic profiling (VSP), and other downhole and crosshole seismic imaging 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. To achieve this we have taken approaches using three different frequency ranges. The first uses full waveform acoustic logging, with a frequency range of 1 to 10 kHz and a depth of investigation of a meter or less. The second uses hydrophone VSP, with a frequency of around 100 Hz and a depth of investigation of around 10 m. The third uses arrival times from microearthquakes generated by the fractures under hydraulic pumping, with an image area on the order of hundreds of meters.

The research undertaken in the past year consists of (1) theoretical modeling of seismic wave propagation in a borehole with a vertical or horizontal fracture and the testing of the model using laboratory scale model experiments; (2) modeling of the fracture or fracture zone as a porous and permeable material and comparison of field data with theoretical results; (3) tomographic inversion of travel time data from microearthquakes generated in a geothermal reservoir to delineate the fracture planes and the velocity structure around them; and (4) modeling of the fracture as rough surfaces in contact.

GRANTEE:	**MASSACHUSETTS INSTITUTE OF TECHNOLOGY** Earth Resources Laboratory Department of Earth, Atmospheric, and Planetary Sciences Cambridge, Massachusetts 02139
GRANT:	**DE-FG02-89ER14084**
TITLE:	**Reservoir Characterization by Crosshole Seismic Imaging**
PERSON IN CHARGE:	**R. Turpening** (617-253-7850; FAX 617-253-6385; E-mail roger@erl.mit.edu) and **M. N. Toksöz** (617-253-7852; FAX 617-253-6385)

The seismic techniques needed for detailed characterization of known hydrocarbon reservoirs are in the early stages of development. To get the needed resolution it is obvious that we must place both the seismic source and the receiver in boreholes and that these boreholes must straddle the region of interest. To get reasonable coverage of the region of interest the boreholes must be much deeper than the reservoir. To achieve some characterization of the reservoir, in addition to its image, one must use shear wave sources in addition to compressional wave sources. Furthermore, for the results to be of use, the work must be conducted over typical oil well spacings, not special research situations.

The Earth Resources Laboratory (ERL), in cooperation with Sandia, is conducting a multi-year research effort at ERL's Reservoir Delineation Research Facility in northern Michigan. There, in a carbonate setting, all of the above requirements are met. Two deep (6800 ft) boreholes, separated by 2000 ft, straddle a 70-acre producing reef. The rough shape and position of the reservoir is known from low-frequency 3-D reflection and VSP images. Low-resolution characterization of the reservoir has been done with additional nine-component VSPs. This program focuses on mid-band (30–300 Hz) and high-frequency (400–2200 Hz) crosshole imaging. The anisotropic features of the reservoir will be seen when the mid-band SV (FY 91) and SH (FY 92) Sandia sources are used.

In October 1990 the feasibility of high-frequency P-wave propagation over long distances (2800 ft) was demonstrated at the Michigan test site. The cylindrical bender source required only sixteen sweeps to be stacked for each trace. Source and receiver interval spacings are 10 ft over an aperture of 2000 ft in each borehole. The peak P-wave frequency is approximately 1700 Hz, which yields a wavelength of 12 ft. This is a thirty-four-fold reduction in wavelength over the energy used in the conventional reflection and VSP images of the reef. A commensurate increase in resolution of the reef and details in the reef will be seen when the survey is complete.

That complete survey is made up of 40,000 ray paths. The data quality is excellent even though the energy has propagated long distances—through a porous reservoir—and across several strong impedance contrasts.

Complementary theoretical studies are being carried out for the interpretation of the crosshole data. These include: (1) P- and S-wave radiation patterns from a piezoelectric (cylindrical bender) clamped axial vibrator and a torsional (SH only) vibrator. These studies are important for interpreting observed P- and S-wave amplitudes. (2) Synthetic seismogram calculations for crosshole geometry using both complete elastic wave solutions and high-frequency ray approximations. Items (1) and (2) have been completed. (3) Putting bounds on the resolution and accuracy of tomographic inversion of P- and S-wave travel times for a given ray coverage. Unlike the linearized or Backus-Gilbert inversions, the quantification of the resolution or errors does not exist for nonlinear tomographic inversions. (4) Since some parts of the section in Michigan are anisotropic, we are developing forward modeling and inversion for crosshole data in anisotropic media.

GRANTEE:	**UNIVERSITY OF MINNESOTA** Department of Geology and Geophysics Minneapolis, Minnesota 55455
GRANT:	**DE-FG03-89ER14051**
TITLE:	**Experimental Investigations of Magma Rheology and Numerical Simulations of Caldera Collapse and Magma Withdrawal**
PERSON IN CHARGE:	**D. A. Yuen** (612-624-1868; FAX 612-624-6369)

This is a collaborative study with F. J. Spera (University of California at Santa Barbara). Research carried out at UCSB includes high-temperature experimental rheometry and numerical simulations of magma withdrawal. A fluid dynamical model based on solution of the conservation equations for mass, momentum, and species has been applied to the withdrawal of magma from magma bodies that are strongly zoned with respect to composition. Dimensional, scaling, and numerical experiments provide insights into the interpretation of commonly observed correlations between stratigraphic height and composition. Natural eruptions span the dynamic range from the viscous regime to the inertial regime. For central vent eruptions from flat-roofed, layered magma bodies, eruptive intensity varies as σ^{-1}, $\sigma^{-3/5}$, and $\sigma^{-1/2}$, where σ is the super-hydrostatic (effective) pressure, $\sigma = p' + \tau_b$. Effective pressures needed to drive an eruption are proportional to $\dot{M}$, $\dot{M}^{5/3}$, and $\dot{M}^2$ in the viscous, sub-inertial, and inertial regimes, respectively. Typical driving pressures are around 10^3 Pa in the viscous and sub-inertial regimes and roughly 10^6 Pa in the ultraplinian regime, where $\dot{M}$ can be as large as 10^9 kg/s. Tidal stresses, maximum values of which are on the order of 10^4 Pa, are sufficient to drive eruptions in the viscous or sub-inertial regime. The time interval during which upper layer magma is a significant component of the eruptive products (t_{ss}) depends on the thickness of the upper layer, the effective pressure, and the viscosity contrast. When the layers have different viscosities, t_{ss} is proportional to $\eta_r^{0.46}$, where η_r is the relative viscosity of the layers. Simulations of central vent and ring fracture eruptions from flat-roofed and sloped-roof magma bodies with layered compositional profiles show that compositional gaps in ignimbrites may be artifacts of the withdrawal process.

The rheological behavior of dilute emulsions of GeO_2 containing from 0.8 to 5.5 vol% air bubbles has been measured experimentally between 1100 and 1175°C at 1 kPa at shear rates between 0.05 and 7 s^{-1}. At constant bubble volume fraction, the rheological behavior of the emulsions is modeled by a power-law constitutive relation. The power-law emulsions are pseudoplastic (shear-thinning), having a flow index of 0.87 to 0.93. Bubble deformation is promoted by shear and opposed by surface tension. Two dimensionless parameters governing bubble deformation are the capillary number $Ca \equiv \dot{\gamma}\eta_m r_b/\sigma$ and viscosity ratio $\lambda \equiv \eta_b/\eta_m$ determined from melt viscosity η_m, bubble viscosity η_b, bubble radius r_b, shear rate $\dot{\gamma}$, and vapor-melt interfacial tension σ. The capillary number is a measure of the relative importance of shear and interfacial stresses. Low-λ bubbles may attain very elongate stable shapes, and high shear rates are required before fragmentation occurs at a critical capillary number $Ca_{crit,f}$. Bubble fragmentation has consequences for observed bubble size distributions both in post-experimental counts and in nature. Bubble fragmentation by the fracture mechanism is unlikely (or at least not dominant) in most natural magmatic flows. Instead a sub-critical instability known as tip-streaming can occur at a much lower capillary number, $Ca_{crit,ts} = 0.56$. This mechanism produces much smaller daughter bubbles than that of fracture but is more relevant to magmatic flows. Normal stress differences amounting to several percent of the total shear stress can be produced at shear rates of less than 10 s^{-1}. In rotating rod rheometry, this leads to rod-climbing behavior (Weissenberg effect).

GRANTEE:	**UNIVERSITY OF MINNESOTA** Department of Geology and Geophysics Minneapolis, Minnesota 55455
GRANT:	**DE-FG02-91ER14212**
TITLE:	**Physical Modeling of Sedimentary Basins, Magma Mechanics, and Molecular Dynamics of Aqueous Solutions**
PERSON IN CHARGE:	**D. A. Yuen** (612-624-1868; FAX 612-624-6369)

This is a collaborative project with F. J. Spera (University of California at Santa Barbara) to conduct numerical modeling of three problems of relevance to the geoscience mission of the DOE. The three areas include (1) thermo-mechanical modeling of sedimentary basins, including porous media convection; (2) molecular dynamical investigation of the physical and chemical properties of aqueous solutions in the temperature and pressure regime characteristic of continental lithosphere; and (3) magma dynamics with emphasis on magma withdrawal and caldera resurgence. The detailed work plan includes (1) the dynamical influences of lithospheric phase transitions on the thermal-mechanical evolution of sedimentary basins; (2) the coupling between mantle convection and, in particular, mantle plumes on the thermal regime and subsidence history of rift-related sedimentary basins; (3) numerical modeling of heat and solute transport driven by thermal and salinity gradients in a fractured and/or granular porous medium as commonly encountered in sedimentary basins undergoing diagenesis and lithification; (4) the thermodynamic and electrostatic properties of water determined by state-of-the-art molecular dynamics (MD) methods, taking into account effects such as oxygen polarization and molecular dissociation in order to account for the dielectrical properties of water at conditions characteristic of the crust and lower lithosphere; (5) the dynamics of magma removal from large crustal reservoirs for magma treated as a Bingham plastic fluid; and (6) the dynamics of the resurgence of volcanic calderas in continental regions.

GRANTEE:	**NATIONAL ACADEMY OF SCIENCES** **NATIONAL RESEARCH COUNCIL** Washington, D.C. 20418
GRANT:	**DE-FG05-89ER14061**
TITLE:	**Basic Energy Science Studies**
PERSON IN CHARGE:	**K. C. Burke** (202-334-2744; FAX 202-334-3362; E-mail KBURKE@NAS.BITNET)

A. Board on Earth Sciences and Resources *(K. C. Burke [202-334-2744; FAX 202-334-3362; E-mail KBURKE@NAS.BITNET])*

The Board on Earth Sciences and Resources, under the Commission on Geosciences, Environment, and Resources of the National Research Council (NRC), coordinates the NRC's advice to the federal government on earth science issues, ranging from basic research to applications. Such advice includes (1) identification and enunciation of the opportunities for advancing basic earth science research and understanding, (2) analyses of the scientific underpinnings and credibility of earth science information for resource and other earth science applications and decisions, and (3) the science, technology, economics, industrial activity, educational programs and governmental policies and programs related to hydrocarbon resources, metallic and other energy resources, and non-metallic mineral resources. The Board's actions address the overall health of the earth science disciplines that are vital to the nation in maintaining and increasing its capability to make wise use of the Earth and its resources.

The Board has under way a major report, a study entitled *Status and Research Opportunities in the Solid-Earth Sciences—A Critical Assessment*, and has just published a report entitled *Undiscovered Domestic Oil and Gas Resource Estimates*.

B. U.S. Geodynamics Committee *(K. C. Burke [202-334-2744; FAX 202-334-3362; E-mail KBURKE@NAS.BITNET])*

The U.S. Geodynamics Committee (USGC) was established in 1969 to foster and encourage studies of the dynamic history of the Earth, with appropriate attention to both basic science and applications. The USGC also serves as the U.S. counterpart to the International Lithosphere Program. The USGC work is based largely on the recommendations developed by its reporters (currently 26, including 12 corresponding to special topics of the International Lithosphere Program) and their associated groups. In 1976, at the request of the Geophysics Research Board, the USGC began planning U.S. research activities in solid-earth studies in the 1980s. This led to the report *Geodynamics in the 1980s*, which emphasizes the origin and evolution of continental and oceanic crust, the continent-ocean transition, the relation of mantle dynamics to crustal dynamics, and a geodynamic framework for understanding resource systems and natural hazards. Major accomplishments include the initiation of the continental scientific drilling program and designing and conducting the North American Continent-Ocean Transects Program. Other topics emphasized by the USGC are deep seismic reflection profiling, geodynamic data, chemical geodynamics, crustal and mantle dynamics, marine geology and geophysics, fluids in the crust, seismic networks, and sedimentary systems.

Activities emphasized during the past year (and resultant reports) include addressing the present status and needs (over the next five years) and the question of priorities, especially in time sequence, of four classes of instrumentation for earth materials research

(Facilities for Earth Materials Research); looking into the broad national effort in geomagnetic research; providing input to the International Decade for Natural Disaster Reduction (two draft working documents— one regarding the adequacy of the knowledge base for understanding various hazards and another regarding volcanic hazards); providing guidelines regarding key topics for the International Lithosphere Program in the 1990s; developing a plan toward digitizing present and future transects—this plan in effect set the standards for the Global Geoscience Transects Project that is modeled on the successful North American Transect Program. Plans for a magnetic workshop are in an advanced state.

C. Studies in Geophysics *(T. M. Usselman [202-334-3349; FAX 202-334-2854; E-mail USSELMAN@NAS.BITNET])*

The Geophysics Study Committee is conducting a series of studies dealing with timely scientific and societal aspects of geophysics and the corresponding demand on geophysical knowledge. The studies include (1) problem-oriented studies such as demands on geophysical knowledge in connection with climatic variations, fresh-water resources, mineral resources, geothermal and other energy resources, natural hazards, and environmental maintenance and (2) science-oriented studies such as fluids in the crust and paleoenvironments. Each study is conducted by a panel selected for the specific purpose. The preliminary findings of each study are presented to the scientific community for comment at a suitable symposium. One or two studies are expected to be completed each year. The committee recently issued two studies: (1) *Sea-Level Change* (1990) and (2) *The Role of Fluids in Crustal Processes* (1990). Two additional studies are in preparation: (1) *Global Surficial Fluxes* and (2) *The Effects of Past Global Change on Life.*

D. Studies in Seismology *(K. C. Burke [202-334-2744; FAX 202-334-3362; E-mail KBURKE@NAS.BITNET])*

The research objectives of the Committee on Seismology are to influence major trends in seismology and identify related developments in other fields; conduct studies for government agencies; provide advice on U.S. government-supported seismic facilities; maintain cognizance of and provide advice on international seismological activities, including seismic verification of nuclear test ban treaties; and coordinate within the National Research Council (NRC) activities in engineering seismology, rock mechanics, geodesy, geodynamics, geology, and seismic verification of nuclear test ban treaties. The committee meets twice a year to discuss current topics of major importance relevant to seismology; review with government agency personnel, in particular, the actions that have resulted from recommendations of the committee and its panels; and take actions to assure a healthy science that is in a position to provide maximum benefits to the nation and to society. Panels are established to conduct ad hoc studies on topics specified by the committee.

The report of the Panel on Regional Seismic Networks was published in 1990 under the title, *Assessing the Nation's Earthquakes.* The report of the Panel on Real-Time Earthquake Warning will be published in 1991.

Future activities include: (1) a review of the Loma Prieta earthquake; (2) a workshop and plan for a more mitigative approach to the collection, storage, and use of strong-motion data; and (3) an assessment of the role of seismology in the earth sciences, in societal problems, and as a scientific discipline in its own right.

E. Studies in Geodesy *(K. C. Burke [202-334-2744; FAX 202-334-3362; E-mail KBURKE@NAS.BITNET])*

Activities of the Committee on Geodesy are aimed at the encouragement of the use of geodetic techniques to solve problems in the physical, oceanic, and atmospheric sciences; to foster the development of improved geodetic technology; and to assist government agencies in the solution of their particular problems.

As we live on a dynamic planet where both horizontal and vertical positions, to a varying degree, are constantly changing, positions in land and ocean areas must be monitored for their effect on tides, crustal deformation, and global change. Specifically, the committee is involved in the following activities:

- The committee, in conjunction with The International Association of Geodesy, is studying the need for an international network of fiducial stations, whose positions will be precisely determined and monitored and at which numerous earth monitoring systems will be established.
- As local geodetic networks play a significant role in the monitoring of local crustal motion, the committee encourages the continued use of Very Long Baseline Interferometry (VLBI) and Satellite Laser Ranging systems, which provide very precise data.
- As much of the geodetic data are obtained through use of the Global Positioning System (GPS), and as that system is controlled by the Department of Defense, the scientific community is adversely affected by data classification and signal deniability.
  The committee actively seeks the declassification of data and the easing of anti-spoofing and selective availability.
- The proper use of geodetic information is critical to the solution of scientific problems. The committee is examining the present status of education in geodesy and the role of agency extramural activities.
- As there are a number of government agencies involved in geodetic activities, the committee meetings permit the exchange of information on present and future plans between agencies and the scientific community.

GRANTEE:	**UNIVERSITY OF NEW MEXICO** Albuquerque, New Mexico 87131-1126
GRANT:	**DE-FG02-90ER14149**
TITLE:	**Chemical Transport through Continental Crust**
PERSON IN CHARGE:	**J. J. Papike** (505-277-1644; FAX 505-277-3577)

The Long Valley-Mono Craters volcanic complex is the most active major silicic system within the continental United States. The last major eruption of the system occurred only 550 years ago, and minor eruptions may have occurred as recently as 100 years ago. Present tectonic activity suggests a rejuvenation of the magmatic system. The main objective of this research is to study the state and evolution of the magmatic-hydrothermal system in Long Valley. Research in progress has the following goals:

- Characterize the chemical and mineralogical zonation of the system.
- Identify and evaluate the chemical, thermal, and mineralogical effects of magmatic versus post-emplacement hydrothermal fluid-rock interaction.
- Propose overall modal-chemical mass balance equations to account for the observed metasomatic effects on the Bishop tuff and related lithologies.

Our research, thus far, has emphasized portions of the system sampled by Phase I of the Magma Exploratory Hole LVF51-20. The first phase of the Magma Exploratory Hole on Long Valley Caldera's resurgent dome reached 839.4 m depth in 1989. Phase II drilling, to a depth of ~ 2300 m, is planned for Summer 1991. The hole is planned for a final depth of 6 km, in the vicinity of the caldera's central magma chamber. The history of this chamber is recorded by surface eruptive activity and presumably by a subsurface array of intrusions and frozen chamber remnants. The first phase of drilling encountered a swarm of five such igneous units (or perhaps intersected five segments of the same irregular body) from 624.8 m to 829.3 m, intrusive into welded and devitrified Bishop Tuff. The intrusions are similar-appearing aphyric, microcrystalline rhyolite and exhibit an obsidian border phase at contacts. Thickness (intersected length) of the intrusions varies from 0.2 to 71.7 m. The longest continuously cored segment (782.7 m to 810.6 m) was chemically analyzed along its length. The intrusion is a high-silica (76.1 ± 0.8 wt.% SiO_2) rhyolite with high K_2O/Na_2O (~ 2) and high Ba content (1182 ± 70 ppm). These chemical signatures closely resemble eruptions of the voluminous early rhyolite sequence. The intrusion is probably a feeder for this sequence and was likely emplaced about 10^5 years after caldera collapse. Igneous-like compositions are confined to within about 3 m of the upper contact. Deeper samples show depletion in Na_2O (factors to 0.1), Rb (to 0.3), Sr (to 0.3), and Ba (to 0.1) and enrichment in S (to 10), Fe (to 10), Zn (to 5), and As (to 5), presumably reflecting hydrothermal leaching and deposition of pyrite. The occurrence of igneous compositions near the contact and the preservation of obsidian at the contact requires that only minor syn- or post-emplacement hydrothermal activity occurred there.

GRANTEE:	**CITY UNIVFRSITY OF NEW YORK, QUEENS COLLEGE** Department of Geology Flushing, New York 11367-0904
GRANT:	**DE-FG02-88ER13961**
TITLE:	**Evaporites as a Source for Oil**
PERSON IN CHARGE:	**B. C. Schreiber** (718-997-3300; FAX 718-793-3006)

Evaporitic environments are the site of a high level of biological activity and are very favorable for the formation, accumulation, and preservation of organic matter. Such sedimentary sections have rarely been the objects of a coordinated and detailed sedimentary analysis together with their associated organic geochemistry. However, this integrated approach is necessary in order to determine the relationship of the actual biological precursors, their milieu of deposition within the sediments, and their diagenetic evolution during burial. The basins chosen in this project as study areas are sites of Tertiary to Recent deposition. This choice is particularly interesting because the organic matter is largely immature and *in situ*. Most of these basins are largely marine-fed and undergo episodes of stratification and hypersalinity ("pre-evaporitic" deposits), culminating in the deposition of halite and gypsum. From the rock record thus far studied we see that the periods of restriction result in accumulation and preservation of organic matter as well as diverse sedimentation, including evaporites. The biomarker signatures of the organic matter are highly variable, depending on the specific conditions of the water body (bed by bed), and represent biotas that are largely from restricted marine waters. Nonmarine organic accumulations are also present, though rare, and are associated with the uppermost evaporite sequences (when the basins actually dry out).

The Recent, marine-fed water bodies that have been sampled in this study include salinas at Santa Pola (Spain) and Margherita di Savoia (Italy) and provide us with modern chemical, mineralogical, and organic models for the Tertiary sediments. Comparison between these modern deposits and the older but immature basin accumulations permit biomarker fingerprinting of the individual organic contributions.

GRANTEE:	**STATE UNIVERSITY OF NEW YORK AT PLATTSBURGH** Center for Earth and Environmental Science Plattsburgh, New York 12901
GRANT:	**DE-FG02-87ER13747**
TITLE:	**Depositional and Diagenetic History of the Edgecliff Reefs (Middle Devonian Onondaga Formation of New York and Ontario)**
PERSON IN CHARGE:	**T. H.Wolosz** (518-564-4031; FAX 518-564-7827)

An understanding of the biological and physical environmental factors which controlled the growth of ancient reefs is critical to the successful prediction of the subsurface location of these potential hydrocarbon reservoirs. Studies of Edgecliff reefs along the Onondaga strike belt from south of Albany westward into Ontario, Canada, have produced the following results.

An east to west trend of increasing stromatoporoid abundance across New York and into Ontario, Canada, indicates that these reefs grew in temperate waters. Growth in "cool" waters would explain the unusual nature of the Edgecliff reefs (i.e., no stromatoporoid framework, no calcareous algae). The temperate water hypothesis is further supported by the identification of shallow water facies in the vicinity of Port Colborne, Ontario, Canada, which do not match the standard Bahamian (tropical water) model. These consist of shaley limestones with flaser bedding which grades into small mounds of coral rubble. Preliminary stable isotope data for non-luminescent brachiopods (average $\delta^{18}O \approx -3.00$ to -4.00, $N = 14$) also support this hypothesis.

A much greater diversity of growth patterns has been revealed than had previously been documented. In the eastern portion of the state (Utica to Albany), a depth related reef trend has been determined. "Calcisilt mounds" dominated by small, delicate, branching tabulate corals characterize deepest (or quietest) water conditions; at shallower depths, increased levels of water turbulence led to the development of dense colonial rugosan successional mounds, which gave way to thicket/bank structures (interbedded crinoidal grainstone and colonial rugosan thickets) under shallowest water conditions.

Analysis of large central New York mound/bank reefs (gas producing in the subsurface) indicates cycles of growth within these large structures attributable to relative sea-level fluctuations. These shallowing/deepening cycles are related to the interplay of central basin subsidence and early faulting or folding causing gentle uplift along the subsurface reef trend.

Cathodoluminescence examination of samples from all reefs reveals a simple sequential cementation pattern of dark, bright, and dull cement precipitation. Cessation of cementation, leading to preservation of primary porosity, followed precipitation of initial dull cements and is characteristic of the upper central portions of rugosan mounds from central New York westward. The lower and lateral portions of these mounds are tightly cemented, with complete pore occlusion by late stage dull cements.

GRANTEE: **STATE UNIVERSITY OF NEW YORK AT STONY BROOK**
Research Foundation of SUNY
Albany, New York 12201

GRANT: **DE-FG02-85ER13416**

TITLE: **Geochemistry and Origin of Regional Dolomites**

PERSON IN CHARGE: **G. N. Hanson** (516-632-8210; FAX 516-632-8240)

The goals of this project are to develop geochemical approaches for testing models describing the geochemistry and dynamics of fluid systems responsible for the development of regional dolomites which are major reservoirs for petroleum. The rocks we initially selected for a very detailed petrographic and geochemical study are the Mississippian (Osagean) Burlington-Keokuk formations of Iowa, Illinois, and Missouri. While the Burlington-Keokuk formations are not a major reservoir for oil, mid-Mississippian shelf dolomites closely akin to the Burlington dolomites, in terms of petrography, apparent nature of porosity, and paleogeographic setting, are major reservoirs of oil and gas in many regions of North America. Moreover, similar dolomites with "sucrosic" textures, dominated by intercrystalline and moldic porosity, also are common in shelf-carbonate sequences of other ages and regions.

We are applying a large range of trace elements (REE, Pb, Zn, Ba, B, LiSr, Mg, Fe, and Mn) and isotopic systems (Pb, B, Sr, Nd, S, C, and O) to help discriminate among potential fluids responsible for the diagenesis of sedimentary carbonates. The analytical techniques for the trace element studies include isotope dilution, plasma spectrometry, electron microprobe, and synchrotron X-ray microprobe. Our modeling has shown that bivariate plots using a range of trace elements and isotopes can be used to evaluate the type of fluids involved and the water-to-rock ratios necessary for a diagenetic carbonate to reach its present composition.

Our approach has been to apply new geochemical techniques to the Burlington-Keokuk formations. After evaluating their usefulness, the most appropriate techniques are applied to sequences that have quite different tectonic or sedimentary settings. Besides studying the dolomites in the Burlington-Keokuk formations, we are also studying dolomites in (1) the Canning Basin, Western Australia, formed in Devonian reef complexes and platform carbonates fringing a Precambrian massif landward and a large synsedimentary graben (Fritzroy Trough) basinward; (2) Neogene carbonates formed in reefal and perireefal facies in island settings in the Mediterranean and the Netherlands Antilles; and (3) the Wahoo Formation (Penn.) in Prudhoe Bay, Alaska, which is a typical shallow marine carbonate sequence and a major hydrocarbon reservoir.

GRANTEE:	**THE OHIO STATE UNIVERSITY** Department of Welding Engineering Columbus, Ohio 43210
GRANT:	**DE-FG02-89ER13749.A001**
TITLE:	**Investigation of Ultrasonic Wave Interactions with Fluid-Saturated Porous Rocks**
PERSON IN CHARGE:	**L. Adler** (614-292-1974)

In this research project we conducted an investigation of ultrasonic surface wave and bulk wave propagation in fluid-filled rocks and other porous materials. In our previous work on surface wave interaction with fluid-filled porous materials, we were using slightly corrugated interfaces to generate both Rayleigh and Stonely type surface modes. In our new direct excitation experimental technique for surface and interface wave generation, we have used a conventional contact transducer. We used this technique to generate both Rayleigh and Stonely waves at the interface of the liquid-fluid saturated materials. We were able to generate both of these surface waves on fluid-natural rock interfaces. In our experiments, we were using several different types of natural rocks without any particular treatment of the surface. With this direct excitation technique, we may be able to study boundary conditions related to open or closed pore structure in rocks.

We have developed a new experimental technique for studying acoustic wave propagation in fluid-filled thin porous materials, which is based on the generation and detection of the so-called Lamb modes. These waves are guided along a plate, and their velocities depend on the frequency and thickness of the plate. We developed both analytical and experimental methods using these waves for porous materials and showed that there are additional modes which appear when slow waves are present. Furthermore, these Lamb modes, which show up as resonances in the plate, are affected by the boundary conditions, i.e., the pores are open or closed. We have shown that the resonances due to slow waves will disappear when the surface pores are closed.

Our previous results showed that certain material parameters, such as grain size and the degree of consolidation, can be assessed from either the fast compressional or shear wave attenuation and velocity. Other parameters, such as tortuosity, pore size, porosity, and permeability, are assessable from slow compressional wave measurements only.

We continued to study different aspects of slow wave propagation in material rocks by both experimental and theoretical means.

We have structured our measuring system so that higher sensitivity can be achieved and have automated the process via direct computer control. Previously we were able to detect slow wave propagation in rocks with 400 mdarcy or higher permeability up to 150 KHz. With our modified system, we can study the frequency dependent behavior of both slow wave velocity and attenuation. Several geophysical parameters of importance can be derived from these measurements, e.g., frequency dependent (complex) tortuosity, dynamic permeability, pore size, etc.

We found that tortuosity can be assessed from the high-frequency, more-or-less dispersion-free velocity of the slow wave. Furthermore, the pore size can be readily estimated from the low-frequency, strongly dispersive slow wave velocity.

GRANTEE:	**THE OHIO STATE UNIVERSITY** Department of Geological Sciences Columbus, Ohio 43210
GRANT:	**DE-FG02-91ER14206**
TITLE:	**Construction of a Calibrated Sea Level Curve: Mid-Cretaceous through Mid-Tertiary**
PERSON IN CHARGE:	**D. Sahagian** (614-292-2721; FAX 614-292-7688)

This research program is based on the identification of a stable reference frame for measurement of sea level. Numerous errors have crept into previous eustatic sea level curves because they have relied on unstable reference frames such as passive margins. A stable frame of reference is found in the Russian Platform and allows for the construction of a eustatic curve without the uncertainties introduced by subsidence and other corrections on passive margins and other subsiding basins. The stability of the Russian Platform is indicated by flat-lying Mesozoic-Cenozoic sediments which have remained undeformed and untilted since deposition. These sediments are no thicker than 200 m throughout the Russian Platform, so factors such as compaction and loading are very small, and the elevation of these deposits is a measure of post-depositional sea level change. The tectonic stability of the Russian Platform allows eustatic curves to be constructed through two complementary methods. The first uses backstripping of well data to calculate sea level changes from one geologic stage to another. The application of this method to the mid-Jurassic through the mid-Cretaceous has generated a sea level curve in which the net sea level rise throughout that time is 110 m. The second method uses the elevation of former shoreline (or very shallow marine) deposits to calculate the net sea level change from a former sea level to the present sea level, thus relating the results of the first method to modern sea level. Mesozoic-Cenozoic outcrops can be found in three main regions on the stable part of the Russian Platform near Moscow, Kirov, and Penza. A eustatic sea level curve for the mid-Cretaceous through the mid-Tertiary is now being constructed using both methods with outcrop and well data from these regions.

GRANTEE:	**UNIVERSITY OF OKLAHOMA** School of Geology and Geophysics Norman, Oklahoma 73019
GRANT:	**DE-FG05-85ER13412**
TITLE:	**A Study of the Source Materials, Depositional Environments, Mechanisms of Generation, and Migration of Oils in the Anadarko and Cherokee Basins**
PERSON IN CHARGE:	**R. P. Philp** (405-325-3253; FAX 405-325-3140)

The major objectives of this research continue to be aimed at studying the origin and migration pathways of oils in the Anadarko basin, Oklahoma. The organic geochemical approach makes extensive use of biomarker concepts for unraveling source relationships and migration pathways. If relationships can be established between specific families of oils and their suspected source rocks in this basin, it will provide an opportunity to study both the mechanisms of primary and secondary migration and the effects of migration on crude oil composition. The use of extensively explored areas such as the Anadarko Basin provides a natural laboratory in which we can refine and develop novel geochemical approaches to improve these exploration efforts.

Our work during the past year has continued to diversify into a number of areas which are directly related to the major goals of our study. We have collected and characterized over 220 samples of potential source rocks from the Viola, Sylvan, Springer, and Morrow Formations throughout the basin. In the past much effort has been placed on the examination and characterization of the Woodford Shale as a potential source rock, but the other formations have received much less attention. These samples were initially screened by Rock Eval pyrolysis and TOC determination. From the original 220 samples, approximately 80 were selected as having good source potential. These samples are now being extracted and the saturated and aromatic hydrocarbon fractions are being analysed by GC, GCMS, and GCMSMS. We have tried as far as possible to collect samples so that we can also examine areal variations in the composition of the organic matter over the basin. At the same time we are in the process of collecting and characterizing oils from the western and northern parts of the basin. Comparison of the data from the source rocks and the oils will enable us to see whether there are any correlations between them. In addition to undertaking the conventional types of geochemical analyses, we have also examined some of these oils using high temperature gas chromatography columns. Performing the analyses in this manner, we have observed that some of the oils and their associated waxes contain saturated hydrocarbons extending to at least C_{20} and probably higher. The fact that many of these higher molecular weight components are waxes that precipitate in the pipelines and not in the oil has led us to the conclusion that, in many cases, the composition of the oil collected at the wellhead is not necessarily the same as the composition of the oil in the reservoir. We are now in the process of trying to obtain fresh reservoir cores so that we can compare the composition of the oil in place with that collected from the wellhead.

We are continuing to develop sets of geochemical parameters that can be used to define particular types of depositional environments. The aim of this work is to be able to apply these sets of parameters to define and recognize ancient depositional environments. In this part of the study we are examining small intervals of well-characterized core from the Woodford shale and have carried out detailed geochemical analyses on samples from the core.

GRANTEE:	**UNIVERSITY OF OKLAHOMA** School of Geology and Geophysics Norman, Oklahoma 73019
GRANT:	**DE-FG05-91ER14208**
TITLE:	**Sedimentary Basin Geochemistry and Fluid Interaction Workshop**
PERSON IN CHARGE:	**R. P. Philp** (405-325-3253; FAX 405-325-3140; E-mail pphilp@geoadm.gcn.uoknor.edu)

The BES/Geosciences program for several years has supported research projects which may be thought of as falling under the general title of Sedimentary Basin Geochemistry and Fluid-Rock Interactions. There are plans to hold a two-day review of these projects at the School of Geology and Geophysics, Sarkeys Energy Center, University of Oklahoma, Norman, on November 18 and 19, 1991. This workshop will follow a format similar to that used for the program review of High Resolution Underground Imaging recently held in Berkeley.

In the workshop, the PIs of the groups designated by the BES/Geosciences Program are to give presentations of their research activities. For the most part, these presentations are scheduled to last 30 minutes, including questions. Presentations at the review are limited to the PIs in the program and one or two invited talks from researchers outside of the program. Attendance at the meeting is limited to PIs and any project personnel they wish to bring plus a small number of additional invited observers and/or others suggested by the Program Office. An extended abstract is required, and a book of extended abstracts will be available at the meeting.

The workshop will be held in a review type format so that ample time will be available for discussion of results and future directions of research. It is also hoped that the invited speakers from industry will provide a perspective on how the research carried out under this program can be of value to industry.

Representatives from a number of other DOE programs and other agencies are also invited in order for them to obtain information on the direction this program is taking and possible areas of collaboration or interaction.

GRANTEE:	**UNIVERSITY OF OKLAHOMA** School of Geology and Geophysics Norman, Oklahoma 73019
GRANT:	**DE-FG05-89ER14075**
TITLE:	**Regional Assessments of the Hydrocarbon Generation Potential of Selected North American Proterozoic Rock Sequences**
PERSON IN CHARGE:	**M. H. Engel** (405-325-3253; FAX 405-325-3140; E-mail AB1635@UOKMVSA)

A geochemical survey study of over 500 core and outcrop samples that represent more than a dozen U.S. Middle and Upper Proterozoic sedimentary formations has been undertaken to assess their potential for oil and gas generation. Comprehensive sedimentologic/organic geochemical studies on three depositionally distinct units that experienced mild to moderate thermal histories are nearly completed. These include the ~1.1 Ga Nonesuch Formation (Oronto Group, northeastern Wisconsin/Upper Peninsula Michigan), the ~1.3 Ga Dripping Spring Quartzite (Apache Group, Arizona), and a series of black shales from the 1.2 to 1.3 Ga Lower Tindir Group (east-central Alaska). Depositional environments represented by these three units are lacustrine rift deposits, marine shelf deposits, and glacio-marine deposits, respectively.

Based on percent total organic carbon (TOC), kerogen type, and maturity, it appears that several intervals of the Nonesuch Formation qualify as moderate to good source rocks. Intervals of organic-rich rocks are particularly prevalent in the vicinity of the White Pine Mine and the Presque Isle River (Ontonagon and Gogebic Counties, Michigan, respectively). Moderate to good gas potential is likely for several intervals throughout the basin.

Despite TOC levels exceeding 3%, Rock Eval data indicate a limited source potential for oil from the black shale facies of the Dripping Spring Quartzite. The rocks may have experienced alteration by hydrothermal fluids. However, given an appropriate geologic setting, a significant gas potential cannot be precluded at this time. Similarly, black shales of the Lower Tindir Group, whilst containing up to 6.5% TOC, appear to be overmature. At this present level of maturity the Lower Tindir Group exhibits good potential for gas generation. However, given the geographic extent of this formation and limited knowledge of its burial history, the potential for oil generation cannot be entirely discounted.

Our results to date indicate that there are numerous organic-rich North American Proterozoic rock units that, based on conventional criteria, appear to be moderate to good source rocks. It remains to be demonstrated whether geologic factors affecting hydrocarbon generation, migration, accumulation, and preservation will prove to have been appropriate for the commercial production of oil and/or gas in these frontier basins.

GRANTEE:	**UNIVERSITY OF OKLAHOMA** School of Geology and Geophysics Norman, Oklahoma 73019
GRANT:	**DE-FG05-91ER14209**
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**
PERSON IN CHARGE:	**R. D. Elmore** (405-325-3253; FAX 405-325-3140; E-mail AB1635@UOKMVSA)

Investigations of fluid migration in the subsurface are often hindered by a lack of temporal control and a fundamental appreciation of the potential for alteration of fluid composition by means of fluid-rock interactions. There is little doubt that the ability to constrain the time of oil migration and a better understanding of potential changes in oil composition during migration would be of significant benefit for oil exploration. For the past several years we have worked on the development of a paleomagnetic method for dating hydrocarbon migration. The refinement and field tests of this dating method are the primary objectives of this proposed study. In addition, we plan to test and compare the paleomagnetic dating approach with another hydrocarbon dating method, Pb-Pb radiometric dating recently developed by John Parnell (Queen's University, Belfast) and his colleagues. A secondary objective of this study will be to document some of our previous observations concerning the effects of rock-fluid interactions on the composition of crude oils. One of the proposed study areas, an exposed reservoir in northwest Colorado (Schoolhouse Member, Maroon Formation), provides us with an opportunity to continue our assessment of the potential for chemical and stable isotopic alteration of crude oils resulting from fluid-rock interactions. Whereas we have conducted numerous studies of geochromatographic effects in the laboratory, it is important that we continue to compare the results of this work with natural systems.

The research will involve both field and laboratory studies. Field tests will be conducted on three units. One test will focus on the Schoolhouse Member of the Maroon Formation (Pennsylvanian), an exposed reservoir in northwest Colorado. A second test will be performed on Paleozoic rocks (Old Red Sandstone) in Great Britain that contain uraniferous bitumen from which independent Pb-Pb dates for hydrocarbon migration can be determined. A third test will be on Triassic-Jurassic redbeds and volcanics in the Hartford Basin, Connecticut, that contain veins with hydrocarbons. We will also determine if the units in North America we plan to study or have studied in the past are suitable for Pb-Pb dating. Laboratory studies will include additional organic geochemical and rock magnetic studies on hydrocarbon impregnated Permian calcite speleothems and laboratory simulation experiments in order to better understand the mechanism of magnetite precipitation.

Results of these studies should provide additional constraints on the mechanism(s) of magnetite precipitation (and nature of rock-fluid interactions) as well as allowing for an evaluation of the applicability of the paleomagnetic approach for dating hydrocarbon migration. In addition, the results should permit an evaluation of the Pb-Pb dating approach in comparison with the paleomagnetic approach.

GRANTEE:	**OREGON STATE UNIVERSITY** College of Oceanography Corvallis, Oregon 97331-5503
GRANT:	**DE-FG06-89ER14057**
TITLE:	**New Approaches to the Estimation of Magnetotelluric Parameters**
PERSON IN CHARGE:	**G. D. Egbert** (503-754-2947; FAX 503-737-2604; E-mail egbert@oce.orst.edu)

To use magnetotelluric (MT) data to image crustal structure one must first reduce long time series of electric and magnetic fields to transfer functions (TFs) which determine the frequency dependent impedance tensor. Because neither the natural source signal nor the dominant noise sources are well modeled as stationary Gaussian processes, standard least squares TF estimation methods often perform very poorly. As a result, MT experimentalists have developed a variety of *ad-hoc* schemes, such as coherency sorting, to eliminate noisy data segments and achieve stable and repeatable impedance estimates. More recently, rigorously justifiable outlier-resistant data processing methods (based on regression M-estimates; RMEs) have been applied to long period magnetotelluric (MT) and magnetovariational data. In this research project we are developing and testing improved methods for processing shorter period (0.001–100 Hz) MT data relevant to geophysical prospecting and imaging of crustal structure. We have adopted a general strategy based on a combination of coherence sorting and the RME. We have demonstrated the superiority of such hybrid methods for single station estimates in low signal-to-noise environments (in particular in the "dead band," 0.1–10.0 Hz), and are now concentrating on the extension of these methods to remote reference estimates, which are based on data from two or more simultaneously operating stations. We are focusing in particular on the development of methods which work in areas where data is severely contaminated by cultural electromagnetic noise. Although some effort has been devoted to formal methodological issues, we have concentrated on testing various possible approaches on real data sets. The goals of the research are to document the performance of a range of alternative processing methods and to develop and make available to the exploration community optimal practical working algorithms.

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)

The purpose of this work is to expand our data base and understanding of the thermochemistry of minerals and related materials through a program of high temperature reaction calorimetric studies. The technique of oxide melt solution calorimetry (in molten $2PbO \cdot B_2O_3$) has been extended to volatile-bearing phases. Calorimetric conditions under which H_2O and CO_2 reach a well-defined final state upon reaction with molten lead borate have been perfected. These involve calorimetry under a flowing gas atmosphere, which purges all H_2O and CO_2 in the gas phase, leaving essentially none to interact with the solvent (R. Rapp and others).

The projects on phlogopite-eastonite structure and thermodynamics (S. Circone) and on H_2O-cordierite interactions (W. Carey) have been submitted for publication. A. Pawley returned to Princeton to use our improved techniques to refine some calorimetric data on tremolite-richterite.

The role of large highly charged cations in glasses and crystals was investigated by A. Ellison. This work included calorimetry and EXAKS of K_2O-La_2O_3-SiO_2 glasses and a study of the heat of formation of zircon. This work is now published or in press. Crystals and glasses of $K_2ZrSi_3O_9$ and $K_2TiSi_3O_9$ have also been studied by solution calorimetry.

Two new projects have been initiated. L. Chai is studying the energetics of the $CaCO_3$-$MgCO_3$-$FeCO_3$ system. He has determined, using oxide melt calorimetry, the energetics of calcite, magnesite, and dolomite and is synthesizing iron-bearing samples. He has also checked his methodology by measuring the enthalpies of the reactions calcite + quartz = wollastonite + CO_2 and magnesite + quartz = enstatite + CO_2. I. Petrovic's thesis concerns zeolite thermochemistry. He is attempting to separate the energetic influences of (a) cage and framework topology, (b) Al/Si substitution, and (c) ion exchange and hydration. Calorimetric study of a series of almost pure SiO_2 zeolites, the first step in this work, is essentially finished.

These studies taken together begin to unravel the simultaneous energetic effects of coupled ionic substitutions, of framework topology, and of water and carbon dioxide content in complex chain, sheet, and framework silicates and in carbonates. The thermodynamic properties of such phases are important in diagenesis, metamorphism, rock-water and rock-CO_2 interactions, and nuclear waste disposal.

GRANTEE:	**PRINCETON UNIVERSITY** Department of Geological and Geophysical Sciences Princeton, New Jersey 08544
GRANT:	**DE-FG02-91ER14197**
TITLE:	**The Effects of Natural and Radiation Induced Defects on Noble Gas Transport in Silicates: A Study of Argon Using Laser, X-Ray, and Electron Microprobes**
PERSON IN CHARGE:	**T. C. Onstott** (609-258-6669; FAX 609-258-1274; E-mail tullis@warbler.princeton.edu)

$^{40}Ar/^{39}Ar$ laser microprobe results indicate that the radius of diffusion is on the order of the grain size for hydrous silicates but that the shapes of the concentration profiles are often distinctly non-Fickean, suggesting that volume diffusion is not the sole mechanism of argon transport. We suspect that short-circuit diffusion due to structural defects plays an important role in these minerals and in complexly exsolved and altered K-feldspars. We are currently undertaking experimental determinations of $^{40}Ar/^{39}Ar$ spatial gradients in K-feldspars. These gradients will be modeled with a numerical code for one- and two-dimensional concentration profiles for a continuum, multipath diffusion model which we have recently developed.

The density of structural defects is an important parameter in the multipath diffusion model. We have also recently developed an etching technique which permits imaging of the defects at the microscopic scale, thus eliminating the enormous tedium and expense of TEM mosaics.

Inversion of detailed thermal histories from two-dimensional concentration distributions is feasible by means of the numerical modeling that we intend to develop. If the multipath diffusion model proves to be an accurate replication of nature, then the delineation of the thermal histories of rocks and the dating of their magnetizations by the K-Ar system will be greatly improved. This approach will be compared with the method currently in vogue of deriving diffusion information from in vacuo step-heating on the same samples. In order to understand the mechanism of argon release in vacuo, detailed isothermal analyses will be performed on fine-grained K-feldspar samples irradiated for varying durations.

We are also exploring newer types of pulse lasers to increase the surface absorption coefficient of the incident beam for K-feldspar, a relatively transparent mineral, in order to limit the internal scattering of the laser beam by defects, which increases the degassing volume well-beyond the diameter of the laser beam.

GRANTEE:	**PURDUE UNIVERSITY** Department of Earth & Atmospheric Sciences West Lafayette, Indiana 47907
GRANT:	**DE-FG02-89ER14082**
TITLE:	**Models of Natural Fracture Connectivity: Implications for Reservoir Permeability**
PERSON IN CHARGE:	**A. Aydin** (now at Stanford University; 415-725-8708; FAX 415-724-0979)

This is a cooperative project between researchers at Stanford University and Purdue University to characterize the geometry of natural fracture systems in rock and to elucidate the mechanical aspects of their evolution. This project is a key element in a broader effort to understand the factors which influence the flow of hydrocarbons and ground water in the Earth's crust. This understanding is vital to the energy industry, both for oil and gas production and for nuclear waste isolation.

Within sedimentary layers, fracture geometry (e.g., spacing, aperture, and length distribution) is largely controlled by mechanical interaction between adjacent fractures. In contrast, interfaces between different lithologic members of a sequence and their contrasting physical properties play the most important roles in controlling the geometry of fracture sets that transect many layers. Research at Purdue University focuses on fracture propagation across multi-layered sequences with thin shale units.

Field-based research on the role of interfaces in fracture propagation consists of documenting fracture geometry and determining the kinematics of fracturing across common types of interfaces. The field data are then used to develop mechanical models for the observed effects of interfaces on the propagation and the continuity of fractures across rock layers with various physical properties (elastic moduli, Poisson's ratios, and fracture toughnesses) and loading conditions. It is expected that both the field work and the numerical models will lead to a greatly improved conceptual basis for evaluating the geometry and the connectivity of fractures and their role in either improving or impeding fluid flow in typical fractured reservoir rocks such as sandstone, shale, and limestone.

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

GRANT:	**DE-FG02-90ER14113**

TITLE:	**Hyperfiltration-Induced Fractionation of Lithium Isotopes in Geologic Systems**

PERSON IN CHARGE:	**S. J. Fritz** (317-494-3276; FAX 317-494-0776)

Hyperfiltration through clay membranes induces isotopic fractionation in which a solute's heavy isotope is depleted on the clay membrane's high-pressure side. It should thus be possible to delineate regions of high and low hydrostatic heads in the subsurface by plotting distributions of elements' isotopic ratios obtained through analyses of samples collected from opposing sides of aquitards.

High degrees of hyperfiltration-induced fractionation should result when ions of a low-atomic-weight element are hydraulically forced through a highly ideal clay membrane. This study gauges the magnitude of $^{7}Li/^{6}Li$ fractionation during hyperfiltration through clay membranes. The results will yield baseline data against which hyperfiltration-induced isotopic fractionation of higher-atomic-weight elements should be compared in future hydrogeochemical investigations.

Because the high-pressure test cell is not yet fully fabricated, an experiment was devised to gauge the potential isotopic fractionation of lithium isotopes in an osmotic mode. In this experiment, 45.93 g of 0.9088 Formal LiCl solution was placed in a sealed dialysis membrane having a molecular weight cutoff (MWCO) of 3500 Å. Reagent-grade LiCl was used whose $^{6}Li/^{7}Li$ ratio was 0.08059 (relative to NBS standard L-SVEC). As expected, ^{6}Li diffused out of the dialysis bag faster than ^{7}Li, with the result that the maximum fractionation of lithium isotopes in the dialysis-bag solution was −11 per mil relative to the input stock solution.

GRANTEE:	**UNIVERSITY OF SOUTHERN CALIFORNIA** Department of Geological Sciences Los Angeles, California 90089-0740
GRANT:	**DE-FG03-87ER13807**
TITLE:	**Continental Scientific Drilling Program: The Seismology of Continental Thermal Regimes**
PERSON IN CHARGE:	**K. Aki** (213-740-5830; FAX 213-740-0011) E-mail Aki%sei@gamera.usc.edu)

This program was started as an involvement in two major geothermal projects, namely, the Hot Dry Rock Geothermal Energy Project of Los Alamos National Laboratory and the Magma Energy Project of Sandia National Laboratories. The theory and methods developed for interpretation of various seismic experiments conducted at Fenton Hill, New Mexico, and Kilauea Iki, Hawaii, however, found a variety of applications to other geothermal areas and volcanoes, and our research has been evolving into what might be called volcanic seismology.

In this program we are applying the methods of passive seismology using natural seismic sources occurring in geothermal areas as well as active seismology using artificial sources to the candidate sites for the CSDP in order to delineate the geothermal and mechanical properties as well as the mass and energy transport mechanism of the geothermal system.

In the past year, we finally succeeded in separating the scattering Q^{-1} from intrinsic Q^{-1} for crustal shear waves in the frequency range from 1 to 20 Hz. The success is due partly to the elimination of local site effect from the observed seismic energy by the coda method and partly to the application of a new method based on measuring seismic energy contained in several non-overlapping time windows as a function of distance. The frequency dependent scattering Q^{-1} and intrinsic Q^{-1} obtained for Long Valley, Island of Hawaii, and central California revealed a unique difference in small-scale structure between volcanic and seismic regions.

In addition to the above stochastic modeling approach, we are also pursuing a deterministic approach toward seismic imaging of subsurface structures using the T-matrix method applied to the waveform data. The goal of this approach is to design effective configurations of seismic source-receiver that give satisfactory images of the structures. We apply these interpretation methods to seismological data from the CSDP candidate sites, including Mt. Katmai, Long Valley, Valles Caldera, the hot dry rock sites, and other continental geothermal areas.

GRANTEE:	**STANFORD UNIVERSITY** Geophysics Department Stanford, California 94305-2215
GRANT:	**DE-FG03-88ER13601**
TITLE:	**Porosity with Fluids: Origin and Effects on Physical Properties of Crustal Rocks**
PERSON IN CHARGE:	**A. M. Nur** (415-723-9526)

Our studies are focused on five important problems in rock physics: shear strength of rocks and its relation to petrography and petrophysical properties; critical porosity of porous and cracked rocks and unconsolidated sediments; quantitative analytical estimates of permeability in saturated rocks using attenuation and seismic velocity data; laboratory measurements of velocity and attenuation anisotropy in shales; and relating rock physics from the laboratory to *in-situ* velocity tomograms.

Shear strength in rocks. Laboratory tests of uniaxial confined compression were performed on tight gas sandstones and shales. Using these results to relate rock strength and formation properties, we distinguish two regimes: (1) For clay volume fractions less than 17 percent, strength is strongly dependent on confining pressure and porosity. (2) For clay volume greater than 17 percent, strength is sensitive to confining pressure and weakly sensitive to clay content. Our results give the basis for the determination of *in-situ* rock-mechanical properties based on petrography and petrophysics.

Critical porosity. The critical porosity is the transition porosity between solid matrix-supported and fluid matrix-supported mechanisms in rocks. We examined several theoretical descriptions of multicomponent materials to formulate the critical porosity of saturated rocks with and without clay phase, ranging from marine suspensions and unconsolidated sediments to porous and cracked rocks. We find that the self-consistent approach with flat-oblate or penny-shaped inclusion models can approximately describe formation properties below and above the critical porosity. This theoretical investigation allows us to realistically quantify velocity-porosity relations in saturated rocks.

Permeability and attenuation in fractured rocks. Employing the concept of a complex elastic modulus, we use our model for pore fluid dynamics to find P-wave attenuation and velocity. We calculate permeability as a function of pore geometry and relate this parameter to the attenuation. These theoretical results demonstrate good correlation with published experimental data for sandstone samples. Our model can qualitatively explain the attenuation-permeability relationship for fractured rocks.

Velocity and attenuation anisotropy in shales. New experimental data on dynamic elastic properties of siltstone samples were obtained, revealing velocity and attenuation anisotropy. The measurements were conducted using the pulse transmission method with corrections on the energy transmission coefficients and geometric diffraction loss. These data on anisotropy of the Freeman shale might be used to interpret *in-situ* seismic measurements.

Relating rock properties to in-situ velocity tomograms. Laboratory-derived relations between seismic measurements and rock properties were applied to interpret data obtained in the field. A specific goal was to derive the images of porosity and shaliness from the velocity tomogram. In a particular Gulf Coast example, we have found that using well log data, velocity can be related empirically to porosity and clay volume, with very high correlation. The best porosity images were obtained using a combination of rock physics and geostatistics methods.

GRANTEE:	**STANFORD UNIVERSITY** Department of Applied Earth Sciences Stanford, California 94305-2115
GRANT:	**DE-FG03-85ER13319**
TITLE:	**Structure and Vent Geometry of the Novarupta Caldera, Valley of Ten Thousand Smokes, Katmai National Park, Alaska**
PERSON IN CHARGE:	**D. D. Pollard** (415-723-4679; FAX 415-725-0979; E-mail dpollard@denali.stanford.edu)

The goal of this project is to provide constraints on the subsurface geometry of the vent, feeder conduit(s), and possible intrusive bodies in the Novarupta basin, Valley of Ten Thousand Smokes (VTTS), Katmai National Park, Alaska. Our results have guided site selection and targets for the Katmai Drilling Project and have contributed to the understanding of silicic volcanic systems. This new knowledge of the subsurface geometry of the vent is essential for accurate modeling of the present thermal regime in the vent region and the eruption dynamics. In more general terms, this project contributes to our understanding of geothermal energy resources and volcanic hazards. This project is nearing completion: Peter Wallmann has successfully defended his Ph.D. thesis on these subjects; one manuscript is published; one is in press; and three are in preparation.

Four sets of structures are interpreted to reflect the extent of the Stage I vent at Novarupta basin: (1) truncated topography along the northern and southern basin margins; (2) arcuate grabens on the eastern margin; (3) translational block slides and gulls on the north and south margins; and (4) a monoclinal fold in the tephra blanket along the western margin. These structures define a roughly elliptical vent with axial lengths of 2.5 and 3 km. Other surficial structures include radial slides and fissures, perhaps related to passage of a dike which fed Novarupta Dome. Topographic cross sections, the inferred depth to a possible magma chamber, and the surficial fractures suggest that the subsurface geometry is a flared vent with steeply dipping walls to the north and south and more gently dipping walls to the east and west.

A large faulted mound of tephra, the Turtle, was produced northeast of the Stage II vent during the last eruption phase. The dominant structures on the Turtle are two graben systems which intersect at nearly right angles. Two conceptual models are proposed for their doming of the tephra by a shallow igneous intrusion and their compaction of the tephra pile. Numerical modeling of these processes, combined with field observations, suggest the Turtle formed by inflation of a shallow igneous intrusion. Measurements of extensional strains across fissures and grabens in the Novarupta basin and VTTS have been used to constrain numerical models for compaction of the ash. These models provide estimates for the bedrock topography beneath the compaction structures. Apparently, the western margin of the basin is underlain by a convex-upward, flared vent. In contrast, the geometry of the vent along the eastern margin is inferred to be concave upward and steep-sided. This geometry probably represents truncation of a preexisting topographic saddle by growth of the flared vent.

GRANTEE:	**STANFORD UNIVERSITY** Department of Applied Earth Sciences Stanford, California 94305-2115
GRANT:	**DE-FG03-89ER14081**
TITLE:	**Models of Natural Fracture Connectivity: Implications for Reservoir Permeability**
PERSON IN CHARGE:	**D. D. Pollard** (415-723-4679; FAX 415-725-0979; E-mail dpollard@denali.stanford.edu)

This is a cooperative project between researchers at Stanford University and Purdue University to characterize the geometry of natural fracture systems in rock and elucidate the mechanical aspects of their evolution. This project is a key element in a broader effort to understand the factors which influence the flow of hydrocarbons and ground water in the Earth's crust. This understanding is vital to the energy industry, both for oil and gas production and for nuclear waste isolation.

Within sedimentary layers fracture geometry (e.g., spacing, aperture, and length distribution) is largely controlled by mechanical interaction between adjacent fractures. In contrast, interfaces between different lithologic members of a sequence and their contrasting physical properties play the most important roles in controlling the geometry of fracture sets that transect many layers. Research at Stanford focuses on fracture geometry within individual layers.

A series of model experiments have been designed to understand the behavior of single fracture sets within thinly layered brittle materials. In these experiments a PMMA sheet is coated with a brittle lacquer and subjected to plane deformation. In these non-destructive tests the PMMA acts as the load-carrying medium and stabilizes fracture growth in the brittle coating. Here the characteristic length scale for fracture interaction is the thickness of the brittle coating.

Strain cycling. The effect of uniaxial strain cycling on the development of a single set of fractures in layered brittle materials was studied. Changes in five geometric parameters (total number of cracks, total length, average length, average spacing, and spatial density) were recorded during each experiment. Two major factors, strain rate and strain magnitude, were considered. These investigations provide us with an understanding for certain surface textures commonly found on the faces of natural opening-mode fractures (joints) in reservoir rocks. These textures, called hesitation lines, are indicative of cyclic loading.

Relaxation. Another important loading condition in a layered mass involves initiation and propagation under stress relaxation. A series of model experiments have been conducted under a constant strain field transmitted by the PMMA sheet. The changes in number and length of cracks, spacing, spatial density, and propagation velocity have been studied. These investigations show the effect of time on the geometric patterns of fractures.

Numerical analysis. A three-dimensional finite element analysis is being developed for modeling fracture sets within thin layers. This will enable us to extend the laboratory results to material properties more suitable for rock and environmental parameters appropriate for reservoir conditions. Using these numerical experiments we can relate the degree of connectivity among fractures to the state of stress and material properties of the rocks and, in turn, be in a position to evaluate the influence of these factors on permeability and fluid flow.

GRANTEE:	**STANFORD UNIVERSITY** Department of Geology Stanford, California 94305-2115
GRANT:	**DE-FG03-90ER14154**
TITLE:	**Fluid Flow, Element Migration, and Petrotectonic Evolution of the Early Mesozoic Central Klamath Island Arc, Northwesternmost California**
PERSON IN CHARGE:	**W. G. Ernst** (415-723-2750; FAX 415-725-6566)

Continuing investigations in the central Klamath Mountains have documented the presence of a polymetamorphosed suite of highly magnesian basaltic rocks, the so-called Yellow Dog greenstones, in the Sawyers Bar terrane (= North Fork ophiolite) of the western Triassic and Paleozoic belt. The Yellow Dog metavolcanics display apparent komatiitic chemical affinities; if correctly interpreted, such an occurrence could have important significance for the thermal and petrotectonic evolution of the early Mesozoic Klamath island arc. The metabasalts were initially thought to reflect the Permo-Triassic to Middle Jurassic overriding of an oceanic hot spot by the stable, nonsubducted arc-capped North American lithospheric plate, but are now regarded as metamorphosed, mildly alkaline oceanic island lavas (OIBs) and surmounting immature calc-alkaline arc basalts (IATs). These igneous rocks are interlayered with, and are interpreted to largely overlie, distal turbidites. The assemblage was laid down, altered, and metasomatized during the hypothesized collapse of a Philippine Sea-type marginal basin which brought the westerly Sawyers Bar oceanic arc terrane into juxtaposition with the inboard, pre-existing Stuart Fork subduction complex in an immature island-arc setting.

Supporting research has concentrated on elucidating the areal extent and structural/stratigraphic relations of these mafic/ultramafic Yellow Dog metavolcanic units and has documented the insignificant degree of crustal contamination of the melts by associated terrigenous metasediments. The physical conditions of metamorphism and of water-rock interaction accompanying island-arc accretion have been determined as follows: Middle Jurassic regional metamorphism of the Sawyers Bar/Stuart Fork amalgamated terrane took place at 350–500°C and 2.5–4.5 kbars; contact aureoles peripheral to the mid-Jurassic calc-alkaline plutons reached maximum physical conditions of 500–600°C at 2.0–3.5 kbars. Intrusion of the post-collisional granitoids mobilized alkalies, silica, rare earths, and, especially, oxygen isotopes in the sedimentary strata intimately interlayered with the Yellow Dog greenstones, overprinting the effects of an inferred earlier seafloor alteration in the mafic volcanics. The thermal structure and its evolution in the central Klamath Mountains evidently reflects surfaceward advective transport of magmatic energy derived from the partly fused downgoing oceanic slab, as well as hydrothermal fluid circulation. Clarification of the element migration, volatile pathways, and thermal evolution of this crust-constructional event in the immature island arc are the goals of the research now underway, employing both field and geochemical methods.

One postdoctoral fellow and two Ph.D. candidates as well as the P.I. are involved in the project. We have nearly finished a regional reconnaissance map showing the distribution of the OIB and IAT lavas throughout the California part of the Klamath Mountains. Investigation of the regional and contact metamorphism/metasomatism of the Sawyers Bar area is in progress. A manuscript demonstrating the presence of at least two ages of diabase dike/sill emplacement is ready for submission to a journal, and a 1:24,000-scale colored map of the Sawyers Bar area is approaching completion.

GRANTEE:	**STANFORD UNIVERSITY** Department of Geophysics Stanford, California 94305-2215
GRANT:	**DE-FG03-90ER14152**
TITLE:	**Seismicity Induced by Hydrocarbon Production**
PERSON IN CHARGE:	**P. Segall** (415-725-7241; FAX 415-725-7344 E-mail segall@kilauea.stanford.edu)

The goal of this project is a fundamental understanding of induced seismicity, including the coupling between pore fluid flow and rock deformation. Seismic data from a number of active oil and gas fields clearly show that earthquakes are occurring near fields where pore pressures have declined by several tens of MPa. These observations cannot be explained by changes in effective stress alone, which predict that decreasing pore-fluid pressures tend to stabilize faults. We believe that poro-elastic stresses resulting from pore-fluid extraction are responsible for earthquakes in these situations.

We are working in collaboration with J. R. Grasso (University of Grenoble) to characterize the induced seismicity and deformation occurring above a particularly well studied gas field in southwestern France. At this locality good seismic coverage, extensive well-log, gas production, reservoir pressure, and repeated precise leveling data are available, which permit us to test the hypothesis that production-induced seismicity can be explained by poro-elastic stressing. Recently, the local seismic network was augmented to provide better earthquake locations and focal mechanisms. The project plan is to develop a continuum mechanical model of the reservoir and its surroundings and to test the model by comparing predicted pore-pressure changes and surface displacements with available leveling and reservoir pressure data. If this is successful, we will compare the computed poro-elastic stresses with earthquake locations and orientations deduced from relocated hypocenters and earthquake focal mechanisms. To accomplish this we are extending analytical poro-elastic models for general axi-symmetric geometries and exploring appropriate numerical methods to analyze production-induced stressing in three-dimensional heterogeneous reservoirs.

GRANTEE:	**TEXAS A&M UNIVERSITY** Department of Geology College Station, TX 77843
GRANT:	**DE-FG05-87ER13767**
TITLE:	**Sedimentologic and Diagenetic History of the Mission Canyon Formation (Mississippian) and Stratigraphic Equivalents, Southwestern Montana and East-Central Idaho, and Determination of Rare Earth Element Abundances in Diagenetic Carbonates**
PERSON IN CHARGE:	**S. L. Dorobek** (409-845-0635; FAX 409-845-6162)

The Mission Canyon Formation and its stratigraphic equivalents in Montana and Idaho were deposited during collision of the western continental margin of North America with an inferred volcanic arc (Antler orogeny). An integrated petrographic and geochemical study of the diagenetic history of the Mission Canyon Formation is being carried out within the sedimentologic context established by field studies. Petrographic and geochemical data from individual diagenetic phases are being used to interpret extent of diagenetic alteration, sources of ions incorporated into cements, and paleohydrology of diagenetic fluids.

We have documented third- to fifth-order scale (10^6 to 10^4 yr) cyclic sedimentary sequences in shallow platform to deep basin environments. The third-order cycles have been correlated from the Antler foredeep, across the platform, and into the Williston Basin to the east, an area approximately 1200 km wide (nonpalinspastic). This study has established criteria for recognizing third-order (and smaller-scale) cycles in deep water deposits.

We also have completed a regional study of Late Devonian through Late Mississippian subsidence in Montana and Idaho. The analyses have shown that subsidence in the Antler foredeep and on the Montana platform are coupled. Conceptual geodynamic models for the coupled response of the proximal foredeep and adjacent cratonic platform incorporate flexure (vertical loading) and in-plane stresses (horizontal loading). Subsidence analyses suggest that the large-scale sequence stacking patterns within the Devonian-Mississippian platform stratigraphy probably are caused by spatial and temporal changes in subsidence, not by long-term sea level fluctuations.

Regional petrographic and geochemical trends in carbonate diagenetic phases also have been documented in the Mission Canyon Formation. Extensive meteoric diagenesis was related to regional subaerial exposure of the entire platform during post-Mission Canyon time. Meteoric groundwaters caused recrystallization of early-formed dolomites and precipitated calcite cements which occluded most porosity in the Mission Canyon Formation. Petrographic and geochemical data from Mission Canyon dolomites allow identification of two end member dolomite types: (1) precursor "evaporative" dolomite (zoned to irregular cathodoluminescence, Ca-rich, variable $\delta^{13}C$, positive $\delta^{18}O$, enriched trace element content) and (2) meteorically altered dolomite (homogeneous nonluminescence, stoichiometric, invariant $\delta^{13}C$, negative $\delta^{18}O$, low trace element content). Most dolomites are intermediate in composition between these two end members. These data suggest that the chemistry and petrography of many ancient dolomites might be explained by an episode of shallow-burial meteoric alteration. Rare earth element (REE) abundances in diagenetic phases have been used in our research as a geochemical tracer. Because of their extremely low concentrations in most natural solutions, very high fluid-rock ratios are required to produce REE abundances in diagenetic phases which are much different from those of the original carbonate sediment. Therefore, the REE may provide an additional constraint on the amount of fluid-rock interaction in carbonate diagenetic systems.

GRANTEE:	**TEXAS A&M UNIVERSITY** Center for Tectonophysics College Station, Texas 77843-3113
GRANT:	**DE-FG05-87ER13711**
TITLE:	**Mechanical Properties and Modeling of Seal-Forming Lithologies**
PERSON IN CHARGE:	**A. K. Kronenberg, J. E. Russell, and N. L. Carter** (409-845-0132; FAX 409-845-6780)

The goal of this research is to evaluate the roles of deformation and the occurrence of weak sedimentary lithologies subjected to gravitational loads in shaping conventional and unconventional oil and gas reservoirs. Two sedimentary lithologies that influence the geometries, physical properties, and heterogeneities of oil and gas reservoirs are shale and rock salt. Both form effective barriers to the flow and communication of petroleum and gas and, in many cases, form the seals to major reservoirs due to their low permeabilities. Both are actively deformed in depositional environments due to their low strengths relative to gravitational loads applied. Thus the shapes of seal-forming units and the nature of fractures and faults that may breach them depend upon the mechanical properties of shale or those of salt and upon the loading histories to which they have been subjected.

The fracture and flow properties of shales are not well constrained, and we are currently investigating these properties experimentally. The rheology of rock salt, on the other hand, is well known, and we believe that the time is right to apply the experimentally constrained constitutive relations for rock salt to deformations in the Earth.

During the first half of this year, we have completed our experiments on micaeous schists, research funded by DOE to investigate anisotropic yielding of foliated rocks at high temperatures and pressures. Microstructural studies of the deformed samples have revealed many of the deformation mechanisms that are operative in polycrystalline aggregates made up of layer silicates as well as the sources of inelastic anisotropy. Foliated schists may be regarded as coarse-grained analogues to bedded, clay-bearing shales, sharing in their textural character and mechanical properties, and we have initiated our study of shales with this premise. Triaxial, constant strain rate experiments to date reveal transitional brittle-ductile behavior for an illite- and muscovite-bearing shale from Louisiana over the confining pressure interval 60 to 200 MPa with an anisotropic yield envelope remarkably similar in form to slates and layer-segregated schists.

The main objective of our modeling efforts is to determine the influence of mobile salt and shale bodies and associated growth faults in the development of hydrocarbon traps and seals in the Gulf of Mexico. Deformation rates for salt related structures are about 10^{-10} to 10^{-14} s^{-1}, far lower than can practically be achieved in laboratory experiments. In the Gulf of Mexico the down termination of the major growth fault structures is still unknown because it is beyond seismic resolution. Even if resolution is not a problem, the subhorizontal termination of these faults is not within the normal time recording length (5–6 s TWT). A numerical model is therefore necessary to evaluate the influence of deformation on the evolution of the structures in question. Initially our attention is on developing a conceptual model which must account for the geometric scale and number of spatial dimensions, driving mechanism, conservation principles that control the process, boundary conditions, material models, and equations of state. Our work currently involves backstripping and subsidence analysis within the Gulf of Mexico in order to model the sedimentary loading history.

GRANTEE:	**UNIVERSITY OF TULSA** Department of Geosciences Tulsa, Oklahoma 74104
GRANT:	**DE-FG05-88ER13417**
TITLE:	**Stability of Natural Gas in the Deep Subsurface**
PERSON IN CHARGE:	**C. Barker** (918-631-3014; FAX 918-631-2286)

The main aim of this research program has been to establish the composition of very deep gas and understand the factors that control its composition. A combined theoretical and experimental approach has been used. Gas composition is being calculated with a minimum free energy thermodynamics program that can handle up to 70 components in up to 25 phases. Actual deep gas composition is difficult to obtain by direct analysis because of the lack of wells that have penetrated deeper than 30,000 feet in sedimentary sections. Fluid inclusions offer one possible source of information. Fluid inclusions are microscopic defects in crystals that have trapped small volumes of the fluids present at the time of mineral growth, and so they provide a way of getting samples of the gases that were present in the environment where the mineral grew. They are not inherently limited by either depth or age, and the gases are protected from both loss and contamination. We have continued to develop our computer-driven, dual mass spectrometer system for analyzing the bursts of gas released as individual inclusions rupture on heating. In the past year the data handling software has been moved from a SUN computer system to HP/Apollo workstations. This provides advantages of increased processing speed, increased memory, easier access, graphics with better resolution, and more portable software (using X-windows).

We have continued to evaluate the limits of applicability of the analytical procedures. The method has been used successfully to analyze gases in fluid inclusions in opaque minerals (which cannot be studied by traditional methods) and in melt inclusions in rhyolite and basalt. The latter showed some of the highest concentrations of sulfur dioxide found so far. The burst temperature for a fluid inclusion can be retrieved by the software along with inclusion size. Graphic displays of inclusion size versus burst temperature have been developed and may be useful in helping identify stretched inclusions. If inclusions are buried deeply after formation, internal pressures can become high enough to stretch the host mineral and increase the volume of the inclusion. On subsequent heating in our analytical system these inclusions will rupture at higher temperatures. The degree of stretching is size dependent, so that the shape of the distribution for a large number of bursts on a temperature-size plot may indicate the degree of stretching for that sample. Preliminary results are encouraging.

Inclusions from the cementing sandstones that form the top pressure seal for abnormally pressured natural gas reservoirs in the Anadarko basin have been analyzed. They are water-dominated and contain very little methane, suggesting that the calcite formed by rather complete oxidation of the methane or that the seal developed before the gas accumulated. Preliminary analyses have been made for samples from the Arbuckle of the Arkoma basin and the Brown Zone of the Criner uplift. In both cases the rocks have been considerably deeper and hotter in the past, so that present gas composition was probably controlled by the deep burial. The samples analyzed so far have had little methane and no hydrogen sulfide. Thermodynamic calculations suggest that for the reservoir mineralogies sampled, even with considerable additional anhydrite, the expected hydrogen sulfide concentration will be low.

GRANTEE:	**U.S. GEOLOGICAL SURVEY** Reston, Virginia 22092
GRANT:	**DE-FG05-91ER14210**
TITLE:	**Interagency Coordinating Group/Continental Scientific Drilling**
PERSON IN CHARGE:	**D. P. Russ** (703-648-6640; FAX 703-648-6683)

This grant was initiated to cover the DOE portion of the costs incurred by the Department of Interior, U.S. Geological Survey, for support of the Interagency Coordinating Group for Continental Scientific Drilling (ICG/CSD). Under the provisions set forth in the Continental Scientific Drilling and Exploration Act of 1988, PL 100-441, the ICG/CSD is responsible for implementing the United States Continental Scientific Drilling Program (US CSDP) and is to be composed of members from DOE/OBES, DOI/USGS, and NSF.

The ICG/CSD is jointly responsible for

- Preparation and submission of an annual report from the three agencies to Congress.
- Support and operations of the annual Forum for Continental Scientific Drilling.
- Support and operations of the review committee Council for Continental Drilling.
- Support of technical workshops as required to define unique scientific opportunities.
- Identification and notification of opportunities for research, consistent with each agency's guidelines and operating methods.
- Preparation of the Environmental Impact Statement for Scientific Drilling at the Katmai National Park, Alaska, as required by the National Park Service prior to issuance of a drilling permit.
- Other expenses needed to fulfill its role in implementing and coordinating activities within the scope of the United States Scientific Drilling Program.

To fulfill these responsibilities, the ICG/CSD meets on a monthly basis to exchange information and to coordinate activities. The ICG/CSD shares costs to implement the US CSDP.

GRANTEE: UNIVERSITY OF UTAH RESEARCH INSTITUTE
Earth Science Laboratory
391-C Chipeta Way
Salt Lake City, Utah 84108-1295

GRANT: DE-FG02-90ER14133

TITLE: **Investigation of High-Temperature, Igneous-Related Hydraulic Fracturing as a Reservoir Control in the Blackburn and Grant Canyon Oil Fields, Nevada (Including Phase 2—Assessing the Role of Active and Paleo-Hydrothermal Systems in Oil-Reservoir Evolution)**

PERSON IN CHARGE: **J. B. Hulen** (801-524-3446; FAX 801-524-3453)

Results of petrographic and fluid-inclusion research in progress at UURI have strongly supported high-temperature hydrothermal fracturing as a reservoir control for the Blackburn oil field, in the Basin and Range province of eastern Nevada. Here, oil-bearing dolomite breccias show textures indicating explosive rock rupture rather than tectonic breakage. These breccias are cemented with secondary dolomite precipitated from hydrothermal brines at temperatures exceeding 350°C and indicating a contemporaneous igneous heat source. For the geologically similar Grant Canyon/Bacon Flat field (Railroad Valley, Nye County, Nevada), the origin of texturally similar breccias remains ambiguous; fluid-inclusion homogenization temperatures for secondary quartz cementing the breccias of this field average only about 120°C. However, the quartz at Grant Canyon does host primary oil, oil/aqueous, and aqueous fluid inclusions which document a direct geothermal connection for petroleum migration and entrapment. Moreover, the 120°C homogenization temperature is the same as the current reservoir temperature at Grant Canyon, and there is no fluid-inclusion evidence that temperatures since quartz precipitation have ever dipped much below this point. These relationships suggest that the Grant Canyon field is very young and may have formed as an integral portion of a convecting, moderate-temperature geothermal system. Such a system, still active, may also have helped form the Blackburn oil reservoirs: a nearby, travertine-precipitating hot spring (90°C) also produces "live" oil and methane. It seems likely that hydrothermal systems may have played a much more comprehensive role in formation of many Basin and Range oil fields than simply creating secondary porosity (hydrothermal fractures and breccias) for oil entrapment. We are investigating this broader geothermal connection by expanding our breccia research at Blackburn and Grant Canyon/Bacon Flat to encompass the influence of paleo- and active hydrothermal systems in oil-reservoir evolution.

GRANTEE:	**UNIVERSITY OF UTAH RESEARCH INSTITUTE** Earth Science Laboratory 391-C Chipeta Way Salt Lake City, Utah 84108-1295
GRANT:	**DE-FG02-91ER14207**
TITLE:	**Participation in the Creede Scientific Drilling Project as On-Site Principal Investigator**
PERSON IN CHARGE:	**J. B. Hulen** (801-524-3446; FAX 801-524-3453)

The U.S. Geological Survey's Creede caldera scientific drilling project will commence in September and October 1991 with completion of two continuously cored holes in the moat sedimentary sequence of this 25.9 m.y.-old caldera in the central San Juan caldera cluster. This initial phase of the project, undertaken as part of the U.S. Continental Scientific Drilling Program under the aegis of the Interagency Coordinating Group, is designed to test the hypothesis that the moat furnished the saline fluids which ultimately deposited the Creede mining district's rich silver/base-metal ores. Two holes will be drilled—one to a nominal depth of 1 km in the presumed recharge area for the fossil Creede hydrothermal system and the other at a location several kilometers distant in relatively fresh "background" moat sediments to a depth of about 0.5 km. The Creede project will naturally complement past and ongoing OBES-sponsored CSDP efforts in the nearby, analogous but active, high-temperature geothermal system in the Quaternary Valles caldera of northern New Mexico. Combined research from both projects will provide an unprecedented understanding of magmatically heated, ore-depositing hydrothermal systems in large silicic caldera complexes. Achieving the multiple scientific goals of the Creede project will involve not only successful completion of the coreholes but also coordination and planning of on-site experiments as well as preparation, in "real time," of a detailed preliminary lithologic, alteration, fracturing, and vein mineralization log for the recovered core. UURI's on-site Principal Investigator will work closely with Chief Scientist Phillip M. Bethke to help manage these activities and assure that the project realizes its optimum scientific benefit.

GRANTEE:	**UNIVERSITY OF UTAH RESEARCH INSTITUTE** Earth Science Laboratory 391-C Chipeta Way Salt Lake City, Utah 84108-1295
GRANT:	**DE-FG02-89ER14083**
TITLE:	**Tensor, Controlled-Source Audiomagnetotelluric Survey over the Sulphur Springs Thermal Area, Valles Caldera**
PERSON IN CHARGE:	**P. E. Wannamaker** (801-524-3445; FAX 801-524-3453)

We have recently completed the acquisition of a tensor, controlled-source audiomagnetotelluric (CSAMT) survey at the Sulphur Springs geothermal area of the Valles caldera, New Mexico. This survey is in support of scientific interpretation of CSDP drillholes VC-2A and VC-2B. Purposes of the CSAMT survey include establishing basement relief, mapping stratigraphy, estimating relative fluid content or alteration, inferring relative permeability, delineating possible vapor regimes, and establishing geometric controls on the hydrothermal system. There is an overall goal to calibrate the resistivity expression of the system with other geological and geophysical models. Moreover, the survey should evaluate the viability of the tensor approach to CSAMT measurements. This approach should have the advantage of independence of source field polarization and a complete estimation of the resistivity response regardless of dimensionality.

The CSAMT soundings, 45 in all and obtained with our own equipment, were concentrated over the Sulphur Springs area, but some were taken as much as 2–3 km away for control. The frequency range of the data spans 4.1 kHz down to 1 Hz for almost half of the sites, and down to 4 Hz for the remainder, allowing tight control of near-surface variations, but also providing information on structure to depths approaching 2 km. Acquiring the electric field component across strike with contiguous bipoles (EMAP mode) ensures against undersampling the lateral response variation. The tensor nature of the data is very desirable to strengthen the interpretation and take advantage of the precise and versatile modeling techniques developed at ESL/UURI. This data set furthermore should be highly valuable in testing two- and three-dimensional MT inversion algorithms currently under development.

The main field trip for the project was undertaken in May and June of 1991. A transmitter of crossed bipoles each slightly over 2 km in length was emplaced about 13 km from the VC-2B wellhead. Typically 20 A of current was achieved after substantial current electrode preparation. Good electric and magnetic field signals with quite independent polarizations for the two bipoles were measured over the survey area. Comparison with existing natural field MT sites is excellent for apparent resistivity, impedance phase, and the vertical magnetic field over the common span of periods. Near-field effects were observed in the CSAMT data at 1 and perhaps 2 Hz, which is the bottom of our period range of interest. However, the natural field MT data will extend the possible investigation by plane waves to substantially greater depths. In addition to addressing the geological goals summarized above, this unique data set will be interesting in terms of the CSAMT method itself. Issues here include stability and accuracy of scalar versus tensor estimates, theoretical versus observed field patterns over the survey area, and controls on near-field effects defined using CSAMT and natural field data both inside and outside the caldera.

GRANTEE:	**VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY** Department of Geological Sciences Blacksburg, Virginia 24061
GRANT:	**DE-FG05-88ER13951**
TITLE:	**Zircons and Fluids: An Experimental Investigation with Applications for Radioactive Waste Storage**
PERSON IN CHARGE:	**A. K. Sinha** (703-231-5580; FAX 703-231-3386; E-mail GEOLSCI@VTVM1 (Bitnet)) and **K. L. Chyi**

Although experiments on the hydrothermal stability of $ZrSiO_4$ are still in progress, we have begun to develop the physical correlation between volume expansion associated with alpha decay and induced stress. We have gathered new analytical data that draw a relationship between development of "hot spots" due to incorporation of radioactive waste (in $ZrSiO_4$ host), volume expansion due to metamictization, and increase in porosity/permeability associated with the development of fractures.

Density and sonic velocities have been measured on large single crystals (4 cm to 8 cm along c-axis) on loan from the Smithsonian Museum, Washington, D.C. Calculated Vp and Vs in km/sec range from 5.561/2.860 to 8.222/4.456, and bulk modulus varies from 1.888 to 0.813. The lower velocity is probably attributed to fractures present in the crystal. Using a published value of 5.07% volume change associated with total metamictization, and assuming a spherical geometry with a core region undergoing volume change, we have calculated both radial normal stress and tangential normal stress values for concentric spherical geometry (where inner radius (A) is the metamict domain and radius (B) is the original sphere radius). Calculated values of pressure at the contact of the two spheres can be as high as 450 Mpa. Using an assumed value of 0.5% of the Young's modulus values of zircons as representing failure stress values, a volume expansion of 0.7% will induce a pressure of 1.4×10^{10} dyn/cm^2 at the contact between the concentrically zoned sphere and can easily generate fractures in zircons.

The current research program is integrating physical and chemical data that will provide a comprehensive model of the stability of $ZrSiO_4$ as a host for radioactive waste.

GRANTEE:	**VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY** Fluids Research Laboratory Department of Geological Sciences Blacksburg, Virginia 24061

GRANT:	**DE-FG05-89ER14065**

TITLE:	**PVTX Properties of Fluid Systems: $NaCl\text{-}CaCl_2\text{-}H_2O$**

PERSON IN CHARGE:	**R. J. Bodnar** (703-231-7455; FAX 703-231-3386; E-mail: RJB@VTVM2), **J. M. Simonson, and C. S. Oakes**

Most geologic processes occurring in the Earth's crust proceed in the presence of one or more fluid phases. In order to better understand the important role that fluids play in controlling the magnitude and extent of mass and energy transfer in the crust requires knowledge of the physical and thermochemical properties of fluids present. The long-term goals of this research program are to experimentally determine the phase equilibrium (PTX) and volumetric (PVT) properties of geologically relevant fluids over the complete range of crustal PTX conditions. These data provide the basic information required to (1) interpret natural fluid inclusions trapped in crustal rocks and (2) develop empirical to semi-theoretical equations of state to predict thermodynamic properties of fluids.

Our current research efforts are focused on the geologically important $NaCl\text{-}CaCl_2\text{-}H_2O$ system. Fluids approximated by the $NaCl\text{-}CaCl_2\text{-}H_2O$ system include basinal brines associated with many hydrocarbon occurrences and many terrestrial geothermal systems, such as the Salton Sea geothermal system in California. Our data will permit workers to refine fluid-flow and fluid-rock interaction models related to hydrocarbon occurrences and will provide geothermal energy producers with basic information required to predict conditions for optimum energy output from geothermal systems and to avoid potential problems related to corrosion and salt precipitation in power plants.

Phase equilibrium and volumetric properties of $NaCl\text{-}CaCl_2\text{-}H_2O$ fluids are being determined using synthetic fluid inclusions trapped at known PTX conditions, combined with information obtained using a vibrating U-tube densimeter. Experiments are being conducted at Virginia Tech and at the Chemistry Division of Oak Ridge National Laboratory. Upon completion of the experimental portion of this study, the data will be used to develop an equation of state for the $NaCl\text{-}CaCl_2\text{-}H_2O$ system that will permit thermodynamic properties to be calculated over a significant portion of crustal PTX conditions.

GRANTEE:	**UNIVERSITY OF WASHINGTON** Geophysics Program Seattle, Washington 98195
GRANT:	**DE-FG06-89ER14064**
TITLE:	**Two- and Three-Dimensional Magnetotelluric Inversion**
PERSON IN CHARGE:	**J. R. Booker** (206-543-9492; FAX 206-543-0489; E-mail booker@geophys.washington.edu)

We have developed a fast algorithm to invert large magnetotelluric (MT) data sets for multi-dimensional structure. The method is iterative and approximates lateral derivatives of the electric and magnetic fields inside the model by their values from the previous iteration. This leads to "pseudo-1-D" inverse problems at each measurement site that can be solved very efficiently. The pseudo-1-D inversions are interpolated to form an improved multi-dimensional model, and the multi-dimensional forward problem is solved to improve the fields for the next iteration. This cycle is repeated until a measure of model complexity is minimized subject to a specified misfit to the data. At convergence, we have a solution to the fully multi-dimensional inverse problem. We call the method the Rapid Relaxation Inverse (RRI). A two-dimensional (2-D) code, including color animation of the convergence, has been installed at the USGS and is being released more generally.

Our effort has been split between improving the 2-D code and developing a three-dimensional (3-D) version. We have developed inversion strategies to remove distortions to 2-D inversions due to near-surface 3-D effects. We have also developed an FDA for the forward problem that permits boundaries between discrete media to have an arbitrary spatial relation to the node network. This can be used to incorporate surface topography in the inversion. We have done the theory for pseudo-1-D partial derivatives that explicitly account for the charges that build up at long period in laterally varying media. This can improve the accuracy of TM mode inversions. We have also developed the theory necessary to inclusion of the vertical magnetic field in the inversion. The key to RRI is that MT data are strongly affected by perturbations in the structure directly beneath each site. Vertical field data do not obviously have this property. We have therefore developed a method to combine data from several adjacent sites to form a new datum that is suitable for the pseudo-1-D approach of RRI.

RRI can be generalized to 3-D by replacing the 2-D interpolation and forward modeling steps by their 3-D equivalents. We have developed an iterative solution to the 3-D forward problem of calculating the electric and magnetic fields in a smoothly varying but otherwise arbitrary conductivity model that is numerically very efficient. The matrices generated are not as sparse as for 2-D (12 as opposed to 5 non-zero diagonals), and a different iterative scheme (pre-conditioning by Incomplete Cholesky factorization of Conjugate Gradients, ICCG) has proven more efficient than Incomplete Lower-Upper (ILU) decomposition used for 2-D. However, we have found that our code fails to correctly calculate the charge accumulations produced by lateral gradients of conductivity. This failure manifests itself as a failure of current conservation and is generic to FDA and finite element methods. We have developed a strategy to enforce current conservation by embedding a solution using an approximate Greens function technique within the ICCG iterations.

GRANTEE:	**WASHINGTON STATE UNIVERSITY** Department of Geology Pullman, Washington 99164
GRANT:	**DE-FG06-91ER14172**
TITLE:	**Origin of Flood-Basalt Volcanism on the Columbia Plateau: An Integrated Approach Using Geology, Geophysics, and Petrology**
PERSON IN CHARGE:	**S. P. Reidel** (509-335-7621, -3009; FTS 444-9932; FAX 509-335-7816)

This study is being done in collaboration with the Westinghouse Hanford Co.

Continental flood-basalt volcanism, although relatively rare in the geologic record, is an important part of the evolution of the Earth, Moon, and the terrestrial planets. The massive outpourings of basaltic lava over relatively short periods of time present a formidable problem as to the thermal tectonic conditions that trigger the eruptions and the physical and chemical processes that govern the evolution of the lava flows.

One of the best known and most extensively studied flood-basalts is the Columbia River Basalt Group of the Pacific Northwest. The principal objective of this investigation is to contribute to understanding flood-basalt volcanism by analyzing and integrating a large geological and geophysical data set obtained as part of previous U.S. DOE projects on the Columbia Plateau. The goal of this research is to develop a comprehensive volcanic and tectonic model of this major eruptive event.

In order to achieve this objective, five major areas of study will be undertaken: (1) a study of the Columbia River Basalt Group, with emphasis on the main eruptive unit, the Grande Ronde Basalt, which was an outpouring of 148,600 km^3 of basalt in about 1.5 million years; (2) the structural development of the Columbia Plateau before, during, and after the eruption of the Columbia River Basalt Group; (3) the timing and rates of structural deformation on the Columbia Plateau and their relationships to the timing and rates of eruption of the Columbia River Basalt Group; (4) an assessment of the tectonic implications of paleomagnetic and other geophysical data; and (5) a synthesis of these studies with previous studies on volcanism and tectonism in the Columbia Plateau and Pacific Northwest.

This study also will provide information relevant to important geologic problems on the Columbia Plateau, such as ground-water resources and the hydrocarbon potential of the Columbia Basin, one of the largest frontier petroleum provinces in the continental United States. Detailed data on the nature of flood-basalt volcanism and the style of deformation associated with it will be invaluable to the present planetary science missions that are dedicated to improving our understanding of the geologic evolution of Mars and Venus.

GRANTEE: WASHINGTON STATE UNIVERSITY TRI-CITIES
Department of Environmental Sciences
Richland, Washington 99352

GRANT: DE-FG06-91ER14217

TITLE: **Transport in Porous and Fractured Media of the Creede Formation**

PERSON IN CHARGE: J. L. Conca (509-375-3268/4787; FAX 509-375-4838)

The objective of this investigation is to determine the hydrologic transport parameters of Creede formation rocks for use in transport model development and for image analysis of transport pathways to produce a porosity/permeability evolution curve to support geochemical and isotopic water/rock interaction models. The ultimate goal of research drilling in the Creede mining district is characterization of the paleohydrologic cycle and mass transfer environment in the Creede hydrothermal system. This goal requires knowledge of the transport parameters of the media with respect to the fluids, species, and conditions of interest. The hydraulic conductivity, K, and diffusion coefficient, D, are key input parameters to existing and developing models of mass transport that have traditionally been difficult to measure directly in fractured and porous media, and have generally been inferred from porosity information. In addition, the actual transport pathways in the fractured media are also inferred from hand specimen and thin section analysis, and not directly determined. This study proposes to directly measure the hydraulic conductivity, the diffusion coefficient, and the actual fluid flow paths in rocks of the Creede area for use in transport model development and for image analysis of transport pathways. Samples will include host rocks of varying degrees of mineralization to establish changes in transport properties as a function of time and position in the hydrothermal system. Results of this study will also be applicable to remediation and site restoration of mining areas where predictive models of mass transport and contaminant release require transport parameters for these materials and where development of remediation technologies and strategies require material properties. Results will contribute to general theories for porosity-controlled hydrothermal ore deposition in caldera complexes.

GRANTEE:	**UNIVERSITY OF WISCONSIN** Department of Geology and Geophysics Madison, Wisconsin 53706
GRANT:	**DE-FG02-84ER13184**
TITLE:	**Thermal Stress Microfracturing of Crystalline and Sedimentary Rock**
PERSON IN CHARGE:	**H. F. Wang** (608-262-5932; FAX 608-262-0693; E-mail wang@geology.wisc.edu)

The goal of this research program is to understand mechanisms of thermal cracking in granitic and sedimentary rocks. Slow uniform heating of crustal rocks is both a pervasive geologic process and an anticipated by-product of radioactive waste disposal. A fracture mechanics model has been applied to quantify the cracking mechanism in thermally cycled granites. The numerical model has the potential to predict cracking events as a function of temperature and confining pressure. Numerical simulations were performed to evaluate the roles of thermal expansion anisotropy and volumetric thermal expansion mismatch in the grain boundary microfracture of granite. The simulations employed a two-dimensional plane stress model consisting of four hexagonal, thermally anisotropic grains embedded in an infinite, elastic homogeneous, isotropic medium. In heating, the relatively small volumetric thermal expansion of feldspar grains along the facet face and the relatively large thermal expansion of quartz grains along either edge of the facet favor cracking. In cooling, the large volumetric contraction of quartz grains along the facet face and the relatively small contraction of feldspar grains along the facet edges favor cracking. The simulations yield percentages of cracked facets as a function of pressure and temperature that match acoustic emission events and crack density counts obtained previously for Westerly granite.

Healed cracks are commonly found in the quartz phase of igneous and metamorphic rocks. They have one or more preferred orientations, which indicate the direction of the paleostress field during their formation. The micromechanical, four-grain model was used to simulate intragranular cracks produced during primary cooling of a granitic pluton in an anisotropic stress field. The sharpness of the distribution peak increases with the ratio of the maximum to minimum horizontal stress. When applied to data on Precambrian granites from Wisconsin and Illinois, the micromechanical model suggests that the stress ratio was four. The healed crack orientations are useful indicators of the paleostress field and may be used as a tool for orienting core that has undergone the same stress history as a control.

GRANTEE: WOODS HOLE OCEANOGRAPHIC INSTITUTION
Department of Chemistry
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 508-457-2193; E-mail jwhelan@red.whoi.edu)

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. We are the principal organic geochemical arm of a recently formed Global Basin Research Network (GBRN), an ambitious attempt to create 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.

The GBRN has developed as a major scientific initiative involving a consortium of eight university partners and 11 corporate affiliates representing a variety of geological and geochemical expertise. Formed in 1989, GBRN is using coastal regions of the Gulf of Mexico as a focal point of investigation to produce a model on the supercomputer at Cornell University that explains the fluid migration, past and present, and to test this integrated model against an observational database gathered over the last 50 years by oil and mineral companies as well as universities. The overall goal of the GBRN is to develop a general modeling-observational approach that is applicable to any basin.

The Woods Hole organic geochemical group is currently working on two specific tasks for the GBRN. First, we are inserting the extensive data base on Gulf Coast gas and oil compositionals gathered by the Texas A & M University Geochemical and Environmental Research Group into the GBRN "data cube." This three-dimensional computerized picture shows visually how reservoired oil and gas compositions relate to temperatures, pressures, salt topography, and sediment depocenters. Initial work has been completed for a 20 × 40 km area in the highly productive Eugene Island/S. Marsh Island area. Contours of this initial limited hydrocarbon data set are remarkably consistent with the superimposed geothermal, geopressure, and salinity data in showing a "hot spot" at Eugene Island Block 330, where gas condensate may be squirting upward in the vicinity of a fault at the present time.

The second part of the Woods Hole effort is to obtain kinetic parameters for gas generation and expulsion processes using high pressure isothermal heating experiments of potential Alaskan N. Slope and Gulf Coast source rocks by means of procedures similar to hydrous pyrolysis. The resulting kinetic parameters will be plugged into the GBRN computer model currently under development at Cornell. Our high pressure apparatus is different from any previously used to mimic oil and gas generation because of the elimination of the gas head space in the vessel by using an expandable gold bag. We are currently testing the system to see if this approach will yield field gas compositional and isotopic data better than previous hydrous pyrolysis experiments, because the gas is not allowed to escape from the reactive zone. Thus this approach should better reproduce the actual conditions found in the geological system.

GRANTEE:	**YALE UNIVERSITY** Department of Geology and Geophysics New Haven, Connecticut 06511
GRANT:	**DE-FG02-90ER14153**
TITLE:	**Reactive Fluid Flow and Applications to Diagenesis, Mineral Deposits, and Crustal Rocks**
PERSON IN CHARGE:	**A. C. Lasaga** (203-432-3114; FAX 203-432-3134) **and D. M. Rye**

This project is obtaining new results and developing new techniques along three directions: (a) experimental studies of water-rock reactions, (b) theoretical modeling of coupled fluid flow-chemical reactions, and (c) isotopic measurements of both regional isotopic compositions as well as isotopic zoning within individual mineral grains. An important part of the project is the integration of all three approaches into a concerted effort aimed at new understanding of the behavior of fluids and their chemical reactions with minerals in the crust.

The main thrust of the theoretical modeling has been to develop further 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. We have found that the mixing of fluids in two-dimensional models (from processes such as dispersion) has profoundly different chemical patterns from those found in the one-dimensional models.

We are applying the two-dimensional code 2DREACT to the study of reactive flow in hydrothermal systems. The code calculates heat transfer and hydrodynamic flow in a convecting hydrothermal system, and these calculations are then coupled to those of reactive transport. A novel feature is full basis switching within the finite difference scheme. A new method was developed whereby it is possible to write the reactions at each grid point in terms of the dominant species (and the dominant redox couple) and to correct the fluxes between adjacent grid points where the reactions are written using different basis sets. The code has been run with as many as 42 aqueous species (13 of which are actually independent), 18 minerals, and 800 grid points, although most runs have been carried out with 400 grid points. We have carried out the simulations for as long as 50,000 years using time steps ranging up to 5 years.

Our results indicate that substantial reaction occurs before a hydrodynamic steady state is attained. This observation is particularly important because the reactions may result in a change in the permeability of the medium. We are studying this problem by comparing simulations with and without porosity/permeability change due to mineral dissolution and precipitation reactions. The results are very sensitive to the initial diameter of the fractures (i.e., the hydraulic radius), but as an example, for an initial porosity of 1% and a permeability of 3 mD, we find an order of magnitude increase in the permeability of the medium in the initial stages of the hydrothermal system even over relatively short time scales.

As a first step in using isotopic data in metamorphic systems, we have developed one-dimensional isothermal steady-state flow path isotopic exchange models for both veins and wall rocks. These models incorporate diffusion, advection, and isotopic exchange (assuming first order kinetics). We find that even for relatively rapid isotopic exchange rates and small fluid fluxes, significant oxygen isotope disequilibrium between fluid and wall rock can be maintained for long distances for long periods of time along the flow path. The model has been used to interpret a set of oxygen isotope data from veins and wall rocks from the Wepawaug Schist of south-central Connecticut.

TABLE 1
DOE/OBES GEOSCIENCES RESEARCH
HISTORICAL SUMMARY
(OPERATING FUNDS - THOUSANDS)

ON-SITE	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	FY 1990	FY 1991
ANL	$ 330	$ 330	$ 360	$ 360	$ 355	$ 340	$ 335	$ 440	$ 454	$ 385
BNL	-	-	-	-	-	-	50	90	49	-
LANL	1,375	1,684	2,343	2,289	2,263	2,603	2,868	2,638	2,613	2,518
LBL	1,180	1,405	1,485	1,596	1,632	2,162	2,100	2,265	2,372	2,109
LLNL	1,110	1,280	1,815	1,898	1,521	1,837	1,732	2,121	2,169	2,103
ORNL	430	430	470	480	492	690	785	944	1,226	1,097
PNL	520	520	578	595	605	725	850	848	819	735
SNL/A	1,546	1,682	2,087	1,861	2,256	2,462	2,711	2,213	1,828	2,167
WHL	-	-	-	-	-	-	-	-	-	44
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TOTAL ON-SITE	6,491	7,331	9,138	9,079	9,124	10,819	11,431	11,559	11,530	11,158
TOTAL OFF-SITE	3,141	4,523	3,308	4,260	3,508	4,453	4,868	5,755	5,685	5,987
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TOTAL OPERATING	9,632	11,854	12,446	13,339	12,632	15,272	16,299	17,314	17,215	17,145
TOTAL EQUIPMENT	900	890	960	1,100	1,094	1,150	1,150	1,150	1,150	1,110
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TOTAL GEOSCIENCES	$10,532	$12,744	$13,406	$14,439	$13,726	$16,422	$17,449	$18,464	$18,365	$18,255

TABLE 2
DOE/OBES GEOSCIENCES RESEARCH
HISTORICAL SUMMARY/OFF-SITE
(OPERATING FUNDS - THOUSANDS)

INSTITUTION (PI)	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	FY 1990	FY 1991
U/Alaska (Lee)	$ 113	$ 117	$ 120	$ 126	$ 126	$ 128	$ 140	$ 143	$ 140	$ 145
Am. Geophys. Union (Spilhaus)	-	-	-	-	-	-	-	5	-	-
U/Arizona (Anovitz)	-	-	-	-	-	-	-	-	60	47
U/Arizona (Hill)	99	101	90	121	-	101	103	121	120	126
U/Arizona (Norton)	60	48	-	-	-	-	-	-	-	-
Arizona St. (Fink)*	-	-	-	22	23	11	-	-	-	-
Arizona St. (Navrotsky)	66	123	-	-	-	-	-	-	-	-
Arizona St. (Williams)	-	-	-	-	-	-	-	-	-	108
Bechtel (Harper)	-	-	-	-	25	-	-	-	-	-
Brown U (Hermance)*	165	333	-	166	-	150	150	-	-	-
Brown U (Yund)	-	-	-	-	-	-	-	-	70	71
Cal Tech (Ahrens)*	-	72	81	160	-	150	100	-	-	-
Cal Tech (Stolper)	-	-	-	50	98	-	78	82	85	87
Cal Tech (Wasserburg)	-	-	-	-	-	-	200	250	250	300
U/California-B (Carmichael)	-	-	-	-	-	-	-	-	-	117
U/California-B (Helgeson)	-	204	-	120	120	135	116	121	120	135
U/California-B (Reynolds)	150	165	196	233	200	200	210	236	245	245
U/California-LA (Anderson)	-	-	60	74	-	23	-	-	-	-
U/California-LA (Boehler)	-	60	66	75	-	-	-	-	-	-
U/California-LA (Ernst)	-	-	-	-	-	64	69	-	-	-
U/California-LA (Harrison)	-	-	-	-	-	-	-	54	54	54
U/California-LA (McKeegan)	-	-	-	-	-	-	-	-	-	64
U/California-R (McKibben)*	-	-	-	50	-	40	-	77	49	-
U/California-SB (Spera)	-	-	-	-	-	-	-	64	47	101
U/California-SD (Chave)	-	-	-	-	-	120	-	-	-	-
U/California-SD (Craig)	-	-	35	41	41	42	35	-	-	-
U/California-SD (Harding)	-	-	-	-	-	-	-	63	-	-
U/Chicago (Anderson)	38	98	NFX	46	-	-	-	-	-	-
U/Colorado-B (Spetzler)	-	-	-	-	-	95	87	91	NFX	50
Colo Sch Mines (Cross)	-	-	-	-	-	-	10	-	-	-
Colo Sch Mines (Larner)	-	-	-	-	-	-	-	192	195	200

TABLE 2 (CONTINUED)

(OPERATING FUNDS - THOUSANDS)

INSTITUTION (PI)	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	FY 1990	FY 1991
Columbia U (Engelder)	156	289	-	150	75	-	-	-	-	-
Columbia U (Jacob)	318	337	359	360	360	360	360	290	203	-
Columbia U (Walker)	-	-	73	79	106	-	85	90	127	127
U/Conn (Torgerson)	-	-	-	-	-	-	-	-	4	-
U/Delaware (Wood)	-	-	-	-	-	-	-	62	56	67
DOSECC (Barber)	-	-	-	6	-	-	66	-	-	-
DOSECC (Friedman)*	-	-	-	-	-	-	-	-	65	70
Geochem Res Assoc (Ortoleva)	-	-	-	-	-	50	100	-	-	-
Harvard U (Thompson)	-	372	-	115	-	18	-	-	-	-
U/Hawaii (Manghnani)	88	96	99	200	-	100	100	-	-	-
U/Houston (Chafetz)	-	-	-	-	-	69	-	-	-	-
U/Houston (McDonald)	-	-	-	-	-	-	-	273	295	221
Headquarters Services	6	1	3	15	5	3	3	3	5	2
Indiana U (Hayes)	-	-	-	-	-	-	186	162	150	NFX
Indiana U (Ortoleva)	-	-	-	-	-	-	-	-	-	80
Johns Hopkins U (Veblen)	-	-	-	-	-	-	-	63	66	135
Louisiana St. (Ferrell)	-	-	-	-	-	60	59	64	NFX	127
U/Maryland (Valette-Silver)	-	-	-	43	-	-	-	-	-	-
Michigan St. (Vogel)*	-	-	-	31	31	34	-	-	-	-
Michigan Tech. (McDowell)*	-	-	-	50	-	-	-	-	-	-
U/Minnesota (Johnson)	57	-	-	-	-	-	-	-	-	-
U/Minnesota (Yuen)	-	-	-	-	-	-	-	48	42	102
MIT (Aki)	151	158	147	-	-	-	-	-	-	-
MIT (Simmons)	106	106	110	80	80	-	-	-	-	-
MIT (Toksoz)	-	-	-	-	142	-	113	370	498	485
Montana Bu. Mines & Tech. (Bartholomew)	-	-	-	-	-	-	8	-	-	9
NAS/NRC (Carter)	-	-	-	-	-	-	-	3	3	-
NAS/NRC (Hart/Long/Burke)	282	-	200	187	124	202	132	100	105	200
NAS/NRC (Corell)	-	-	-	-	-	-	5	-	-	-
Natl Ctr Atm Res (Herring)	-	-	-	-	-	10	-	-	-	-
NSF (Johnson)	-	-	-	-	-	-	-	30	-	-
NSF (Wright)	-	-	-	-	-	200	-	-	-	-
U/Nevada (Peppin)*	-	-	-	-	143	-	-	-	-	-
U/Nevada (Ryall)*	75	87	95	-	-	-	-	-	-	-
U/New Mexico (Papike)	-	-	-	-	-	-	-	-	200	-
CUNY-B (Friedman)	-	-	-	95	86	100	50	-	-	-
CUNY-Q (E. Schreiber)	81	49	-	116	-	-	-	-	-	-

TABLE 2 (CONTINUED)
(OPERATING FUNDS - THOUSANDS)

INSTITUTION (PI)	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	FY 1990	FY 1991
CUNY-Q (C. Schreiber)	-	-	-	-	-	-	101	105	NFX	119
SUNY-A (Harrison)	39	136	-	58	60	54	52	-	-	-
SUNY-P (Wolosz)	-	-	-	-	-	72	-	56	42	-
SUNY-SB (Hanson)	-	112	118	120	120	128	128	120	119	124
U/N Carolina (Glazner)	-	-	-	38	39	-	35	-	-	-
Ohio St. (Adler)	-	-	-	-	-	50	52	55	54	56
Ohio St. (Sahagian)	-	-	-	-	-	-	-	-	-	40
U/Oklahoma (Elmore)	-	-	-	-	-	-	-	-	-	109
U/Oklahoma (Engel)	-	-	-	-	-	-	-	112	106	-
U/Oklahoma (Philp)*	-	-	-	-	28	-	-	-	-	-
U/Oklahoma (Philp)	-	-	-	84	88	106	110	124	121	143
U/Oregon (Weill)	-	103	94	-	-	-	-	-	-	-
Oregon St. (Egbert)	-	-	-	-	-	-	-	43	41	-
Oregon St. (Fehler)	38	-	-	-	-	-	-	-	-	-
Penn St. (Given)	-	-	100	-	-	-	-	-	-	-
Princeton U (Navrotsky)	-	-	-	100	-	85	120	125	123	125
Princeton U (Onstott)	-	-	-	-	-	-	-	-	-	103
Princeton U (Phinney)	-	-	-	-	-	-	-	97	-	-
Purdue U (Aydin)	-	-	-	-	-	-	-	56	56	-
Purdue U (Fritz)	-	-	-	-	-	-	-	-	71	44
Purdue U (Hinze)	-	-	-	-	-	8	-	-	-	-
RPI (Friedman)	99	150	-	-	-	-	-	-	-	-
Rice U (Ave Lallement)	-	120	121	-	-	-	-	-	-	-
San Diego St. (Jiracek)	-	-	-	-	-	-	-	-	5	-
S Dakota Sch M&T (Papike)	67	100	130	150	99	100	105	115	-	-
U/S California (Aki)*	-	-	-	150	150	155	159	164	147	160
SMU (Blackwell)	70	-	-	-	-	-	-	-	-	-
Stanford U (Ernst)	-	-	-	-	-	-	-	-	100	101
Stanford U (Liou)	34	45	-	-	-	-	-	-	-	-
Stanford U (Nur)	125	160	172	172	165	165	170	175	328	-
Stanford U (Parks)	57	56	56	-	-	-	-	-	-	-
Stanford U (Pollard)*	-	-	-	39	42	44	70	73	30	-
Stanford U (Pollard)	-	-	-	-	-	-	-	79	75	183
Stanford U (Segall)	-	-	-	-	-	-	-	-	80	-
U/Rochester (Gove)	-	-	-	-	-	8	-	-	-	-
U/Texas-Arl (Self)*	-	-	-	43	NFX	80	-	-	-	-
U/Texas-Aus (Barker)	-	54	-	-	-	-	-	-	-	-
U/Texas-D (Mitterer)	-	-	-	-	-	-	-	-	119	112

TABLE 2 (CONTINUED)

(OPERATING FUNDS - THOUSANDS)

INSTITUTION (PI)	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	FY 1990	FY 1991
Texas A&M (Carlson)	-	-	-	-	98	-	-	-	-	-
Texas A&M (Carter)	-	-	70	-	-	-	-	-	-	-
Texas A&M (Dorobek)	-	-	-	-	-	52	55	57	-	-
Texas A&M (Friedman)	200	201	93	100	194	-	-	-	-	-
Texas A&M (Gilbert)	-	-	-	-	98	88	101	10	-	-
Texas A&M (Kronenberg)	-	-	-	-	-	117	156	197	149	143
U/Tulsa (Barker)	71	75	80	80	81	133	-	76	71	84
USGS (Morgan)	-	-	-	-	-	35	-	-	-	-
USGS (Russ)	-	-	-	-	-	-	-	12	-	137
USGS (Wesson)	-	-	-	-	-	-	6	-	-	-
U/Utah (Neilson)*	-	-	-	-	114	-	-	-	-	-
U/Utah (Hulen)*	-	-	-	-	-	-	125	-	85	126
U/Utah (Wannamaker)	-	-	-	-	-	-	-	91	-	-
VPI & SU (Bodnar)	-	-	-	-	-	-	-	114	78	-
VPI & SU (Sinha)	-	-	-	-	-	-	82	60	87	74
U/Washington (Booker)	-	-	-	-	27	30	-	78	81	-
U/Washington (Malone)	-	-	-	-	-	-	32	32	-	-
Wash. St.-R (Reidel)	-	-	-	-	-	-	-	-	-	45
Wash. St.-R (Thiessen)	-	-	-	-	-	103	-	-	-	-
Wash. St. Tri-Cities (Conca)	-	-	-	-	-	-	-	-	-	95
U/Wisconsin (Wang)	-	-	48	52	97	84	87	92	-	97
Woods Hole (Hunt)	150	190	208	-	-	-	-	-	-	-
Woods Hole (Whelan)	-	-	-	223	223	226	238	220	208	197
Woodward-Clyde (Burdick)*	100	100	100	40	-	-	-	-	-	-
U/Wyoming (Surdam)	-	-	-	-	-	65	65	-	-	-
Xdata (Dines)	54	66	-	-	-	-	-	-	-	-
Yale U (Gordon)	26	39	184	-	-	-	-	-	-	-
Yale U (Lasaga)	-	-	-	-	-	-	-	-	50	91
Other	-	-	-	-	-	-	254	160	5	4
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OFF-SITE TOTALS	$3,141	$4,523	$3,308	$4,260	$3,508	$4,453	$4,868	$5,755	$5,685	$5,987

*Continental Scientific Drilling Activity

TOPICAL INDEX

GEOLOGY, GEOPHYSICS, AND EARTH DYNAMICS

GEOCHEMISTRY

ENERGY RESOURCE RECOGNITION, EVALUATION, AND DEVELOPMENT

SOLAR, SOLAR-TERRESTRIAL, AND ATMOSPHERIC INTERACTIONS

INDEX OF TECHNICAL CONTRIBUTORS

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