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Summaries of Physical Research in the Geosciences

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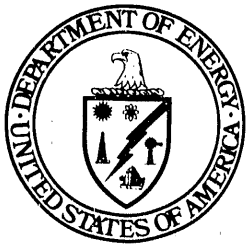

U.S. Department of Energy
Office of Energy Research
Division of Engineering & Geosciences
Washington, D.C. 20585

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, industry, universities, 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 content 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, university, college, corporate, not-for-profit, and other Federal agency laboratories supported by this program frequently have components in more than one of the categories or subcategories listed.

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. Tectonic Evolution of the Midcontinent Rift System *(L. D. McGinnis [708-972-8722; FAX 708-972-7819; E-mail B35698@ANLEES.Bitnet])*

This program involves a study of the dynamics of Precambrian rifting and its processes relative to the production and preservation of hydrocarbons in the Midcontinent Rift (MCR). Sedimentary basins of rift origin are noted world-wide for their hydrocarbon productivity. Rift basins of Precambrian age have only recently been recognized as potential sources of hydrocarbons, following their discovery and exploitation on other continents. Although petroleum reserves have not been identified along the Midcontinent Rift System, oil seeps emanate from the Nonesuch Shale in the White Pine mine on the Keweenaw Peninsula. Because the MCR is the best preserved and largest example of Precambrian rifting on earth, it is also integral to fundamental research on continental evolution.

An orthogonal grid of 1837 line kilometers of seismic reflection, gravity, and magnetic profiles in Lake Superior (which comprises 20% of the total area of the MCR) has been acquired. This comprehensive data set permits unique solutions to problems of structure and stratigraphy beneath the lake. Analysis of the data has led to the discovery of several distinct basins and interconnecting troughs, a large anticline, and major boundary faults and folds. In addition, locations and characteristics of previously known boundary faults have been revised.

Lake Superior is underlain by a continuous series of rift basins having variable width and depth, that descend to more than 24 km in places. A newly discovered basin, east of the primary axial trend, is separated from the continuous series of basins by a narrow arch at the far eastern end of the lake. The basins are filled partially with sediments and volcanic flows of Keweenawan age (~1.1 billion years) resting on older basement. The rift is associated with as many as four major strike faults. Strike faults and hinge lines form the graben boundary. These lineaments were reactivated during late Keweenawan plate convergence, so their latest record of activity involves folding, thrusting, and crustal shortening of 30 to 40 km.

Contractor:	ARGONNE NATIONAL LABORATORY Argonne, Illinois 60439
Contract:	109 ENG 38
Category:	Geochemistry
Person in Charge:	N. C. Sturchio

A. Hydrothermal System Evolution *(N. C. Sturchio [708-972-3986; FAX 708-972-5287; E-mail B33251@ANLCMT.Bitnet])*

The objective of this program is to achieve a better understanding of water-rock interactions that occur in shallow portions of the Earth's crust, with emphasis on the sources of hydrothermal fluids and their dissolved components, the rates and mechanisms of hydrothermal transport processes, and the relation of hydrothermal systems to larger-scale tectonomagmatic and climatic processes. These problems are approached through field-based studies that involve detailed elemental and isotopic analysis of the materials comprising natural hydrothermal systems. Such work is of basic importance to a variety of energy-related concerns involving mass transport in groundwater systems.

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

Recent work at Yellowstone has centered on thermal waters and travertine deposits in the northern part of the park. The isotopic systematics of B, S, Sr, Ra, and U have been defined from analysis of numerous representative thermal water discharges. Potential applications of Ra isotopes for age determinations of travertines were investigated through studies of the terraces at Mammoth Hot Springs. Ages of numerous travertine deposits in the area have been determined by the ^{230}Th-^{234}U method; their geologic relations with glacial deposits, and certain aspects of their elemental and isotopic composition, are being examined. These data will establish the glacial chronology in the area, as well as the influence of glaciation on, and the spatial and temporal continuity of, the hydrothermal circulation system.

Age determinations of hot spring deposits in the Long Valley caldera provide evidence for substantial episodes of thermal water discharge at >250 ka and at <40 ka, but not during intervening time. These results support thermal models involving an early heat source associated with the resurgent dome and a later heat source associated with volcanic activity in the western moat.

Volcanic hydrothermal systems in Colombia are being studied in collaboration with volcanologists from Louisiana State University, INGEOMINAS (Colombia), and the University of Tokyo. Analyses of thermal water and fumarolic steam from Galeras Volcano have shown evidence for increased volatile input from recent magmatic resurgence that may be premonitory

to an eruption. Studies at Purace Volcano have established both the nature of hydrothermal circulation within the volcano and the origin of the sulfur deposit at El Vinagre mine.

B. Deep Carbon Geochemistry *(T. Abrajano [708-972-4261; FAX 708-972-5287; E-mail B34538@ANLCMT.Bitnet] and B. D. Holt)*

Our present studies are designed to elucidate the process of organic matter alteration in high temperature (metagenic) environments. 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. Field-based studies of carbonaceous sediments that were metagenically altered by magmatic activity are being pursued. Laboratory step-combustion experiments on kerogen are being performed to understand the mechanism and magnitude of isotopic fractionation that may be experienced by carbonaceous materials in metagenic environments.

Our principal approach is to study the process of organic matter alteration in "fossil" magma-sediment systems through detailed mineralogic, organic geochemical, and isotopic studies of samples collected from drill cores, quarry exposures, and natural outcrops. Initial work has focused on the carbonaceous formations from the Early Proterozoic Animikie Basin (Minnesota) that were variably metamorphosed by the emplacement of the Duluth Complex (1.1 Ga). In this system, extensive dehydration and decarbonation of metamorphosed Animikie Basin sediments are indicated by the systematic conversion of hydrated silicates and carbonates to anhydrous silicates and the relatively low amounts of total carbonate carbon in samples collected closer to the intrusion. The highly variable $\delta^{13}C_{carbonate}$ (–13.7 to –3.6 ‰) and $\delta^{18}O_{carbonate}$ (12.0 to 23.8 ‰) values measured for the residual carbonates appear to reflect primary variations that are unrelated to metamorphism. In contrast to the depletion of carbonate carbon, the total "organic" carbon content (polycondensed residual carbon plus graphite) of the highly carbonaceous Intermediate Slate Unit of the Biwabik Iron Formation showed a clear enrichment within the thermal aureole of the intrusion. This enrichment may reflect mobilization of hydrocarbon residues in response to the thermal conditions imposed by the emplacement of the Duluth Complex. Similar studies of the Mesozoic Deep River (North Carolina) and Culpeper (Virginia) Basins are also underway.

As a complementary approach, we are interested in simulating the metagenic alteration of carbonaceous materials in the laboratory, where environmental conditions can be controlled. For example, the total yields and isotopic compositions of carbon species released during step-combustion experiments on Green River kerogen were investigated (parallel pyrolysis/GC/MS experiments are also in progress). A bimodal total carbon release pattern was observed from 220°C to over 600°C, with CO_2 dominating the overall yield (CO and unoxidized hydrocarbons comprise the balance). Carbon isotopic compositions measured for the entire temperature range vary by 5 ‰ (CO_2) to as much as 15 ‰ (CO). Both the yields and isotopic compositions at each temperature step were invariant for heating durations beyond a few hours. These results imply that isotopic fractionation could accompany systematic destruction of individual kerogen functional groups in metagenic environments.

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Contract:	DE-AC02-76CH00016; AS-132-AAP
Category:	Geochemistry
Person in Charge:	K. W. Jones

A. Trace-Element Microdistribution in Coal *(K. W. Jones [516-282-4588] and A. Kolker [516-282-2229])*

Focused synchrotron radiation is being used for fine scale (≤ 10 micron) x-ray fluorescence analysis of a range of trace elements in coal samples from the Illinois Basin, the San Juan and Raton Basins of New Mexico, and the Appalachian Foreland Basin of Pennyslvania. By analyzing coal components that formed at different stages of diagenesis, emphasis is placed on understanding the diagenetic and coalification history of a given basin. By analyzing fracture-filling minerals that precipitated from basin fluids, changes in the trace-element chemistry of these fluids can be traced. In addition to its implications for understanding coal genesis, this technique is an important new method for assessing coal quality.

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, N. E. Goldstein, K. H. Lee [415-642-3804; FAX 415-486-5686; E-mail kiha@lbl.gov], and H. F. Morrison, 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. Two facilities provide data for the initial testing of such numerical algorithms: (1) an EM scale model facility and (2) a small scale field test facility at the Richmond Field Station, University of California.

The scale model consists of a container of size 9' × 15' × 4' filled with 10 S/m salt water. Graphite blocks are used as targets, and an array of transmitter and receiver coils is used to measure the resulting magnetic fields. The system has been designed such that data are collected while the transmitter moves continuously and the receivers are in a fixed position. This provides for both low noise measurements and relatively quick acquisition.

For the small scale field experiment more than 20,000 gallons of seawater will be injected into a shallow underground aquifer and the associated change in subsurface conductivity will be monitored with EM measurements in boreholes spaced 50 meters apart, straddling the injection well. The crosshole EM system consists of a borehole transmitter and a computer controlled receiver section. The crosshole survey will utilize multiple transmitter and receiver positions for a total of more than 400 separate measurements. A complete set of data will be collected before injection begins and daily during the saltwater injection and withdrawal. Numerical modeling calculations have indicated that the field data need to be repeatable to within 1 percent to permit imaging of the saltwater plume. Preliminary field measurements have shown that this level of accuracy is achievable with this field system.

B. Center for Computational Seismology *(T. V. McEvilly and E. L. Majer [415-486-6709; FAX 415-486-5686; E-mail elmajer@lbl.gov])*

Continuing base level support of CCS has provided a facility which has aided not only BES programs but other DOE, government, and private industry cooperative ventures. CCS offers 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.

During the last year the CONVEX C-1/XP was augmented by a Solbourne 602. The Solbourne is a dual processor (upgradable to four processors) machine running a SUN UNIX (UNIX is a Bell

labs trademark) operating system. This machine will act as a file server for work stations and as a pre- and post-processor for the CONVEX. Graphics and text processing, in addition to light computational duties, will now be done on the Solbourne, which has a capacity of 50 MIPS and 10 Mflops. During the last year full use was made of the CONVEX C-1/XP computer, with down time averaging a few hours per month, including routine maintenance. An additional 4 Gbytes of disk space was added to bring the capacity to over 10 Gbytes.

On the scientific front, CCS continued support of the Cajon Pass project in the interpretation of the VSP data, CALCRUST, and several projects for the DOE nuclear waste program. In these projects significant progress has been made in the areas of the application of seismic tomography for the imaging of fractured rocks and in using VSP data for the detection of anisotropy.

Some examples of CCS's role in seismic research are (supporting agency given in parenthesis):

(a) A facility to analyze seismic data for CSDP and thermal regimes programs as well as other BES projects at LBL and other national laboratories (BES)

(b) Development of seismic exploration and monitoring techniques for the geothermal industry (DOE geothermal and private industry)

(d) Fracture detection research using VSP/tomographic techniques (DOE geothermal, waste isolation, and private industry)

(f) Data processing center for CALCRUST: a consortium of four universities using seismic reflection methods for intermediate and deep crustal structural analysis (NSF and private industry).

(g) A base of computational support for software and hardware development of field systems for seismic monitoring (BES, DOE geothermal, waste isolation, private industry).

Presently there are over 60 routine users on CCS. Ninety-two scientific publications have been produced with CCS report numbers.

C. Microcrack Growth in Crystalline Rock *(L. R. Myer [415-486-6456; FAX 415-486-5686; E-mail mcevilly@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 problem requiring knowledge of the mechanical properties of rock masses.

Previous theoretical work resulted in new crack models which 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 to investigate crack interaction in failing rock have been carried out.

In FY 1989 this previous work was extended to a study of the microstructure of rock during indentation experiments. Such experiments are important to understanding the mechanisms of rock failure associated with drilling processes. The experiments focused on evaluating the relative contribution of pore collapse and chip formation to failure of the rock beneath the indentor. Tests were carried out on a sample of highly porous refractory brick, in which failure

was solely by pore collapse, and samples of limestone and Berea sandstone. For both rocks there was a region of compaction beneath the inductor. The region was more extensive and more clearly defined in the sandstone. For the sandstone this compaction zone was formed by extensively broken quartz grains which gradually increased in size as the external boundary was approached. Debris from the broken grains filled the pore spaces. Microcracking outside the compaction zone was observed in both rocks but was more prevalent in the limestone.

Results indicated that during indentation the mechanism of failure of porous rock under large hydrostatic stress is controlled by pore collapse and compaction. When indentation begins, pore collapse predominates. Once a compaction zone is created in the material, this zone acts as a nucleus of expansion, introducing tensile stresses in the material surrounding the compacted zone and thus developing other mechanisms of failure. Outside the boundary of the compacted zone, the overall failure of the material is no longer governed by the details of stress field under the indenter but instead by the stress field imposed in the material by the expanding compaction zone.

D. Process Definition in Fractured Hydrocarbon Reservoirs *(L. R. Myer [415-486-6456; FAX 415-486-5686; E-mail mcevilly@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 single fracture networks of heterogeneous geometry, and hardware development for seismic imaging.

The first phase of laboratory tests to study the effects of thin liquid layers on transmission of seismic waves across a single fracture was completed. These tests indicated that chemical interactions at the solid-liquid interface, in addition to liquid viscosity and film thickness, strongly affect the amplitude of the transmitted shear wave. The nature of the interactions is now being investigated in more detail.

Laboratory measurements of fluid flow in a single fracture were also undertaken. The purpose of these tests was to investigate the effect of tortuosity on flow through a natural fracture. Measurements were carried out on a siltstone sample obtained from a petroleum reservoir. The geometry was such that linear flow conditions could be maintained in the single fracture. Flow measurements were made over a range of apertures, from conditions where the two surfaces of the fracture were mechanically held apart by shims up to 0.01 inch thick, to conditions where the two surfaces were in contact and under moderate stress. Analysis of the flow measurements revealed deviations from ideal "cubic law" behavior over a wide range of apertures. By cubic law is meant that flow is proportional to the cube of the fracture aperture. Flow rates in the tests with surfaces held apart were slower than those predicted by the cubic law; the difference was nearly constant for six different apertures. When the fracture surfaces were in contact and under low stress the flow rate was not proportional to the cube of the mechanical aperture, but instead to a higher and variable power. At the highest stress levels flow rate asymptotically approaches a constant value independent of further decreases in mechanical aperture. Departure from the cubic equation for all measurements except those at the highest stress level is attributed to effects of tortuosity, which can be quantitatively related to the roughness of the fracture surfaces.

Diffraction tomography, a full waveform acoustic inversion technique, was developed and successfully applied to data from the Grimsel test site. The test site geometry permitted four sided coverage of a 10×21.5 m area. A new data processing scheme and 2.5-D corrections were developed in order for the inversion to be applicable to the data. For simplification the field data were also approximated by an acoustic medium, so that only P-wave data was inverted. The numerical results showed various fracture zones which correlated well with the core samples taken from the boundaries of the medium being imaged.

Work on electromagnetic diffusion tomography continued with the completion of a 3-D tomographic inversion code. This program was developed to evaluate the detection of tabular fractures illuminated by a dipolar alternating magnetic field. It provides for the use of a solenoidal transmitter in one borehole while the vertical component of the magnetic field is detected in another borehole some distance away. The code was verified for accuracy against other accepted numerical methods by using a specially assembled laboratory scale model. Numerical experiments with the new code indicate that one can realistically expect to map fractures in typical petroleum reservoirs. A full report on this subject constitutes the basis for a Ph.D. Thesis, completed in December 1989.

In the study of methods for integrating geophysical data into hydrologic models, work continued on development of an inversion technique called simulated annealing, which can be used to construct an equivalent discontinuum model for fractured rock which behaves in accord with the hydrologic test observations. Sensitivity analyses and a statistical method called cross-validation were used to assess model performance, with good results. Using a synthetic case, the algorithm converged to solutions with the same connectivity, independent of the connectivity of the initial configuration. This is important, since it implies that any solution will have approximately the same connectivity. Cross-validation was used to find an estimated prediction error for steady-state head values in the end solution given by the simulated annealing model. Work also began on a Bayesian interpretation of a fracture hydrology inverse model. In a second hydrologic study, theoretical approaches were developed to simulate transport in fractured media containing multiple fractures with variable apertures. These were applied to 3-D field data in a granitic fractured medium in Stripa, Sweden.

Finally, in the development of the down-hole shear wave source, the electronic feedback control system needed to check the drift of the driving coil was completed and made ready for bench testing. The coil is centered by using the amplified output of a control transformer chip. This chip compares the instantaneous position of the coil as sensed by a capacitor sensor, and the requested center of motion, as sensed by a LVDT (linear voltage differential transformer). The output from the control transformer is integrated to form an error signal. If the motion of the coil is not centered about the requested center, a DC error signal results. This error signal is amplified and used to correct the position of the coil by passing the amplified signal through the coil.

E. Coupled THM Processes in Petroleum Reservoirs *(C.- F. Tsang [415-486-5782; FAX 415-486-5686; E-mail chinfu@lbl.gov] and J. Noorishad)*

Various aspects of petroleum reservoir engineering, such as isothermal and non-isothermal 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 both to improve the numerical solution approach used in the code and to enhance its modeling capability. The

former has been achieved by implementation of an incremental loading scheme, a Newton-Raphson linearization scheme, dynamic storage allocation, an efficient equation solver, and a weighted predictor-corrector time integration method. For the latter, a realistic joint model has replaced the old ideal elasto-plastic model. Preliminary work for the development of various material constitutive models has been done. Partial and full verification of all the changes pertinent to hydraulic, mechanical, and coupled hydromechanical aspects have been achieved. Testing and revision of the heat transport counterpart of ROCMAS have been the focus of recent work. The lack of performance of the basic finite element method in solving hyperbolic equations is well known in the modeling field and is the reason for the emphasis on research in this area.

Preliminary findings have revealed potential ways for improving the classical Galerkin methods for solution of the transport equations. These enhancements seem to improve the performance level of the finite element method to a level above the finite difference methods (including IFDM). At present, work is underway to evaluate the effects of multidimensionality, source/sink, and transient time generalizations on the procedure.

F. Advanced Geoscience Research Concepts *(T. V. McEvilly [415- 486-7347; FAX 415-486-5686; E-mail mcevilly@lbl.gov])*

This activity provides support to encourage the 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. A study of the possible application of position electron tomography (PET) for imaging two phase flow in fractured rock was initiated last year and was continued through the current reporting period.

Experiments demonstrated that PET is feasible as a method to non-invasively image the fluid distribution in rough-walled rock fractures. The Donner 600 Crystal PET originally developed for medical research at Lawrence Berkeley Laboratory was used to image the fluid in fractures in granite cores (2" diameter) and a tuff block (8" linear dimension). The images clearly indicate the heterogeneous nature of the pore space of the rock fractures. Methods to quantify these results are being developed.

Exploratory laboratory tests to evaluate the feasibility of *in situ* hydrogenation of heavy oil were completed. An experiment to measure hydrogen uptake by heavy oil from the Ugnu field, Alaska, at 300°C and 2000 psi H_2 was terminated after 3 months of operation. Samples of the gaseous residue were analyzed by gas chromatography and found to contain nearly 40 volume percent methane.

Finally, in a new effort, a search for underground workings (mines and civil works) that would provide access for an underground geosciences research facility is being carried out. The facility would permit development of techniques and experiments to examine the full-scale mechanical, hydrological, and chemical responses of a rock mass to construction of openings and to hydraulic and thermal perturbations.

G. Gravity Field Monitoring at Yellowstone *(T. V. McEvilly [415-486-7347; FAX 415-486-5686; E-mail mcevilly@lbl.gov])*

The pair of feedback-controlled Lacoste-Romberg Model G gravimeters have been coupled through antialias filters and 16-bit digitizers to a pair of data platforms transmitting to the NOAA

GOES satellite-based data collection system. Control is through laptop computers for field use, and the two systems are designed for remote field deployment. With resolution of a fraction of a microgal (one count), the pair of meters forms a differential gravity detection system for use in monitoring the short-term (minutes to days) characteristics of vertical deformation in extremely active tectonic environments such as those in which volcanic uplift is occurring. The project was proposed at the time (1987) when the maximum uplift rate at Yellowstone was as much as 1.5–2.5 cm/yr and several microgals of related change could be expected annually. A maximum of around 30 microgals differential change accompanied some 15 cm of uplift between the 1977 and 1987 precision microgravity surveys (see Smith et al., EOS, Feb. 21, 1989), so the planned experiment at Yellowstone offered promise of reasonable success in producing data of value in modeling tectonic/magmatic/seismic processes operating in the subsurface to produce the uplift. Unfortunately, unrelated occurrences have combined to put the project on hold. First, the uplift rate at Yellowstone has decreased substantially. The recent park fire also has complicated access for the field test. Finally, and most disconcerting, is our discovery of an unexplained noise source in the difference signal, producing unacceptably large and random changes in its trend, necessitating updating of the electronics. The revised system will remain available for deployment when an appropriate opportunity arises, but the Yellowstone project will not be carried into FY 1991.

Contractor: LAWRENCE BERKELEY LABORATORY
University of California
Berkeley, California 94720

Contract: DE-AC03-76SF00098

Category: Geochemistry

Person in Charge: T. V. McEvilly

A. Thermodynamics of High-Temperatures Brines *(K. S. Pitzer [415-486-5456; FAX 415-642-8359; E-mail kspitzer@lbl.gov])*

This project covers theoretical and experimental studies concerning the thermodynamic properties of aqueous electrolytes at high temperatures. The components important in natural waters and brines 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 at 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.

A theoretically based equation has been developed for the near-critical and supercritical properties of NaCl-H_2O and KCl-H_2O. Parameters were fitted to the vapor-liquid coexistence surface for temperatures to 600°C and compositions from pure H_2O to that of the liquid on the three-phase line. Heat capacities and enthalpies were then predicted by this equation and agree satisfactorily with the available experimental data.

B. Studies of the Interactions between Mineral Surfaces and Ions in Solution *(D. L. Perry [415-486-4819; FAX 415-486-5686]*

The x-ray fluorescence microprobe technique, using a synchrotron radiation source, has been employed to study the surface of oxidized galena (PbS) and its reactions with high oxidation metal ions in solution. These reactions, conducted at 100°C in order to increase the kinetics and the extent of the reactions, are shown to vary greatly from the analogous reactions in which the reacting substrate is an unoxidized, "clean," galena surface. The resulting surfaces are observed to be much more heterogeneous than the comparable reactions involving the clean surfaces.

One good example of a reaction system that gives dramatic results in this series of studies is that of the solution interaction of aqueous chromium with the oxidized surface. Mapping of that reaction surface using the x-ray fluorescence microprobe indicates enriched chromium in areas that have been shown previously to include both hydrated chromium(III) oxide hydrates and

mixed chromium-lead oxides. Past studies in this laboratory also indicated the existence of segregated islands on the surface that are enriched in chromium; the amount of chromium varies from as little as 35 pg/g to as much as 100 pg/g. Some of the chromium-rich islands at the highest concentrations are as wide as ~100 microns. Again, these variations merely mirror the difference in the chromium (III, VI) chemical phases on the galena surface.

It is clear from these experimental data that the galena surface involved in solution interface reactions as described here cannot be satisfactorily described as a homogeneous surface available for dissolution or other subsequent reactions. Rather, the solid/solution interface reaction processes involving these surfaces can only be modeled as ones which must include a multiplicity of chromium(III), chromium(VI), and lead(II) phases. These (and related) reaction systems of metal ions will be studied further with respect to the reaction products, mechanisms, and kinetics. The synchrotron-related experimental work is being balanced with traditional x-ray photoelectron, Auger, and other types of spectroscopy in order to provide rigorous experimental data for input to such models.

C. Chemical Transport in Natural Systems *(C. L. Carnahan [415-486-6770; FAX 415-486-5686; E-mail chalon@lbl.gov] and J. S. Jacobsen)*

The objective of this research is to gain increased understanding of processes affecting the movement of chemically reactive solutes in groundwater flow systems. Our approach has been to investigate these processes theoretically while using reported experimental data for model evaluation. We have developed computer programs that solve the nonlinear, partial differential, and algebraic equations describing movement of dissolved, reactive chemicals in geological media.

The thermodynamics of irreversible processes is being applied to theoretical investigations of coupled processes active in low-permeability, permselective materials such as certain clays and shales. This method was used to develop a theoretical description of the distribution of water adsorbed by clay in the presence of a steady thermal gradient. The theory was applied to data from experiments on water distributions in heated bentonite. Measured isotherms for adsorption of water and heats of immersion for bentonite were used in the analysis. The analysis indicated the possible existence of coupling among flows of water and air in the experiments and provided tentative values of a coupling coefficient. The computer program TIP was used to solve the equations governing simultaneous flows of heat, volume, and solute mass driven by evolving gradients of temperature, hydraulic head, and composition in bentonite and kaolinite, using coupling coefficients reported in the literature. The simulations of transient and steady-state isothermal advection, diffusion, chemical osmosis, and ultrafiltration in the bentonite showed that this particular material, with a reflection coefficient of 0.01, could not be effective in creating osmotic pressure differences comparable to some reported in the field, nor in concentrating salts by ultrafiltration. On the other hand, simulations of thermal osmosis in the kaolinite showed that in the presence of temperature gradients of about 2 K/m, this material could support thermal osmotic volume fluxes two orders of magnitude larger than those predicted from Darcy's law.

The computer program THCC, constructed to simulate movement of solutes in the presence of homogeneous and heterogeneous chemical reactions, was modified to account for feedback from chemical reactions to fluid flow. The new program, THCVP, simulates changes of permeability (and, thus, fluid flux) caused by precipitation or dissolution of reactive solids during advective transport of reactive chemicals. The effects of varying temperature on chemical reactions can be included.

Extensive computations required by these investigations are made possible by OBES-supported access to the NMFECC Cray X-MP computer. Our fundamental research has led to support by other DOE offices for applications to their particular interests.

D. Impacts and Mass Extinctions *(F. Asaro [415-486-5433; FAX 415-486-5401], H. V. Michel, and W. Alvarez)*

One of the major objectives of this project is to determine the relationship between asteroidal or other large-body impacts on the Earth and repeated massive extinctions of life that have occurred in the last 570 million years (m.y.). The primary mechanism for this research consists of intensive chemical and selective mineralogical studies (on sediments near both major and minor extinction boundaries) that are run in parallel with floral and faunal fossil studies by collaborating geologists and paleontologists. Another major objective is to determine a series of time markers of very high precision and accuracy (in the form of Ir and other geochemical anomalies) for relative dating and correlation of sediments in many different parts of the world. A minor objective is to evaluate the major chemical and mineralogical alterations that have occurred in the sedimentation of the 67 m.y. old Cretaceous-Tertiary (K-T) boundary (the one most closely linked to a large-body impact) in order to predict the behavior expected in other boundaries.

The Iridium Coincidence Spectrometer (ICS) was significantly improved so that it now measures the abundances of 13 other elements (Ag, Ce, Co, Cr, Cs, Eu, Fe, Hf, Sb, Sc, Se, Ta, and Th) simultaneously with the measurement of Ir abundances. With the new instrument the K-T boundary region was studied in cores taken from Ocean Drilling Program Hole 752B in the Indian Ocean west of Australia.

The large iridium spike characteristic of marine K-T boundaries and generally believed to be due to the impact of a large body on the Earth was found within 1 cm of the position where the extinction of a number of species of foraminifera took place. Large enrichments of iron and other elements were also found in the same region. As their abundances were too large relative to Ir to be explained as impact debris or a changing sedimentation rate, the best explanation is that there was a pulse of basaltic volcanism at the same time as (and possibly caused by) the impact of the asteroid or comet responsible for the K-T iridium.

About 2 m.y. of sedimentation from a 35 m.y. old section from Massignano, Italy, was studied. An Ir anomaly of 150 parts per trillion similar to that found at other Late Eocene sites of comparable age was found. These data confirm the worldwide distribution of the Late Eocene Ir anomaly in the northern as well as the southern hemispheres. Three smaller close-lying Ir anomalies were found which will be compared with other sections to determine if there was a cluster of large-body impacts in the Late Eocene which distributed Ir worldwide and were hence large enough to cause extinctions.

The existence of an Ir anomaly (possibly related to an impact) was also confirmed in 10-12 m.y. old sediments from a deep sea core taken off of Antarctica in the same position as previously found. As a further test of background, besides the 1 m.y. of deposition previously studied, an additional 3 m.y. of deposition was measured with no Ir peak of consequence being found. This study suggests such Ir anomalies are rare.

E. Center for Isotope Geochemistry *(D. J. DePaolo [415-486-4975; FAX 415-643-9980; E-mail stborg@lbl.gov])*

Understanding of complex earth processes relating to energy and energy by-product management, such as fluid-rock interactions, solute transport in porous media, climate change, sedimentary basin evolution, and magmatic processes, is greatly enhanced by study of natural systems — both active and fossil. Natural and introduced isotopic tracers are excellent tools for characterizing the transport properties of natural media on all time and length scales and thus are indispensable for model verification and the ultimate development of predictive capabilities for Earth processes.

The purpose of the Center for Isotope Geochemistry is to (1) make available to the DOE Geoscience community a resource for high quality isotopic measurements, (2) facilitate the integration of isotopic and trace element geochemistry into ongoing geoscience research, (3) develop new and improved techniques for sampling and analyzing Earth materials, (4) develop dynamical process models coupling isotopic ratios to transport processes, and (5) facilitate the education of future geoscientists in state-of-the-art geochemical methods.

In this, the second year of operation, analytical capabilities were established in both solid source mass spectrometry (Sr, Nd, Ca, Pb isotopes, plus isotope dilution trace element concentration determinations) and stable isotope mass spectrometry (O isotopes), concentrating on both high throughput systems and techniques for low-blank, small sample analysis. A microsampling facility provides the capability to sample rock materials with 50-μm resolution. Automated chemical separation systems for small samples are now being designed. Other efforts have been in (1) developing analytical and numerical models for isotopic ratio variations in saturated geologic media undergoing reactive-advective fluid transport, (2) measuring global paleo-weathering rates using Sr and O isotopes in oceanic sediments and igneous rocks to aid in quantifying the long term carbon and CO_2 budget of the Earth, (3) quantifying transport processes in thermal regimes in the crust of the Earth using measurements on rocks and fluids, and (4) determining the magmatic and thermal evolution of the deep continental lithosphere in areas undergoing extension.

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Contract:	DE-AC03-76SF00098
Category:	Energy Resource Recognition, Evaluation, and Utilization
Person in Charge:	T. V. McEvilly

A. Hydrothermal Chemistry *(H. A. Wollenberg [415-486-5344; FAX 415-486-5686; E-mail mcevilly@lbl.gov])*

These activities are primarily associated with the thermal regimes sector of the Continental Scientific Drilling Program. The study of rock-fluid interactions in hydrothermal systems emphasizes caldera systems. Strong collaboration continues with colleagues at the Los Alamos National Laboratory and the U.S. Geological Survey. 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. O, H, C, and Sr isotope ratios trace the paths of hydrothermal fluids from precipitation in recharge areas, through the hydrothermal systems to surface manifestations. At Long Valley, California, a Sr-isotope gradient of fracture-filling calcite and a systematic variation in Sr-isotopic ratios in thermal waters support the concept of contact of hydrothermal fluids with basement rocks, then upward flow of the fluids in the caldera's west moat and their subsequent eastward movement in the caldera fill. Alteration-mineral assemblages in cores from DOE, industry, and municipally drilled holes have clay-mineral transitions that indicate earlier higher-temperature conditions in some sectors of the caldera and the widespread effects of the hydrothermal system in the west moat. Investigations of rock-fluid interactions in precaldera basement rocks should be augmented in the next few years by core, cuttings, and fluid samples from further drilling in the Long Valley caldera. In addition, a recharge zone of a hydrothermal system may be accessed by a hole proposed for the eastern part of the Valles caldera, New Mexico.

B. Aqueous Solutions Database *(S. L. Phillips [415-486-6865; FAX 415-486-5401])*

It is the objective of this work to provide computerized tabulations of consistent thermodynamic data which are useful to simulate and predict the magnitude of geochemical processes. The thermodynamic property values tabulated are standard Gibbs free energy of formation, enthalpy of formation, and entropy and heat capacity for minerals, gases, and aqueous species. These values are obtained from our and other critical evaluations of selected laboratory information. They are consistent with the 1989 CODATA Key Values, internally consistent within the data base, and reproduce selected experimental work generally within the uncertainty of the experiments. During the year, a computer preprocessor was designed and implemented to use thermodynamic data for calculating solubility and complex ion apparent equilibrium constants. These calculations are for use in performance assessment calculations for the Waste Isolation Pilot Plant. A report was completed consisting of a critical evaluation of thermodynamic data for the five monomeric hydrolysis products of aqueous U(IV) including recommended values. Both linear and nonlinear regression analyses were used for data fitting.

C. Geophysical Measurements Facility *(T. V. McEvilly [415-486-7347; FAX 415-486-5686; 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 the field deployments and operations. Examples of activities during this reporting period are: operation and maintenance of microearthquake networks in use at Long Valley, The Geysers, Coso, and Parkfield; operation and maintenance of the logging trucks and Vibroseis units used in several projects; deployment of the downhole fluid sampler at Valles; hydrological field studies at the Kesterson and Stillwater study areas; operation of the aquifer test facility at Richmond; field and technical support for the 10-company/DOE research in Texas on crosshole EM imaging; 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.

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A. Search for Nemesis (R. A. Muller [415-486-7430; FAX 415-486-5686; E-mail ramuller@lbl.gov] and S. Perlmutter)

Otherwise unrelated geophysical and astrophysical observations can be consistently accounted for by postulating that the Earth has been subjected to comet storms. The phenomena include features of the fossil record, impact craters and glass, geomagnetic reversals, and cosmic ray exposure ages of H-chondrite meteorites. Monte Carlo analyses of both the extinction data and the crater data suggest that these data are periodic. Theoretically, periodicity in impacts on the Earth requires that the impacting bodies arrive in large numbers, as in a comet storm. A number of causes have been suggested for periodic storms of comets, but presently only the Nemesis hypothesis of a solar companion star is consistent with all the known data.

The search for this star is being carried out by measuring the parallax of faint red stars that would have been missed in catalogues of bright and nearby stars. So far, about 40% of the 2615 stars in our list of candidates in the northern hemisphere have been rejected. Until recently it has not been possible to observe the brighter objects in our candidate list without either saturating our chip or underexposing background reference stars. We are now beginning to observe these stars by summing several successive images in software. We expect to complete parallax measurements of our northern hemisphere candidate list by the end of FY 1990.

Because the parallax search method depends upon the availability of a complete catalog of faint red stars in the northern hemisphere, a different approach will be necessary to extend our search to the southern hemisphere (for which no such catalog is available). A promising technique which might allow us to distinguish red dwarf stars from red giant stars photometrically is being studied. Recently Djorgovski, Thompson, and Greenstein have defined a new color, DG, which provides a clear differentiation between dwarfs and giants which are redder than type M4, precisely the class of stars which must be distinguished in our search. Using this technique, it would be possible to gather a large field of images with many stars, locate all of the red stars, and then select out the dwarfs from the giants. Another advantage of this method is that the stars can be immediately classified by color. The parallax method is much more time-consuming, since one must wait for the Earth to move sufficiently in its orbit to make a useful pair of measurements.

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A. Rheology of Partially Molten and Melt-free Crustal Rocks *(F. J. Ryerson [415-422-6170; FAX 415-422-4198; E-mail Ryerson@S91.es.llnl], W. B. Durham, and B. P. Bonner)*

Granite magmatism is a major process in determining the constitution of the continental crust. Granite plutons form the cores of most mountain belts, and the ascent of granitic magma from either the upper mantle or lower crust into the upper crust is the primary mechanism by which heat-producing elements are redistributed. Geochemical studies of granites are voluminous and have led to a better understanding of differentiation trends, magma sources, etc. Yet the details of many of the physical processes involved in granitic magmatism remain problematical, controversial, or difficult to quantify because of the absence of relevant rheological data. The goal of this project is to provide rheological data relevant to (1) the ascent of granitic diapirs (i.e., mixtures of melt and crystals) through the crust, (2) the segregation of magma from crystals, and (3) inversion of lower crustal seismic data.

We are currently developing the methods to fabricate and deform fine-grained aggregates of minerals and partial melts. Current work concentrates on quartz-bearing aggregates. The sample powders are being produced by spray drying components which are either totally in solution or in colloidal suspension. The results of these experiments are encouraging, as subsequently hot-pressed samples made from colloidal silicate result in quartz aggregates while those made from metal alkoxide solutions result in glass. Hence, crystal glass aggregates can be fabricated by mixing colloidal silica solutions with metal alkoxide solutions of the appropriate composition prior to spray drying. Potassium- and sodium-bearing quartz-glass aggregates fabricated in this fashion are fully dense, with an average grain size of ~ 5 mm and a uniform melt distribution. Preliminary deformation experiments indicate that the presence of a melt may reduce the strength of quartzites by up to a factor of 10.

B. Diffusion in Silicate Materials *(F. J. Ryerson [415-422-6170; FAX 415-422-4198; E-mail Ryerson@S91.es.llnl.gov] and W. B. Durham)*

The goal of this project is to determine the diffusion coefficients and diffusivities of various geochemically important elements in rock-forming minerals and melts, and then to apply these data to a variety of geochemical problems. Restitic accessory minerals carried to the upper crust by granitic magmas carry information regarding their time-temperature history; this information is carried in the form of diffusion profiles in radiogenic elements such as Pb, Sr, and Nd. In order to invert this compositional information, diffusion coefficients for the elements of interest are required. Measurements of Pb and Sr diffusion have been made for apatite, zircon, and sphene between 900°C and 600°C at one atmosphere. The technique used combines ion implantation of the tracer followed by annealing and subsequent analysis of the diffusion profiles by Rutherford

backscattering. The Pb and Sr data for apatite are in good agreement with those from previous high temperature measurements, and yield an activation energy of 62 kcal/mol. The results of Pb diffusion experiments are very well behaved, yielding a well-constrained Arrhenius line with an activation energy of 34 kcal/mol. However, the diffusion coefficients are as much as 5 orders of magnitude greater than those obtained by geochemical inference. This appears to be the result of radiation damage during implantation, which renders the zircons metamict. For both apatite and zircon, no change in diffusion mechanism is observed to temperatures as low as 600°C. Pb diffusion in titanite does show a change in activation energy from 44 kcal/mol above 800°C to 12 kcal/mol below 750°C. Oxygen diffusion measurements in diopside have also been performed between 1100°C and 1250°C, yielding an activation energy of 114 kcal/mol with a preexponential term of 53.4 $cm^2\ s^{-1}$. The activation energy observed under these anhydrous conditions is much higher than the value of 54 kcal/mol measured under hydrous conditions at 1 kb, and may be due to the presence of dissolved hydrogen species in "anhydrous" diopside.

C. Electrical Conductivity, Temperature, and Radiative Transport in the Earth *(A. G. Duba [415-422-7306; FAX 415-423-3107; E-mail duba@S61.es.llnl.gov], joint research with T. J. Shankland, LANL)*

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. The results apply to inference of upper mantle temperatures from electrical data. We have now extended our calculations of the equilibrium concentrations of point defects in the test case (Mg,Fe)O to more complex materials, specifically olivine $(Mg_{1-x},Fe_x)_2SiO_4$. 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. In the key step we iteratively solve the coupled nonlinear equations using the Newton-Raphson method together with experimental and theoretical activation enthalpies selected from the literature. Our results suggest that the defects are, in general, trivalent iron on Mg-sites and electrons. At high f_{O_2} Mg- and Si-vacancies become important; at low f_{O_2} Mg- and Si-interstitials are abundant. Oxygen interstitials and vacancies also appear at high and low f_{O_2}, respectively. Using synthetic olivine single crystals grown at LLNL we have shown that addition of Fe increases conductivity as $x^{1.8}$ for x = 0.8 to 0.33—in agreement with predictions from the theory above. These results unequivocally tie olivine conductivity to the presence of iron. Further, we were able to theoretically define the threshold concentration above which Fe determines defect concentrations as a function of f_{O_2} and temperature. In another significant step Constable and Duba addressed the problem that literature values for electrical conductivity of rocks are usually higher than values for the single crystals that comprise the rocks. They measured conductivity under controlled oxygen fugacity of a relatively unaltered dunite (composed dominantly of olivine) from Jackson County, North Carolina; the results show that conductivity is about 0.3 log units less than that calculated from the conductivity tensor of San Carlos olivine. We can thus argue that intercrystalline grain boundaries within this rock, which has grain sizes of order 1 mm, do not significantly enhance its conductivity. With this major uncertainty diminished, we feel much more confident about using single crystal data from mantle-derived crystals to calculate conductivities for polycrystalline assemblages using the averaging schemes of Shankland and Duba. Thus, mantle temperatures inferred from these conductivities are on a much firmer basis.

D. Attenuation and Dispersion in Partially Saturated Rocks *(J. G. Berryman [415-423-2905; FAX 415-422-3013; E-mail Berryman@lcdc.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, particularly hydrocarbon and geothermal exploration and resource assessment. The results also are relevant to code calculations which simulate explosion induced high amplitude wave propagation; such code calculations are used to investigate nuclear test containment and to evaluate seismic treaty verification issues. This project has continuing experimental and theoretical components: (1) Our experimental efforts are aimed at verifying theoretical predictions for wave propagation in fluid bearing porous media. Many of our wave propagation experiments apply novel techniques developed for nondestructive evaluation to geophysical problems. We have continued to collaborate with the Ultrasonics Group, Department of Welding Engineering, Ohio State University. Using a new experimental technique developed at Ohio State which employs air coupled ultrasonic waves, we have observed Biot's slow compressional mode in natural rocks for the first time. Samples of Berea and Massillon sandstone were carefully selected based on our measurements of permeability and formation factor. New techniques to prepare extremely thin samples (1–2 mm) were developed at LLNL to overcome the severe attenuation of the slow wave. Since the slow mode involves a coupled motion of the pore fluid and solid frame, observations of its speed and attenuation may provide a direct acoustic means of determining formation tortuosity and permeability. The existence of the slow mode was first predicted in 1956. (2) Acoustic microscopy shows promise as a new tool to evaluate the morphology of porous rock. We have demonstrated that images of sandstones and limestones comparable to those obtained by electron microscopy can be made by acoustic imaging at 200 MHz.

E Surface Wave Method for Determining Earthquake Mechanisms with Applications to Regional Stress Field Studies *(H. J. Patton [415-422-3924; FAX 415-422-7315; E-mail patton@S52.es.llnl.gov] and G. Zandt)*

The primary purpose of this work is to use surface-wave data to obtain source mechanisms and depths for earthquakes in the western United States. Our objective is an improved characterization of the regional stress field to gain better understanding of the geophysical processes that control continental rifting in the Basin and Range and the styles of extensional deformation. In addition to our studies of earthquake mechanisms, we have also accrued a considerable amount of information about the propagation speeds and attenuation rates of surface waves in the western United States. This information has been used for structural interpretations including the mapping of lateral variations of shear-wave velocities across the study area. The results of these structural studies are also valuable for understanding the processes of lithospheric extension. There are vital national facilities located in the Basin and Range and other areas of the western United States that will benefit from more complete understanding of the lithospheric structure and the processes modifying this structure. These facilities include the Yucca Mountain Waste Storage Facility, where long-term stability of geologic repositories of radioactive waste is a key environmental and health issue and the Nevada Test Site, where a concern is the safe conduct of underground nuclear explosions. In addition, the findings should be beneficial for assessments of geothermal and natural resource potential.

In the past year we have made significant progress in the characterization of the regional stress field. Over 50 earthquake mechanisms have been determined using the moment tensor inversion technique applied to events in the 3.5 to 5.5 magnitude range. The results are beginning to show consistent regional patterns in the stress for both northern California and the Basin and Range province. The state of stress on the San Andreas fault system has been the subject of several important studies which have shown the maximum horizontal compressive stress to be almost normal to the trend of the fault in central and southern California. This fault-normal compression is at odds with predictions from classical shear faulting theory and appears to support the contention that the fault has segments with low shear strength. The observations for northern California in these studies are far fewer and show far more scatter than in other areas of California. Our results show very uniform patterns of maximum compressive stress throughout the study area, with no evidence of fault-normal compression in northern California. Indeed, the observations are consistent with faulting theory. This could be an indication of greater effective shear strength of the northern fault segment than the segment in central California, and this would have important implications for understanding the mechanical behavior of the fault system as a whole. In the Basin and Range, our results show distinct differences in the style of deformation between the Battle Mountain region in the north, which is characterized by mainly normal faulting, and the shear zones in southern Nevada, characterized by strike-slip deformation. Also, directions of crustal extension show differences between north and south, with extension more east-west in the north than in the south, although this may be controlled by the orientation of seismically active faults.

F. Thermal Stress Microfracturing of Crystalline and Sedimentary Rock *(B. P. Bonner [415-422-7080; FAX 415-423-1997] and B. J. Wanamaker)*

Large changes in temperature occur during natural geologic processes and as a result of the application of energy technologies, including radioactive waste isolation, geothermal production, and enhanced oil recovery. These effects can alter critical physical properties of the rock mass, such as strength, elastic constants, and fluid permeability, which can affect the successful outcome of the application. The underlying mechanism for these phenomena is the formation of microfractures at the grain scale. Cracking occurs through the action of internal thermal stresses arising from local mismatches in elastic constants and thermal expansion. Our objective is to develop a predictive capability for microcrack generation for relevant temperature/pressure paths by integrating results from a wide-ranging experimental program. Work is under way at LLNL and at the University of Wisconsin under the direction of our collaborator, Professor H. Wang, and includes acoustic emission, compressional and shear velocity and attenuation, precision compressibility measurements, and direct observations with the scanning electron microscope.

We have previously found that low confining pressure, 7 MPa, suppresses acoustic emission in Westerly granite less effectively than post-test measurements of crack porosity predict. These events seem to result from some other source, such as sliding on preexisting fractures, decrepitation of fluid inclusions, or an increase in energy release rate that increases seismic efficiency. We are investigating the origins of this apparent surplus of acoustic emission by conducting a series of broadband acoustic emission measurements without confining pressure, to produce the most dramatic effect. Changes in wave speed and attenuation are sensitive indicators of fracturing in rock. Acoustic emissions begin at lower temperature than that which changes the wave propagation parameters. We have measured attenuation and modulus for Westerly granite at low frequencies to determine if microcracking is the only source of recorded acoustic emissions and to verify that ultrasonic results can be safely extrapolated to the seismic

range. If a competing mechanism, such as decrepitation of fluid inclusions, dominates intergranular microcracking as an acoustic emission source, then estimates of thermal damage based on acoustic emission will be systematically high.

We found previously that high confining pressure displaces the onset of thermally induced acoustic emissions to higher temperature. Although much of our effort this year has been on rebuilding our pressure system to meet more stringent safety requirements and to add automatic control, we have continued a series of acoustic emission experiments for granite from Stephenson Co., Illinois, to generalize this result.

G. Quantitative Image Analysis to Determine Rock Properties *(J. G. Berryman [415-423-2905; FAX 415-422-3013; E-mail Berryman@lcdc.llnl.gov] and S. C. Blair)*

The objective of this project is to use advanced image processing and analysis techniques to characterize the physical properties of rocks. Image processing techniques are already used routinely to analyze pictures of cross sections of rocks to determine the porosity and specific surface area. More sophisticated computer analysis will provide estimates of various statistical measures of the topology of rocks. One approach that has already proven successful is to estimate the permeability of sandstones by combining data obtained from spatial correlation functions for cross sections with an approximate formula for permeability obtained from a Kozeny-Carman relation. Better understanding of the dependence of physical properties on pore structure will benefit DOE projects involving fluid and gas flow in both sandstone reservoirs and unconsolidated sediments or projects designed to model fluid flow through rock. DOE interests such as nuclear weapons testing, seismic verification, radioactive waste isolation, and deep drilling are all potential beneficiaries of this research.

Progress last year was focused on moving image processing software from a mainframe based imaging system to a desktop color graphics workstation based system. Codes originally written in Fortran were rewritten in C and upgraded to take advantage of graphics hardware and software available on the workstations. This work was completed and our capabilities have been both restored and enhanced. The new capabilities include display and visualization of three-point correlation functions for rocks. The report on our new image processing routines for general use has been published in the form of a manual with over 100 pages of detailed documentation. Hardcopy of the rock images and the two- and three-point correlation functions is now easily accomplished using the photographic equipment attached to the workstation system. A new digitizer has now been installed, so that our analog SEM images of rocks may be conveniently digitized in a form readily available to the workstations. Another color graphics workstation is about to be added to our system.

We are pursuing a collaborative effort with L. Myer and N. Cook at LBL regarding use of imaging techniques to characterize the relations between pore structure and relative permeabilities of wetting and nonwetting liquid phases in porous media.

We are in the process of developing a suite of rocks for which many physical properties have been measured and for which we have analyzed images of cross sections. The main thrust of this work is to develop and implement methods to estimate elastic constants of geologic materials, based on three-point correlation functions measured for pores of real materials. Most of our previous work has been limited to analysis of two-point correlations and applications to estimates of fluid permeability. Our ongoing work continues to show that this approach is very successful at correctly predicting the permeabilities for sandstones.

Longer term efforts include an expansion of our data base to include pore structures of a diverse variety of geologic materials such as: sandstones and other sedimentary rocks with a wide range of grain and pore size distribution, unconsolidated sediments, fractured rocks, and anisotropic rocks. We will also evaluate various techniques for imaging microstructure in the laboratory and the field, study higher order statistical quantities, and address multiphase materials by using mineral identification as an added parameter in the description of the microstructure.

H. Nonlinear Sources for Seismic Imaging *(B. P. Bonner [415-422-7080; FAX 415-423-1997], Joint research with T. J. Shankland and P. A. Johnson, LANL, 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. One objective is to study the feasibility of producing a collimated, low frequency source by nonlinear ultrasonic mixing of two high frequency signals; this will be accomplished by conducting nonlinear experiments in rocks using various source arrays to optimize generation and transmission of the nonlinear beam. Other 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. The measurements will be used in the theoretical calculations as means of understanding and defining conditions for nonlinear wave generation. We have now designed an array of transducers that will be used to produce the mixed beam and have fabricated the separate transducer holders, each transducer being epoxied to the rock inside its own acrylic housing. One array is composed of transducers placed side by side in a checkerboard fashion with adjacent transducers driven by different frequencies. The plan is to first arrange 9 transducers in a 3×3 array before moving to a larger scale that may be an 8×8 size. A second array consists of two circular, concentric transducers having equal areas. According to preliminary results the pattern of the difference-frequency beams shows the anticipated narrow lobe. After analyzing our new low frequency data and literature data we proposed that strain dependence of attenuation at low frequencies should prove to be a useful quantitative measure of the relative magnitude of the third order elastic constants, which indicate the strength of the nonlinear effect. In other experiments, we have used our low frequency torsional oscillator to directly observe nonlinear behavior in rocks containing macroscopic fractures. Fractured granite specimens show the characteristics of a strong nonlinear response: load-dependent modulus, amplitude-dependent attenuation, and changes in stress-strain hysteresis. We have also reported precision ultrasonic measurements which show that the nonlinear effect for partially saturated rocks (volcanic tuffs) at low stress is one to two orders of magnitude greater than the typical values for rocks.

I. Maximum Resolution Seismic Imaging of the Long Valley Resurgent Dome *(G. Zandt [415-423-6835; FAX 415-422-4198, E-mail zandt@S25.es.llnl.gov])*

This is a new project with goals to develop higher resolution seismic transmission imaging methods and apply them to the study of magmatic structures and processes in the Earth's lithosphere with emphasis on shallow crustal structures. Our long term goal is to develop techniques with resolution in the upper crust that will be complementary to continental drilling. Our immediate objectives are to improve existing tomography algorithms by including new ray-tracing codes to test new approaches (including nonlinear optimization) using synthetic and existing data sets and to conduct preliminary field experiments in order to test new algorithms and field deployment configurations. Our results will have direct application to DOE interests in

continental drilling, resource exploration and analysis, and basic science issues related to continental crustal evolution.

We are investigating several computational/theoretical approaches to increase resolution. A stable, iterative tomographic method has been developed for high wave-speed contrast media using feasibility constraints and has been shown to work for medium contrasts as large as 50% where standard techniques tend to diverge. We are studying nonlinear approaches to seismic tomography, such as simulated annealing. The nonlinear techniques have the potential for use in a no-raytracing, no-inversion method for seismic tomography that takes advantage of rapidly developing parallel processing capabilities. An important step in the eventual utilization of full-waveform inversion methods is to have a better understanding of near-surface effects on seismic waves. We plan to examine scattering, attenuation, and diffraction effects on first arrival travel-times and waveforms.

New algorithms and techniques are initially tested with simulated data; however, testing with real data is a crucial step. Our plan is to test new algorithms with existing data to provide a direct comparison with current state-of-the-art results. For this purpose we have obtained data from Exxon for a dense borehole-to-borehole experiment. We plan to test algorithms with both travel-time and attenuation data from the active-source experiments at Medicine Lake Volcano and Newberry Volcano. We also have local earthquake and teleseismic travel-time data from northern California.

Among our original objectives was the design and execution of a high resolution seismic tomography experiment at the resurgent dome in Long Valley, California. In order to test different field deployment configurations in a major large-scale experiment, we planned two small-scale experiments to analyze fan-profile and under-shooting configurations. The objective of the NTS cavity/rubble zone imaging experiment is to provide a non-aliased high density data set with a "known" target to test new algorithms and provide an analog to the major Long Valley experiment. A preliminary experiment with a fan-profile configuration revealed a significant seismic effect by a small rubble zone in alluvium at Yucca Flat. The objective of the Death Valley experiment is to test the existence of a proposed mid-crustal magma layer using P to-S converted waves from the Moho reflection phase (PmP) generated by explosions at NTS. Data from a preliminary deployment at Death Valley revealed converted S-energy in the appropriate time window following PmP; however, our early examination of phase polarity indicates the mid-crustal feature may be a high-velocity layer.

J. **Advanced Concepts** *(L. W. Younker [415-422-0720; FAX 415-422-4198; E-mail younker@csam.lbl.gov])*

This project involves exploratory research in several geoscience-related areas. 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 and assessing feasibility of research tasks.

Contractor: LAWRENCE LIVERMORE NATIONAL LABORATORY
University of California
Livermore, California 94550

Contract: W-7405-ENG-48

Category: Geochemistry

Person in Charge: L. W. Younker

A. Thermodynamics, Kinetics, and Transport in Aqueous Electrolyte Solutions *(J. A. Rard [415-422-6872; FAX 415-422-4198] and D. G. Miller)*

Transport of dissolved species in water by diffusion is of major importance to a wide variety of geochemical phenomena, including isolation of radioactive and chemical wastes, diagenesis and ore formation, crystal growth, and dissolution kinetics for certain types of minerals. Activity coefficients are required for all chemical equilibrium calculations involving aqueous electrolyte solutions, including calculation of thermodynamic solubility products, calculation of Gibbs energies of formation for solid phases, calculation of vapor pressures of water above aqueous solutions, and speciation calculations. We have been making a variety of experimental measurements to provide some of the required data for aqueous binary and ternary electrolyte solutions at 25°C: (1) Diffusion coefficients have been measured for the major and minor brine salts (except for K_2SO_4 and alkali metal carbonates) and mixtures of NaCl with $MgCl_2$ and with $SrCl_2$. (2) Osmotic coefficients have been measured for all of these electrolytes and for other binary and ternary systems, at least to saturation and generally to considerable supersaturation. (3) Solubilities were measured for many of the binary solutions using the isopiestic method. (4) Densities were measured for solutions used in the diffusion experiments.

This year our experimental program emphasized isopiestic measurements for aqueous mixtures of $NaHSO_4 + H_2SO_4$ and supplemented our earlier work for $NaHSO_4$ and $NaHSO_4 + Na_2SO_4$. Data now extend to about 15 $mol \cdot kg^{-1}$, which is considerably above the solubility limits, and should be completed this year. Previous results are restricted to 3.5 $mol \cdot kg^{-1}$ and lower, and were inadequate to characterize this complex system.

This year we completed the extraction of the diffusion data from all our experimental runs on aqueous $NaCl-MgCl_2$. These data are part of a 10-laboratory international collaboration on the transport properties of this system. Three experimental papers have been published, and one is in press. We have done an extensive analysis of mixture rules for conductance using $NaCl-MgCl_2$ data from the Argentine collaborators. We have examined deviations from "ideal" mixing rules for different conductance representations, including specific, molar, equivalent, and ionic strength conductances at either constant molarity, constant equivalent concentration, or constant ionic strength. The relationships between these three representations have been systematized. Deviations from the ideal mixture rules and the Van Rysselberghe-Nutting rule are smallest at constant normality.

In connection with more general transport property estimation schemes, the transport properties for aqueous NaCl have been critically reviewed based on data obtained since our last review in 1966.

A critical review for aqueous $MgCl_2$ is under way. We have solved the problem of extracting diffusion coefficients from Rayleigh and Gouy data when the diffusion coefficient matrix has equal eigenvalues.

A book chapter on optical methods for diffusion measurements has been prepared for publication by IUPAC.

B. Compositional Kinetic Model of Petroleum Formation *(A. K. Burnham [415-422-7304; FAX 415-443-8779], J. J. Sweeney, and R. L. Braun)*

The objective of this project is to derive and verify quantitative chemical kinetic models of petroleum generation and expulsion from its source rock. We are pursuing parallel tasks in oil generation kinetics, oil cracking kinetics, phase-volume calculations, and geologic modeling to achieve that objective. We test chemical kinetic models of varying complexity in an effort to outline the tradeoffs between simplicity and completeness. This year, we acquired a new instrument for measuring pyrolysis kinetics and measured more accurate rate parameters for twelve oil shales and petroleum source rocks. We also refined and further tested the new models of vitrinite reflectance maturation and petroleum generation, cracking, and expulsion that we reported last year. Finally, we started development of a faster, easier-to-use, and more flexible computer code for calculating petroleum generation, cracking, and expulsion.

Our kinetic model of vitrinite maturation was the first that could account for changes in reflectance at both laboratory and geological time-temperature scales. Additional tests using geological data from the Uinta Basin (obtained from the USGS), the Maracaibo basin (obtained from INTEVEP), and published data from the Alberta Basin have been favorable. However, additional comparisons with unpublished laboratory hydrous pyrolysis data from the University of Texas and Centre National de la Recherche Scientifique have confirmed that the model is not as quantitative as desired for those conditions, indicating that further work is warranted.

We have used PYROL, our detailed generation and expulsion model, to investigate the relative importance of organic type, richness, and heating rate on oil expulsion efficiencies and expelled gas/oil ratios. This required us to estimate the complete set of kinetic parameters for marine kerogens to complement the lacustrine parameters we developed last year. We found that overpressuring depends strongly on heating rate and both organic type and richness. Generated pore pressures reach lithostatic pressure only for rich, lacustrine source rock in rapidly subsiding basins. Expelled gas/oil ratios depend strongly on organic type and richness but only weakly on heating rate. Lean source rocks containing oil-prone kerogen tend to expel mostly gas because substantial oil cracking is required to create enough excess volume for major expulsion. A thorough comparison of model predictions with geological data is still required in order to have confidence in the predictions of this model.

Although PYROL is useful as a research tool, it is too computationally intensive for routine use or for incorporation into 2-D or 3-D models. During the last part of the year, we made significant progress on a second computer code, PYROL JR, which will be more flexible yet computationally more efficient. The chemistry part, which is largely complete, will allow the user to specify the chemical mechanism, ranging from simple to very complex. In one mode, the code will ask the user to supply the appropriate constraints (product empirical formulas and product ratios) from which it will calculate stoichiometric coefficients that conserve elemental balance.

Finally, we acquired a prototype version of a new instrument, PYROMAT II, for measuring pyrolysis kinetics of source rocks by programmed micropyrolysis. This instrument was designed to interface with LLNL kinetic analysis software. After some minor modifications, we were able to achieve good temperature uniformity and properly calibrated thermocouples. Measurements on Green River shale indicated that our previous indirect temperature calibration method was accurate to within 2°C in the 425-450°C region, but slightly high at higher temperatures and slightly low at lower temperatures. The general result is that our more recent kinetic parameters are a few kcal higher than our previous best values from the Rock Eval II instrument and predict petroleum generation temperatures at geological heating rates that are typically 5-15°C higher than our previous results. However, PYROL calculations suggest that vapor pressure effects may cause this type of experiment to slightly overestimate the true chemical activation energy, which would result in overestimating the geological generation temperature by about 5°C. There are still some unresolved issues relating to the application of kinetic experiments to geology.

Contractor:	LAWRENCE LIVERMORE NATIONAL LABORATORY University of California Livermore, California 94550
Contract:	W-7405-ENG-48
Category:	Energy Resource Recognition, Evaluation, and Utilization
Person in Charge:	L. W. Younker

A. Shallow Hole Investigations of Long Valley, Valles, and Salton Sea Thermal Regimes *(L. W. Younker [415-422-0720; FAX 415-422-4198; E-mail younker@csam.lbl.gov], P. W. Kasameyer, and R. L. Newmark, joint research with C. R. Carrigan, SNL)*

This project involves dedicated scientific drilling at Long Valley, California and Salton Sea, California to characterize the near surface magmatic/hydrothermal environments. Work this past year has focused on integrating and publishing the results of two shallow drilling projects, the Shallow Salton Sea drilling project and the Inyo Domes drilling project.

1) Salton Sea Geothermal Field, California

An integrated study of the aeromagnetic and gravity fields at the SSGF has been carried out to identify the three-dimensional subsurface structure of the intrusions inferred to be the source of the thermal anomaly. Intrusion volumes are modeled as homogeneous three-dimensional prismatic blocks. Magnetic and gravity data are used in a nonlinear least squares approach in both two and three dimensions to estimate values of size, depth, orientation, density, and effective susceptibility contrasts of the prisms. The results of this modeling effort are being integrated with the seismic and heat flow observations in the region.

2) Inyo Domes, Long Valley, California

The purpose of this project was to investigate the thermal, chemical, and mechanical behavior of magma during its ascent toward the surface in an igneous system young enough so that it is essentially unchanged subsequent to its emplacement. Four holes were continuously cored in the Inyo chain of rhyolitic domes and craters in Long Valley, California. They confirmed the existence of a dike-like structure beneath the trend, indicated a strong control of degassing upon subsequent crystallization and provided evidence for the role of degassing in the development of the Obsidian flow .

One of the most intriguing results from the project was the degree of chemical heterogeneity observed in the intrusive and extrusive samples. There are at least three independent magma types represented in the 600-year-old Inyo domes. Two models have been developed to explain this observed geochemical variability. In the first model, the chemical patterns observed in the surface and subsurface samples at Obsidian dome are explained by differential draw-up of magma from a stratified reservoir. This differential draw-up is the result of changing flow rates during the course of the volcanic eruption. In the second model, the dike is viewed as initially consisting of heterogeneous magma domains. The zonation observed on the surface of the three domes and

in the conduit of Obsidian dome is ascribed to the tendency of less viscous magma to encapsulate more viscous magma during sustained flow in conduit.

B. Underground Imaging *(W. D. Daily [415-422-8623; FAX 415-422-3013] and J. G. Berryman)*

The goal of the 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 characterize the subsurface environment. 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 data interpretation process. The results of this project will benefit many DOE programs, including nuclear waste emplacement and monitoring, test ban verification through on site inspection and cavity detection, enhanced oil recovery, and basic research through imaging the detailed flow patterns of fluids in fractured rocks. Our work is now being focused more toward underground imaging using electrical methods. The efforts previously carried out on this project on Seismic Tomography are now continuing under the new project on Seismic Transmission Imaging.

Building on the past success of this project in high frequency electromagnetic (HFEM) tomography, the main thrust of the project at present is towards the development of imaging methods that extend our current capabilities to longer ranges. The main approach being considered is Electrical Impedance Tomography (EIT). 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 HFEM tomography; the disadvantage is that new, more sophisticated reconstruction methods must be developed to analyze the data since the location of the 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 originally developed on this project for applications to 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 the reconstructed images are much less susceptible to noise in the data. In order to test this premise with experimental data, the data collection apparatus was modified. Some data were gathered for cross borehole measurements using an electrolytic tank, and further tests are planned. In the past, our emphasis has been on circular and cross borehole configurations.

Work is now in progress on data taken in surface surveys, i.e., current is injected and voltage differences measured only on the surface of the earth (assuming no boreholes). A field demonstration has been completed showing 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 surface measurements alone. An automated data collection system is being built and will be used for three different field tests of EIT planned for later this year.

The main focus of this effort in the future will be towards generalizing the electrical impedance tomography methods and algorithms for a wider variety of applications. Current algorithms are restricted to two spatial dimensions. Work is beginning on generalizing to three dimensional imaging, especially in geometries traditionally used in geophysical surveys. Work is already in

progress on adapting the existing techniques to strictly surface measurement geometry. However, when boreholes are available, more view angles are possible and better reconstructions are expected.

C. Katmai Resistivity Studies *(P. W. Kasameyer [415-422-6487; FAX 415-422-4198; E-mail kasameyer@111-1cc.llnl.gov or kasameyer@s69 es. llnl. gov] and M. Wilt)*

As part of a multi-agency project for the Continental Scientific Drilling Program, we are investigating upper crustal magmatic processes that occurred during the great eruption of 1912 at Katmai in the Aleutian Range of Alaska. The focus of this year's work was a suite of geophysical measurements covering the region near Novarupta, where the eruption vent is thought to lie buried beneath its own ejecta. Our portion of the effort was focused on the collection of data to understand the subsurface distribution of electrical conductivity in the vent area. In addition, we collected gravity data (in a cooperative effort with the University of Alaska) and oversaw the collection of magnetic data and the installation of the measurement grid.

We collected DC resistivity and induction data near Novarupta in August and September, 1989. The purpose of this work was to delineate subsurface electrical conductivity structures caused by groundwater depth variations, regions of intense alteration, and geologic structures. Both methods detected anomalies that coincide with major vent features. The resistivity traverse radial to the eastern vent margin identified a steeply dipping conductive plane beneath the inner of two major arcuate grabens. This may be a zone of pervasive alteration on a vent-bounding fault, but careful modeling of this dataset is needed before a final interpretation can be made.

The most interesting results come from a set of induction soundings conducted along an East-West profile crossing both sides of the Tephra Ring at Novarupta. All soundings were interpreted to determine three-layered structures, and these structures were assembled into a two-dimensional cross section. To the east of Novarupta we find the near-surface materials to be very resistive to about 20–40 m, where the conductivity increases, suggesting that the water table has been reached. A similar profile is found to the west. Near Novarupta, however, there is a much more conductive zone beginning at 80 to 100 m. This zone could reflect high temperatures, but more likely it indicates a zone of intense alteration associated with the Novarupta intrusion.

Difficult weather conditions limited the work we accomplished during the 1989 field season. As a result, we plan to return to the Novarupta area in July, 1990, to complete the electromagnetic induction measurements. We will study the vent boundary, the Turtle, and complete the delineation of the conductive anomaly near Novarupta.

D. CSD Review Group *(L. W. Younker [415-422-0720; FAX 415-422-4198; E-mail younker@csam.lbl.gov]*

The twelve-person group reviews on-going, planned and proposed Continental Scientific Drilling projects in both the thermal regimes and hydrocarbon-related sectors. The review group is made up of scientists from federal agencies, universities, industry and DOE laboratories.

Contractor:	LOS ALAMOS NATIONAL LABORATORY University of California Los Alamos, New Mexico 87545
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 505-667-4739; E-mail 086172@ESSDP1.LANL.GOV] and L. M. Hirsch, joint research with A. G. Duba, 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. The results apply to inference of upper mantle temperatures from electrical data. We have now extended our calculations of the equilibrium concentrations of point defects in the test case (Mg,Fe)O to more complex materials, specifically olivine $(Mg_{1-x},Fe_x)2SiO_4$. 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. In the key step we interactively solve the coupled nonlinear equations using the Newton-Raphson method together with experimental and theoretical activation enthalpies selected from the literature. Our results suggest that the dominant defects are, in general, trivalent iron on Mg-sites and electrons. At high f_{O_2} Mg- and Si-vacancies become important; at low f_{O_2} Mg- and Si-interstitials are abundant. Oxygen interstitials and vacancies also appear at high and low f_{O_2}, respectively. Using synthetic olivine single crystals grown at LLNL we have shown that addition of Fe increases conductivity as $x^{1.8}$ for $x = 0.8$ to 0.33—in agreement with predictions from the theory above. These results unequivocally tie olivine conductivity to the presence of iron. Further, we were able to theoretically define the threshold concentration above which Fe determines defect concentrations as a function of f_{O_2} and temperature. In another significant step Constable and Duba addressed the problem that literature values for electrical conductivity of rocks are usually higher than values for the single crystals that comprise the rocks. They measured conductivity under controlled oxygen fugacity of a relatively unaltered dunite (composed dominantly of olivine) from Jackson County, North Carolina; the results show that conductivity is about 0.3 log units less than that calculated from the conductivity tensor of San Carlos olivine. We can thus argue that intercrystalline grain boundaries within this rock, which has grain sizes of order 1 mm, do not significantly enhance its conductivity. With this major uncertainty diminished, we feel much more confident about using single crystal data from mantle-derived crystals to calculate conductivities for polycrystalline assemblages using the averaging schemes of Shankland and Duba. Thus, mantle temperatures inferred from these conductivities are on a much firmer basis.

B. **Nonlinear Generation of Acoustic Beams** *(P. A. Johnson [505-667-8936; FAX 505-667-8487; E-mail JOHNSON@ESSDP2.LANL.GOV], T. J. Shankland, and J. N. Albright)*

This research is aimed at examining the different kinds of nonlinear elastic interactions and their geometries. In analogy with the case in laser optics two narrow beams of high-frequency sound can interact in a nonlinear medium to produce a narrow beam at their much lower difference frequency. The difference frequency beam has the narrow width of the generating beams, but it can travel farther because of lower attenuation. 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. From designs devised for acoustic resonance studies in LANL's Center for Materials Science we wired a state-of-the-art high frequency mixer and a low frequency mixer. These new devices permit a whole range of new experiments. In particular, we were able to do a previously time consuming sweep across the frequency range for nonlinear wave generation in just a few seconds. Not only was the signal/noise ratio greatly improved, but we observed interference patterns for the driving beams that determined characteristic distances without the need for external measurement, a startling innovation. As an example, we were able to determine distance of travel from the mixing volume and thereby calculate travel time using a known velocity. Distance measurements are just the kind of information needed to locate fractures, free surfaces, or burn fronts in underground exploration or monitoring. Alternatively, using rock dimensions we can obtain the compressional and shear velocities V_p and V_s for the region. These are key properties in any application; for instance, monitoring fluid migration within or outside a reservoir or repository. These new interferometric methods in combination with pulsed wave techniques should allow us to remotely determine distances to geologic features.

C. **Nonlinear Sources for Seismic Imaging** *(T. J. Shankland [505-667-4907; FAX 505-667-4739; E-mail 086172@ESSDP1.LANL.GOV] and P. A. Johnson, joint research with R. J. O'Connell, Harvard, and B. P. Bonner, LLNL)*

This research is aimed at developing directed sources that can be used to probe rock volumes using seismic tomographic techniques. One objective is to study the feasibility of producing a collimated, low frequency source by nonlinear ultrasonic mixing of two high frequency signals; this will be accomplished by conducting nonlinear experiments in rocks using various source arrays to optimize generation and transmission of the nonlinear beam. Other 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. The measurements will be used in the theoretical calculations as means of understanding and defining conditions for nonlinear wave generation. We have now designed an array of transducers that will be used to produce the mixed beam and have fabricated the separate transducer holders, each transducer being epoxied to the rock inside its own acrylic housing. One array is composed of transducers placed side by side in a checkerboard fashion with adjacent transducers driven by different frequencies. The plan is to first arrange 9 transducers in a 3×3 array before moving to a larger scale that may be an 8×8 size. A second array consists of two circular, concentric transducers having equal areas. According to preliminary results the pattern of the difference-frequency beams shows the anticipated narrow lobe. In experiments on low-frequency elastic nonlinearities of rock we have modified our torsional oscillator to directly observe nonlinear behavior in rocks containing macroscopic fractures. Fractured granite specimens show the characteristics of a strong nonlinear response:

load-dependent modulus, amplitude-dependent attenuation, and changes in stress-strain hysteresis.

D. Imaging of Reservoirs and Fracture Systems Using Microearthquakes Induced by Hydraulic Injections *(M. Fehler [505-667-4318; FAX 505-667-8487; E-mail FEHLER@SEISMO5.LANL.GOV] and L. House)*

Microearthquake studies of hydraulic fracturing generally have relied on only the locations of the induced microearthquakes to estimate the location and extent of the fracture system created. This study aims to identify and locate some of the more significant fluid filled fractures from their ability to scatter and reflect seismic energy. In addition, the study aims to better characterize the internal structure of the fracture system through its effects on seismic velocities. Because microearthquakes are more energetic (particularly for shear waves) than artificial sources, using microearthquakes to interrogate the fracture system should considerably increase the amount of information that can be obtained compared to using artificial sources. This study seeks to exploit information in the recordings of microearthquakes that is not generally used for simply locating them. In particular, the seismic coda, or wavetrain following the direct P and S arrivals, contains information about heterogeneities or scatterers that are located within or near the fracture system. In addition, as well as locating the microearthquakes, the times of arrival of the P and S waves can be used to estimate the seismic velocities in the vicinity of the fracture system. This study seeks to use both the scattering and velocity effects to identify some of the more prominent fractures from within the fracture system created.

E. Two- and Three-Dimensional Magnetotelluric Inversion *(B. J. Travis [505-667-1254; FAX 505-665-3687; E-mail BJT@CANOPUS.LANL.GOV] and A. D. Chave)*

The only way to determine subsurface structure on a large scale within the earth is through indirect, non-invasive means such as analysis of seismic signals, interpretation of gravity and heat flux, and deconvolution of electromagnetic surface measurements. Magnetotellurics (the simplest EM method) can provide good resolution of the subsurface electrical conductivity distribution on scales up to several hundred kilometers. Conductivity can then be related to density or other material properties to provide a map of subsurface stratigraphy. While electrical geophysical recording technology has seen great progress in the last decade, interpretation capabilities have lagged behind, due to the high computational cost. New ideas as well as concepts developed in other disciplines must be implemented to reduce computational effort.

The goal of this research project is the development of highly efficient, user-friendly numerical models to solve a variety of 2-D and 3-D forward and inverse problems in geophysical electromagnetic sensing. The approach taken is to obtain as much accuracy as possible with a limited number of nodes and to reduce the need for user intervention to a minimum. The numerical methodology centers on the moving finite element (MFE) concept. In MFE, computational nodes are positioned automatically to achieve optimal or near optimal accuracy with a given set of nodes. Nodes accumulate where electromagnetic field gradients are steep and spread out in shallow gradient areas. Highly efficient sparse matrix solvers based on incomplete factorization with acceleration are at the heart of the model. Additional improvements over conventional numerical methods include use of infinite elements for side and bottom boundaries and higher order elements along material interfaces, where discontinuities in derivatives can exist. Solution of inverse problems is achieved with the regularization approach, which generates the smoothest, least-structure solution. At abrupt changes in structure, the smoothing effect of regularization should be suspended. None of the present inversion methods can find where abrupt

changes occur on their own. We have developed a method to overcome this obstacle by using a parametric representation. Automatic mesh generation complements the 2-D and 3-D computer codes and is virtually essential for complex geological simulations.

F. Advanced Concepts *(C. W. Myers [505-667-3644; FAX 505-667-3494; E-mail MYERS@CSAM.LBL.GOV] and R. W. Charles [505-667-4985; FAX 505-665-3403; E-mail 081948@INCDP3.LANL.GOV])*

Five limited term projects are underway in FY90:

1) Magma Volatiles in the 'New' Geothermal System, Mount St. Helens, Washington

Volcanoes emit gases and heat that affect our atmosphere and climate, erupt lava flows and ash that create hazards to people and property, and contain heat circulating groundwaters that develop into geothermal resources and form ore deposits. Volcanoes also provide us with direct conduits into the Earth's crust and mantle that can provide samples documenting fundamental Earth processes. A new geothermal system was created following the catastrophic eruptions at Mount St. Helens in 1980. Because direct evidence of a magmatic component has never been found in a geothermal system (although suspected), we have been collecting samples of meteoric waters, 'new' hot spring waters, fumarole condensates, and volcanic rocks to determine conclusively if a magmatic component exists in the system. We have determined that approximately 10% of the thermal fluid consists of condensed magmatic volatiles. We have also recently determined that the tritium content of the magmatic steam is unusually high, which may impact cold fusion theory in the Earth. Efforts this year will allow us to publish our St. Helens results.

2) Thermal Spallation Drilling Research

The overall goal of this project is to renew research in thermal spallation drilling and to evaluate new techniques for spalling common petroleum-bearing reservoir rocks. Thermal spallation drilling technology has the potential to drastically reduce drilling costs and subsurface excavation costs. New energy and mineral resources for the Nation could become more economically attractive through the application of thermal spallation drilling and excavation technologies. The specific objectives of this work are to (1) test the spallability of petroleum-bearing reservoir rocks under various laboratory and *in-situ* conditions, (2) improve the technology of thermal spallation drilling equipment, (3) demonstrate thermal spallation to prospective users in the industrial sector, and (4) provide well documented drilling experiences that can be analyzed by new theoretical models developed for thermal spallation applications. This is a cooperative effort between the New Mexico Institute of Mining and Technology in Socorro, New Mexico, and Los Alamos.

3) Numerical Simulation of Light Hydrocarbon Diffusion from Petroleum Reservoirs

A two-dimensional, heterogeneous diffusion code was developed to solve the problem of high hydrocarbon diffusion through rock strata of varying physical properties and structure. Results for solutions of an anticlinal trap and a faulted trap at depths of about 900 m show development of surface anomalies of several tens and several hundreds of parts per million, respectively, after one-half million years of diffusion. Numerical simulation of light hydrocarbon diffusion from petroleum reservoirs is important because geochemical exploration has only been empirically applied to location of petroleum resources. There are numerous techniques for detecting light

hydrocarbon anomalies in surface rocks and soils above known reservoirs, but inversion of these data to predict depth, size, and structure of a potential unknown reservoir cannot be currently done, because solutions of the forward problem have not been systematically obtained. Study of the basic physics and chemistry of oil and gas will help improve the definition and characterization of fluid flow and reaction pathways which are a fundamental concern in the migration of oil and gas in natural reservoirs.

4) Sensitivity Analysis of Large Aqueous Geochemical Computations

Selected aqueous geochemical codes are being extended to explicitly include methods for estimating the uncertainties and sensitivities of calculated results from geochemical models as a function of input data and corresponding errors. While there are well recognized uncertainties (and even inconsistencies) in geochemical models and databases, the consequences for calculated results have only been evaluated for a few extremely simple systems. The complex geochemical computational models currently in widespread use offer no automated means of evaluating sensitivities and statistical errors. The goal is to provide a framework for systematically estimating uncertainties in geochemical calculations that are relatively automatic, rigorous, available for interpretation of experimental results, and able to enhance experimental efforts.

Emphasis continues to be on application of automatic gradient enhancement methods to distribution of aqueous species calculations at ambient to elevated temperatures and pressures. Sensitivity of ion activity and mineral saturation is evaluated based on estimated analytical uncertainty of input solution concentrations and activities. Application has been made to seawater and dilute hydrothermal solution.

5) Measuring Erosion Rates in Arid Regions Using ^{3}He

The purpose is to apply measurements of the buildup of cosmic-ray produced ^{3}He and ^{21}Ne as a measure of erosion rates. In arid environments like the Southwest United States the most important pathway for release of subsurface materials may be via erosion. Thus, one important area for research is the study of surface erosion. It has recently been shown that noble gas isotopes are produced in measurable quantities in the surface of the earth by interaction with cosmic rays. Because of their low abundance in nature, excesses of ^{3}He and ^{21}Ne are particularly apparent in near-surface rocks. We propose to exploit this build-up of nuclides, which is directly proportional to the residence time of the material on the surface, to study rates and mechanisms of erosion in arid regions. The apparatus is in place for these measurements, and samples have been collected in order to perform analyses on separated minerals.

Contractor: LOS ALAMOS NATIONAL LABORATORY
University of California
Los Alamos, New Mexico 87545

Contract: W-7405-ENG-36

Category: Geochemistry

Person in Charge: D. R. Janecky

A. Uranium-Series Disequilibrium Measurements in Geologic Systems Using Mass Spectrometry *(M. T. Murrell [505-667-4299; FAX 505-665-3403; E-mail 099691@INCDP3.LANL.GOV], S. J. Goldstein, A. M. Volpe, D. R. Janecky, R. E. Perrin, joint research with R. W. Williams, UCSC)*

U-series disequilibrium techniques are well established and valuable tools in geochronology and geochemistry. Such measurements have typically been made by decay counting. However, there is significant interest in the development of mass spectrometric techniques for U-series disequilibrium measurements. We have developed mass spectrometric techniques for the measurement of ^{238}U-^{234}U-^{230}Th-^{226}Ra and ^{235}U-^{231}Pa disequilibria which have resulted in order of magnitude improvements for sample size, precision, and/or counting times over that typically obtained by decay counting techniques. These improvements should help to make the chronology of the last 500 ka much more accessible. Applications include studies of geologic hazard risk assessment, paleoclimate and climate change, as well as basic questions in isotope geochemistry.

We have evaluated the U-Th disequilibrium technique for both geochronological and petrogenetic study of mid-ocean ridge basalts (MORB). Previously, we measured large activity excesses of ^{230}Th relative to ^{238}U in young, axial basalt glasses dredged from the Juan de Fuca (JDF) and Gorda Ridges, typically 13 to 15% but ranging up to 40% in a sample from Endeavour segment (JDF). Subsequently, we have obtained additional young, axial samples to better define the range in initial $^{230}Th/^{232}Th$ values along these ridges. For purposes of age dating, we also analyzed older, off-axis samples of basalt glass from North Gorda Ridge and the Endeavour segment of Juan de Fuca Ridge. Initial values of $^{230}Th/^{232}Th$ ratios based on "zero-age" axial samples are quite uniform within ridge segments (±1% variation), and initial ^{230}Th activity excesses are generally quite large (30–40%). The $^{234}U/^{238}U$ results give no evidence for seawater alteration, and the disequilibrium appears to be a magmatic feature. U-Th ages obtained for off-axis samples, based on constant initial $^{230}Th/^{232}Th$ on eruption, range from 130 to 200 ka and show general agreement with estimated ages based on spreading rates. For Endeavour, ages for off-axis ridges indicate asymmetry in spreading (4.0 cm/yr West and 1.9 cm/yr East) in agreement with predictions based on topographic constraints. The full spreading rate from these U-Th ages (5.9 cm/yr) is in agreement with the spreading rate based on magnetic anomalies in sediments (6.0 cm/yr). For North Gorda, U-Th ages indicate a half-spreading rate (3 cm/yr) also in agreement with the half-spreading rate based on magnetic anomalies (2.75 cm/yr). For both ridges, samples located near the rift axis are typically younger than predicted by spreading rate, suggesting recent eruptive activity over a broad (2–3 km) area. These data represent the first direct isotopic measurement of eruption ages and spreading rates for ocean spreading centers. Based on these

results, age-dating MORB by ^{238}U-^{230}Th disequilibrium appears quite promising and should have much utility in understanding the processes which create oceanic crust.

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 presently being combined with enthalpy data from ORNL to provide a complete thermodynamic model 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, and D. L. Bish)*

Rock varnish, a ubiquitous, manganese- and iron-rich coating on rock surfaces in arid and semi-arid regions, has long been of interest as a potential age indicator. Recent work has demonstrated that rock varnish is an effective medium for dating geomorphic surfaces and surficial deposits over an age range of several thousand to more than a million years. However, such dating relies on ratios of several minor elements in the varnish calculated for a specific geographic area. Relationships between varnish mineralogies, varnish elemental contents, varnish diagenesis, and the mechanism of varnish formation are not yet understood. In addition, it is not clear what effect these various varnish attributes have on the elemental ratios used in rock varnish dating.

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 composition of rock varnish as a function of local geology, geochemical environments, and varnish source environments. Included within this work are examinations of (1) variations in varnish composition existing both laterally throughout the varnish horizons and vertically from the varnish/substrate interface to the varnish surface; (2) the effect of varnish age on varnish composition; and (3) the relative effects of local and regional geology on varnish composition. Inherent in such studies will be an evaluation of paleoclimatic variations as recorded in rock varnish stratigraphy.

Interpretation of analytical data will result in a means by which to refine empirically derived rock varnish cation-ratio curves for geomorphic surfaces. Such refinement 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. Rock varnish dates of young (< 1.0 Ma) tectonic events will be of significant value to enhanced resolution of mantle/crust interaction, improved seismic risk evaluations, and improved characterization of sites for nuclear power plants and toxic and nuclear waste disposal.

D. Geochemistry of Technetium *(D. B. Curtis [505-667-4498; FAX 505-665-3403; E-mail 083769@INCDP3.LANL.GOV], J. Fabryka-Martin, M. Attrep, Jr., R. Aguilar, R. E. Perrin, and F. Roensch)*

The objective of this work is to study the geochemistry of long-lived radioactive species, ^{99}Tc, ^{129}I, and ^{239}Pu, in uraniferous rocks. Work during the past year addressed fundamental questions regarding the processes controlling their production rates by measuring ^{239}Pu concentrations in several uranium ore deposits representing a variety of geochemical conditions. The ores are from unaltered and unweathered ore zones and were selected as being likely to represent geologically closed systems. The measured concentrations correspond to Pu production rates of 60–360 atoms ^{239}Pu/mgU/yr. No correlation exists between $^{239}Pu/U$ ratios and uranium content, and considerable variability in $^{239}Pu/U$ ratios is seen even within a single deposit. The measurements as well as predictions from our modeling study indicate that *in-situ* neutron fluxes, which control ^{239}Pu production rates, are probably influenced as much by the composition of adjacent (generally lower %U) mineralogy as by that of the analyzed ore sample. Consequently, one cannot interpret measured $^{239}Pu/U$ ratios in terms of degree of retention without some independent measure of the in-situ neutron flux.

We have continued to improve our ability to model radionuclide production rates in uranium deposits, using a Monte Carlo Neutron Transport Code to model neutron-induced reactions (i.e., ^{239}Pu production, ^{235}U fission) and introducing increasingly complex geometries for the ore body. Model calculations show that ^{239}Pu production rates are significantly reduced near the outer edge of ore bodies due to neutron leakage. However, the extent of reduction is not a simple function of distance from the edge; production is even enhanced in the outermost centimeter of the deposit due to increased thermalization of the neutron flux, sufficient to offset the decrease in total flux due to neutron leakage. The influence of a better-thermalized neutron flux is even more dramatic in the case of neutron-induced fission of ^{235}U, such that maximum fission rates are predicted to occur in the outer centimeter of the deposit, more than 50% greater than the rate predicted for the center.

Based on these results, our present views on radionuclide concentrations at secular equilibrium are: (1) in general, no correlation should be expected between ^{239}Pu and fission-product concentrations in primary ore deposits, although one parameter may serve to set bounds on the other; (2) $^{36}Cl/Cl$ should be a good *in-situ* measure of the ^{235}U fission rate in most cases but

should not be expected to show a correlation with $^{239}Pu/U$; and (3) considerable variability should be expected in $^{239}Pu/U$ and $^{129}I/U$ ratios within a given deposit, even on the scale of centimeters, due to the effects of elemental heterogeneities on neutron fluxes and hence on production rates.

E. Rock-Water Interactions and Element Migration (D. R. Janecky [505-665-0253; FAX 505-665-3403; 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, and G. K. Bayhurst)

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 terrains 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 water-rock reaction processes at near critical conditions. 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 and Asteroid Impacts at Extinction Boundaries *(C. J. Orth [505-667-4785; FAX 505-665-3403; 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 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).

Our primary effort has been directed at the 93-Ma Late Cenomanian extinction of marine animals. Several years ago we discovered two closely spaced Ir abundance anomalies in marine rock sequences exposed near Pueblo, Colorado. In last year's summary we reported finding the anomalies throughout the western interior of North America and also in England and Germany. The anomalies are strongest in the southern portion of the North American Cretaceous seaway (Texas, New Mexico, and Colorado) and drop off rapidly to the north and are also weak in the European sections. Also present with the Ir in anomalously high abundances are Sc, Ti, V, Cr,

Mn, Co, Ni, Pt, and Au. In order to localize the source of the anomalies, we examined cores collected by the Deep Sea Drilling Project. We found weak anomalies in cores taken from the western equatorial Pacific and from the Atlantic west of Senegal, Africa, and southwest of Ireland. We did not find the anomalies in cores taken from the Atlantic near Morocco, from the Kerguelen Plateau in the southern Indian Ocean, and from the Caribbean basin. Although we did not detect the anomalies in the Caribbean core, a picture is emerging in which the source was intense spreading-center activity in the Late Cenomanian proto-Caribbean or nearby Atlantic. The elemental abundance patterns are similar to those in ocean ridge basalts and not to those in Solar-system bodies (meteorites).

We examined samples collected by a Chinese collaborator from the 245-Ma Permian-Triassic boundary and from the 365-Ma Frasnian-Famennian boundary in south China. No evidence of a large-body impact was detected at either boundary, although these boundaries represent two of the largest extinctions in the fossil record.

We continued to study the 66-Ma Cretaceous/Tertiary (K/T) boundary. In North America we found further evidence from Ti/Al ratios in the two thin boundary clays to support the hypothesis that they are from the same impact; low angle ejecta (lower clay) overlain by back angle ejecta (upper clay) that fell later from the stratosphere. We also examined more samples collected by Indian and Japanese collaborators from central India and from Hokkaido. No evidence of the K/T boundary was found in either of these sections. Contrary to their claims, we suspect that the boundary is not preserved at these sites. In the Indian suite of samples more Deccan basalts were analyzed, and, as before, we found very low Ir concentrations (0.006 ppb). Arguments that the Deccan flood basalts were the source of the K/T Ir anomaly are unfounded.

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], D. R. Janecky, and P. S. Z. Rogers)*

Optical spectroscopies, including conventional uv electronic absorption, Raman scattering, and resonance Raman scattering, 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 geothermal, oil field, and environmental systems.

The current focus is on halide complexation/interaction with dissolved metals, especially from the platinum group elements (PGE's). Although classically regarded as magmatically placed ore systems, geologic field work in places like the Bushveld Complex (South Africa) indicate hydrothermal dissolution, re-transport, and precipitation/adsorption/reduction from sulfide minerals to form other veins. Laboratory work here involving systematic changes in pH and [Cl^-] has determined that Pd-Cl species persist to higher pH's than originally thought. Because the Pd-Cl complexes (especially $PdCl_4^{2-}$) have significant solubility in water, these experiments add support to the field hypotheses. Presently, we are extending these studies to higher temperatures.

Another current interest continues to be organic acid complexation/interaction with silicates and aluminum silicates. The importance of such interactions have been established, and we are involved in quantifying the characteristics of complexation as a function of pH, pressure, and temperature. Because silicates and aluminum silicates are ubiquitous matrices, such interactions have important implications for mineral dissolution, groundwater and geothermal transport and precipitation, and fossil fuel/reservoir interactions.

Contractor:	LOS ALAMOS NATIONAL LABORATORY University of California Los Alamos, New Mexico 87545
Contract:	W-7405-ENG-36
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. The project is jointly managed by Los Alamos, University of Utah Research Institute, and Sandia National Laboratories.

Further studies of structures in VC-2b and the 528-m deep companion hole VC-2a confirm that of three spatially coincident caldera cycles, only the youngest, the Valles caldera, experienced structural doming during resurgence. The mylonitized contact of Precambrian and Paleozoic rocks appears to represent deep thrust faulting probably associated with regional compression that occurred during the Laramide event (locally about 65 Ma). All other low angle faulting, slumping, and/or tilting of units seen in the research holes occurred in one event, during structural doming of the Valles (1.12 Ma) caldera. These Valles-related structures constitute the main reservoir conduits for the active hydrothermal system.

The hydrothermal system penetrated by these bores consists of a shallow vapor- rich cap, which has evolved in the last 0.6 Ma from an earlier 200°C liquid-dominated system, overlying stacked, liquid-dominated zones up to about 300°C. Geochemistry of mud returns collected during drilling had suggested chloride- rich geothermal fluids were entering the bore and mixing with the drilling fluids in the fractured lower Paleozoic and Precambrian sections. A major effort this year has been to characterize these fluids from the open-hole section of VC-2b between 1697 and 1762 m within fractured Precambrian quartz monzonite. A specially developed titanium in-situ sampler was run in the hole in May, 1989. At this time, the well had not been purged of all drilling fluids. In spite of the contamination with residual drilling fluids the sample contains 762 mg/kg Cl and anomalous quantities of As, B, and Li, indicating, indeed, formation water is entering the bore below 1697 m. VC-2b was then stimulated with a nitrogen lift, purging the residual drilling fluids and inducing self-sustained flow for 30 hours until the well was shut in. Tritium analyses of the produced fluids were less than 0.7 T.U., indicating successful purging. Deep, high temperature, down-hole sampling efforts were intermittently staged through January, 1990, using two experimental tools. The suite of samples collected indicate that the fluid column in the upper

part of VC-2b is substantially boiled. In addition, a recently developed temperature tool, with on-board dewared data acquisition system, has been tested in VC-2b, and a U.S. Geological Survey experiment to grow fluid inclusions in quartz was suspended in the hole at 1710 m for four weeks. The trapping temperatures of the synthetic fluid inclusions average about 292°C, compared to the measured temperature at that depth of 293°C. Another similar experiment and one more down-hole sampling session are scheduled for spring 1990. In summer 1990, the casing of VC-2b will be perforated to allow testing and sampling of thermal aquifers above 1697 m.

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. 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.

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 Geotech, 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. Valles Caldera Workshop Held in Los Alamos, New Mexico, in October 1989 *(G. Heiken [505-667-8477; FAX 505-665-3285; E-mail 082844@ESSDP1.LANL.GOV])*

A workshop to evaluate scientific drilling in the Valles/Toledo caldera complex was held October 18, 19, and 20, 1989 in Los Alamos, New Mexico, with about 50 attendees. The purpose of the workshop was to review progress of the drilling program and to consider the scientific merit of continuing core hole drilling, as was proposed in the original scientific and management plan.

The group discussed the drilling sites proposed in the original scientific plan and added several new sites, based on data acquired during the drilling of holes VC-1, VC-2A, and VC-2B. It was agreed that the next core hole, designated VC-4A, should be sited in the eastern half of the Valles caldera. The site is located inboard of the inferred ring fractures, on a line between the post-caldera rhyolite domes, and at the base of the resurgent dome.

The key scientific problems to be addressed in this proposed project include caldera-forming eruptions, the mechanics of caldera collapse and resurgence, hidden hydrothermal systems within the caldera framework, and the processes of ore deposition.

What new problems will this core hole resolve? Most of the drilling in the Valles/Toledo caldera complex has been in the western half. Little is known about subsurface structure, stratigraphy, or hydrothermal systems in the eastern half of the caldera. Gravity surveys indicate that there may be a very thick sequence of caldera fill, perhaps as much as 3 km thick. If this is the case, these may be trapdoor calderas, thickening to the east. It has been inferred by some investigators that this thick section may contain a hidden hydrothermal system and by others that this is the recharge area for the hydrothermal systems located in the western part of the caldera. A few of the problems outlined that can be tested only by drilling are hydrothermal processes within thick sections of intracaldera volcanism, sedimentation that followed collapse of both the Valles and Toledo calderas, location and characteristics of the ring fracture zone, and studies of the most complete sections of Bandelier Tuff.

Drilling at this site is proposed to be completed in two stages; the first stage involves coring to a depth of 2 km or the top of the lower member of the Bandelier Tuff (VC-4A), and the second stage involves drilling through the floor of the caldera or to a depth of 5 km (VC-4B). This science plan will address problems to be studied within the 2 km core hole, VC-4A.

It was proposed by the workshop attendees that the moat core holes proposed at Creede caldera, Colorado, by the U.S. Geological Survey be drilled immediately after the Valles core hole VC-4A by the same drilling and science teams. The goals are similar, with cores and data from both fossil and active caldera/hydrothermal systems. We feel that this symbiosis will increase the scientific benefits and our understanding of caldera-forming processes and caldera-hosted hydrothermal systems and volcanogenic mineral deposits. The overall Valles/Creede project will involve proposals to the U.S. Department of Energy, the U.S. Geological Survey, and the National Science Foundation.

Contractor:	LOS ALAMOS NATIONAL LABORATORY University of California Los Alamos, New Mexico 87545
Contract:	W-7405-ENG-36
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@ESSDP2.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. Specifically, we use electron and ion distribution functions observed by Los Alamos plasma instruments on scientific satellites 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 1989 has been our improved understanding of the Earth's magnetopause through the use of computer simulations. The magnetopause represents the boundary between the plasma and magnetic field of the solar wind and those of the Earth's magnetosphere. Recent analyses of the magnetopause have concluded that plasma diffusion across this boundary is unimportant. Our simulations have demonstrated that at least two of the assumptions underlying these analyses are incorrect and indicate that cross-field transport at the magnetopause may indeed contribute to solar wind-magnetosphere coupling.

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 models of the structure and dynamics of the magnetosphere.

Our most important achievements in 1989 were made in the analysis of auroral images taken from outer space and in the theoretical interpretation of these images. We have found that during very quiet geomagnetic conditions the region of auroral emission assumes a unique configuration that we have named the "horse-collar aurora." We have now used an empirical model of the magnetospheric magnetic field to show that closed field lines in the magnetotail do indeed map to a horsecollar shape on the Earth's surface and that increased geomagnetic activity or a strong east-west component of the solar wind magnetic field alters this characteristic shape. This success confirms the procedure for mapping local auroral phenomena to specific regions of the magnetosphere and enhances our ability to understand precipitation mechanisms associated with the various types of aurorae.

C. Energetic Particle Acceleration *(T. E. Cayton [505-665-2582; FAX 505-665-3332; E-mail 084731@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. By energetic particles we mean that population of ions and electrons that extends from just above the bulk thermal plasma population all the way to the highest velocity charged particles of the measurable plasma energy distribution function, so that our studies examine energetic particle phenomena from a few keV to many MeV.

Our most important result of 1989 has been the demonstration that both energetic electrons and energetic ions observed at geosynchronous orbit exhibit characteristic two-Maxwellian velocity distributions. The more tenuous, hotter (T ~ 200 keV) electrons show very little temperature change on a substorm time scale of hours, whereas the more dense, less hot (T ~ 25 keV) electrons are much more variable and are characterized by strong substorm-related injections. In contrast, it is the hotter (T ~ 100 keV) proton component which exhibits the greater variability, especially during solar flare proton events, whereas the less hot (T ~ 30 keV) proton component is characterized by quasiperiodic fluctuations of approximately 27-day periodicity.

D. Radiation from Space and Astrophysical Plasmas *(G. 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 1989 has been a combined computational and theoretical analysis of the heating and acceleration of electrons trapped on magnetic field lines between approaching magnetic mirrors. Our relativistic, three-dimensional, collisionless test particle simulations show that an initial thermal electron distribution is bulk heated while a few individual electrons are accelerated to many times their original energy before they escape the trap. Results from this study are applicable to acceleration of electrons at the Earth's bow shock, in solar flare shocks, and in supernova remnant shocks in the interstellar medium.

Contractor: OAK RIDGE NATIONAL LABORATORY
Martin Marietta Energy Systems, Inc.
Oak Ridge, Tennessee 37831

Contract: DE-AC05-840R21400

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)*

Our work combines complementary research in seismic imaging and geochemistry to investigate the spatial configuration of magmatic and hydrothermal systems. It involves the acquisition of experimental data for a well-defined object in the field and the use of those data to develop and test seismic imaging algorithms.

The object of our experiment is an artificial lava lake formed by melting rock and soil, which subsequently recrystallizes, during the In Situ Vitrification (ISV) test at the Oak Ridge National Laboratory. The dimensions of the artificial lava lake are several meters on a side and approximately 2.5 m deep. Seismic data are recorded using surface sources, 3-component geophones on the surface, and hydrophones in boreholes to produce a sequence of images of the parent material before it is melted, at several stages as melting proceeds, and at intervals during recrystallization. Temperatures during melting and recrystallization are monitored using a combination of optic fiber thermometry and high-temperature thermocouples. Vapors and particulates released during the melting period are collected, analyzed, and correlated with geophysical, thermal, and geochemical characteristics of the liquidus. Following recrystallization, the mass will be core drilled for geochemical and petrologic characterization that will provide information for comparison with the seismic images.

Contractor: OAK RIDGE NATIONAL LABORATORY
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Contract: DE-AC05-840R21400

Category: Geochemistry

Person in Charge: R. E. Mesmer (615-574-4958; FAX 615-576-2912; E-mail rem@msr.emp.ornl.gov)

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

In natural waters, the hydrolytic aluminum species, $Al(OH)_x^{3-x}$ (x = 0–4), dominate the chemistry of aluminum and the solubility of aluminosilicate minerals over a wide range of temperatures and compositions. In order to determine the stability fields of the stepwise hydroxyl species, solubility and emf studies are under way. The formation constant of $Al(OH)^{2+}$ has been measured in 0.1 molal NaCl in the range 25–175°C by potentiometric titrations using a hydrogen electrode concentration cell. The solubility of gibbsite — $Al(OH)^3$ — has been measured as a function of pH in 0.1 molal NaCl solutions at 50°C. The pH was controlled in the range 3 to 9 by several organic buffers, acetate, Tris, and Bistris, with experiments performed over a range of total buffer concentrations at each pH. After subtracting out the contributions due to interactions of aluminum species with the buffers, as discussed below, the solubility of gibbsite in acetate, Bistris, and Tris buffers forms a smooth, continuous solubility curve, with a minimum near 10^{-8} molal total aluminum at a hydrogen ion concentration of $10^{-5.5}$ at 50°C in 0.1 molal NaCl. The measured solubilities in the pH ranges of 3–4.5 and 6–9 are in quantitative agreement with the emf results discussed above, coupled with gibbsite solubility measurements in NaCl-HCl and Na-K-OH-Cl solutions conducted in a parallel program funded by the Geothermal Technology Division. An additional species, probably $Al(OH)_2^+$, is needed over a very narrow pH range in order to quantitatively explain the entire solubility curve. Modeling of these results is now under way.

B. Complexation of Metal Ions by Organic Ligands in Aqueous Solutions *(D. J. Wesolowski [615-574-6903; FAX 615-576-2912], D. A. Palmer, and S. E. Drummond, joint research with T. H. Giordano, New Mexico State University)*

Measurements of gibbsite — $Al(OH)_3$ — solubility in acetic acid/sodium acetate buffers (total acetate concentrations of 0.001, 0.005, and 0.01 molal) in 0.1 molal NaCl solutions at 50°C demonstrate that acetate forms a strong complex with Al^{3+} in solutions similar to oilfield brines. The calculated formation constant for the monoacetate aluminum complex of 10^2 at 50°C is in quantitative agreement with results of potentiometric titrations of acetate buffers with $AlCl^3$ in 0.1 molal NaCl, which indicate a formation constant ranging from 10^2 at 50°C to $10^{4.4}$ at 150°C. The formation constant for the diacetate aluminum complex was also determined from the potentiometric studies, ranging from $10^{3.3}$ at 50°C to 10^8 at 150°C in 0.1 molal NaCl. These results, together with earlier potentiometric studies of the complexation of Zn^{2+} and Fe^{2+} by acetate, indicate that the generation of carboxylic acids (acetate, propionate, oxalate, etc.) during maturation of hydrocarbons in sedimentary basins and geothermal systems may have a profound

influence on secondary porosity development, the paragenesis of diagenetic and alteration mineral assemblages, and possibly Mississippi-Valley-Type ore deposit formation.

Gibbsite solubility measurements in slightly basic 0.1 molal NaCl solutions at 50°C indicate that $Al(OH)_4^-$ forms an even stronger complex (formation constant of approximately $10^{2.6}$ at 50°C) with Bistris, a sugar-like polyhydroxyl organic pH buffer. The Bistris complex was confirmed by Raman spectroscopy and additional gibbsite solubility measurements in NaOH-Bistris solutions. Tris buffer, which is structurally similar to Bistris, does not interact significantly with any aluminum species, suggesting that the spacing of hydroxyl groups on the polyhydroxyl ligand is critical in determining its interaction with aluminate anion. Dextrose forms a much weaker complex with aluminate, but sucrose, mannitol, ethylene glycol, and glycerol do not interact significantly with aluminate in the 25–50°C range. Because polyhydroxyl sugar-like compounds and organic acids are abundant in shallow environments, these results have important implications for the mobility and toxicity of aluminum in groundwaters and waste disposal sites, as well as in sedimentary basins.

C. Solubilities of Calcite and Dolomite in Hydrothermal Solutions *(D. R. Cole [615-574-5473; FAX 615-576-2912] and S. E. Drummond)*

Highly accurate measurements of the solubilities of calcite and dolomite are needed in order to model diagenesis and the development of secondary porosity in sedimentary basins, because calcite is a common diagenetic phase and the dolomitization of limestone involves a 14.2% volume reduction. Calcite is also one of the major scales which develop in geothermal reservoirs and production wells. Previous studies demonstrated that the logarithm of the equilibrium constant for the reaction $CaCO_3 + CO_2 + H_2O \rightleftarrows Ca^{2+} 2HCO_3^-$ at 300 bars total pressure decreases from –4.86 at 100°C to –9.98 at 300°C. At 1000 bars, the equivalent log K values are 3.98 at 100°C and –8.05 at 300°C. For the reaction $\frac{1}{2} CaMg(CO_3)_2 + CO_2 + H_2O \rightleftarrows \frac{1}{2} Ca^{2+} + \frac{1}{2} Mg^{2+} + 2HCO_3^-$, the log K values at 300 bars range from –4.35 at 100°C to –8.56 at 300°C. This year, these reactions were studied at 50°C and 300 bars, giving log K values of –4.09+0.02 for the calcite reaction and –4.41+0.02 for the dolomite reaction. The kinetics of dissolution are extremely sluggish at these conditions, resulting in very time-consuming experiments. A series of Ca-Mg cation exchange experiments with calcite-dolomite mixtures at 25, 50, and 70°C and 1 bar were also initiated during this period. A value of 0.445 was obtained for the equilibrium $\log(Ca^{2+}/Mg^{2+})$ value at 50°C. Accurate data of this type are needed in order to predict the onset of dolomitization or dedolomitization in coupled reaction-transport computer codes.

D. Stable Isotope Exchange in the System Calcite-CO_2-H_2O at Elevated Temperatures and Pressures *(D. R. Cole [615-574-5473; FAX 615-576-2912] and T. Burch, joint research with A. C. Lasaga, Yale University)*

In order to examine the effect of fluid composition on the rates and mechanisms of carbon and oxygen isotope exchange between calcite, CO_2, and H_2O, we have conducted experiments from 300°C, 250 bar to 700°C 1.0 kbar at % X_{CO_2} = 0, 2, 4, 5, 11, 18, and 100. A minimum of four runs lasting 72–1200 hours were performed at each P,T,X condition to constrain the time dependence of isotopic exchange. The experimental conditions cover a wide range in calcite solubility and CO_2-H_2O miscibility and re-examine the $CaCO_3$-CO_2 and $CaCO_3$-H_2O subsystems. SEM observations show that essentially no grain growth occurs when CO_2 is present in any amount, even at 700°C, whereas recrystallization and growth in pure H_2O is extensive, in support of previous pseudo-first-order kinetic models for calcite-water exchange. Based on the SEM observations, we have modeled carbon and oxygen isotope exchange using a combination

of diffusion and surface reaction rate models. The experimental data demonstrate the following: (1) carbon isotope exchange occurs primarily by diffusion, even at 700°C, 1.0 kbar and X_{CO_2} = 0.02, (2) oxygen isotope exchange is faster than carbon for all X_{CO_2}, by more than one order of magnitude in some cases, (3) oxygen exchange rates in pure H_2O are much faster than in H_2O + CO_2, except at 300°C, and (4) annealing of grains leads to lower fractions of exchange than predicted from initial rates due to a reduction of specific surface area and elimination of defects. The reduced rates of isotopic exchange for calcite in the presence of CO_2 + H_2O has profound implications for the attainment of isotopic equilibrium in hydrothermal/metamorphic systems.

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

Carbon and oxygen isotopes in soil carbonates are useful tracers of the influence of climate on soil-forming processes. We have used this approach to delineate paleoclimatic conditions for caliches deposited in fluvial and supratidal rocks of the Abo Formation (Permian), south-central New Mexico. Stable oxygen isotopes are similar in fluvial and supratidal caliches, ranging from 21.6 to 30.5 °/oo (SMOW) with $\delta^{18}O$ enrichment correlated with decreasing age. Consideration of these data in the context of δ-temperature relationships suggest that (1) surface waters responsible for caliche formation increased in $\delta^{18}O$ (from roughly –8 to 1 °/oo) over the 8 m.y. time interval that separated the lowest stratigraphic nodule horizon from the highest, and (2) the increasing $\delta^{18}O$ values reflect a warming trend (approximately 15 to nearly 30°C) in the mean monthly temperature over this same time period, with perhaps an associated increase in Permian ocean temperature. The persistence of caliche and the paucity of gleization support the view that the paleoclimate became warmer and drier with time. Caliches in the Abo are enriched in heavy carbon (–7.2 to –1.5 °/oo PDB) compared to that of soil carbonate derived exclusively from C_3 plants (–12 °/oo PDB), with the supratidal caliches containing somewhat heavier carbon (av = –3.0 °/oo PDB) compared to the fluvial caliches (av = –5.3 °/oo PDB). The $\delta^{13}C$ values for both environments increase with a decrease in caliche age. These results indicate that as the temperature increased and rainfall decreased with time, the level of C_3 plant productivity apparently declined, allowing a greater influx of atmospheric CO_2 into the soil. This process seems to have been somewhat more pervasive in the supratidal environment.

F. Stable Isotope Trends in Fossil Geothermal Systems *(D. R. Cole [615-5745473; FAX 615-576-2912], joint research with B. S. Smith, LBL, and T. Albinson, MAGSA, Mexico City)*

Isotopic data on fossil geothermal systems in central Mexico have provided insight into the nature of the mineralizing fluids responsible for metal transport and deposition (e.g., boiling, mixing). A correlation between increasing $\delta^{18}O$ values with decreasing salinity and depth is indicative of enrichment due to boiling (e.g., Catorce). Mixing systems seem to exhibit a trend of decreasing $\delta^{18}O$ values with decreasing salinity and depth (e.g., Colorada). In general, the oxygen isotopic compositions of fluids responsible for the mineralization in Ag-Pb-Zn epithermal deposits in central Mexico are very enriched, namely +2 to +10 °/oo. Fluids from the high end of this range are typically from boiling horizons. Hydrogen isotope analyses have also been obtained in both altered whole rocks and fluid inclusion waters from Sombrerete and Colorada. The fluid inclusion δD values range from –45 to –83 °/oo for Stage 1 quartz plus sulfide mineralization at Sombrerete and –66 to –89 °/oo for Colorada mineral stage quartz plus sulfides. These values are similar to those reported for the nearby Santo Nino vein: –30 to –74 °/oo. The δD values for fluids assumed to have equilibrated at 250°C with altered whole rock (–72 to –86 °/oo) at Sombrerete are similar to the fluid inclusion values: approximately –62 to –76 °/oo. The range

in these δD data is similar to that given for magmatic waters, but is also in the same range as local meteoric water. Our hypothesis is that these relatively low salinity fluids (av wt % NaCl < 5) are probably either highly evolved meteoric waters or formational waters that have interacted on a regional scale with a thick sedimentary sequence composed of graywacke, shale, and limestone, which underlie the volcanic-hosted deposits. At 250°C and a water/rock ratio of one or less, fluids could exhibit $\delta^{18}O$ values as low as approximately +3 (equilibrated with clastics) to as high as +18 (equilibrated with carbonates). Batholithic-scale intrusions at depth provide both the source of heat and the volcanics which act as a host for the mineralization.

G. H_2O Fugacity Effects on the Oxidation State of Silicate Melts *(M. T. Naney [615-576-2049; FAX 615-576-2912], joint research with D. Hamilton, University of Manchester)*

Experiments are being conducted in our hydrogen service internally heated pressure vessel (IHPV) at 1150°C and 200 MPa with H_2O saturated liquid compositions produced by melting U.S. Geological Survey rock standards RGM-a, VHVO-1, linear combinations of RGM-1 and BHVO-1, and per-alkalinesilicic compositions from Pantelleria. In these experiments, $a_{H_2O}^{vapor} = a_{H_2O}^{melt} = 1$ (i.e., the silicate melts are saturated in water). The f_{H_2} is buffered by H_2-Ar gas mixtures in the IHPV. These compositions will be subjected to f_{H_2} values up to approximately 100 MPa to investigate T-f_{O_2} conditions ranging from hematite-magnetite to magnetite-wustite. These experiments are designed to test the Kilinc et al. (1983) model for relating the melt Fe^{3+}/Fe^{2+} ratios to f_{O_2} and bulk composition in hydrous silicate systems. The experiments will permit an independent test of the Kilinc equation, which is currently being used by a number of investigators to determine magmatic f_{O_2} conditions from natural glass volcanic rocks. If these results are consistent, experiments with H_2O-vapor-absent melts will be performed to investigate X_{H_2O}–f_{H_2O} relations in H_2O-vapor-absent or mixed volatile systems.

H. Chemistry, Mineralogy, and Textural Development of Silicic Magma in Volcanic and Subvolcanic Environments *(M. T. Naney [615-576-2049; FAX 615-576-2912], joint research with R. G. Gibson, AMOCO)*

Results of detailed mineralogical analysis of silicic lavas from the Inyo volcanic chain support the hypothesis that magma mixing was the primary process responsible for the bimodal mineral chemistry and banded texture typical of these rocks. Samples obtained from the surface and drill holes were subdivided into three types based on microscopic texture, mineralogy, and mineral chemistry: (I) non-banded tephra and dike samples from the Inyo Craters containing andesine phenocrysts, Mg-rich orthopyroxene, and abundant ilmenite; (II) non-banded samples from the upper part of the Obsidian Dome tephra and the dike near Obsidian Dome containing oligoclase+alkali feldspar phenocrysts, Fe-rich ferromagnesian silicates (biotite, hornblende, orthopyroxene, clinopyroxene), and no ilmenite; and (III) banded samples from the early Obsidian Dome tephra, the conduit beneath Obsidan Dome, and the body of the Glass Creek, South Deadman, and Obsidian Domes. Banding is defined either by variations in glass color, reflecting variations in chemistry, or variable microlite abundance. Compositions of all minerals in type III samples are bimodal, and these mineral composition groups can be correlated with diagnostic textural features. Mineral grains with compositions similar to those measured in type I samples occur in brown glass or microlite-rich bands, whereas grains with compositions like their type II counterparts occur in microlite-poor bands of colorless glass. The observed features of the type III samples are interpreted to be the result of mechanical mixing between two crystal-bearing siliceous magmas. On the basis of phenocryst compositions and glass chemistry, the mixing end-members are interpreted to have been of rhyolitic (T = 40–800°C, log f_{O_2} = –14.0 to –15.2, f_{O_2} = 27.417 bars) and dacitic (T = 825–925°C, log f_{O_2} = –10.9 to –12.7, $f_{O_2} \geq 100$ bars) compositions.

Mixing probably occurred while the two end-members were being drawn simultaneously through the subvolcanic conduits from a zoned dike. Banding in the type III samples formed either as (a) samples of the commingled magmas were immediately vented to the surface and quenched, preserving bands of two distinct glass compositions, or (2) bands of the hotter dacitic magma precipitated microlites when commingled with the cooler rhyolitic magma in response to changing temperature and/or dissolved water content.

I. Unit Cell Parameters of Synthetic Paragonite-Muscovite Micas *(J. G. Blencoe [615-574-7041; FAX 615-576-2912]*

Felsic igneous rocks commonly contain small to moderate amounts of Na-bearing muscovite. Therefore, an improved understanding of the crystallization histories of these rocks can be gained through experimental investigations of the geochemistry of muscovite and paragonite-muscovite crystalline solutions. To augment the body of information available on the geochemistry of paragonite-muscovite micas, unit-cell parameters of 1M and $2M_1$ synthetic Na-K paragonites and muscovites (Pa-Mu micas) synthesized at 2, 4, and 8 kbar, 400°–775°C have been reinterpreted. Micas synthesized at 2 and 4 kbar are 1M polytypes; however, at 8 kbar, 1M micas crystallized at low temperatures and with increased temperature, 1M–2M mixtures and finally just $2M_1$ polytypes were obtained. X-ray powder-diffraction data were used in the refinement of unit-cell parameters for each mica, and the results of these refinements indicate that: (1) in general, the unit-cell dimensions of 1M Pa-Mu micas decrease slightly with increased synthesis pressure; (2) there are small increases in the a and b cell edges and large increases in the c cell edge, with increasing K/Na ratio; (3) the unit-cell parameter values for $2M_1$ micas are significantly more precise than comparable values for 1M micas; and (4) the unit-cell parameter values for $2M_1$ micas are in excellent agreement with corresponding values obtained by Flux and Chatterjee. Evaluation of published molal volume equations for Pa-Mu micas suggests that excess molal volume for these micas is continuously positive with a maximum between 0.6 and 0.7 joules/bar-gfw.

J. An Attempt to Observe "Cold Fusion" in Deuterated Palladium and Titanium at 4 kbar *(J. G. Blencoe [615-574-7041; FAX 615-576-2912], M. T. Naney, D. J. Wesolowski, and F. G. Perey)*

In March 1989, Pons and Fleischmann announced that they had achieved "cold fusion" by electrolyzing D_2O at palladium and titanium cathodes in an LiOD solution. Shortly after that time, Steven Jones at BYU reported similar results and presented arguments which suggested that such a process might (a) explain the $^3He/^4He$ data from volcanoes and mid-ocean ridges and (b) might provide an energy source for deep mantle processes. The hypothesis at that time was that, because large quantities of deuterium can dissolve in palladium, fusion of the deuterons occurred inside the cathode. Recognizing that stoichiometrically similar amounts of deuterium could be forced into palladium using our group's high P-T hydrogen pumping system, we decided to do some experiments of this type. A pressure vessel was designed and constructed and a sophisticated neutron (a fusion product) detection system was set up. Samples of palladium and titanium metal were subjected to temperature cycling from liquid nitrogen temperatures to room temperature at D_2 gas pressures ranging from 1 to 4000 atmospheres. A number of high-sensitivity neutron detection experiments were conducted which have been reported in the literature and at a DOE workshop in Santa Fe. All of our results were negative, and our major contribution was in demonstrating that (a) very high D_2 gas pressures do not enhance the likelihood of "cold fusion" in these metals and (b) that the BF_3 and ^3He detectors used in these and a large number of other experiments worldwide are subject to electronic and mechanical

noise, which can lead to apparently anomalous neutron emissions which are not due to "cold fusion."

K. Crustal Stability of C-O-H Fluids *(J. G. Blencoe [615-574-7041; FAX 615-576-2912], S. E. Drummond, and M. T. Naney)*

The principal objective of this research is to establish the equilibrium proportions of methane, carbon dioxide, water, and hydrogen in C-O-H gas mixtures at pressure-temperature conditions up to 10 kb and 1100°C. Preliminary experiments have been conducted to evaluate the performance of a vibrating-tube densimeter (VTD) designed to measure the P-V-T properties of C-O-H gases. The experimental strategy adopted for determining the P-V-T properties of pure C-O-H gases is to: (1) measure the vibrational periods of suitable standards (H_2O, Ar, N_2, and, at low pressures, He) under isobaric, isothermal conditions; (2) make corresponding measurements on one or more "unknown" gases (e.g., CH_4); (3) develop a calibration equation from data obtained in step 1 using published P-V-T equations for the standard gases; and (4) calculate the volumes of the "unknown" gases using the data obtained in step 2 and the calibration equation developed in step 3. Scoping experiments completed to date have employed CO_2 as a pure "unknown" C-O-H gas. The goal of these experiments is to evaluate the performance of the VTD over pressure-temperature conditions where the available P-V-T equations of state for the standards and CO_2 are generally regarded as highly accurate (500–1000 bars, 50–400°C). Results obtained at 500–1000 bars, 50°C, reveal that vibration period-squared vs. density data for the four standards are almost perfectly linear. This result indicates that the VTD is exhibiting theoretically "ideal" behavior. Volumetric data for CO_2 obtained at the same pressure-temperature conditions are in excellent agreement with data obtained by previous investigators.

L. Hydrothermal Stability of Organic Acids *(J. L. S. Bell [615-576-4600; FAX 615-576-2912], S. E. Drummond, and D. A. Palmer)*

Experiments conducted over the past year indicate that quartz and pyrite have minimal catalytic effects on acetic acid/acetate decarboxylation. (Surface areas for these minerals have not yet been measured; however, data obtained previously at ORNL indicate that—beyond a minimum threshold value—surface area has only a minor effect on decarboxylation.) Calculated first-order rate constants for these minerals—approximately 10^{-19} at 100°C—are virtually indistinguishable from the rate constants for decarboxylation of acetic acid/acetate in the absence of mineral surfaces. In contrast, it was observed that hematite had a profound effect on decarboxylation rates. In experiments performed with this mineral, the periods required to achieve a 50% reduction in acetic acid concentration ($t^{1/2}$) were 200 hours at 335°C and 75 hours at 355°C. Compared with a noncatalytic mineral such as quartz ($t^{1/2}$ – 1.5 years at 335°C and 0.4 years at 355°C), it is evident that hematite is an effective catalyst for acetic acid/acetate decarboxylation. Unfortunately, however, slow conversion of hematite to magnetite during the course of the hematite experiments means that an accurate rate constant cannot be derived for this mineral. A series of follow-up experiments have been initiated in which the initial concentration of acetic acid was varied while the surface area of the hematite was held constant. It is hoped that, despite slow conversion to magnetite, initial rates of decarboxylation obtained from these experiments will be representative of the true effect of hematite on acetic acid decarboxylation. Finally, it was observed that iron-bearing montmorillonite (3.6% Fe^{3+} as Fe_2O_3) had a significant catalytic effect, which tended to diminish with run time, suggesting, together with the hematite results, that decarboxylation may be homogeneously catalyzed by Fe^{3+} or other oxidized metal ions in solution. Calcium-montmorillonite has a moderate catalytic effect on the rate of decarboxylation.

M. Salinity Effects on Oxygen and Hydrogen Isotope Partitioning between Geothermal Brines and Other Phases at Elevated Temperatures *(D. R. Cole [615-574-5473; FAX 615-576-2912] and D. J. Wesolowski)*

Equilibrium isotopic fraction factors for D/H and $^{18}O/^{16}O$ exchange between silicate minerals and NaCl solutions have been estimated to 300°C, based on sparse literature data and our results for liquid/vapor D/H exchange as a function of NaCl concentration at 70 and 100°C. Between 25° and 300°C, salinity effects for both oxygen and hydrogen exhibit a complex, nonlinear temperature-composition dependence that is difficult to predict from electrolyte theory. The salt effect can be as large as 3.5 permil for oxygen and 12 permil for hydrogen at temperatures above 150°C. If ignored, the salt effect associated with a 4 molal NaCl solution can lead to errors in geothermometry estimates of 30° to 50°C. In boiling hydrothermal fluids, the presence of NaCl profoundly influences the $^{18}O/^{16}O$ and D/H partitioning between liquid and vapor. As an extreme, at 250°C in the pure water system, the $\delta^{18}O$ values of liquid and vapor continually increase as boiling proceeds, whereas with NaCl present the general trend is one of *depletion* in $\delta^{18}O$ for both liquid and vapor. Quartz precipitated from these two systems would mimic these dissimilar trends. The magnitude of the salinity effects on rates of exchange and equilibrium fractionations are far too great to be ignored and must be accounted for when modeling data from natural systems and experiments.

A major effort was expended during this period in assembling and critically reviewing the available data, including past results from this program, on the effect of dissolved NaCl on the rates of D/H and $^{18}O/^{16}O$ exchange and the equilibrium fractionations between aqueous NaCl solutions and other phases, including silicate minerals and the vapor phase. We have demonstrated that rates of isotopic exchange are greatly enhanced by interaction of a mineral or rock with NaCl solutions relative to interaction with pure water. This rate increase is due to either the more rapid transformation of the reactant phase to a new phase (e.g., sanidine to albite) or recrystallization of the reactant compared to pure water systems. For example, at 250°C the rate of oxygen isotopic exchange for sanidine-H_2O is $10^{-9.0}$ moles $O/m^2/sec$ versus $10^{-7.8}$ for the interaction of sanidine with 2–3 molal NaCl solutions. The time required to obtain 90% equilibration in the systems sanidine-H_2O-NaCl, quartz-H_2O-NaF, and calcite-H_2O-NH_4Cl has been calculated using a modified surface-exchange rate model for closed systems. These calculations indicate that below 300°C the rate of isotopic equilibration can be 2 to 50 times faster than in pure H_2O, depending on the mineral and type and concentration of electrolyte.

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

Potentiometry measurements of protolytic aqueous reactions using hydrogen-electrode emf cells constitutes one of the most productive and accurate methods of obtaining quantitative data on important hydrothermal processes. Our current effort involves expanding the capabilities of this methodology to temperatures of 450°C and pressures to 1 kbar by constructing a flowing emf cell fitted with hydrogen electrodes, but having no vapor space, and using yttria-stabilized cubic zirconia single crystals as the inert insulator and pressure vessel. The cell will operate in a continuous-flow mode, with residence times in the hot zone of only a few tens of seconds. This will enable studies of systems containing species metastable in the presence of molecular hydrogen (e.g., sulfate) as well as systems containing volatile species.

A parallel effort is under way to develop geological applications for our newly acquired Cameca ims/4f ion microprobe. Our principal interest is in developing quantitative analyses of the light stable isotopes (C,O,H) in natural samples and experimental charges at a resolution of 1 permil for beam diameters from 10 down to 1 micron. However, we are also developing analytical methods for routine trace element analysis in geologic materials.

Contractor: PACIFIC NORTHWEST LABORATORY
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Contract: DE-AC06-76RLO 1830

Category: Geochemistry

Person in Charge: J. C. Laul

A. Chemical Migration in Continental Crustal and Geothermal Systems *(J. C. Laul [509-376-3539])*

This research program focuses on gaining a quantitative understanding of chemical migration over a range of temperatures in diverse geological media and geothermal systems. The study includes the understanding of dispensing solutions into country rocks, partitioning of elements between minerals and solutions derived from granite and pegmatite, and composition and evolution of the solutions.

The proposed sites are the Harney Peak Granite in the Black Hills, South Dakota, and carbonatite intrusions (rich in REE, U, and Th) in the Bear Lodge Mountain, Wyoming. As part of the CSDP, we plan to participate in the chemical study of cores from the Long Valley caldera, California. These studies focus on some 40 elements, with specific emphasis on the REE, Ba, Sr, K, Rb, Cs, As, Sb, Pb, Zr, Hf, Ni, Th, and U, which are analogs of radwaste radionuclides.

A suite of altered and unaltered samples from the Valley of Ten Thousand Smokes in Alaska has been studied for various trace elements. The concentrations of rare earth elements (REE) range from La as 40× to 100× (chondrites), and the REE patterns are nearly flat except that the Eu anomaly varies significantly. The altered samples lack a negative Eu anomaly, while the unaltered samples show a strong negative Eu anomaly. This alteration is related to the Eu anomaly, which in turn seems related to the plagioclase content in the sample.

For geothermal systems (water/rock interaction), the proposed site is Valles caldera VC-2A and V2C-2B in New Mexico. The emphasis is on natural radionuclides of ^{238}U and ^{232}Th series and REE in thermal fluids and cores. The study will provide information on the *in situ* retardation and sorption/desorption parameters for transport models of various elements and their associated kinetics (residence time), past migration of radionuclides in cores, and source region geochemistry and mixing of groundwaters.

The granite/pegmatite and Long Valley studies are in collaboration with J. J. Papike, University of New Mexico, Albuquerque, New Mexico, who is responsible for geologic, petrographic, and petrologic systematics. Our focus will be on the chemical systematics of some 40 elements by XRF, AA, INAA, and ICP-MS.

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 [509-376-8425; FAX 509-376-5368; E-mail ed%vistal@pnlg.pnl.gov]

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 106 to 108 data values, and thus are of the same order of size as multispectral satellite data sets. In the past year, we have extended our work with two-dimensional data sets to the more general problem of visualization of multidimensional spatial and temporal 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. One of the areas of particular attention is the Valles caldera in New Mexico, a Continental Scientific Drilling site where an extensive geologic and geophysical database exists. For this location, we have registered Landsat and SPOT satellite imagery, geologic, gravity, and digital elevation data sets. We are evaluating techniques for displaying geologic cross sections in the context of the other data sets. We are developing an approach in which the apparent viewpoint moves from one point of interest to another, and geologic cross sections can in effect be lifted out of the surface for detailed viewing.

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, K. A. Hoover, and P. G. Heasler)*

We are developing an automated pattern-recognition system for spatial analysis and synthesis of digital topographic, geologic, and geophysical data. Our emphasis is on identifying the tectonic conditions and 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 to (1) semiautomatically 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 fault and fracture systems manifested at the Earth's surface, (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 topography, we are also studying the noise and error structures of digital elevation models and the way in which those errors are propagated through our analyses.

The Remote Geologic Analysis system is currently operational at the level of our first objective, 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.

Contractor:	PACIFIC NORTHWEST LABORATORY Battelle Memorial Institute Richland, Washington 99352
Contract:	DE-AC06-76RLO 1830
Category:	Solar, Solar-Terrestrial, and Atmospheric Interactions
Person in Charge:	E. W. Kleckner

The insolation/aeronomy program encompasses the area of aeronomy in the upper atmosphere and the area of insolation and radiative transfer in the lower atmosphere. Specifically, the aeronomy program is concerned with the plasmasphere/magnetosphere regions and the ionosphere/upper atmosphere regions. Significant advances have been achieved over the past two decades in expanding our basic knowledge of the Earth's atmosphere and magnetosphere and the Sun as an interacting system. The physics of this coupling region must be well understood to obtain definitive solar-terrestrial cause-effect relationships.

The insolation program relies on a data base of direct and diffuse solar radiation measurements made in visible and near-infrared spectral passbands. The research has two goals. One is to quantify the spectral characteristics of scattered and direct sunlight. This is germane to energy generating solar technologies, including photovoltaics and daylighting. The primary emphasis of the insolation task, however, is to characterize the influence of trace species in the troposphere and lower stratosphere on solar radiation. These man-made or naturally produced trace species include aerosols, molecules, and clouds.

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

The Rattlesnake Mountain Observatory data set of direct solar measurements (1977–1989) has been analyzed. Based on these data, we have extracted the effect of volcanic aerosols on the stratospheric aerosol burden. In particular, a detailed examination of the effect of the El Chichon eruption has been made. The outstanding features of the stratospheric data are the El Chichon peak and a seasonal modulation of the exponential decline. This modulation, which persists until the perturbation has entirely decayed, suggests meridional transport of aerosol-laden air between arctic and equatorial regions. We have made a wavelength-dependent inversion of this turbidity data to cover the aerosol size distributions as a function of time.

A unique instrument, the rotating shadowband radiometer (RSR), was developed for making measurements of the direct, diffuse, and horizontal solar flux density. This low-cost, low-maintenance device has significant advantages over the instrumentation that is traditionally used for solar resource assessment. Our investigations show that this device can also be used for monitoring atmospheric visibility changes through measuring atmospheric transparency. A detection limit of 0.01 optical depths (representing about a one-percent change in atmospheric transparency) is achievable, which should be adequate to track visibility changes in Class I areas of the United States, where scenic vistas are to be protected.

We use mid- and high-latitude auroral and ionospheric phenomena to reveal solar-terrestrial relations involving wide-ranging and complex interactions. A major goal of the aeronomy program is to investigate the coupling of the ionosphere, plasmasphere, and magnetosphere, primarily through the use of optical remote sensing. To accomplish this, a network of automatic photometers was engineered and deployed to acquire synoptic observations of the aurora and airglow above major portions of the North American continent. Catalogs of all data available through the middle of 1990 have been created and are available for research studies by outside users.

An extensive examination of this database, along with a search of the entire Dynamics Explorer-2 satellite data base yielded approximately 30 periods of coincident measurements during Stable Auroral Red (SAR) arc events. Approximately 50 additional instances of the satellite passing through SAR arc regions while at 300 km to 500 km altitude have also been identified. Data from the satellite during these periods are currently being examined to identify any perturbations of the ionic or neutral components of the thermosphere as compared to expectations based on current models.

A series of studies with the University of Michigan has used our photometric data, together with satellite data sets, to attempt identification of regions within the ring current that are associated with SAR arcs. The satellite data used to characterize the composition and energy spectra of the ring current population are combined with the ground-based photometric observations. A model being developed then compares predictions of energy influx and resulting emission intensities from selected events. These studies have also sought to explain seasonal and solar cycle variations of SAR intensities that have become evident in the PNL data base.

Construction of a new solid-state, intensified imager for use in extremely low light-level conditions has been completed. The sensor element is a charge coupled device (CCD) consisting of an array of 384 × 576 diodes. The optical train preceding this device consists of interchangeable lenses to control field-of-view, a filtering section to control wavelength discrimination, and a microchannel plate image-intensifier capable of approximately 50,000 gain. Initial testing of the instrument has shown the system to exceed design criteria for detection of very low levels of illumination with the visible spectrum. The system is operational and is being used for a variety of studies. Data analysis of measurements made by the MASP network and the CCD Imager during a recent chemical release experiment above Canada has proven these data to be of considerable importance .

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 505-846-3464]

A. Crustal Strain (J. B. Rundle [505-844-8158])

A great number of critical energy facilities, including power plants, pipelines, power lines, and national laboratories, are located in regions of frequent and pronounced crustal instability. Examples of such tectonic instabilities include the October 17, 1989, Loma Prieta earthquake and the January 24, 1980, Livermore earthquake that affected the San Francisco Bay area. Thus it is of considerable importance to understand the physical mechanisms by which earthquakes and other crustal instabilities arise. The objective of this research is to develop physical models to explain geodetic strain changes observed at the Earth's surface over a period of years, as well as associated seismicity and other data. Laboratory data such as that obtained from experiments involving frictional sliding of rocks can also be used as a guide to the appropriate physics of the processes.

Emphasis in the past was on constructing and using kinematic Green's functions for interpretation of time dependent crustal deformations following earthquakes, gravity changes for layered inelastic media, and pore fluid and thermal changes due to internal sources of strain in the earth. Current emphasis is being placed upon the investigation of a variety of simple nonlinear dynamical models for nucleation phenomena, earthquakes, and frictional sliding. These models have appealing analogies to nonclassical nucleation phenomena in thermal and magnetic systems. As a result, productive interaction with theorists from the condensed-matter physics community is occurring.

B. Acoustic Emissions and Damage in Geomaterials *(D. J. Holcomb [505-844-2157])*

Under compressive stresses, brittle polycrystalline materials fail as the result of the accumulation of multiple microfailures. Constitutive laws for such materials must incorporate the effects of the microfailures, in particular the inelastic strain and reductions in elastic moduli. A method of incorporating accumulating failures into a continuum model is to replace the details of crack density, size, orientation, and development with a material property which is commonly called damage. Although a number of theories of damage have been proposed, there is no generally accepted technique for detecting and measuring damage. The purpose of this research is to develop such techniques, using acoustic emissions as the basic tool, and to apply the techniques to study the development of damage in geomaterials. Damage surfaces obtained for Tennessee marble, which undergoes a transition from brittle to ductile behavior at pressures above 20 MPa, are pressure-dependent in the brittle regime and independent of pressure in the ductile regime. The orientation of the inelastic strain increment vector, a macroscopic measure of damage, was studied. It was found that the inelastic strain nearly obeys normality if the yield surface is assumed to be the same as the damage surface determined using the acoustic emission (AE)

method. This links the microscopic results obtained from AE work to the macroscopic formulations used in continuum damage mechanics.

A paper entitled "Combining Acoustic Emission Locations and a Microcrack Damage Model to Study Development of Damage in Brittle Materials" was prepared for the 31st U.S. Symposium on Rock Mechanics. The goal was to compare the observed damage as determined from locating AE events with the damage calculated from a microcrack damage model. Reasonable agreement was obtained although it was clear that there were features in the damage distribution that the model was not reproducing. A repeat of the test is in progress with a more elaborate sensor network and using the upgraded AE acquisition system. The system is now capable of acquiring about 10 events per second on a sustained basis from a network of 16 transducers.

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

Anelastic strain recovery (ASR) measurement of oriented core is a technique that can, in some cases, provide important information about *in situ* stresses. In addition, the ASR measurements appear to indicate to what extent rock core has been disturbed from its *in situ* state by drilling. This study and previous work have shown that microcracks are induced by the coring and relaxation process, and it has been suggested that relaxation cracks are grain-boundary cracks that open more in the direction of maximum expansion. Accordingly, relaxation microcracks may be responsible for the anisotropy of petrophysical properties found in core from many tight reservoirs, and their closure may have a significant role in restoration of core to its *in situ* state. In order to determine the effect of relaxation microcracks on petrophysical properties at elevated pressure, deformation (strain), compressional velocity, and permeability measurements have been made at confining pressures to 60 MPa in two directions that were parallel to principal strain recovery directions of low porosity sandstone cores. The cores were from wells that were 1.5 to 2.5 km deep and had large strain recovery, velocity, and permeability anisotropy. The slowest velocity and highest permeability were in the maximum strain direction. With increasing confining pressure, velocity increased and permeability decreased as microcracks closed, but significant differences in the two directions were still present at confining pressure equal to the effective overburden stress. Velocity and permeability became isotropic at pressures that are nearly twice the effective overburden stress. These results indicate that relaxation microcracks are largely responsible for the velocity and permeability anisotropy in these cores at elevated pressure because the anisotropy is (1) aligned with the strain recovery directions, (2) principal horizontal strain recovery and *in situ* stress directions are aligned, and (3) petrographic observations of thin sections of the core did not show tectonic or intergranular cracks, sedimentary fabric, or alignment of grains or minerals. For tight rock, this implies that restoration of a core to its *in situ* state may be strain-history dependent, and requires higher stresses than *in situ*.

D. Transport Properties of Fractures *(S. R. Brown [505-846-0965])*

Fluid flow in fractured rocks is of primary importance to oil and gas production from fractured reservoirs, reservoir stimulation by hydrofracturing, hazardous waste isolation, and geothermal energy extraction. Central to these applications is the measurement of the hydraulic conductivity of a single fracture. Measurement of the electrical conductivity is a possible way to estimate the hydraulic properties both quickly and inexpensively. The purpose of this work is to better understand the physics of transport of fluid and electric current through fractures and the scale dependence of these properties. The work has three main parts: (1) laboratory measurements

leading to a complete description of the topography of fracture surfaces, including their scaling properties and the degree to which they are correlated with each other; (2) numerical simulations of transport properties of rough fractures with the goal of reducing the description to a minimum number of free parameters; (3) laboratory measurement of the dependence of hydraulic and electrical transport on fracture surface roughness and comparison of these results to predictions based on numerical simulations.

In support of the laboratory studies, a surface profiler and a rock core permeability system have been built, calibrated, and tested. The profilometer is being used for a study of the statistics of fracture surface roughness and aperture, including measurement of anisotropy of the aperture distribution in the fracture plane. Further numerical simulations are being done to study the effect of anisotropic roughness of the aperture distribution on the transport properties.

Previous theoretical and numerical results show that the electrical resistivity of a single fluid-filled fracture is strongly dependent on both the separation and roughness of the contacting surfaces. Initial experiments have been performed to test these results quantitatively. The specimens consisted of plastic replicas of actual fractured rock specimens filled with a strong electrolyte. Before the resistivity measurements were made, topographic profiles of both contacting surfaces were measured with the profilometer to allow computation of the aperture distribution. The aperture of the fracture is varied by placing various loads on the sample column and externally measuring the incremental closure of the fracture as a function of load. The value of resistivity at each step is converted to an equivalent parallel-plate aperture and is then compared to theoretical analyses such as effective medium theory and to previously obtained numerical results. The effective electric aperture decreases more rapidly than the fracture closure in the manner predicted by these models. If verified by fluid-flow experiments in progress, the models will give error bounds on the prediction of hydraulic aperture from electrical resistivity measurements.

E. Reservoir Characterization: Reef Type Reservoir *(G. J. Elbring [505-846-3463], H. C. Hardee, and S. Ballard)*

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 and clamping mechanisms. Gas supply systems are also under development to allow extended downhole operation. This source will be ready for deployment in late FY90 to collect the SH-wave crosshole data set. A prototype for the SH-wave source has been bench tested and is under further development. It is anticipated that integrated crosshole P-, SV-, and SH-wave data sets will provide not only better spatial resolution as compared to surface seismic methods, but also greater information on the properties of the reservoir itself.

F. Advanced Concepts *(R. K. Traeger [505-844-2155; FAX 505-846-3464])*

This program involves exploratory research in several geoscience areas. Typically, such research efforts are of a short-term nature and may be oriented toward assessing feasibility of a particular research task.

1) Simulation of Coupled Heat Transfer and Mass Transport Processes *(R. T. Cygan and C. R. Carrigan)*

We have completed a theoretical study to examine the coupling behavior of heat transfer and mass transport processes. The mass transport response of a chemical system to a thermal gradient, commonly known as thermal (Soret) diffusion, has often been invoked as a mechanism for significant chemical fractionation in geochemical systems. Numerical calculations of the coupled processes for time dependent and nonlinear temperature fields indicate very limited separations of an idealized chemical component for a variety of thermal and chemical conditions. These results support our earlier calculations which were restricted to fixed linear temperature profiles. The calculations were performed to evaluate Soret cell experiments (aqueous sodium chloride solutions) and the thermal boundary layers associated with magmatic intrusions (silicate melts). Sensitivity analysis of selected model parameters was performed to examine the net effect upon the steady state fractionation.

2) Calculation of Flow and Diffusion via Lattice Gas Automata (LGA) *(H. W. Stockman)*

Currently, only LGA holds promise of exactly and efficiently solving Navier-Stokes and diffusion equations in geologic media of arbitrary complexity. LGA are collections of discrete particles constrained to move on a fixed hexagonal grid; the particles undergo simple, momentum-conserving collisions, and macroscopic momentum averages over time and space obey the Navier-Stokes equations. We have developed two-dimensional LGA codes and applied them to modeling effects of viscosity and surface tension on the segregation of immiscible liquids. The system began with a random, fine emulsion in a planar channel; a pressure gradient along the channel caused the fluids to flow. One fluid was 6 times more viscous than the other. Simple stability theory predicts that the high-viscosity fluid should segregate in the center of the channel to minimize shear. This "minimum energy principle" has been used to explain the segregation of variable viscosity magmas flowing through the throats of volcanoes, a phenomenon discovered through Inyo CSDP, and has been used to increase flow rate of oil in pipelines by sheathing the oil with water. With the LGA models, we observe the expected segregation of the high-viscosity liquid into the middle of the channel, provided that surface tension effects are kept small. The technique is also applicable to environmental problems, through calculations of fluid flow and contaminant dispersion in fractured porous media.

Contractor:	SANDIA NATIONAL LABORATORIES Albuquerque, New Mexico 87185
Contract:	DE-AC04-76DP00789
Category:	Geochemistry
Person in Charge:	R. K. Traeger [505-844-2155; FAX 505-846-3464]

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

Analyses of volcanic rocks have shown that the volatile contents of silicic magmas (H_2O, F, Cl, and S) decrease markedly during volcanic eruptions. The goal of this project is to understand the degassing process and its control of eruptive behavior by determining the pre- and syneruptive volatile content of silicic magmas, measuring the kinetics of bubble nucleation and growth that occurs during volcanic eruptions, and examining the process of bubble resorption after magma emplacement. This work also includes laboratory development of microanalytical techniques using the electron and ion microprobe for the analysis of volatile components from silicate glass inclusions trapped within phenocrysts. Analyses of matrix and inclusion glasses from the Katmai volcanic region are currently under way. Recent work has focused on the development and refinement of stereological techniques using a SEM with a digital image analyzer in order to characterize the bubble densities of vesiculated volcanic glasses. This work is being applied to experimental studies evaluating the effect of decompression upon the kinetics of bubble nucleation and growth. Progress has also been made refining an eruption model for silicic lava flows using the results of low-pressure bubble resorption experiments. Recent tests have incorporated D/H isotopic tracers to monitor water diffusion in and out of the vesiculated glasses in order to determine the timing and extent of gas release during magma decompression.

B. Diagenetic Processes *(W. H. Casey [505-846-0196], H. R. Westrich, R. T. Cygan, and M. E. Thompson)*

The development of sedimentary rocks and coupled evolution of fluids in sedimentary basins involves reactions related to the formation, alteration, and dissolution of common rock-forming silicate minerals. Our research has focused on understanding the dissolution mechanism(s) of two common silicate minerals, quartz and feldspar, and includes characterization of the reacted surface by ion beam (ERD/RBS), optical (FTIR), and x-ray (TEM, SEM/EDS) analytical techniques. Other work includes measurement of batch dissolution rates as a function of temperature (25-80°C), solution pH (2–12), and plagioclase feldspar composition ($NaAlSi_3O_8$-$CaAl_2Si_2O_8$), as well as theoretical analysis of oxide-fluid hydrolysis reactions using molecular-orbital calculations. The calculations suggest that the rate-controlling step in simple oxide hydrolysis involves hydrogen-transfer from water to a bridging bond at the oxide surface, and predict that quartz dissolution should be about 20–30% slower in D_2O than in H_2O, a prediction we have subsequently confirmed by experiment. Identification of the rate-controlling step and prediction of reaction rates by theoretical calculations have broad implications to our understanding of mineral dissolution in diagenetic processes.

Another aspect of diagenesis is macroscale chemical migration. We have developed a computational method for predicting solute transport through fractures with rough surfaces. Our

results indicate that calculations of fracture transport based on smooth-channel models are inaccurate. We have been able to relate transport rates to fundamental geometric properties of natural fractures, such as percent contact area. The codes are currently being extended to include phase change effects and will be used to predict simultaneous mass transport and precipitation/dissolution in fractures.

Contractor:	SANDIA NATIONAL LABORATORIES Albuquerque, New Mexico 87185
Contract:	DE-AC04-76DP00789
Category:	Energy Resource Recognition, Evaluation, and Utilization
Person in Charge:	R. K. Traeger [505-844-2155; FAX 505-846-3464]

A. CSDP High-Temperature Geophysical Research Techniques *(H. C. Hardee [505-844-2257] and G. J. Elbring)*

The objective of this task is the development of new or refined concepts and techniques in thermal and seismic methods to locate and define subsurface anomalous thermal areas. Surface or near-surface thermal instrumentation includes development and testing of thermopile heat flux sensors and *in situ* permeable flow sensors. Seismic techniques involve use of downhole seismometers and surface geophone receivers and a downhole controlled seismic source capable of swept-frequency operation at 250°C and eventually at 500°C. An oriented, 3-axis seismometer for use in drill holes has been developed. Two downhole, controlled, seismic shear-wave sources have been developed and field tested. These sources provide control of energy content and frequency of the downhole seismic signal. The instruments are being used in both hole-to-hole and hole-to-surface seismic experiments. In addition to the instrumentation and field experiments, research is underway on methods to interpret the data. Current effort is concentrated in the following areas: (1) a third-generation downhole, controlled, seismic shear-wave source is being field tested, (2) a second generation *in situ* permeable flow sensor has been field tested and a set of third generation sensors are being fabricated for a field test at Savannah River Laboratory this year, (3) a new type of geologic heat flow sensor that is capable of making triaxial heat flow measurements is undergoing long-term field tests, (4) a new sensitive geologic heat flow field technique is being evaluated at the Jornada LTER station.

B. Katmai Research Drilling Project *(J. C. Eichelberger [505-844-5929])*

The objectives of this project are to determine the mechanisms and rates of release of heat and volatiles, as well as the associated migration of metals during the emplacement of silicic magma in the upper crust. The approach is to use coordinated surface and drilling observations of a simple, large, 78-year-old, still-cooling igneous system at the Valley of Ten Thousand Smokes, Katmai, Alaska. Geophysical investigations were undertaken in the summer of 1989 to define the vent for the great 1912 eruption. A surveyed grid with 150 points was established over a 6 km^2 area spanning the geologically inferred site of the 1912 vent. Precise gravity and magnetic measurements were made at these points. Other geophysical surveys were located with reference to grid points. Seismic refraction lines were run across the western margin of the vent below Falling Mountain. An electrical resistivity traverse was made across faults marking the eastern margin of the vent. Time-domain magneto-telluric measurements were made on an east-west line spanning the vent. Significant geophysical anomalies were delineated and are now being interpreted. A dense (4-m spacing) array of shallow heat-flow measurements was made at a large thermal area 1 km east of Novarupta. Measured values ranged up to a few thousand HFU. Bench marks were installed on Falling Mountain, Novarupta, and Baked Mountain and distances between them measured precisely. Seventeen of the grid points were set up for reoccupation as

gravity and magnetic stations by driving metal fence posts to just below the surface. Rock samples were collected for geochemical and rock magnetic studies. Mapping of vent structures, begun in 1987, was largely completed.

The surface-studies phase of this project involves three universities, two national laboratories, and the U.S. Geological Survey. Sandia geoscientists are responsible for coordination of the scientific program, conduct of the geochemical and heat flow studies, and collaboration with GRDO in developing the drilling plan.

C. Geoscience Research Drilling Office *(P. Lysne [505-846-6328])*

The GRDO is responsible for implementing the OBES/Geoscience-sponsored drilling efforts in the Continental Scientific Drilling Program. This implementation involves design, budgetary, and field responsibility for drilling operations. GRDO participation starts at the conception of a drilling idea and often continues through hole abandonment. This year the GRDO participated in logging and fluid sampling studies in support of the VC-2B hole drilled in 1988. GRDO also generated an operations plan for the proposed Katmai Drilling Project. The operations plan will provide the basis for the Environmental Impact Statement required for access to Katmai National Park. GRDO maintains a suite of high-temperature logging tools, and upgrades to this suite were made by the development of memory-type tools for use in holes above 300°C.

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))

The basic plasma processes associated with magnetic reconnection in the Earth's magnetosphere are studied in our proposed project. In the past year, several problems associated with the 2-D and 3-D nonlinear reconnection processes were investigated. The theoretical and simulation results from the present magnetosphere study are also applicable to plasma research in the other fields, such as thermonuclear fusion, solar physics, and astrophysics.

A new theory for nonlinear fast steady-state magnetic reconnection is proposed. The inflow region possesses highly curved magnetic field lines, which differ from that in the classical model of Petschek. A separatrix jet of plasma is ejected from the central diffusion region along the magnetic separatrix. Two types of outflow are studied, the simplest one possessing a potential outflow magnetic field and the other containing weak standing shock waves attached to the ends of the diffusion region.

In the 3-D MHD simulations, frayed magnetic flux ropes are found to be formed during the dayside magnetic reconnection process. Strong flux-rope-aligned plasma flows are observed. Simulations of the driven reconnection process also indicate that the focusing of the Poynting flux has an important effect on the onset of reconnection and the location of reconnection sites. Magnetic reconnection tends to take place in the region which is near the focus of the Poynting vector imposed at the boundary.

The structure of the reconnection layer at the dayside magnetopause is also studied based on 2-D MHD simulations. It is found that in a symmetric configuration, the reconnection layer is bounded by a pair of slow shocks as predicted in Petschek's model. Under the asymmetric conditions typical of the dayside magnetopause, the reconnection layer is found to be bounded by an intermediate shock on the magnetosheath side and a weak slow shock on the magnetospheric side. Contact discontinuities and slow expansion waves can also be identified in the reconnection layer in some simulation cases.

Our previous simulation results indicate that the formation of non-switch-off shocks may result in the lack of large-amplitude rotational wave trains at slow shocks in the deep magnetotail. Our recent particle simulation results show that the interaction between particles and downstream wave field may lead to the overlapping of wave-particle resonances, resulting in the stochastic motion of particles and the damping of waves. The trajectories of particles in the rotational wave field are calculated. The results indicate that the strong wave damping occurs if the intermediate Mach number M_{An} of the slow shock is smaller than a critical Mach number M_c. The damping of the wave is accompanied by the heating of downstream plasma, which is consistent with observation of slow shocks in the magnetotail.

Grantee:	UNIVERSITY OF ARIZONA 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; E-mail sclera@soliton.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 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 a time series of diameter measurements that are accurate to parts per million over extended time periods. Observations are made for as long as 12 hours per day over times spanning as much as 8 months per year.

New diameter observations were obtained using the observational facilities and techniques developed at SCLERA. Between March 20 and June 26, 43 days of data were obtained, and between September 14 and December 12, 21 days of data were obtained.

Data obtained in 1973, 1979, 1981, 1983, 1984, and 1986-1989 have been analyzed for changes in the limb darkening function as reflected in differential radius observations. These observations are utilized in such a way that effects of solar activity are minimized in order to reveal the more fundamental structure of the photosphere. The results of observations made during solar cycle 21 at various solar latitudes indicate that a measurable change did occur in the global photospheric limb darkening function. It is proposed that the residual luminosity change not accounted for by sunspots and faculae in satellite radiometric observations is associated in part with this change in limb darkening. From 1980 to 1986, the ratio of the fractional change in the residual luminosity $\delta L/L$ to the fractional change in differential radius $\delta(\Delta R/R)$ is $(\delta L/L)/\delta(\Delta r/R) = -7$. It is noted that this hypothesized correlation may explain the discrepancy between observations obtained by ACRIM and ERB and predictions based on some models of solar luminosity change from 1978 to 1981. 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 possibly have consequences for the Earth's climate.

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. Numerous tests were conducted on the observed properties of these modes and further statistically significant evidence of mode coupling was found. The long period gravity modes may be relevant to understanding luminosity variations because of the long lifetime of these modes. Mode coupling is relevant to the same point because it indicates that these modes may alter the neutrino and fusion-energy production rates in the core of the Sun.

Grantee:	UNIVERSITY OF ARIZONA Department of Geological Sciences 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 in order 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 is currently underway on the synthesis of the necessary materials and construction of additional equipment. In addition, modeling of existing data has been completed on the join diopside–enstatite, which is necessary if the binary data collected in these experiments are to be combined into a ternary model for Ca–Fe–Mg pyroxenes. This re-examination was necessary because currently available models for this join predict that end-member diopside is metastable with regard to subcalcic diopside and wollastonite.

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 fluid-saturated rocks and the rate of transport along these boundaries are important questions for many applications, including the migration of components in nuclear repositories and of hydrocarbons in geological environments. Grain boundaries and microcracks in natural fine-grained quartz and feldspar aggregates will be characterized using transmission electron microscopy (TEM) and scanning electron microscopy (SEM), and then these samples will be used to determine the rate of transport of stable isotopes of oxygen and various cations. Preliminary data indicate that these measurements can be made over wide temperature and pressure intervals.

The analytical procedure involves a depth profiling technique using the ion microprobe (SIMS), developed previously for determining volume diffusion rates in these same minerals. 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-grained size also ensures a strong analytical signal and eliminates thermal cracking of the samples. Using numerical solutions appropriate to the boundary conditions employed, the product of the grain boundary diffusion coefficient (D') and the effective grain boundary width (δ) can be 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. The effective grain boundary width will be correlated with fluid composition of the experiment and the grain boundary microstructure determined using TEM. These results should provide for a much better understanding of grain boundary diffusion rates in rocks under a wide range of natural conditions and allow an estimation of diffusion rates in rocks for which the grain boundary microstructure is known.

Grantee:	CALIFORNIA INSTITUTE OF TECHNOLOGY Seismological Laboratory Division of Geological and Planetary Sciences Pasadena, California 91125
Grant:	DE-FG03-85ER13422-AT
Title:	*In Situ* Stress in Deep Boreholes
Person in Charge:	T. J.Ahrens (818-356-6096)

The holographic stressmeter is an instrument which measures, by interference holography, *in situ* stress in a fluid filled borehole. By drilling a series of small, stress-relieving side holes into the borehole wall at the proper orientations, all six components of the far field *in situ* stress tensor are obtained. This method will prove useful for both scientific and industrial applications, as complete knowledge of the state of stress is vital to effective stimulations of hydraulic fractures for resource recovery in the oil and gas industry. Other applications of *in situ* stress measurement and data include geothermal resource exploitation and the design and monitoring of underground mines and structures, including radioactive and chemical waste isolation facilities. A better understanding of the state of stress in the crust will also improve our knowledge of regional tectonic processes.

During the last year we have completed construction of the 6-inch holographic stressmeter and its support equipment, and we have begun field testing in a borehole in the Mojave Desert of southern California, near the San Andreas fault. The instrument itself is 11 m in length, containing computer-controlled mechanical, electronic, optical, and hydraulic components. The operator communicates with the instrument through a computer interface based in the logging truck. Commands are sent through a seven-conductor cable to the instrument, which is constantly communicating its status to the computer at the surface. In addition to carrying out the user's direct commands, the internal computer regulates gas pressurization within the optical cavity to a few psi greater than the ambient borehole fluid pressure to prevent damage to the optical components. Other features of the instrument include a water flushing system designed to clear the borehole fluid in the region of the camera; a mud cake removal system; an optical video system to monitor the borehole wall drilling process through the clear, flushed liquid; and the ability to measure the elastic modulus of the borehole wall rock by the indention technique.

In addition to field testing of the instrument, in the last year we have completed a theoretical analysis of the displacements that occur as a result of drilling the stress-relief hole, in an effort to improve our modeling and analysis of the holographic data. Previous work had modeled the borehole wall as a thin, elastic plate with a through-going hole. This model, while adequate, was not capable in every case of fitting the observed interference fringe patten within 2 radii of the sidehole. Several holograms had been obtained, particularly in regions with low levels of borehole wall stress, which could not be modeled satisfactorily. The new model relaxes the assumption inherent in the thin plate model that the body is in a state of plane stress everywhere in its interior. A comparison of results from data fit by the two models gives approximately the same result; however, in the new model, the uncertainties in these values are significantly reduced.

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 could also 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 to 850°C and pressures between 2 and 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.

We are also studying the concentrations of water and carbon dioxide in glass inclusions in phenocrysts from the Bishop and Toba tuffs and from the climactic phase of the eruption of Mt. Mazama. We have discovered that water and carbon dioxide contents in inclusions from the eruption of the Bishop tuff magma about 700,000 years ago (which led to the formation of Long Valley caldera in central California) are inversely correlated. Crystallization of a vapor-saturated magma in which the water-rich, carbon dioxide-poor residual liquid concentrates upward in the magma body could be responsible for these trends. According to this view, the vapor at depth would have been rich in both water and carbon dioxide.

It has been known for several decades that the chemical diffusion coefficient of total water in silicate glasses increases strongly with the water content of the glass, and there has been much speculation on the cause of this strong concentration dependence of water diffusivity. As part of this project we have demonstrated that in volcanic glasses, this concentration dependence is related to the fact that water dissolves in glasses in two distinct forms — water molecules and hydroxyl groups — but that the diffusivity of water molecules is orders of magnitude greater than that of hydroxyl groups. The uniqueness of our approach stems from our ability to measure the concentration profiles of these separate species with high precision and at high spatial resolution, 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. This work has implications for understanding rates of exchange of oxygen and hydrogen isotopes between hydrothermal solutions and crystalline and glassy 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)

Studies in this laboratory have shown that, using improved sensitivity, it is possible to measure, by thermal ionization mass spectrometry, 5×10^9 atoms of ^{234}U or ^{230}Th to better than 5 ‰. These new techniques for U and Th isotope ratios have greatly improved data precision and allow the application of the U-Th disequilibrium systematics to many investigations for which the α-counting techniques lack sensitivity. We have applied these techniques to the dating of corals in areas of neotectonic activity. A completed initial study of solitary corals has provided high-precision U-series dating of emergent Quaternary marine terraces outside tropical latitudes. Corals were obtained from known stratigraphic locations at selected terraces along the California coast. The range of the ^{230}Th-^{234}U ages of the Cayucos and Shell Beach specimens (113–126 ky) is similar to the range of ^{230}Th-^{234}U ages of reef-building corals from several tropical localities. It is believed that these reef-building corals were deposited during the last interglacial event and high sea level stand around 120 ky ago. Our data do not indicate a very narrow time band but rather a more broadly defined time zone or zones, some of which are related to "The" last interglacial. We note that the age of the Nestor terrace is distinctly older and lies between 133 and 145 ky and cannot be correlated with the time of the last interglacial. The ^{230}Th-^{234}U ages yield average uplift rates of the coastal terraces, assuming the sea level elevation at the time of deposition. For the Cayucos terrace, the average uplift rate is essentially zero, which implies long term stability for this region. For the Shell Beach terrace, the average uplift rate is 0.11 m/ky. For the Nestor and Bird Rock terraces, the average uplift rate is 0.16 m/ky.

A detailed study of the ^{238}U-^{234}U-^{230}Th ages was made for different coral species from two Bahaman reefs using techniques for the measurement of U and Th isotopes. Thirty-seven coral samples were analyzed in replicate. Typical errors at 125 ky are ±1.5 ky (2σ). This high precision permits detailed chronologic study with time resolution adequate to define stages of the reef's history. The ^{230}Th ages of corals from the Bahamas suggest that the period of the Sangamon high stand of sea level began as early as 132 ky and certainly 129 ky ago, with sea level reaching +6 m above present mean low sea level. After about 120 ky ago, with the onset of Wisconsin glaciation, sea level fell rapidly at about 2 m/ky and terminated the reef cycles. The period of the Sangamon high stand (132 to 120 ky ago) slightly precedes and substantially postdates the maximum summer insolation at 65°N latitude which occurred 128 ky ago.

We have developed a resonance ionization mass spectrometric technique for high sensitivity, *in situ* analysis of Re and Os. This work was performed in cooperation with the Materials Science and Chemistry Divisions at the Argonne National Laboratory. A useful yield of 1% and a detection limit of 7 ppb atomic were demonstrated for Os. The capabilities for quantitative elemental analysis were investigated in a study of Os concentrations in synthetic metal alloys and iron meteorites. The measured Os^+ ion signal is linearly correlated with the Os concentration in the samples over a range of nearly 10^4 in Os with an accuracy of ±10% (2σ).

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 (415-642-1251; FAX 415-643-9980;
E-mail oelkers@violet.berkeley.edu 2

Understanding the chemistry of fluid flow and water-rock interaction in geochemical processes requires thermodynamic and transport properties of hydrothermal fluids, as well as comprehensive mass transfer computer codes. Toward this end we have focused during the past year on characterizing speciation in concentrated supercritical aqueous electrolyte solutions, generating tracer diffusion coefficients for organic species and developing computer algorithms to calculate the growth rate of hydrothermal alteration zones.

Revised interpretation of conductance measurements reported in the literature indicates that the solute in supercritical aqueous alkali metal halide solutions is present predominately as single ions and neutral ion pairs only in the dilute concentration range at supercritical pressures and temperatures. For example, calculations indicate that the degree of neutral ion pair formation in NaCl solutions at 600°C and 2 kbar maximizes with increasing concentration at ~0.2 M and becomes negligible at higher concentrations (1 M), where triple ions predominate. This behavior is a consequence of the low dielectric constant of H_2O at supercritical temperatures and pressures. By analogy with the behavior of electrolytes in low-dielectric constant solvents at low temperatures and pressures, it appears likely that in addition to triple ions, higher order complexes such as quadruple, quintuple, etc. species sequentially predominate with increasing concentration in supercritical solutions of single electrolytes.

Analysis of tracer diffusion coefficients (D°) for aqueous organic species reported in the literature indicates that D° can be described as a linear function of the reciprocal square root of the alkyl chain length of the species. The temperature dependence of D° can be represented by a modified Arrhenius equation. These two relations permit calculation of tracer diffusion coefficients for a wide variety of aqueous organic species at temperatures to 350°C.

The growth of hydrothermal alteration zones can be characterized as a function of time and distance using a numerical algorithm which permits simultaneous solution of homogeneous equilibrium constraints and diffusion equations coupled to reversible and irreversible mineral dissolution/precipitation reactions. A computer code is being developed to compute the diffusional growth rate of hydrothermal alteration zones using a quasi-stationary state approach to integrate the mass transport equations over geologic time frames. The rate at which the primary rock reacts is limited in the code by kinetic rate laws for the hydrolysis of minerals. The algorithm will be used to study alteration halos such as those associated with hydrothermal veins in porphyry copper deposits and metamorphosed dolomites.

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

Grant: DE-FG02-87ER13667

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

Person in Charge: J. H. Reynolds (415-642-4863; 642-2260; FAX 415-643-8497; E-mail reynolds@garnet.berkeley.edu)

The RARGA laboratory studies noble gas systematics in fluid reservoirs. Present interest is the source and migration of noble gas components (e.g., mantle, crustal etc.) in natural gas traps, especially the source of ^{3}He excesses in CH_4-rich traps. It is well documented that many CO_2 wells contain excess ^{3}He (R/Ra > 1.0; Ra is the ^{3}He/^{4}He ratio in air), anomalous neon, and excess ^{129}Xe, which in sum indicate a MORB source. In CH_4-rich fields, ^{3}He/^{4}He ratios are typically low (R/Ra < 0.1), consistent with a crustal origin. Some CH_4 fields, however, have ^{3}He/^{4}He ratios > 0.1 Ra and therefore outside the accepted range for average crustal radiogenic helium. Ascribing the excess ^{3}He to a mantle source in such fields, if not associated with recent volcanics (e.g., Alberta, Texas, Oklahoma), means that the injected mantle component must have migrated over great distances and/or is a remnant of the thermal history of the sedimentary basins. To help identify the source of the excess ^{3}He we, in collaboration with LANL, are augmenting the fluid studies with analyses of U, Th, K, and Li in reservoir and source rocks for the natural gas. Bulk samples and mineral separates from cores from four wells in the Texas Panhandle are being analyzed. Inconsistencies between ^{40*}Ar/^{4}He, ^{136*}Xe/^{4}He and local K/(U+Th) ratios can tag elemental fractionation related to migration or extraction. Li concentrations are essential for evaluating locally enhanced ^{3}He production. Other more exotic sources, such as cosmic dust or spallation, are also being evaluated. Additional RARGA projects include studies of geothermal fluids and continued attention to the Great Artesian Basin, Australia.

Our group has continued to study fluid inclusions (FI) in metamorphic minerals using a sensitive mass spectrometer coupled with a laser microprobe. Scope includes (1) elemental and isotopic calibration by measurements of Ar, Kr, and Xe in synthetic FI; (2) testing, after neutron irradiation, of synthetic FI spiked with known concentrations of K, Cl, Br, and I, thus calibrating production of ^{39}Ar, ^{38}Ar, ^{82}Kr, and ^{128}Xe by neutron irradiation of natural samples; (3) studying "excess" Xe, relative to argon and krypton, that has been found in some natural mineral samples containing FI. Results show that we can measure K, Cl, Br, and I and naturally occurring noble gas isotopes in individual cubic FI, < 50 microns on a side, containing a solution 0.6 m in KCl and 100 ppm in Br and I. Our synthetic FI give neutron irradiation yields consistent with other monitors. In quartz they sometimes contain excesses of Xe similar to the natural counterparts.

A third paper on noble gases in diamonds is in preparation, based on more measurements on composite samples of small diamonds from the Western Australia lamproite pipes, where previously, but not this time, we saw weak indications of solar-like helium and neon. Implantation of energetic ^{4}He, Xe fission fragments, and ^{3}He ions from the surrounding lamproite can explain much of what we have seen in this new study.

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

Grant: DE-FG02-87ER13722 A003

Title: Energy Related Studies Utilizing Microcline Thermochronology

Person in Charge: T. M. Harrison (213-825-7970; FAX 213-825-2779)

$^{40}Ar/^{39}Ar$ results on K-feldspar and muscovite aggregates and K-feldspar single crystals give quantitative estimates on heating duration and provenance ages for sands from the Salton Sea geothermal field. Provenance ages span the Tertiary through Proterozoic, but cluster at Oligocene, Late Cretaceous, and Proterozoic ages, suggesting that the detritus was transported by the Colorado River from detachment terranes to the northeast. Single crystal analyses, which provide both estimates of ^{40}Ar loss and the kinetic data needed to constrain argon retentivity, suggest that the present temperatures in several wells have not been maintained for greater than 1000 years. Our conclusion suggests that the geothermal field is somewhat younger than predicted through modeling of geothermal data.

We have analyzed detrital K-feldspar from a number of accretionary prism environments to assess whether these environments have experienced appropriate thermal histories for hydrocarbon maturation during ridge subduction. Samples from southwest Alaska and Japan, inferred from vitrinite reflectance data to have been heated to ~200°C by the subducting ridge, yield contrasting results. Samples from the Kenai Peninsula, Alaska, yield an age of heating of 63.0 + 3.5 Ma, in excellent agreement with the estimate of 59 Ma for the time of ridge subduction. However, our argon data for samples from the Hioki complex, Japan, do not support a thermal anomaly during Miocene ridge subduction. Other results from the California coast (e.g., Cambria Slab) suggest Tertiary temperatures between ~150 and 200°C; appropriate conditions for source rock maturation.

We have completed two furnace systems for analysis of very small quantities of argon. The laser system has an ^{40}Ar blank of $\sim 10^{16}$ mol for typical heating plus cleanup times. Our second-generation double-vacuum resistance furnace has a higher ^{40}Ar blank which increases with temperature, but is still only $\sim 5 \times 10^{16}$ mol at 900°C and $\sim 2 \times 10^{15}$ mol at 1200°C. We have the flexibility of using either system and exploiting the benefits particular to each. For instance, total fusion experiments are best carried out using the laser system, whereas analysis of a K-feldspar for which kinetic data is needed requires use of the resistance furnace.

A new theoretical model of K-feldspar age spectra and associated Arrhenius data, arising through collaboration with Oscar Lovera and Frank Richter of the University of Chicago, suggests that many samples contain a distribution of diffusion domain sizes. We have confirmed this prediction by performing many non-conventional Ar extraction experiments. The appropriate domain distribution can be chosen through fits to both the age spectrum and Arrhenius plot. This approach optimizes the thermochronological information attainable from $^{40}Ar/^{39}Ar$ analyses of K-feldspar. Small (~ 450 μm), single crystal analyses indicate that the domains are an intrinsic property of K-feldspar not separable at the micron scale, thus requiring these deconvolution techniques. As a consequence, a single feldspar can reveal a broad segment of a cooling history, rather than a single datum.

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

Grant: DE-FG03-88ER13806

Title: Thermal and Petrotectonic Evolution of the Central Klamath Island Arc—Phanerozoic Komatiitic Lavas in Northwesternmost California

Person in Charge: W. G. Ernst (now at Stanford University, 415-723-2750; FAX 415-725-6566)

The region of geochemical/petrologic investigation is the Sawyers Bar terrane of the so-called Western Triassic and Paleozoic Belt (WTrPz). The mapped area constitutes a lithotectonic zone lying between the southern portion of the Marble Mountain terrane and the northern extension of the North Fork-Salmon River composite terrane, within the central Klamath province. Elevations range from approximately 2000 to 7500 feet. The region is heavily vegetated and weathered, hampering mapping efforts and geochemical assessments. Most of the studied tract consists of mildly alkalic oceanic crust (OIB) and immature island-arc basalts (IAT) and distal turbidites of the WTrPz belt, but the southeasternmost part contains subduction-zone units of the Stuart Fork terrane. Nevadan age English Peak and Russian Peak granodioritic stocks subsequently invaded the complex on both the west and southeast.

The WTrPz in this area consists of recrystallized units of the North Fork and possibly, on the west, the eastern Hayfork formations. More than 600 thin sections have been studied petrographically and 160 rocks analyzed by XRF for major element concentrations. Mineral separations have provided suitable materials for radiometric and $^{18}O/^{16}O$ analyses. Microprobe analysis of coexisting minerals has documented a gradual northward increase in intensity of pre-Nevadan metamorphism. On the southeast, this complex is structurally overlain by approximately 220 m.y. old Stuart Fork mafic blueschists and related rocks; protoliths of this high-P assemblage consisted of predominant oceanic tholeiites associated with minor siliceous and graywacke-type clastic sediments. Lithologic contrasts between the Stuart Fork and Sawyers Bar terranes define a major tectonic contact. These two pre-existing complexes were brought together by convergent plate motion along the accreting North American continental margin after the Late Triassic subduction event reflected in the Stuart Fork formation and early Mesozoic deposition of the WTrPz belt rocks. The greenschist facies metamorphism, which affected both lithotectonic units, seems to have preceded the local development of contact aureoles that accompanied Late Jurassic emplacement of the calc-alkaline English Peak and Russian Peak plutons.

Geologic relations mapped in this area bear testament to the petrotectonic evolution of a Mesozoic island arc. Work by the P.I. has documented the possible presence of Permo-Triassic Mg-rich, refractory lavas in the Sawyers Bar area; ongoing regional mapping is being conducted to delineate the lateral extent of these significant petrologic units. Stable isotope and major element analyses of coexisting minerals now underway, combined with mineralogic thermobarometers, will allow the thermal history of the polymetamorphic volcanogenic arc to be deciphered. A better understanding of the P-T evolution of this early Mesozoic complex should result in more efficient utilization of geothermal energy in modern, active, convergent continental margins and island arcs.

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 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, pH, and oxidation state during hydrothermal mineralization. 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 co-existing fluids are known. Therefore, 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. 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.

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 precision stainless steel leak valve.

The inclusions are opened by mechanical decrepitation. This involves a custom built crushing chamber, which has provisions for entrapment of dust generated from the crushing of the sample, the backflushing and removal of the dust from the filter assembly by helium to minimize contamination, and small, modular design to minimize surface area and ease of operation.

Currently, we are analyzing fluid inclusions from several active geothermal systems, including Valles caldera in New Mexico, and Salton Sea, Coso Hot Springs, and The Geysers in California.

Grantee: UNIVERSITY OF CALIFORNIA AT SAN DIEGO
Scripps Institution of Oceanography
La Jolla, California 92093

Grant: DE-FG03-89ER14073

Title: Seismic Imaging of Anisotropy and Cracks in the Upper Oceanic Crust at the East Pacific Rise

Person in Charge: A. J. Harding (619-534-4301), P. M. Shearer, and J. A. Orcutt

Evidence for anisotropy and cracking in the upper oceanic crust is being sought through a combination of the analysis of expanding spread, multichannel seismic data, and the development of asymptotic ray tracing methods for anisotropic media. The degree and form of anisotropy can be related to properties of the medium such as porosity and crack aspect ratio using standard theories for cracked media. One means of diagnosing the presence of anisotropy from conventional single component data is by constructing independent P- and S-wave velocity profiles assuming isotropy. The presence of vertical anisotropy is revealed by discrepancies between the two profiles such as unusually low Poissons ratio or mismatches in reflector depths, since P- and S-wave anisotropies are different in nature.

Expanding spread profile data from along the rise axis at 9 N on the East Pacific Rise has been inverted for P- and S-wave velocity structure down to the top of the axial magma chamber. Observable S wave energy is generated at the relatively undisturbed, large impedance contrast interface at the base of seismic layer 2A. Estimated Poissons ratios are high, > 0.4, in layer 2A and low, < 0.22, in the remainder of layer 2.

In order to model these observations, we are implementing a ray tracing algorithm for anisotropic media which will enable the construction of unified models satisfying both the P- and S-wave data. Included in the algorithm are cylindrically symmetric anisotropic models such as might be produced by vertically or horizontally aligned cracks. The models obtained from this analysis will be used to place constraints on crack parameters, e.g., porosity, crack aspect ratio, and crack orientation, by using theories which describe the effects of cracks on the properties of elastic rocks.

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. Work done at UCSB includes field, laboratory, and simulation studies.

A field study was also undertaken of a caldera-associated volcanic system from the Miocene of Gran Canaria, Canary Islands. This study was an effort to deduce the temporal relationship between caldera collapse (the Tejeda caldera) and the eruption of compositionally zoned magmas from central vent and ring fracture conduits. We found that a compositional gap in the extra-caldera stratigraphy is an artifact of the change in pyroclastic deposit depocenter due to the collapse of the 16×20 km Tejeda caldera about 14 Ma ago. Viscous relaxation of the middle and lower crust beneath the Tejeda volcanic center is spatially associated with resurgent volcanics of phonolitic affinity.

The dynamics of central vent and ring fracture eruptions and the removal of zoned magma from magma bodies of various shapes and sizes have been considered in detail utilizing a finite element code capable of handling a wide variety of boundary and initial conditions and variable magma properties (e.g., density, viscosity, etc.). It is found that the natural eruptions fall into one of three dynamical categories depending on eruptive intensity (mass discharge rate): viscous, sub-inertial, or inertial. The parametric relationship between the discharge, the basal driving stress, and the time period of mixed-magma eruption is developed from scaling arguments and verified quantitatively.

We have also conducted rheometric experiments utilizing the concentric cylinder rheometer for UCSB on a number of melts and multiphase magmatic mixtures. In particular, the rheological properties of dacite and GeO_2 melt, and dilute emulsions of air bubbles (volume fraction vapor < 0.1) in GeO_2 melt, have been carried out using the technique of concentric cylinder viscometry in order to better understand the relationship between microscopic and macroscopic structure and momentum transport in magmatic systems.

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)

Laboratory measurements are in progress to examine the independence of the inelastic damping of seismic waves in sedimentary rocks on parameters that are known to be significant for different proposed attenuation mechanisms. The expected data are needed to gain a better understanding of the attenuation mechanisms of seismic waves as an important parameter for the lithological interpretation of seismic data. Samples of sedimentary rock will be subjected to harmonic stress, both shear and longitudinal. The inelasticity and the moduli will be measured by determining the resulting complex strain by means of optical interferometry. The strain amplitude will be in the range of 10^{-6} and smaller in order to meet linearity conditions. These measurements will be performed in the frequency range 0.01 to 300 Hz under confining pressure up to 100 MPa (1 kbar). The temperature range will be between 20 and 100°C. Variations of the mechanical and thermal properties of the pore fluids and different degrees of saturation will be explored to establish relationships between these parameters and attenuation. This information will be very helpful for identifying the attenuation mechanisms in the seismic frequency range. Knowledge gained from these experiments will help in the identification of and characterization of fossil fuel resources as well as in monitoring the conditions of potential and active toxic and nuclear disposal sites.

To date we have developed an optical interferometer to measure the small displacements involved in the attenuation measurements. We are in the process of adapting it to make the measurements under pressure. This includes the construction of high pressure feedthroughs for the laser beams and arranging the beams' paths in the pressure vessel. A unique and very important aspect of our experimental approach is the measurement of both the longitudinal and shear attenuation in the same experimental setup without removing the sample. Other unique features of our experiments are multiple deformation measurements and variable stress applications which enable us to measure and minimize unwanted modes such as flexure and bending. This will give great confidence in the characterization of the sample and allow attenuation calculated for other modes of deformation. The interferometer has an ultimate sensitivity of 10^{-7} wavelength of the laser light, i.e., approximately 10^{-13} m. This type of resolution is necessary in order to measure small values of absorption (high values of Q) at strain amplitudes corresponding to those of seismic waves.

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. Larner (303-273-3428; FAX 303-273-3278; E-mail klarner@shrock.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 in the earth while facilitating the accurate and efficient computation of seismic wavefields. Today, computer models of the Earth's subsurface are typically limited to simple geologic layers, with the surfaces bounding the layers represented by single-valued functions of depth. While such models are simply implemented and permit fast numerical computations of seismic waves, they also inhibit the representation and imaging of complex but common geologic structures, such as overhanging salt diapirs and inhomogeneous reservoirs. To this end, we have developed an interactive algorithm that characterizes geologic structure as a *Delauney* mesh, an optimum triangulation of a medium based on supplied node points. Current work is aimed at determining the data structure best suited for efficient ray tracing in 2-D and 3-D models, for use in high-resolution imaging and interactive estimation of velocity in media in which velocity varies both laterally and vertically.

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. Conventional seismic wavefield approximations, such as the WKBJ approximation, fail to predict the complexity or even the first arrival times of such horizontally traveling seismic waves. 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. To address this problem, we have implemented 2-D finite-difference modeling of elastic waves for study of seismic waves that propagate rather parallel to bedding. Snapshots of the propagating waves generated and displayed during the course of computation on a high-speed, interactive workstation show tunneling of evanescent waves, a phenomenon not predictable from the ray theory that is the basis of current velocity-determination methods. Accurate solutions from this program will be our standard for analysis of the more efficient, approximate (e.g., modified ray theory and paraxial wave equation) methods that we are developing.

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

Grant: DE-FG02-88ER13221

Title: Seismotectonics of the Eastern Aleutian Arc and Associated Volcanic Systems

Person in Charge: G. Abers (914-359-2900; FAX 914-359-5215; E-mail abers@lamont.ldgo.columbia.edu), J. Taber, and K. Jacob

Physical processes of subduction are investigated throughout the active Alaska-Aleutian arc-trench system. In the Shumagin Islands we study a 300-km long arc segment by operating a digital seismic network with 14 remote stations linked by telemetry. This segment is a seismic gap with a high probability for a large or great earthquake in the next two decades. Applications concern the geothermal energy potential of the Aleutian arc, and seismic, volcanic, and tsunami hazard reduction to off-shore oil lease sales areas directly adjacent to the Shumagin seismic gap and the Gulf of Alaska.

In the last year, stress indicators throughout Alaska have been compiled, and the state of stress in the region has been assessed. Plate boundary interaction between the Pacific Plate and North America controls much of the stress pattern. Broad curvature of stress orientations is observed in the Alaskan interior with maximum horizontal stress apparently radiating outwards from the northernmost Gulf of Alaska.

Estimates of the likelihood of plate boundary earthquakes throughout the Queen Charlotte-Alaska-Aleutian boundary have been updated, with consideration being given to aseismic slip and to variation in both repeat times and sizes of characteristic earthquakes. Seven segments of the seismic zone have high ($\geq 60\%$) conditional probabilities for the recurrence of either large (M_S = 7 to 7.7) or great ($M_S \geq 7.8$) earthquakes within the next 20 years. Azimuthal variations in surface wave amplitude were analyzed for the 1917 Shumagin Islands earthquake, and are best explained by westward propagating rupture for this event. The earthquake (M_W = 7.5) is the last large event to rupture the eastern half of the Shumagin seismic gap. Smaller Shumagin events in 1985 (M_S = 6.6) and 1987 (M_S = 6.2) ruptured only small patches of the main plate interface. These two similar-sized events were well recorded by the network and show different precursory patterns. Estimates of attenuation (Q^{-1}) were made in the Shumagin Islands area. Attenuation appears to be significantly greater in the Shumagin Islands region than in either of the two other parts of Alaska that have been studied, the Adak region and south-central Alaska.

In order to obtain and use on-site, near source recordings of large earthquakes, we have installed a digital strong ground motion accelerograph in Dutch Harbor. Such data are important for design and engineering of earthquake resistant structures. It is the only such instrument in the long Fox Islands section of the Aleutian arc where large earthquakes can be expected.

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 based solely on 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:	THE UNIVERSITY OF CONNECTICUT Department of Marine Sciences Groton, Connecticut 06340
Grant:	DE-FG02-90ER14123
Title:	Chapman Conference on "Crustal Scale Fluid Transport: Magnitude and Mechanisms"
Person in Charge:	T. Torgersen (203-445-3441)

A Chapman Conference on "Crustal Scale Fluid Transport: Magnitude and Mechanisms" was convened in Snowbird 4–8 June 1990. The conference was attended by over seventy researchers from the diverse and wide ranging fields of the Earth sciences to focus on (i) the magnitude of mass transport and net fluid flow in the Earth's crust, (ii) the horizontal and vertical extent of fluid transport in various regions, (iii) the temporal continuity of fluid flow and its accompanying mass transport in various regions, and (iv) the capability and limitations of potential mechanisms by which to explain this temporal and spatial extent of fluid mass transport in the Earth's crust. This field forms a critically important bridge between basic research into the Earth's crustal processes and the applied research of direct and immediate interest to the nation and the mineral/energy industries.

The results of the meeting indicate that there is a contradiction between (i) the near hydrostatic pressure conditions and the continuity of the Darcy-like fluid flow description and (ii) the rock record, which demands a time dependent, discontinuous, and episodic process with both fracture-controlled flow and high pressure (near lithostatic) conditions. The fluid flow effects observed in the rock have not been described in a form that can be incorporated into the apparently dominant topographically driven fluid flow mechanism for the bulk crust.

This interplay between fluid pressures, fracture formation, fault-valves, rock mechanics, net fluid flow, and the chemical and physical properties of the crust is of critical importance, and an understanding of these processes will have direct effects on our exploration strategies for minerals and energy and our concepts of (e.g.) nuclear waste disposal, earthquake prediction, and the strength of the crust. It was the general consensus that the problem has not been solved, that the problem is far from being understood, and that many disciplines are needed to contribute to the database necessary to properly address the problem. A clearly identified and critical need is a mechanism by which to scale the micron- to 100-m scale processes that are observed in the rock to the kilometer- to regional-scale processes that are the space scale of crustal fluid flow and the realm of the modeler.

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)

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 pressure near 350 bar. 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 bar. These 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. 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 HAWAII AT MANOA
School of Ocean and Earth Science and Technology
Mineral Physics Group
Honolulu, Hawaii 96822

Grant: DE-FG03-88ER13418

Title: Physical Characterization of Magma Samples

Person in Charge: M. H. Manghnani (808-956-7825)

The main objectives of this project are (1) to carry out a systematic study of compressional velocity and attenuation in natural and synthetic silicate melts, in order to understand their high-temperature elastic and viscoelastic behavior and gain knowledge of thermodynamic properties pertaining to geothermal exploration and thermal modeling in a volcanically active area as they are affected by a total environmental system, (2) to investigate interrelationships between the various physical, elastic and anelastic, and thermodynamic properties of silicate melts, and (3) to develop a Brillouin scattering technique for measuring the elastic and anelastic properties of melts in a wide range of temperature and pressure.

Such data are needed for acquiring a better knowledge of the fundamental *in situ* high-temperature physical and viscoelastic properties of rocks and their melts relevant to geothermal exploration and to projects such as the Continental Scientific Drilling Program. To accomplish these goals, we are conducting laboratory studies on natural rocks and synthetic silicate samples and their melts in three research areas: (1) characterization of physical, elastic and anelastic (V_p, V_s, Q^{-1}), and electrical properties of samples from Kilauea Iki lava lake and other related types of basalts; (2) development of Brillouin and Raman scattering measurements on synthetic and natural silicates and their melts, first as a function of temperature and then as a function of temperature and pressure, in an effort to understand the structure-property relationships in silicate melts; and (3) investigation of electrical conductivity of molten and partially molten rocks and silicates to understand the role of partial melting.

Ultrasonic measurements have been carried out on the melts of several types of natural basic rocks (basalts, picrites, and komatiites) and on selected synthetic systems such as diopside ($CaMgSi_2O_6$)-anorthite ($CaAlSi_2O_8$), albite ($NaAlSi_3O_8$)-anorthite ($CaAlSi_2O_8$) to 1625°C and in the frequency range 3–22 MHz. These measurements have enabled us to establish the velocity-density-composition (Birch's linear law) and attenuation-temperature-frequency systematics and to interpret the viscoelastic properties such as viscosity, relaxation time, and relaxed moduli in terms of their composition and structure. A direct relationship between attenuation, Q^{-1}, and viscosity has also been established. We have begun Brillouin scattering measurements from room temperature to high temperatures through melting to study the effect of partial melting on the elastic and viscoelastic properties. We are currently carrying out preliminary measurements in a diamond-anvil cell to study the compressibility of silicate melts at high pressures.

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)

Our research is directed at increasing the resolution of the seismic method for improved oil recovery by one to two orders of magnitude. Traditionally the seismic method employed has been to place sources and receivers on the surface of the Earth, and to generate and record and interpret seismic waves reflected from interfaces in the subsurface. Unfortunately the smallest feature that can be resolved by this method has a size of the order of 100 ft. Thus, one of the aims of the present research is to improve this resolution to between 10 ft and 1 ft.

Although the resolution of the surface seismic method can be improved it appears that the greatest improvement will be achieved by removing both the sources and receivers from the surface of the Earth. When both source and receiver are removed from the noisy environment of the near surface, higher frequencies can be generated and recorded.

This research program is being carried out in conjunction with Bureau of Economic Geology (BEG) of the State of Texas and the Southwest Research Institute (SwRI). Contact with the BEG has enabled us to obtain access to a strandplain clastic reservoir in Duval County, Texas, which is owned by the State of Texas. This is a reservoir which, at abandonment, will have produced only about 38% of the original oil in place. Thus, this is a particularly good reservoir for studying improved recovery techniques. The State has a requirement to drill a new well (or dry hole) every 90 days. Any improvement in seismic resolution in this field could directly influence the drilling program and improve recovery.

Measurements have been made of transmitted seismic signals between holes with separations ranging from 50 ft to 600 ft. Preliminary results are very encouraging using both a cylindrical bender piezoelectric source and an air gun source. Despite the fact that the sediments have relatively low compressional velocities and are poorly consolidated seismic waves with frequencies over 1000 Hz have been transmitted over several hundreds of feet. At these frequencies it should be possible to achieve resolution in the range of feet.

Grantee: INDIANA UNIVERSITY
Biogeochemical Laboratories
Departments of Geology and of Chemistry
Bloomington, Indiana 47405

Grant No: DOE-FG02-88ER13978

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

Person in Charge: J. M. Hayes (812-335-5610; E-mail biogeo@iubacs (Bitnet) or biogeo@ucs.indiana.edu (Internet)), L. M. Pratt, and A. H. Knoll

The Nonesuch Formation was deposited about 1100 million years ago during the post-volcanic stage of subsidence in the Midcontinent Rift System. Active petroleum seeps and cellular microfossils in the Nonesuch at the Copper Range mine near White Pine, Michigan are well known. Together with numerous other deposits, they sustain interest in the possibilities that late Precambrian organic matter (i) has significant petroleum potential and (ii) encodes information about global biogeochemistry during an interval of marked climatic variations. In order to evaluate the biological source and thermal maturity of organic matter in the Nonesuch, we have undertaken sedimentological, organic geochemical, and micropaleontological studies of about 200 samples collected from outcrops, cores, and subsurface mine excavations.

Bulk organic geochemical properties of the Nonesuch Formation are being characterized by elemental analysis of whole rock samples (carbon and sulfur), elemental analysis of isolated kerogens (carbon, oxygen, nitrogen), Rock-Eval pyrolysis of both whole rock and kerogen samples, and carbon-isotopic analyses of kerogen samples. Samples of Bitumen extracted from the Nonesuch and of petroleum collected from mine seeps are being characterized by gas chromatography of the saturated hydrocarbons and gas chromatography-mass spectroscopy of the saturated and aromatic hydrocarbons. Thermal maturity is being evaluated on the basis of pyrolysis yields and various molecular ratios (biomarker indices). The hopane ratio of 22S/(22S + 22R) and the phenanthrene index appear to be the most useful molecular indicators of thermal maturity for the Nonesuch study. Carbon-isotopic ratios of individual hydrocarbon compounds will be used to determine the relative proportions of algal and bacterial inputs to Nonesuch sediment. Through these and correlative studies of other deposits, we will work toward development of a more detailed view of late Precambrian carbon cycles.

Well-preserved microfossils in the Nonesuch shales include spherical vesicles (probable reproductive cysts), filamentous cyanobacteria, and, possibly, eukaryotic algae. The preserved microfossil assemblage is similar to other Middle Proterozoic assemblages from North America, Australia, and the Soviet Union and stands in strong contrast to microfossil assemblages from younger Proterozoic sequences. Biostratigraphic subdivision of the Nonesuch or biostratigraphic correlation between the Nonesuch and other Middle Proterozoic strata is the goal of these micropaleontological investigations.

Grantee: THE JOHNS HOPKINS UNIVERSITY
Department of Earth and Planetary Sciences
34th and Charles Streets
Baltimore, Maryland 21218

Grant: DE-FGO2-89ER 14074

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

This project utilizes high-resolution and analytical transmission electron microscopy (HRTEM and AEM) to study geochemically important aspects of porphyry copper systems: (1) geochemical behavior of trace and minor metals (copper); (2) alteration reactions in the silicates, the sequence of alteration products, and their implications for evolving fluid chemistry in the hydrothermal system; and (3) characterization of phase assemblages at the submicroscopic level. Results of a reconnaissance study involving rocks from four porphyry copper deposits indicate that (1) the previously unidentified high-Cu domains in biotite and chlorite are mixed-layer sheet silicates with alternating 12- to 14-Å and 10-Å layers; (2) anomalous copper typically is not in solid solution but is discrete, submicroscopic crystals of native copper in the interlayer regions of biotite and its alteration products. Previous studies of the same samples with electron and ion microprobes suggested that biotite became enriched in Cu during the magmatic/hydrothermal event and that Cu was in solid solution.

We have now made significant progress toward demonstrating the generality of our initial observations and understanding the environment of copper inclusion formation. Contrary to much of the literature, high-Cu biotites, and hence the Cu inclusions, apparently are formed during low-temperature alteration (weathering) and not during the magmatic or main-stage hydrothermal events. Our conclusions are based on a comparison of our initial work with recent TEM observations of biotites experimentally reacted with $CuSO_4$ solutions at 25°C and 1 atm and on TEM study of a suite of core samples from the partially weathered Cyprus Grande porphyry copper deposit in Arizona. TEM methods can define the exact structural and chemical state of minor elements, and in this case they can distinguish unambiguously between subtle weathering processes and hydrothermal alteration. Further research on the core samples is yielding new insights on the geochemical behavior of base metals during weathering reactions. Primary Cu-bearing sulfides are oxidized, and Cu in solution subsequently reacts with and is immobilized by biotite. The mode of copper enrichment in biotite is much more complicated than we originally thought, occurring by sorption into expanded interlayers, by growth of submicroscopic Cu inclusions, by incorporation into submicroscopic goethite inclusions, and by formation of copper-rich inclusions within submicroscopic chrysocolla intergrowths. The TEM data from our studies specifically show how base metals migrate and are demobilized during supergene ore-forming processes, but other practical benefits include understanding the chemistry of acid mine drainage, improving *in situ* mining techniques, suggesting more judicious use of biotite as a pathfinder to Cu ore deposits, and general understanding of trace metal mobility and demobilization under low-temperature conditions in soils and porous rocks.

Grantee:	LOUISIANA STATE UNIVERSITY Basin Research Institute/Diagenesis Group 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 and L. B. Williams (504-388-8328)

An understanding of the nitrogen chemistry of organic-rich environments may be useful in evaluation of hydrocarbon maturity and migration. This research consists of field investigations of the interaction of clay minerals with nitrogen produced from hydrocarbons during diagenesis. Nitrogen is released from organic compounds throughout organic matter decay, thermal maturation, and migration. 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.

Earlier work showed that fixed-NH_4 concentrations increase with organic maturity, and that hydrocarbon migration paths may be indicated by anomalous fixed-NH_4 concentrations in sandstones. Current investigations focus on (1) determining which factor, $NH_4^+{}_{aq}$ concentration or fixation mechanism (adsorption or authigenesis), is responsible for anomalous fixed-NH_4 concentrations observed and (2) establishing reaction mechanisms. Of course mineralogy, porosity, and chemical conditions also play a role in NH_4-fixation, and the relative importance of these factors is being considered.

More than 250 samples have been analyzed from Gulf Coast, Colorado, and California oil fields to determine the influence of different types of organic matter and geologic environments on fixed-NH_4 concentrations. The diagenetic changes in fixed-NH_4 concentrations are being examined in black shales near the Walsenburg Dike, Colorado, and in the Salton Sea area, California, where the geothermal gradient is high and mineralogical studies are well documented. Current experimental work focuses on establishing equilibrium conditions between $NH_4^+{}_{aq}$ and illite (illite/smectite) in an attempt to model a proposed miscibility gap at diagenetic temperatures and its effect on observed fixed-NH_4 anomalies.

The completion of this research will lead to a better understanding of the nitrogen cycle in terms of organic/silicate interactions in hydrocarbon-rich basins undergoing diagenesis. The results 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. Toksoz (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 *in situ* fractures for the purpose of hydrocarbon production from fractured reservoirs, nuclear waste disposal planning, and geothermal energy development.

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, including the attenuation of the borehole Stoneley wave by the fracture and the conversion of the Stoneley wave into other body wave types by the fracture, and the testing of the model using laboratory scale model experiments; (2) measurement of *in situ* velocity anisotropy using full waveform acoustic logs and vertical seismic profiles, and the estimation of in-situ permeability from velocity anisotropy using a crack model; (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.

Grantee:	MASSACHUSETTS INSTITUTE OF TECHNOLOGY Earth Resources Laboratory Department of Earth, Atmospheric, and Planetary Sciences Cambridge, Massachusetts 02139
Grant:	DE-FG02-89ER 14084
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. Toksoz

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 receiver in boreholes and that these boreholes must straddle the region of interest. To get a 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 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 Hz to 300 Hz) and high frequency (400 Hz to 3200 Hz) crosshole imaging. The anisotropic features of the reservoir will be seen when the mid-band, Sandia, vertically polarized shear wave source (FY 91) and horizontally polarized source (FY 92) are used.

A central feature of the research program is the modeling, including anisotropy, necessary for the design of data acquisition efforts. The overall goal of the project is the tomographic inversion of the massive data sets and the interpretation of those images in terms of reservoir properties.

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)

This research on the modeling of magma withdrawal and caldera dynamics has been conducted in collaboration with Dr. Frank J. Spera at the University of California at Santa Barbara. Numerical simulations were conducted at the Supercomputer Center of the University of Minnesota.

We have successfully investigated the time-dependent dynamics of the thermomechanical behavior of caldera formation and associated resurgence. The modeling was accomplished by means of a finite-element code, cast in the large-amplitude Lagrangian formulation, which assumes an elastic-visco-plastic rheology for the crustal medium and includes the thermal equations governing heat transport and mechanical dissipation. The time history of an idealized caldera is modeled in two stages:

(a) A doming phase corresponding to the growth of the magma chamber. This stage is found to be constrained by the amplitudes and relaxation times of the regional doming and by a range of realistic over-pressures. The uplifts are due to the plastic deformation within the crust, whose rheology strongly depends upon the stress and temperature fields.

(b) A resurgence phase which results from caldera collapse due to the rapid expulsion of magma from a crustal reservoir. This is accompanied by an instantaneous change in the shape of surface topography. The magma chamber assumes then a passive role and mechanically behaves similarly to the crater relaxation process.

The dynamics of central vent and ring fracture eruptions and the removal of zoned magma from magma bodies of various shapes and sizes has been considered in detail utilizing a finite-element code capable of handling a wide variety of boundary and initial conditions and variable magma properties (e.g., density, viscosity, etc.). It is found that the natural eruptions fall into one of three dynamical categories depending on eruptive intensity (mass discharge rate): viscous, sub-inertial, or inertial. The parametric relationship between the discharge, the basal driving stress, and the period of time that mixed magma is erupted are developed from scaling arguments and verified quantitatively.

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, organized under the Commission on Geosciences, Environment, and Resources of the National Research Council (NRC), has replaced two standing Boards, the Board on Earth Sciences and the Board on Mineral and Energy Resources. The charge to the new board encompasses those of its two predecessors: to provide oversight of the earth science and resource activities within the NRC, a review of research and public activities in the solid-earth sciences, and analyses and recommendations relevant to the supply, delivery, and associated impacts of and issues related to hydrocarbon, metallic, and nonmetallic mineral resources. The board monitors the status of the earth sciences, assesses the health of the disciplines, identifies research opportunities, and responds to specific agency requests for advice.

The Board has under way two major reports: (1) a study on Status and Research Opportunities in the Solid-Earth Sciences—A Critical Assessment and (2) a study on 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: assessing the singular suitability of Katmai for a proposed scientific program involving drilling at Katmai *(Volcanic Studies at Katmai);* preparing an overview of the transect program *(North American Continent-Ocean Transects Program);* 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 panels of the USGC); 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.

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.

Reports of the Panel on Real-Time Earthquake Warning and the Problems of Regional Seismic Networks are under review and will be published in 1990. Future studies will include an assessment of the global seismic network and a review of the Loma Prieta earthquake.

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

The Committee on Geodesy's report, *Geodesy* in *the Year 2000*, has been published by the National Academy Press. The report considers the oceanic, solid earth, and atmospheric concerns that might benefit from improved geodetic positioning expected during the 1990s. The objectives of the Committee on Geodesy are to encourage 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 conduct studies for government agencies. The Committee has formed a Panel on A Global Network of Fiducial Sites. The Panel will evaluate the scientific impact of a proposed global network of fiducial sites, monitored very precisely, using a combination of surface- and space-geodetic techniques; examine possible strategies for implementing and operating such a network in the light of the anticipated scientific return, building on existing capabilities whenever possible; and assess whether such a network would provide a suitable global infrastructure for geodetic and other geophysical systems in the next century. The Committee and the panel each meet two to three times a year.

Grantee:	NATIONAL ACADEMY OF SCIENCES NATIONAL RESEARCH COUNCIL Washington, D.C. 20418
Grant:	DE-FG05-88ER13815
Title:	Support of the Numerical Data Advisory Board/STI Board
Person in Charge:	G. C. Carter (202-334-2755; FAX 202-334-2791; E-mail CCARTER@NAS.BITNET)

The Numerical Data Advisory Board has expanded its charge and changed its title to the Scientific and Technical Information Board (STIB). This board retains the mandate to examine data quality and needs and adds an additional mandate to study how generic problems arising from the continuing expansion and creation of scientific databases can be better managed in the light of the rapid developments that are occurring in information technology.

The STI Board has the view that data issues identified within scientific disciplines are best addressed within the relevant disciplines. However, the assessment and management of existing data are less glamorous than new research programs or pressing environmental problems, so that generic issues or problems related to data use are often given little attention. Interdisciplinary fields often have tremendous problems with database location, accession, and interfacing that are not addressed by any one of the contributing disciplines. Additionally, many such problems are common to widely varying disciplines and thus are amenable to generic solutions that could reduce duplication of effort and the incompatibilities that invariably occur when solutions are developed independently.

An example of a study addressing common issues is the current study by the Committee on Very Large Databases (VLDB) of the STI Board. This committee has identified six major common issues that confront managers of VLDBs and is now seeking to formulate solutions for these issues. One of these generic issues is the general lack of appreciation of the magnitude of the problem of the ever-accelerating collection of data and proliferation of databases, coupled with inconsistency as to content, organization, format, standards, and means of access. Other issues relate to topics such as slow application of the latest methodologies and technologies, lack of knowledge of what databases exist, lack of adequate archiving and cataloging for future access, and the lack of a national scientific and technical information program.

A new study has been initiated by a subcommittee of the U.S. National Committee for the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions—a part of the STI Board. This subcommittee is conducting a Pilot Study on IGBP Database Interfaces as a part of the International Geosphere-Biosphere Program (IGBP). This group focuses on biological, ecological, and environmental databases as tools to study global change. The USNC for CODATA has completed the preparation of the program for the *12th International CODATA Conference*, to be held 15–19 July, 1990 in Columbus, Ohio.

Other STI Board committees include the Committee on Fundamental Constants and Basic Standards and the Committee on Line Spectra of the Elements—Atomic spectroscopy.

Grantee:	UNIVERSITY OF NEW MEXICO Albuquerque, New Mexico 87131-1126
Grant:	DE-FG04-90ER14149
Title:	Chemical Transport through Continental Crust
Person in Charge:	J. J. Papike (505-277-1644; FAX 505-277-3577)

We will continue to address the evolution and regional mobility of fluids in the Harney Peak granite-pegmatite-fluid system. In addition, we propose to study fluid-rock interactions in the Long Valley caldera magmatic-hydrothermal system. Specific goals for these two studies are summarized below.

1) Black Hills Granite-Pegmatite-Fluid System, South Dakota

- Further characterize the extreme end-products of magmatic differentiation processes through petrologic studies of the Harney Peak Granite and internal evolution of selected pegmatites. Evaluation of inter- and intra- pegmatite fractionation trends will be accomplished using mineral recorders and whole-rock analyses of pegmatite wall-zone samples.

- Investigate the relative importance of the following processes (and others) in controlling the behavior of REE in a volatile-rich peraluminous granite system: (a) REE compatible accessory mineral crystallization, (b) crystallization in a melt/fluid system in which the melt structure fluctuated rapidly, and (c) subsolidus breakdown of accessory minerals and fluid transport of the REE out of the system.

2) Long Valley Caldera Magmatic Hydrothermal System

- 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 interactions.

- Propose overall modal-chemical mass balance equations to account for the observed metasomatic effects on the Bishop tuff and related lithologies.

Grantee: CITY UNIVERSITY OF NEW YORK, QUEENS COLLEGE
Department of Geology
65-30 Kissena Boulevard
Flushing, New York 11367-0904

Grant: DE-FG02-88ER 13961

Title: Evaporites as a Source for Oil

Person in Charge: B. C. Schreiber (718-520-7981)

It has been demonstrated that deposits of organic matter that form and accumulate within evaporative environments are viable source-rocks for hydrocarbons. This project has identified, studied, and sampled a number of such evaporate deposits, presently at varying degrees of maturity, and has typified many of the component organic constituents that are characteristic of these sediments. The organochemical studies, interesting in themselves, are strongly augmented by the associated sedimentological and stratigraphical analyses that represent powerful tools from which we may begin to understand the source-rock environments in other ancient evaporite deposits.

We have noted that there are several distinctly different evaporative environments with discrete biota, but some populations overlap within these groupings. The biotal components, however, seem to break apart into distinct clusters, depending on the level of chlorinity and the ionic concentrations that are present in the water. The variations in the resulting organic deposits may reasonably be expected to follow the population trends. The evaporative biomarkers we have found are exceedingly complex but in particular the analytical results from two time equivalent, well-delineated and discrete basins in Sicily apparently demonstrate characteristic, almost identical organic compositions, so that we are certain that distinct environmental parameters may be identified. The two sampled Sicilian basins, Gibellina and Cattolica, yielded rock extracts from which the chromatograms of the saturate fractions display major similarities, despite being from different areas. The *n*-alkane distributions are nearly identical, are dominated by lower carbon numbers, and maximize at C_{24}. No odd/even or even/odd predominance is evident in either chromatogram. The regular isoprenoids, pristane (Pr) and phytane(Ph), are present in a ratio of 0.27 in each sample, which is commonly considered an indicator of a reducing environment. The abundance of lower carbon numbers (as low as C_{14}) in the *n*-alkanes, particularly in the shallow-water Cattolica Basin, is an indicator of the presence of pelagic zooplankton. All of these observations are exactly in keeping with the sedimentological and petrological evidence produced by the depositional environment. The most significant difference between the two basins is evident on their chromatograms above the region of C_{28} *n*-alkanes. Although the biomarker signatures in this region of the chromatograms are similar, if not identical, there are major differences in the abundance of the components, as shown by the intensity of the peaks. In both the shallow Cattolica Basin and in the deep-water Gibellina Basin, the sediments and much of the organic material originated in the shallows or in the upper, photic-zone portion of the water column, thus there is the great similarity in the chromatograms below the level of the C_{28} *n*-alkanes. In the Gibellina Basin, however, these components were mechanically reworked into the deep part of the basin, where they were somewhat modified by a secondary population of more diverse bacteria, producing additional triterpenoid compounds (hopanes and hopenes). In this way we may see that the sedimentary petrology matches the observed organochemical variations quite clearly — providing the first well defined tie-in between evaporative sediments and their specific organic components.

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 the 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 westwards into Ontario, Canada, have revealed a much greater diversity of growth patterns 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 while 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. From Rochester, New York, westwards to Port Colborne, Ontario, Canada, all surface exposures of Edgecliff reefs are of the thicket/bank type, attesting to shallow 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 trends.

The unusual nature of the Edgecliff reefs (i.e., no stromatoporoid framework, no calcareous algae) has been determined to be the result of temperate water temperatures. A trend in stromatoporoid abundance from extremely rare in the east to common in the vicinity of Port Colborne, coupled with the first identification of calcareous algae in western reefs, suggests the presence of a temperature gradient, with warming of basinal waters as they flowed northwards (present west) towards the Devonian equator. This suggests that the Edgecliff Reefs are more closely analogous to recent ahermatypic reefs than the tropical coral reefs and presents the Edgecliff as a model for Paleozoic "cool water" carbonate deposition.

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 (516-632-8200; 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, Li, Sr, 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 dolomites. The analytical techniques for the trace element studies include isotope dilution, plasma spectrometry, electron microprobe, and 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 generally has been to apply our new geochemical techniques to the dolostones of the Burlington-Keokuk formations. After evaluating their usefulness, the most appropriate are being applied to sequences that have quite different tectono-sedimentary settings. As a result we have included in our petrographic and geochemical studies other types of regionally occurring dolomites: (1) the dolomites in the Canning Basin formed in Devonian reef complexes and platform carbonates fringing a Precambrian massif landward and a large synsedimentary graben (Fitzroy Trough) basinward; and (2) the dolomites in Neogene carbonates formed in reefal and peri-reefal facies in tectonically active island settings in the Mediterranean, Spain, and the Netherland Antilles.

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 waves and bulk waves with fluid-filled porous materials. First, we concentrated on the propagation of various surface waves on fluid-saturated porous materials, both synthetic and natural rocks. We developed two novel techniques for surface wave studies. One of the techniques was based on the mode conversion of bulk waves on corrugated surfaces, while the second one used direct excitation of surface waves. In order to extend our surface wave studies to other guided wave modes, we formulated the general problem of reflection and transmission of elastic waves through various interfaces of fluid-filled porous materials. We carried out numerical calculations and verified, by experiment, the angular behavior of the reflection and transmission coefficients for both fast and slow waves, as well as for shear waves. We have shown that although the boundary conditions (i.e., open or closed pores at the interface) affect the strength of the transmitted slow waves through the porous materials, a more major role is played by volumetric attenuation. To increase the detectability of slow waves we introduced another new method based on the generation and detection of leaky Lamb waves. We have shown, both experimentally and theoretically, that the lowest Lamb mode is due to the slow wave component in the porous material. This Lamb wave technique shows superior sensitivity compared to the more conventional bulk technique. We developed a new technique based on the transmission of airborne ultrasonic waves through air-saturated porous plates in order to observe slow waves in natural rocks. To the best of our knowledge, our preliminary results represent the first irrefutable evidence of *slow waves* in fluid-saturated *natural rocks*, such as different types of sandstones.

Grantee:	UNIVERSITY OF OKLAHOMA School of Geology and Geophysics Norman, Oklahoma 73019
Grant:	DE-FG05-88ER13412
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 405-325-3180)

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 work has diversified into a number of areas, and in the past year major emphasis has been placed on the characterization of suspected source rocks in the basin. In addition to examining samples of the Woodford shale outcrops we have started to characterize samples from the Viola, Sylvan, Springer, and Morrow Formations. A large number of these samples are being characterized in terms of total organic carbon, Rock Eval type pyrolysis using our PYRAN pyrolysis system, petrographic characterization, and examination of the extractable fractions by GC-MS. With the Woodford shale samples, in addition to examining their potential as a source rock, we have made an extensive study of the effects of weathering on outcrops of the shale. Extensive alteration has occurred with effects of microbial alteration and weathering clearly observable in the surface samples. These observations are extremely important in attempts to recognize the effects of paleoweathering in samples of the shale recovered from deeper parts of the basin. Furthermore it is important to understand the effects of surface weathering so that when outcrop samples of other formations are collected in the basin any such effects will be immediately discernible, preventing invalid interpretations being made. It is anticipated that a comprehensive examination of these potential source formations will provide a better picture of oil generation, both in terms of timing and migration, in the Anadarko Basin than is currently available.

The overall aim of this work is to develop, define, and evaluate new and existing geochemical parameters that can be used in the search for new sources of hydrocarbons. Organic geochemistry has developed very rapidly in the last few years, and with the continuing development of analytical equipment and our knowledge of the fate of organic matter in the sedimentary environment, geochemistry will become an even more important exploration tool in the next few years.

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 405-325-3180;
E-mail AB1635@UOKMVSA)

Comprehensive sedimentologic/geochemical studies on two depositionally distinct, unmetamorphosed units, the Nonesuch Fm. (~1.1 Ga lacustrine rift deposit) and the Dripping Spring Quartzite (~1.3 Ga marine shelf deposit), are nearing completion. In particular, an attempt has been made to (1) identify source rocks by quantification and characterization of constituent organic matter, (2) recognize depositional/diagenetic/catagenetic factors that may have influenced source rock quality, and (3) evaluate the possibility of previous or current hydrocarbon generation and migration.

Organic petrology and geochemical analyses suggest important differences between kerogens in the Michigan (MI) and Wisconsin (WI) Nonesuch Fm. study areas. When considered within a geographic/stratigraphic framework, the Nonesuch Fm. in the MI study area exhibits superior source rock potential. Additional analytical information ($\delta\,^{13}C_{kerogen}$, $\delta\,^{13}C_{carbonate}$, $\delta\,^{15}N_{kerogen}$, pyrolysis/GC/MS), when considered collectively, suggests a fundamental difference in the depositional/diagenetic chemical regime between the two study areas. It is suggested that sedimentary organic matter in the WI area was subject to more extensive microbial alteration during early diagenesis. It is also possible that thermal maturity levels were slightly to moderately higher in WI than MI. Petrologic evidence for migrated bitumens and the stable isotope composition of late vein carbonates suggest, furthermore, that oil generation and migration may have actually been more extensive in the WI study area.

Sedimentologic analysis of the Dripping Spring Quartzite suggests overall deposition as a prograding tidal flat. Two organic-rich units within the formation, the gray and black facies (representing sheet flow deposition on the mixed flat and mud flat portions of the tidal flats, respectively), were described in detail (cores) and sampled for petrologic and geochemical analysis. Gray facies TOC levels rarely exceed 1%, and $\delta\,^{13}C_{kerogen}$ values vary considerably ($\Delta^{13}C$ = 2.9 °/oo). In contrast, black facies TOC levels are consistently high (typically >1%), and $\delta^{13}C_{kerogen}$ variability is limited ($\Delta^{13}C$ = 0.7 °/oo). Whereas few consistent variations in kerogen $\delta^{13}C$ values are noted with lithology or vein frequency, isotope enrichment trends are apparent up section in both units, particularly in the gray facies. Pyrolysis-FID, petrologic, paleontologic, and XRF analyses reveal that isotopic variation between and among these two units resulted both from distinct organic source materials and the selective destruction and possible mineral replacement of organic constituents. Our studies on these organic-rich facies suggest that limited petroleum potential exists as a result of such mineralization processes. In turn, it is speculated that organic matter was responsible for the enhanced concentration of a variety of trace elements.

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 503-737-2064;
E-mail egbert@oce.orst.edu)

We are in the early stages of a research project whose goal is to develop improved procedures for the initial processing and reduction of wide-band (0.01–100 Hz) magnetotelluric (MT) data. We have obtained data, modified programs, started testing robust methods, and begun exploring some extensions to our previous work involving regression M-estimates (RMEs). Initial results are very encouraging — the RME works substantially better than simple least squares estimates of the impedance tensor. However, we have found that wide-band data present some problems which require novel solutions. The simplest application of the RME is not always adequate. The "dead band" (0.1–1.0 Hz) presents a particular problem. Signal-to-noise ratios at these frequencies are often very low, due to low levels of ionospheric signal and high levels of cultural noise. We have found that while the RMEs are typically smoother than the standard least squares estimates, they are often severely biased to very low amplitudes in the dead band. In some circumstances the typical data consist mostly of noise and the unusual, or outlier, data are the rare time segments with useful signal, which the RME throws out. The situation is further complicated by the presence of occasional bursts of noise which can produce large outliers in all data channels. One simple solution, which appears to work reasonably well, is to use the coherence of short segments of data as a preliminary screening criterion before application of the RME. In many cases the combination of coherency pre-sorting with the RME produces much better results than either alone.

Preliminary results indicate that the simplest generalization of the single station RME to a robust remote reference estimator of the MT impedance tensor also performs poorly in low signal-to-noise situations. We are concentrating our current efforts on adapting multivariate statistical methods to develop new approaches to robust remote reference impedance estimation.

We are also working in close conjunction with other DOE funded research on rapid multi-dimensional inversion methods. A major goal of this cooperation is to assess the impact that improvements in initial data reduction can have on the final interpretation of the data in terms of crustal structure of the Earth.

Grantee: PRINCETON UNIVERSITY
Department of Geological and Geophysical Sciences
Princeton, New Jersey 08544

Grant: DE-FG02-85ER13437

Title: Silicate Thermochemistry

Person in Charge: A. Navrotsky (609-258-4674, FAX 609-258-1274)

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. This year a good deal of effort has been put into expanding and developing new calorimetric techniques which will enable us to integrate data on low temperature hydrous phases and on high temperature anhydrous minerals, glasses, and melts. The dissolution of water-bearing and carbonate-bearing phases in molten lead borate is being characterized in detail. Solution calorimetry by R. Rapp of alkali and alkaline earth carbonates provides a reference state for heats of solution involving the alkali and alkaline earth oxides and paves the way for studies of carbonate thermochemistry. Overcoming kinetic problems in the dissolution of rare earth oxides and titanium and zirconium dioxides enables us to determine heats of formation of minerals containing these elements; work on zircon is in progress (A. Ellison).

Several projects involving hydrous phases have been completed. In addition to the tremolite-richterite join studied by A. Pawley last year, S. Circone has completed x-ray, NMR, thermogravimetric, spectroscopic, and solution calorimetric studies of the Mg-Tschermak substitution along the Mg-Al-phlogopite join. $KMg_3AlSi_3O_{10}(OH)_2 - KMg_2Al_3Si_2O_{10}(OH)_2$, using synthetic samples. W. Carey performed a calorimetric study of the energetics of water in cordierite, and P. Maniar studied a series of silica gels and some synthetic pure silica zeolites. These studies taken together begin to unravel the simultaneous energetic effects of coupled ionic substitutions, of framework topology, and of water content in complex chain, sheet, and framework silicates. The thermodynamic properties of such phases are important in diagenesis, metamorphism, rock-water interactions, and nuclear waste disposal.

A. Ellison's work on glasses has focused on the system K_2O-La_2O_3-SiO_2. Several joins in this system show virtually linear heats of solution, implying nearly zero heats of mixing. Coupled with Raman spectra, with EXAFS studies, and with the energetics of phase separation, these observations suggest a constant local environment for La and substantial local "phase ordering" such that macroscopic immiscibility represents a change in the size of domains already present rather than major structural rearrangement. Calorimetric data for these and other simple three-component glasses have been used to predict the structural features and heats of mixing in nuclear waste glasses, and to suggest that heats of mixing between these commercial multicomponent glasses are generally small.

To better understand possible coordination geometries in glasses and crystals containing two or more different cations, A. Ellison has been developing computerized enumeration schemes based on generalizations of Pauling's rules.

Grantee:	PURDUE UNIVERSITY Department of Earth and 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 (317-494-3696; FAX 317-494-0776; E-mail aydin @ purccvm)

This is a cooperative project between researchers at Stanford and Purdue universities to characterize and understand the geometry of natural fracture systems in rocks. The study is motivated by a recently increasing emphasis on the transport of water, oil, and gas in fractured reservoirs. Because fracture permeability is strongly dependent on fracture geometry (spacing, aperture, length, etc.) and connectivity, realistic three-dimensional models for natural fractures are required. We are developing fracture models based on detailed field mapping in the Appalachian and Colorado plateaus and on fracture mechanics analyses. Research at Stanford University focuses on fracture models within massive rocks, where interaction between adjacent fractures controls fracture geometry and connectivity. Research at Purdue University addresses the influence of interfaces on the fracture geometry and connectivity in layered rocks. Field-based research on the role of interfaces on the propagation of fractures involves documenting fracture geometry in multilayered rocks and determining the kinematics of fracturing across common types of interfaces listed below:

- In-plane and continuous fracture propagation across interfaces between similar layers
- Out-of-plane and continuous fracture propagation across interfaces between dissimilar layers
- Out-of-plane and discontinuous fracture propagation across thin inhibiting shales

Numerical models are being developed to investigate underlying mechanical processes relevant to the observed effect of interfaces on fracture development in layered rocks with various physical parameters (elastic modulii, Poisson's ratios, and fracture toughnesses) and loading conditions. Both the field data and the numerical analyses, combined with the findings from massive rocks, will lead to a greatly improved conceptual basis for evaluating the geometry and connectivity of fractures and their possible implication for either improving or impeding fracture permeability in typical 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)

Recent experiments have shown that 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.

The degree of hyperfiltration-induced fractionation is a function of the chemical nature of the solute as well as the clay membrane's ideality. High degrees of hyperfiltration-induced fractionation should result when a low-atomic-weight element is hydraulically forced through a highly ideal clay membrane. Since a clay membrane's ideality is mainly a function of porosity, this study proposes to measure experimentally the magnitude of $^{7}Li/^{6}Li$ fractionation during hyperfiltration through Li-saturated membranes of smectite composition. The results will yield baseline data against which hyperfiltration-induced isotopic fractionation of higher-atomic-weight elements should be gauged in future hydrogeochemical investigations.

Grantee:	SAN DIEGO STATE UNIVERSITY FOUNDATION Department of Geological Sciences San Diego, California 92182
Grant:	DE-FG03-90ER14142
Title:	10th Workshop on Electromagnetic Induction in the Earth
Person in Charge:	G. R. Jiracek (619-594-5160)

Approximately 300 participants attended the 10th International Workshop on Electromagnetic Induction in the Earth held on August 22–29, 1990, in Ensenada, Mexico. The workshop is sponsored every two years by the International Association of Geomagnetism and Aeronomy (IAGA) and the International Union of Geodesy and Geophysics (IUGG). Cosponsors of the 10th workshop included DOE, NSF, Consejo Nacional de Ciencia y Technologia (CONACYT), and the Union Geofisica Mexicana. The primary organizing group for the 1990 workshop was Centro de Investigacion Cientifica y de Educacion Superior de Ensenada (CICESE), Mexico.

The electromagnetic (EM) induction workshop is the primary forum for Earth scientists in the world to share their EM research. The workshop activities included five days of oral and poster presentations, including evening panel discussions. The nine sessions were:

1. Developments in EM instrumentation, data acquisition, and processing.
2. Modeling and inversion.
3. Removal, correction, and decomposition of the effect of local near-surface inhomogeneities.
4. Interpretation of conductivity models of the Earth.
5. Long-period induction studies.
6. Oceanic induction studies.
7. Induction studies of volcanic and geothermal belts.
8. Deep-probing controlled-source methods.
9. General contributions.

The full agenda addressed all major EM activities in the Earth sciences. Several scientists from the United States, Mexico, Canada, Germany, and the Soviet Union were selected to present special tutorial and review talks at the meeting. Besides the purely scientific merits of the meeting, the workshop over the years has fostered many collaborative studies and close personal friendships.

Grantee:	SOUTH DAKOTA SCHOOL OF MINES AND TECHNOLOGY Rapid City, South Dakota 57701-3995
Grant:	DE-FG02-88ER13982
Title:	Chemical Transport through Continental Crust
Person in Charge:	J. J. Papike (now at the University of New Mexico; 505-277-2747; FAX 505-277-3577)

The main objective of these studies is to understand the extent and mechanisms of chemical migration over a range of temperatures and in diverse geologic media. We continue to attack these problems through studies in the granite-pegmatite-fluid system of the Black Hills, South Dakota, and the Long Valley caldera magmatic-hydrothermal system, California. Research in progress includes:

1) Black Hills Granite-Pegmatite-Fluid System, South Dakota

- Refine petrogenetic models of granite formation and evolution by studying in detail compositional and mineralogical variation in the Calamity Peak pluton, an essentially small-scale version of the main Harney Peak Dome.

- Further characterize the extreme end-products of magmatic differentiation processes through petrologic studies of the Harney Peak Granite and internal evolution of selected pegmatites. Evaluation of inter- and intra-pegmatite fractionation trends will be accomplished using mineral recorders and whole-rock analyses of pegmatite wall-zone samples.

- Investigate the relative importance of the following processes (and others) in controlling the behavior of REE in a volatile-rich peraluminous granite system: (a) REE compatible accessory mineral crystallization, (b) crystallization in a melt/fluid system in which the melt structure fluctuated rapidly, and (c) subsolidus breakdown of accessory minerals and fluid transport of the REE out of the system.

2) Long Valley Caldera Magmatic-Hydrothermal System

- 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 interactions.

- Propose overall modal-chemical mass balance equations to account for the observed metasomatic effects on the Bishop tuff and related lithologies.

This research is being done in collaboration with Dr. J. Eichelberger, Sandia National Laboratories, Albuquerque, New Mexico, who is emphasizing the geochemistry and mineralogy of the primary volcanic activity and Dr. J. C. Laul, Battelle, Richland, Washington, who is responsible for the INAA, AAS, and XRF analytical work.

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 (213-743-3510; FAX 213-747-2015;
E-mail Aki%GEO@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 accomplished two major breakthroughs in the interpretation theory of high-frequency seismic data. One is the derivation of an integral equation for time-dependent power spectra, which unified all the existing theories (including the radiative transfer theory for total energy and single and multiple scattering theories based on the ray approach) and offers more complete and economical solutions to the problems of seismic scattering and attenuation. The other is the new formula for synthetic seismograms for layered media with irregular interfaces, combining the T-matrix method for an arbitrary shaped inclusion and the method of global generalized reflection/transmission coefficients for layered media. Both breakthroughs will enable us to deal with seismic observations in complex Earth structures more efficiently and accurately. In the area of experimental studies, we completed the study of seismic sources for the long-period event in Fenton Hill and discovered seismic guided waves trapped in the San Andreas fault near Parkfield, California.

Our goal is to develop an effective interpretation method for seismology in the continental thermal regime, including a computer program for calculating synthetic seismograms for three-dimensionally heterogeneous anisotropic absorptive media with irregularly shaped topography and discontinuities. In parallel with the development of interpretation methods, we shall acquire seismological data from the CSDP candidate sites in continental thermal regimes, including Mt. Katmai, Long Valley-Inyo-Mono Lake, Valles caldera, Fenton Hill hot dry rock site, and Mt. St. Helens. We shall collect both the records of seismic events occurring naturally and the data obtained by the use of artificial sources.

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; FAX 415-723-1188;
E-mail nur@erebus.stanford.edu)

Our studies are focused on four of the most important problems in rock physics: static and dynamic elastic moduli of rocks and their relation to formation properties; realistic and quantitative modeling of effective elastic moduli of porous and unconsolidated rocks; dispersion and attenuation of P and S seismic waves in saturated rocks, influence of grain-scale fluid effects on velocity dispersion, and saturation hysteresis in laboratory measurements of elastic wave velocities; and laboratory and analytical investigation of anisotropy in poroelastic media including shales and some petroleum source rocks.

Static and dynamic moduli. Using laboratory measurements, we investigated the relationship between static and dynamic bulk moduli in gas sandstones representing a wide range of porosity and clay content. In shales the ratio of dynamic to static moduli is rather insensitive to confining stress. In sandstones this ratio exhibits a strong dependence on confining stress. Our results give the basis for understanding the connection between static and dynamic moduli and formation properties.

Effective moduli. The displacement discontinuity method was used to compute the deformation of arbitrarily shaped pores in elastic material under general loading. The effective elastic moduli are computed as functions of pore shape, external loading, rock matrix elastic moduli, and rock matrix dimensions. The interaction of rock grains with friction and slippage was modeled to explain the difference between static and elastic moduli of granular materials. These investigations provide us with realistic and quantitative analytical methods for calculating the effective moduli of natural rocks.

Dispersion, attenuation, and hysteresis. Laboratory data showed a clear dependence of elastic wave velocities on the details of the distribution of water and air in the pore space of a sandstone. When saturation was decreased, pronounced saturation hysteresis was observed for P and S velocities. To describe the process of oscillatory flow in pores the general analytical solution of oscillations of a viscous compressible fluid in a long, arbitrarily shaped pore was obtained. Modeling a local flow in fluid saturated rocks, we discovered the linear relation between shear and bulk wave dispersion, with a well-defined slope. The effects of local flow were quantified by estimating the high frequency unrelaxed shear and bulk moduli.

Anisotropy. New data on dynamic elastic properties of cores from the Bakken Formation were obtained, revealing a strong anisotropy. These properties were analyzed using the concept of a transversely isotropic, periodic thin-layered medium. The effects of transverse isotropy were modeled using reflection coefficients at a single interface. Results show the possibility of mapping kerogen content in the Bakken shale directly from seismic amplitude.

Grantee: STANFORD UNIVERSITY
Department of Applied Earth Sciences
Stanford, California 94305

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, Katmai National Park, Alaska. If the National Park Service grants drilling permits to the Katmai Drilling Project, our work will help guide site selection and identify targets for the drilling program. However, our proposed research will contribute to the understanding of silicic volcanic systems regardless of whether drilling ever takes place. Understanding the subsurface geometry of the vent is essential for accurate modeling of the present thermal regime in the vent region and the eruption dynamics. Determining the origin of surficial fractures should indicate the effect of compaction and consolidation of tephra and orientation of the depositional surface on fracture formation. Our research plan is to (1) complete a detailed topographic–structural map of surface fractures including spatial distribution and relative displacements; (2) carry out numerical modeling studies that relate surface fractures to major subsurface structures; and (3) interpret the origin of surface fractures in light of these model studies.

Field work this past summer discovered two areas in the Novarupta Basin which may display the effects of long term compaction of the fallback tephra filling the vent. A morphologic monocline which extends for some 500 m along the western edge of the basin is interpreted to have formed by deposition and compaction of tephra over a gently sloping vent rim. The other area displaying continued compaction is located along the northern edge of the basin. Examination of photographs from the Griggs expeditions in 1916–1919 and topographic profiling have shown that a new drainage is forming there and that the old drainage has been stranded above the present valley bottom. Both of these structures, along with the densely welded fallback tephra that was ejected during the second day of the eruption, can be used to constrain compaction models of the vent region.

Selected photographs from the Griggs expeditions were rephotographed using the old pictures as guides in relocating the original camera location. These pictures show that the degradation of scarp faces has been significant, although the scarps do not appear to have retreated very far from their original locations. One important result from this comparison is that grabens on the Turtle, a fractured, topographic high in the vent region, may have formed initially as open fractures which then experienced dip-slip movement to become faults. Recent modeling efforts have suggested that the topographic expression of the Turtle is consistent with the emplacement of an intrusion the size of Novarupta Dome 275 m beneath the top of the Turtle.

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 and understand the geometry of natural fracture systems in reservoir rocks. Because fluid transport in oil and gas reservoirs can depend strongly on the geometry of fracture apertures and the connections between fractures, we are developing three-dimensional geometric models for natural fractures based on detailed field mapping. In massive sedimentary layers fracture geometry (spacing, aperture, length, etc.) is largely controlled by the mechanical interaction between adjacent fractures or fracture segments. In contrast, interfaces between different lithologic members of a sequence play the most important role in controlling geometry within layered rocks. Research at Stanford focuses on fracture geometry within massive layers.

Our three-dimensional geometric models provide motivation for numerical and experimental studies of the fracture process (including the initiation, propagation, interaction, and termination of fractures under natural loading conditions) using continuum and fracture mechanics principles. In particular, we are identifying the mechanisms responsible for curving fracture paths, segmentation, and linkage (or lack thereof). By understanding these mechanisms we can relate the degree of connectivity to the geometry, state of stress, and material properties of reservoir rocks and, in turn, be in a position to evaluate the influence of these factors on permeability.

Central to our understanding is the concept that fracture geometry is determined by the path taken by each fracture front during propagation. The path depends on the *mode* of stress intensity factor at the fracture front, and that, in turn, depends on the remote loading conditions. We are developing numerical models of fracture growth that determine the relationship between propagation paths and the state of stress in massive layers. Our two-dimensional numerical models, based on the boundary element method, have considered mixed mode I-II fractures loaded by constant remote stress and internal pressure boundary conditions. These models are now being extended to consider prescribed remote strain rates which are more appropriate when fracture propagation is rapid compared to tectonic strain rates.

Fracture segmentation is known to be caused by heterogeneities in material properties or in the local stress state. Mixed mode I-III fracture loading in an isotropic material will cause breakdown into multiple echelon segments. Some of the theoretical means for studying fracture segmentation are available, but important aspects of the theory remain to be tested experimentally. For example, the theory suggests that continuity of the fracture surface through the breakdown zone is dependent on the stress intensity ratio and on Poisson's ratio. We have designed experiments to investigate these dependences and will attempt to identify the different loading conditions and material properties that would result in a continuous transition (providing good hydraulic connection) or would produce a more limited connection, perhaps only at a point.

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)

Ongoing investigations in the central Klamath Mountains by the P.I. 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 alkalic oceanic island lavas and surmounting immature calc-alkaline arc basalts. These igneous rocks are interlayered with, and 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.

Research supported by the past, now exhausted DE Grant concentrated on elucidating the areal extent and structural/stratigraphic relations of these mafic/ultramafic Yellow Dog metavolcanic units and documented the insignificant degree of crustal contamination of the melts by associated terrigeneous metasediments. The physical conditions of metamorphism and of water-rock interaction accompanying island-arc accretion have been provisionally 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 kbar; contact aureoles peripheral to the Middle/Late Jurassic calc-alkaline plutons reached maximum physical conditions of 500–600°C at 2.0–3.5 kbar. The post-collisional granitoids mobilized alkalis, silica, LREE, and 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 primitive arc are the goals of this research.

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)

Recent seismic studies have shown that earthquakes are occurring near oil and gas fields in Texas; Alberta, Canada; and at Lacq in southwestern France. Pore pressures in these fields have *declined* by several 10's of MPa. These earthquakes cannot be explained by conventional models of induced seismicity, which require *increases* in pore pressure to destabilize faults. We believe that poro-elastic stresses resulting from production-generated decreases in pore pressure are responsible for earthquakes in these fields.

The goals of this new project is a fundamental understanding of the coupling between pore fluid flow and rock deformation. Refinement of the models will allow realistic assessment of deformation, both seismic and aseismic, associated with fluid extraction—deformation which, in extreme cases, can limit the ability to recover energy resources. Finally, it is possible that we can utilize the occurrence of micro-seismicity associated with induced stresses to learn about mechanical and hydraulic properties of rocks at depths that are otherwise not accessible to measurement.

This project is a collaboration with J. R. Grasso (University of Grenoble), who is monitoring induced seismicity and deformation occurring above a major deep gas field at Lacq, in southwestern France. Accurate earthquake locations, 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 stresses generated by fluid extraction. In this project we will (1) obtain and analyze existing well-log data to quantify the structure and properties of the reservoir; (2) develop analytical poro-elastic models for general axi-symmetric geometries; (3) develop appropriate numerical methods to analyze production-induced stressing in three-dimensional reservoir models; (4) extend the linearized theory to include realistic equations of state for gaseous pore fluids and incorporate them in numerical codes; (5) verify the model by comparing predicted pore-pressure changes and surface displacements with available leveling and reservoir pressure data; (6) compare the computed poro-elastic stresses with earthquake locations and orientations deduced from relocated hypocenters and earthquake focal mechanisms.

Grantee: TEXAS A&M UNIVERSITY
Department of Geology
College Station, Texas 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 in Montana and its stratigraphic equivalents in east-central Idaho were deposited during collision of the western continental margin of North America with an inferred volcanic arc (Antler orogeny). The study area includes part of the early Mississippian platform, the platform margin-to-basin transition, and deep basin environments in the Antler foredeep. 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 across the platform and into the Antler foredeep, an area approximately 350 km wide (nonpalinspastic). This study has established criteria for recognizing third-order (and smaller scale) cycles in deep water deposits. In addition, this study has documented how sedimentation in ancient slope and basinal environments responds to relative sea level fluctuations on a shallow carbonate platform which supplied most of the sediment to these environments.

We also have completed a regional study of Late Devonian through Late Mississippian subsidence in Montana and Idaho. The subsidence analyses have shown that subsidence in the Antler foredeep and subsidence on the Montana platform are coupled. 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 is 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. Another important aspect of research on the diagenetic history of the Mission Canyon Formation has been utilization of rare earth element (REE) abundances in diagenetic phases as a geochemical tracer. The REE have proven useful as indicators of redox potential in pore fluids. Because of their extremely low concentrations in most naturally occurring 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

Grant: DE-FG05-88ER13711

Title: Anisotropic Yielding of Rocks at High Temperatures and Pressures

Person in Charge: A. K. Kronenberg and J. E. Russell (409-845-0132; FAX 409-845-6780)

The majority of previous studies of mechanical properties of rocks have assumed that their behavior is isotropic. The current study focuses on the influence of fabric anisotropy on the inelastic yielding of foliated and lineated rocks with a variety of applications including prediction of borehole stability, determination of in-situ stress states from fracture orientations in anisotropic rocks and, in general, evaluation of yield envelopes of major rock types found in the Earth's crust. The results may be summarized as follows:

Gneiss. Fracture strengths of Four-Mile gneiss display significant anisotropy, with orthorhombic symmetry defined by the orientations of foliation S and lineation l. Samples shortened in directions perpendicular and parallel to S are consistently strong while samples shortened at 45° to S are consistently weak. Only small reductions in strength are observed with increasing temperature, and material parameters are nearly the same at T = 700°C as they are at T = 25°C. The observed mechanical anisotropy may be explained by a simple model involving tensile crack nucleation within the brittle framework silicates ahead of and between biotite grains oriented favorably for internal slip and frictional sliding on (001).

Granite. Fracture strengths of Westerly granite are indistinguishable for samples compressed in six orientations with respect to the quarrying planes, the rift, grain, and hardway and compare favorably with the highest strengths exhibited by Four-Mile gneiss. Peak fracture strengths vary from sample to sample by ~14%, and anisotropy below this level cannot be resolved. Nevertheless, experiments repeated 10 times in differing orientations fail to show any systematic differences, even though microcracks within quartz grains are oriented preferentially parallel to the rift.

Schist. Yield strengths of a schist rich in biotite (75%) with foliation S defined by well-oriented mica segregation seams are remarkably similar for samples cored at 45° and 90° to S. Compressive strengths exhibit dependencies upon confining pressure as well as upon temperature and strain rate, a result of deformation accommodated both by brittle and by ductile processes. Frictional sliding and kinking are most important at low pressures, while kinking and dislocation slip take over at high confining pressures. The transitional brittle-ductile deformation of biotite schist appears to be subject to history- and/or path-dependencies. Preliminary results for several other mica-rich schists reveal a wide spectrum of behavior, spanning those of the anisotropic Four-Mile gneiss and the isotropic biotite schist. Inelastic anisotropies of foliated rocks depend critically upon the preferred orientations and spatial arrangements of micas. The influence of oriented microcracks is much less pronounced.

Grantee:	UNIVERSITY OF TULSA Department of Geosciences Tulsa, Oklahoma 74104
Grant:	DE-FG05-88ER 13417
Title:	Stability of Natural Gas in the Deep Subsurface
Person in Charge:	C. Barker (918-631-3014; FAX 918-631-2286)

Fluid inclusions are microscopic defects in crystals that have trapped small volumes of the fluids present at the time of crystal growth. They offer one of the best ways of obtaining samples of the gases present during mineral formation because they are not inherently limited by either depth or age and the gases in the inclusions are protected from 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. The main modification made in the last year has involved designing and building a pulse triggering system that is phase locked to the AC power line. It triggers both mass spectrometers in a way that reduces periodic power line noise and significantly improves signal to noise ratios for small inclusions. Workstation memory has also been extended and data storage in the buffers changed to eliminate "dead time" during transfer of digitized mass spectrometric data to tape. We have built an all-metal gas handling line to provide known gas mixtures for instrument calibration and extended the software to handle this calibration data.

The analytical system has been used to study inclusions in quartz overgrowths. Overgrowths are important in petroleum reservoir rocks because their fluid inclusions sample the fluids present at various times during reservoir development and filling. Unfortunately most inclusions were very small and were close to the analytical limits, but information on methane content that is needed for interpreting phase relationships observed microscopically could be obtained.

We have continued to analyze inclusions in deep fracture filling cements with special emphasis on the deep Smackover formation of the Gulf Coast. Many of these inclusions have high concentrations of H_2S. Analyses of a deeply buried shale (now at the surface in central Pennsylvania) showed methane-bearing inclusions in quartz vein-filling cements. Methane concentrations in overlying units decreased with vertical distance. We have also obtained data for the Carlin gold deposit, Nevada. This formed in a breached oil field. The inclusion data showed that the fluids became more water rich as temperature fell and gold was deposited. These inclusions contain some of the highest concentrations of oxidized sulfur gases (SO_2) observed so far.

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

Grant: DE-FG02-88ER13936

Title: Scientific Drilling to Investigate Hydrothermal Dynamics, Ore Mineralization, and Mechanisms of Caldera Formation—Deep Core Hole VC-2B, Sulphur Springs, Valles Caldera, New Mexico

Person in Charge: J. B. Hulen (801-524-3446; FAX 801-524-3453)

VC-2B is the third Continental Scientific Drilling Program corehole to be completed in the Valles caldera complex. The hole was drilled in the Sulphur Springs area of the caldera complex in 1988 as an intermediate-depth (1762 m) companion to previously completed, shallow (528 m) corehole VC-2A. Whereas VC-2A was drilled primarily to investigate the high-level vapor cap on the active, high-temperature (up to at least 300°C) Sulphur Springs sector of the Valles hydrothermal system, VC-2B was designed to penetrate through that cap into the system's deeper and much more extensive liquid-dominated regions. Continuous core and fluid samples from this pair of scientific coreholes (1) provide an unprecedented glimpse of essentially simultaneous vertical variation in a volcanic-hosted hydrothermal system, (2) permit for the first time detailed reconstruction of the system's hydrothermal history, (3) allow refinement of existing models of fluid flow, fluid-flow interaction, and ore mineralization in such a system, and (4) furnish valuable new clues to the volcanotectonic evolution of the Valles caldera complex and similar felsic volcanic centers in other locales.

In the year since the last "Summaries" was published, much additional work has been completed on the core and fluids from VC-2B (at 295°C and 1762 m, believed to be the deepest, hottest, continuously cored hole yet completed in the United States). Fluid sampling has indicated that the deeper of two currently "stacked" (?) hydrothermal cells postulated last year is probably much less saline than originally envisioned, although still perhaps twice as saline as the cell believed to be confined to high-level intracaldera ignimbrites. Fluid-inclusion studies, however, have demonstrated that aqueous solutions perhaps up to six times as saline as any yet sampled in the active hydrothermal system once circulated in the deeper Paleozoic and Precambrian rock penetrated by VC-2B. These relatively saline fluids may have been responsible for precipitating the corehole's deep suite of base-metal sulfides; high-level dilute fluids probably deposited traces of pyrargyrite above 800 m depth.

Grantee:	UNIVERSITY OF UTAH RESEARCH INSTITUTE Earth Science Laboratory 391-C Chipeta Way Salt Lake City, Utah 84108
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
Person in Charge:	J. B. Hulen (801-524-3446; FAX 801-524-3453)

Many of the unusual oil fields of the Basin and Range physiographic province in eastern Nevada are hosted by fractured, brecciated, and hydrothermally veined Paleozoic dolomites spatially associated with granitic stocks of Cretaceous to Oligocene age. At two of these fields, Blackburn and Grant Canyon, textures of the brecciated reservoir rocks suggest development by explosive hydrothermal fracturing. At Blackburn, preliminary microthermometric analyses of fluid inclusions in associated vein minerals show that high-temperature (> 350°C) hydrothermal fluids conducive to natural hydraulic rock rupture once circulated where oil is now concentrated. Moreover, the Blackburn dolomite reservoir rocks appear to be locally disrupted by stringers of hydrothermally fluidized clastic debris derived from the adjacent stock. These relationships suggest that much of the critical porosity and permeability required for oil entrapment in the carbonate-hosted Basin and Range oil fields may have been developed in overpressured, magmatic- or meteoric-hydrothermal systems driven by cooling plutons. Evidence of yet another geothermal/petroleum connection is preserved in late-stage quartz from the Grant Canyon field. The quartz hosts primary aqueous, oil, and mixed aqueous/oil fluid inclusions, all trapped at approximately the current reservoir temperature (120°C); characteristics of the three-phase oil/water inclusions suggest that at Grant Canyon, oil may have migrated to its ultimate entrapment site as droplets dispersed in dilute aqueous geothermal solutions.

These hypotheses are being tested at the Grant Canyon and Blackburn oil fields using a combination of detailed petrographic work, fluid-inclusion studies, detailed geologic mapping, logging of oil-well cuttings and cores, and structural/stratigraphic analysis to delimit major fluid channels. Confirmation could lead to refinement of Basin and Range petroleum exploration models as well as discovery of additional domestic oil reserves.

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

Grant: DE-FG02-89ER14083

Title: 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)

The goal of this effort is the acquisition and interpretation of a tensor, controlled-source audiomagnetotelluric (CSAMT) survey at the Sulphur Springs geothermal area of the Valles caldera. The survey is in support of scientific interpretation of CSDP hole VC-2A, drilled in the fall of 1986, and hole VC-2B, completed in late 1988. Purposes of the CSAMT survey include establishing basement relief, mapping stratigraphy, estimating relative fluid content or alteration, inferring relative permeability, and delineating possible vapor regimes. A further important purpose of the survey is to calibrate the resistivity expression of the system with other geological and geophysical models.

The CSAMT stations, 50 in all and obtained with our own equipment, are being concentrated over the Sulphur Springs area, but some are being taken as much as 2–3 km away for control. The frequency range of the data spans 4.1 kHz down to 1 Hz, allowing tight control of near-surface variations but also providing information on structure to depths approaching 2 km. The tensor nature of the data is very desirable to strengthen the interpretation and take advantage of the precise and versatile multidimensional 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.

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)), D. A. Hewitt, P. Ribbe, and D. Wayne

During the second year of our project we have completed the physical and chemical characterization of synthetic zircons, as well as 40 natural zircons of varying ages (2700 m.y. to 300 m.y.). Two zircon samples with very distinct total alpha dosages have been investigated for uranium and lead isotopic stabilities at pressures up to 6 kbar and 600°C. Although the composition of fluids plays a marked role in the removal of uranium and lead from the zircons, there is a predictable relationship between the amount of uranium removed from the zircon and the total alpha dosage. For a given experimental solution (2M NaCl) the strongly metamictized zircons ($D^* = 1.5 \times 10^{15}$; uranium = 2000 ppm) lost over 50% uranium, while another test sample with lower uranium content (215 ppm) lost approximately 30%. Our results support our working model that stability of $ZrSiO_4$ in a fluid medium is strongly correlated to total alpha dosage and must be a major factor in designing chemical forms for waste repository hosts.

We have also completed preliminary studies of the solubility of crystalline zircons at low pressures (25 bars) and temperatures (200°C). This environment more closely approximates waste repository conditions. Our solubility data suggest a first order dissolution rate law. The constant ratio in molar Si/Zr (above unity) seen in our experiments suggests that $ZrOCl_2$ may not be as soluble in 3N HCl as in HCl solutions below normality of one.

From these studies we are developing a comprehensive model of the stability of zircons at varying P-T-X conditions.

Grantee: VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
Department of Geological Sciences
Blacksburg, Virginia 24061

Grant: DE-FG05-89ER14065

Tide: PVTX Properties of Fluid Systems: $NaCl-CaCl_2-H_2O$

Person in Charge: R. J. Bodnar (703-231-7455; FAX 703-231-3386), J. M. Simonson, and C. S. Oakes

Experimental data on the PVTX properties of fluids provide the basic information required to develop quantitative models to describe the physical and thermodynamic behavior of natural fluids. These models in turn facilitate the understanding of water-rock and fluid-magma interactions that occur in the Earth's crust.

The system $NaCl-CaCl_2-H_2O$ provides a reasonable approximation of fluids in sedimentary basins (oil-field brines) and many higher temperature metamorphic and magmatic environments. We have begun a study of this important system as part of our continuing program to determine the PVTX properties of geologically applicable fluid systems over the range of pressure and temperature conditions encountered in crustal environments. Experiments have been conducted to determine phase relations in the ice-stable region of this system under vapor-saturated conditions, and an equation has been developed to describe ice-liquid equilibrium (liquidus) as a function of temperature. Densities of $NaCl-CaCl_2-H_2O$ solutions have been determined at 298 and 308 K and 0.1 MPa for ionic strengths ranging from 0.1 to 19.2 $mol \cdot kg^{-1}$, and along the 7 and 40 MPa isobars from 298 to 523 K using a vibrating U-tube densimeter apparatus in the Chemistry Division at Oak Ridge National Laboratory. Experiments to determine the positions of isochores at elevated temperatures and pressures using the synthetic fluid inclusion technique are in progress. These data will be combined with PVTX data obtained using the U-tube technique at lower pressures and temperatures to develop an equation of state for the system $NaCl-CaCl_2-H_2O$.

Results available to date suggest that previously published data for PTX relations in the ice-stable region may contain significant errors. Interpretation of fluid inclusion compositions from the Salton Sea Geothermal System (SSGS) using the older data indicates significant differences between present-day fluids and those present at some time in the past when the inclusions were trapped. The discrepancy is eliminated if the fluid inclusion measurements are reinterpreted using ice-liquidus data from this study. Whether or not the geothermal fluids have changed with time has important implications for the evolution of the SSGS and for hydrologic models used to describe fluid flow characteristics of the SSGS.

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 numerically efficient algorithm to invert large magnetotelluric (MT) data sets for conductivity 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. The model is made unique by minimizing a function which measures the complexity of the model. Our philosophy is to find the model with the least structure for a given level of misfit to the data. We call the method the Rapid Relaxation Inverse (RRI). During the past year, our effort has been split between improving the two-dimensional (2-D) version of our code and developing a three-dimensional (3-D) version. The 2-D work has involved a thorough study of synthetic data generated from known models with random noise added. This study resulted in the implementation of three stabilization schemes. One operates in model space and damps efforts by the algorithm to make the model rough. The second operates in data space and down-weights data with large residuals at each iteration. This means that data that are easy to fit will be fit first. The scheme we use is the robust M-estimate of Huber. The third involves spatially smoothing the residuals at each iteration. This means that the long wavelengths in the data are fit first. We have applied 2-D RRI to several large real data sets: 16 frequencies at 35 sites in Saskatchewan; 30 frequencies at 48 sites in Nevada; and 38 frequencies at 100 sites in Wyoming. All of these data have been inverted on a SPARCstation 1. Total run-times are of order one hour and grow only linearly with number of data (frequencies × sites) inverted. In all cases, we have been able to form images of the electrical structure, which fit the data well, are quite simple, and provide interesting geological insight. The Saskatchewan data in particular, provide a remarkably high resolution image of the structure responsible for the North American Central Plains conductivity anomaly. They show that it very likely consists of series of horizontal strands that lie in a plane dipping westward at 11°. Our 3-D work has commenced with development of a suitable algorithm for computing 3-D electric and magnetic fields. To be useful for inversion, this algorithm must be able to handle essentially arbitrary conductivity variation. Fortunately, the job is made easier because the search for models with minimum roughness removes the difficulties that arise when there are discrete boundaries inside the medium. In this case, appropriate finite difference approximations (FDA) are accurate and they lead to very sparse systems of linear equations. The specific FDA that we have implemented leads to 12 diagonals. We solve it using a conjugate gradient method with incomplete Cholesky factorization pre-conditioning. Convergence is somewhat slower in 3-D than we have generally needed for 2-D (240 iterations to reduce the residual by a factor of 10^{-8} as opposed to 80 or less in 2-D). Nevertheless, the method has proven fast enough that one can actually solve reasonable size 3-D examples on the SPARCstation. We expect to implement the 3-D inversion in the coming year.

Grantee: UNIVERSITY OF WASHINGTON
Geophysics Program
Seattle, Washington 98195

Grant: DE-FG06-88ER13979

Title: Investigation of Subcooled Hydrothermal Boiling in Groundwater Flow Channels as a Source of Harmonic Tremor

Person in Charge: S. D. Malone (206-543-8020; FAX 206-543-0489;
E-mail steve@geophys.washington.edu)

Geothermal ground noise and volcanic tremor are sustained, low level, quasi-periodic vibrations of the ground observed in geothermal areas and at active volcanoes. It has been suggested that geothermal ground noise and volcanic tremor could be caused by vigorous aquifer boiling in hydrothermal systems. We model this potential seismic source as a population of spatially distributed monopole (volume) sources of compressional wave energy emitting discrete pulses randomly in time. Each monopole source of the population consists of a single vapor bubble growing or collapsing in liquid as a result of boiling heat transfer to the aquifer. The hydro-acoustic energy emitted during growth or collapse of the bubble takes the form of a narrow pressure pulse, and is considered to be the direct source of seismic energy in our model. The amplitude and frequency content of the observed seismic signal will depend on: (1) the free-field acoustic power spectrum of boiling, (2) the frequency response functions of the groundwater flow channels in which boiling occurs, (3) the frequency response function of the material through which seismic waves travel to the receiver, and (4) the combined frequency response function of the receiver mechanical and electronic components. As a first step toward assessing the ability of hydrothermal boiling to explain geothermal ground noise and volcanic tremor observations, we are investigating the free-field hydro-acoustic power spectrum of boiling (the "source" spectrum in the above model). We simulate boiling in the lab by injecting steam into a pressure vessel filled with water. The pressure pulses produced by the formation and collapse of steam bubbles at the steam inlet vent of the pressure vessel are measured with a submerged hydrophone, and the hydrophone output is digitized at 2×10^4 samples/second by a computer. The range of pressure and temperature conditions attainable with the laboratory apparatus is limited to < 3.5 bars, $< 139°C$, due to the finite strength of observation windows affixed to the pressure vessel. Therefore, dimensional analysis is used to correlate the experimental results in terms of non-dimensional combinations of the pertinent variables. In addition to investigating the overall shape of the boiling acoustic spectrum, we are investigating absolute spectral levels in the frequency band of geothermal ground noise and volcanic tremor (0.5 – 10 Hz) and the ratio of acoustic energy emitted per bubble to the total available (potential) energy. In the past year, we completed the experimental data collection, reduction, and analysis. An empirical correlation has been found which relates low-frequency (0 – 10 Hz) acoustic energy output to the properties describing the states of the hydrothermal liquid and vapor phases and to the size of vapor bubbles generated by boiling. By making guided assumptions about the range of fluid properties and boiling heat transfer characteristics likely to exist within hydrothermal systems, we can use this correlation to predict expected intensities of ground vibration caused by hydrothermal boiling. This information will allow us to better assess the ability of hydrothermal boiling to produce ground vibration amplitudes in accordance with geothermal ground noise/volcanic tremor observations, and hence will contribute to our knowledge of possible seismic sources in geothermally and volcanically active regions.

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. R. Whelan (508-548-1400, Ext. 2819)

The objective of this program is to develop a better understanding of processes of hydrocarbon generation and migration in coastal and offshore sedimentary basins as an aid in predicting favorable exploration areas for oil and gas. Work is now complete on the Louisiana Gulf Coast East Cameron well, including downhole maturation modeling. Vitrinite reflectance shows an excellent continuous maturation profile through the Miocene section, making this an important "calibration" well for the time-temperature response of a number of geochemical parameters for the Tertiary section of the Louisiana Gulf Coast. Geochemical profiles being used for this purpose include various individual C_{15}^{+} hydrocarbons, light hydrocarbon ratios, and pyrolysis data. Recently completed maturation modelling results, together with the extensive geochemical data for the well, contribute greatly to an interpretation of the geological history of this well, including the timing and effects of geopressuring. For example, early expulsion of light hydrocarbons is occurring just above and throughout the geopressured zone; even the organic matter in this well would not be considered by many to be of sufficient amount or quality to be producing the separate "oil phase" currently thought to be necessary for primary oil migration. These results also may provide experimental information for resolving the debate which currently rages about the major source(s) of the oils in the Gulf Coast.

A new Global Basin Research Network (GBRN) has been formed which allows us to examine our Gulf Coast organic geochemical data together with that of others in a much more comprehensive way than was previously possible. The GBRN includes geologists, geochemists, and geophysicists from Lamont-Doherty Geological Observatory, Cornell University, and Texas A & M University working together with industrial participants, who are contributing expertise in computer modelling and data visualization in petroleum related areas. The goal of this research is to develop a general methodology for looking at the interactions of fluid flow and sedimentary basin development. The data on Gulf Coast gas and oil compositions, inorganic fluid compositions, mineralogies, sediment organic matter, etc., provide tests of whether the processes being simulated by the computer are geologically reasonable. The group has begun to assemble a comprehensive 3-D observational framework which eventually can be compared with 3-D computer models, starting with specific areas of the Louisiana Gulf Coast. The first observational "data cube," which has been completed using AMOCO data of a 20×40 km block of the off-shore Gulf Coast, provides impressive visualization of the relationships of salt topography, surface heat flow, clays and sands, and oil and gas fields with locations of two major faults running through the block. The presence of two major compositional families of oils and gases within the cube suggest that the two fault systems feed two fundamentally different petroleum types into the reservoirs separated by a salt ridge with the seaward reservoirs containing a more sulfur rich (possible more marine) oil.

Grantee:	YALE UNIVERSITY Department of Geology and Geophysics New Haven, Connecticut 06511
Grant:	DE-FG-02-90ER14153
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 a combined theoretical and field study of coupled fluid flow, heat and mass transport, and chemical reaction in hydrothermal and metamorphic systems. An existing computer code developed by the applicants which numerically treats multicomponent, finite-rate reactions combined with advective and dispersive transport in one dimension will be extended to incorporate isotopic exchange and heat and mass transfer in two dimensions. The code we have developed simultaneously solves for mass transport and reaction, thus offering a significant improvement in computational efficiency over existing "batch" reaction path codes. By coupling flow and chemical reaction in a hydrothermal system, we can explicitly investigate the extent to which characteristic flow-reaction paths govern the chemical evolution of the fluids in a hydrothermal system. The concept of a flow-reaction path is particularly important where certain portions of mature hydrothermal systems may exhaust the buffer capacity of the rock as the primary mineralogy is consumed. In these instances, fluids traversing distinct regions within the hydrothermal system may experience very different reaction histories, even where the system can be described as nearly isothermal.

The study of paleo-hydrothermal systems can yield some important insights into the chemical dynamics of hydrothermal systems in general. As an example of a paleo-hydrothermal system, we will consider the geochemical evolution of "porphyry-copper" type mineralization as meteoric fluids encroach on early high-temperature copper mineralization and alteration assemblages. As a field example, we will simulate the hydrothermal system which formed the Butte Main-State copper-zinc veins, where early high-temperature mineralization is redistributed by meteoric waters along through-going fractures.

The sulfur isotopic composition of coexisting sulfide-sulfate pairs may constrain the dynamics of sulfur-rich hydrothermal systems. Since the rate of isotopic equilibration between sulfate and sulfide in solution is slow, the extent to which equilibrium is established may provide information on mixing between various fluids and the rate of fluid flow. In order to determine the utility of this kind of isotopic data in hydrothermal systems, we propose a study of coexisting alunite and sulfides from the highly altered central zone at Butte.

A second field application of the reactive flow modeling will be to the high-grade metamorphic complex at Naxos, Greece. Preliminary data from the complex suggests that isotopic reaction fronts are present where metamorphic fluids have moved from one lithologically and isotopically distinct unit to another. The extent of penetration of the isotopic reaction fronts into a unit may constrain the integrated fluid flux through the contact. The detailed shape of the front may provide constraints on the instantaneous ratio of the isotopic exchange to the fluid flux.

TABLE 1

DOE/OBES GEOSCIENCES RESEARCH
HISTORICAL SUMMARY
(OPERATING FUNDS — THOUSANDS)

ON-SITE	FY 1981	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
ANL	$ 310	$ 330	$ 330	$ 360	$ 360	$ 355	$ 340	$ 335	$ 440	$ 454
BNL	—	—	—	—	—	—	—	50	90	49
LANL	1,500	1,375	1,684	2,343	2,289	2,263	2,603	2,868	2,638	2,614
LBL	1,075	1,180	1,405	1,485	1,596	1,632	2,162	2,100	2,265	2,372
LLNL	1,060	1,110	1,280	1,815	1,898	1,521	1,837	1,732	2,121	2,169
ORNL	380	430	430	470	480	492	690	785	944	1,226
PNL	580	520	520	578	595	605	725	850	848	819
SNL/A	1,310	1,546	1,682	2,087	1,861	2,256	2,462	2,711	2,213	1,828
ON-SITE TOTALS	$ 6,215	$ 6,491	$ 7,331	$ 9,138	$ 9,079	$ 9,350	$10,819	$11,431	$11,559	$11,530
TOTAL OFF-SITE	$ 3,030	$ 3,141	$ 4,523	$ 3,309	$ 4,260	$ 3,507	$ 4,453	$ 4,868	$ 5,755	$ 5,683
TOTAL OPERATING	$ 9,245	$ 9,632	$11,854	$12,447	$13,346	$12,857	$15,272	$16,299	$17,314	$17,213
TOTAL EQUIPMENT	$ 923	$ 900	$ 890	$ 960	$ 1,100	$ 1,094	$ 1,150	$ 1,150	$ 1,150	$ 1,150
TOTAL GEOSCIENCES	$10,168	$10,532	$12,744	$13,407	$14,446	$13,951	$16,422	$17,449	$18,464	$18,363

TABLE 2

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

INSTITUTION (PI)	FY 1981	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
U/ALASKA (LEE)	$ 108	$113	$ 117	$ 120	$ 126	$ 126	$ 128	$ 140	$ 143	$ 140
U/ALASKA (PULPAU)	70	—	—	—	—	—	—	—	—	—
AM GEOPHYS UNION (SPILHAUS)	—	—	—	—	—	—	—	—	5	—
U/ARIZONA (ANOVITZ)	—	—	—	—	—	—	—	—	—	60
U/ARIZONA (HILL)	96	99	101	90	121	—	101	103	121	120
U/ARIZONA (NORTON)	66	60	48	—	—	—	—	—	—	—
*ARIZONA STATE (FINK)	—	—	—	—	22	23	11	—	—	—
ARIZONA STATE (NAVROTSKY)	62	66	123	—	—	—	—	—	—	—
BECHTEL (HARPER)	—	—	—	—	—	25	—	—	—	—
*BROWN U (HERMANCE)	164	165	333	—	166	—	150	150	—	—
BROWN U (YUND)	—	—	—	—	—	—	—	—	—	79
*CAL TECH (AHRENS)	—	—	72	81	160	—	150	100	—	—
CAL TECH (STOLPER)	—	—	—	—	50	98	—	78	82	85
CAL TECH (WASSERBURG)	—	—	—	—	—	—	—	200	250	250
U/CALIFORNIA-B (HELGESON)	—	—	204	—	120	120	135	116	121	120
U/CALIFORNIA-B (REYNOLDS)	144	150	165	196	233	200	200	210	236	245
U/CALIFORNIA-LA (ANDERSON)	—	—	—	60	74	—	23	—	—	—
U/CALIFORNIA-LA (BOEHLER)	46	NFX	60	66	75	—	—	—	—	—
U/CALIFORNIA-LA (ERNST)	—	—	—	—	—	—	64	69	—	—
U/CALIFORNIA-LA (HARRISON)	—	—	—	—	—	—	—	—	54	54
U/CALIFORNIA-LA (WARREN)	121	NFX	—	—	—	—	—	—	—	—
*U/CALIFORNIA-R (McKIBBEN)	—	—	—	—	50	—	40	—	77	49
U/CALIFORNIA-SD (CHAVE)	—	—	—	—	—	—	120	—	—	—
U/CALIFORNIA-SD (CRAIG)	—	—	—	35	41	41	42	35	—	—
U/CALIFORNIA-SD (HARDING)	—	—	—	—	—	—	—	—	63	—
U/CALIFORNIA-SB (SPERA)	—	—	—	—	—	—	—	—	64	47
U/CHICAGO (ANDERSON)	NFX	38	98	NFX	46	—	—	—	—	—
U/COLORADO-B (SPETZLER)	—	—	—	—	—	—	95	37	91	NFX
COLO SCH MINES (CROSS)	—	—	—	—	—	—	—	10	—	—
COLO SCH MINES (LARNER)	—	—	—	—	—	—	—	—	192	195
COLUMBIA U (ENGELDER)	150	156	289	—	150	75	—	—	—	—
COLUMBIA U (JACOB)	318	318	337	359	360	360	360	360	290	203
COLUMBIA U (WALKER)	—	—	—	73	79	106	—	85	90	127
U/CONN (TORGERSEN)	—	—	—	—	—	—	—	—	—	4
U/DELAWARE (WOOD)	—	—	—	—	—	—	—	—	62	56
DOSECC, INC (BARBER)	—	—	—	—	6	—	—	66	—	—
*DOSECC (FRIEDMAN)	—	—	—	—	—	—	—	—	—	65
GEO CHEM RES ASSOC (ORTOLEVA)	—	—	—	—	—	—	50	100	—	—
HARVARD U (THOMPSON)	—	—	372	—	115	—	18	—	—	—
U/HAWAII (MANGHNANI)	—	88	96	99	200	—	100	100	—	NFX
U/HOUSTON (CHAFETZ)	—	—	—	—	—	—	69	—	—	—
U/HOUSTON (McDONALD)	—	—	—	—	—	—	—	—	273	295
HEADQUARTERS SERVICES	—	6	1	3	15	5	3	3	3	5
INDIANA (HAYES)	—	—	—	—	—	—	—	186	162	150

TABLE 2

(OPERATING FUNDS — THOUSANDS)
(CONTINUED)

INSTITUTION (PI)	FY 1981	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
JOHN HOPKINS (VEBLEN)	$ —	$ —	$ —	$ —	$ —	$ —	$ —	$ —	$ 63	$ 66
LOUISIANA STATE (FERRELL)	—	—	—	—	—	—	60	59	64	NFX
U/MARYLAND (VALETTE-SILVER)	—	—	—	—	43	—	NFX	—	—	—
U/MINNESOTA (JOHNSON)	68	57	NFX	—	—	—	—	—	—	—
U/MINNESOTA (YUEN)	—	—	—	—	—	—	—	—	48	42
MIT (AKI)	160	151	158	147	—	—	—	—	—	—
MIT (SIMMONS)	100	106	106	110	80	80	—	—	—	—
MIT (TOKSOZ)	—	—	—	—	—	142	—	113	370	498
*MICHIGAN STATE (VOGEL)	—	—	—	—	31	NFX	34	—	—	—
*MICHIGAN TECH (McDOWELL)	—	—	—	—	50	—	—	—	—	—
MONTANA TECH., BU. MINES & TECH. (BARTHOLOMEW)	—	—	—	—	—	—	—	8	—	—
NAS/NRC (CARTER)	—	—	—	—	—	—	—	—	3	3
NAS/NRC (HART)	168	282	—	200	187	124	202	132	—	—
NAS/NRC (LONG/BURKE)	—	—	—	—	—	—	—	—	100	105
NATL CTR ATM RES (HERRING)	—	—	—	—	—	—	10	—	—	—
28TH INT'L GEOL CONGRESS (NSF) (WRIGHT)	—	—	—	—	—	—	200	—	—	—
NAS/NRC (CORELL)	—	—	—	—	—	—	—	5	—	—
NSF (JOHNSON)	—	—	—	—	—	—	—	—	30	—
*U/NEVADA (PEPPIN)	—	—	—	—	—	143	—	—	—	—
*U/NEVADA (RYALL)	—	75	87	95	—	—	—	—	—	—
U/NEW MEXICO (PAPIKE)	—	—	—	—	—	—	—	—	—	200
CUNY-B (FRIEDMAN)	—	—	—	—	95	86	100	59	—	—
CUNY-Q (E-SCHREIBER)	83	81	49	—	116	—	—	—	—	—
CUNY-Q (C-SCHREIBER)	—	—	—	—	—	—	—	101	105	NFX
SUNY-A (DEWEY)	86	—	—	—	—	—	—	—	—	—
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
SUNY-SB (PAPIKE)	65	—	—	—	—	—	—	—	—	—
U/N CAROLINA (GLAZNER)	—	—	—	—	38	39	—	35	—	—
OHIO STATE UNIV (ADLER)	—	—	—	—	—	—	50	52	55	54
U/OKLAHOMA (ENGEL)	—	—	—	—	—	—	—	—	112	106
*U/OKLAHOMA (PHILP)	—	—	—	—	—	28	—	—	—	—
U/OKLAHOMA (PHILP)	—	—	—	—	84	88	106	110	124	121
U/OREGON (WEILL)	—	—	103	94	—	—	—	—	—	—
OREGON STATE (EGBERT)	—	—	—	—	—	—	—	—	43	41
OREGON STATE (FEHLER)	—	38	—	—	—	—	—	—	—	—
PENN STATE (MARTIN)	83	NFX	—	—	—	—	—	—	—	—
PENN STATE (GIVEN)	—	—	—	100	—	NFX	—	—	—	—
PURDUE UNIV (AYDIN)	—	—	—	—	—	—	—	—	56	56
PURDUE UNIV (FRITZ)	—	—	—	—	—	—	—	—	—	71
PURDUE UNIV (HINZE)	—	—	—	—	—	—	8	—	—	—
PRINCETON U (NAVROTSKY)	—	—	—	—	100	—	85	120	125	123
PRINCETON U (PHINNEY)	—	—	—	—	—	—	—	—	97	—
RPI (FRIEDMAN)	91	99	150	—	—	—	—	—	—	—
RICE (AVE LALLEMENT)	—	—	120	121	—	—	—	—	—	—
SAN DIEGO STATE (JIRACEK)	—	—	—	—	—	—	—	—	—	5

TABLE 2

(OPERATING FUNDS — THOUSANDS)
(CONTINUED)

INSTITUTION (PI)	FY 1981	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
S DAKOTA SCH M&T (PAPIKE)	$ —	$ 67	$ 100	$ 130	$ 150	$ 99	$ 100	$ 105	$ 115	$ —
*U/S CALIFORNIA (AKI)	—	—	—	—	150	150	155	159	164	147
U/S FLORIDA (SACKETT)	34	—	—	—	—	—	—	—	—	—
SMU (BLACKWELL)	54	70	—	—	—	—	—	—	—	—
STANFORD U (ERNST)	—	—	—	—	—	—	—	—	—	160
STANFORD U (LIOU)	—	34	45	NFX	—	—	—	—	—	—
STANFORD U (NUR)	140	125	160	172	172	165	165	170	175	328
STANFORD U (PARKS)	—	57	56	56	—	—	—	—	—	—
*STANFORD U (POLLARD)	—	—	—	—	39	42	44	70	152	105
STANFORD U (SEGALL)	—	—	—	—	—	—	—	—	—	80
U/ROCHESTER (GOVE)	—	—	—	—	—	—	8	—	—	—
*U/TEXAS-AR (SELF)	—	—	—	—	43	NFX	80	—	—	—
U/TEXAS-AU (BARKER)	—	—	54	—	—	—	—	—	—	—
U/TEXAS-D (MITTERER)	—	—	—	—	—	—	—	—	—	119
TEXAS A&M (CARLSON)	—	—	—	—	—	98	—	—	—	—
TEXAS A&M (CARTER)	—	—	—	70	—	—	—	—	—	—
TEXAS A&M (DOROBEK)	—	—	—	—	—	—	52	55	57	—
TEXAS A&M (FRIEDMAN)	202	200	201	93	100	194	—	—	—	—
TEXAS A&M (GILBERT)	—	—	—	—	—	98	88	101	10	—
TEXAS A&M (KRONENBERG)	—	—	—	—	—	—	117	156	197	149
U/TULSA (BARKER)	75	71	75	80	80	81	133	—	76	71
USGS (MORGAN)	—	—	—	—	—	—	35	—	—	—
USGS (RUSS)	—	—	—	—	—	—	—	—	12	—
USGS (WESSON)	—	—	—	—	—	—	—	6	—	—
*UURI (NEILSON)	—	—	—	—	—	114	—	—	—	—
*UURI (HULEN)	—	—	—	—	—	—	—	125	—	85
UURI (WANNAMAKER)	—	—	—	—	—	—	—	—	91	—
VPI & SU (BODNAR)	—	—	—	—	—	—	—	—	114	78
VPI & SU (SINHA)	—	—	—	—	—	—	—	82	60	87
U/WASHINGTON (BOOKER)	—	—	—	—	—	27	30	—	78	81
U/WASHINGTON (MALONE)	—	—	—	—	—	—	—	32	32	—
U/WISCONSIN (WANG)	38	—	—	48	52	97	84	87	92	—
U/WYOMING (SURDAM)	—	—	—	—	—	—	65	65	—	NFX
WASHINGTON STATE UNIV (THIESSEN)	—	—	—	—	—	—	103	—	—	—
WOODS HOLE (WHELAN/FARRINGTON)	—	—	—	—	223	223	226	238	220	208
WOODS HOLE (HUNT)	139	150	190	208	—	—	—	—	—	—
*WOODWARD-CLYDE (BURDICK)	—	100	100	100	40	—	—	—	—	—
XDATA (DINES)	—	54	66	—	—	—	—	—	—	—
YALE U (GORDON)	35	26	39	184	—	—	—	—	—	—
YALE U (LASAGA)	—	—	—	—	—	—	—	—	—	50
OTHER	64	—	—	—	—	—	—	254	160	5
OFF-SITE TOTALS:	$3,030	$3,141	$4,523	$3,309	$4,260	$3,507	$4,453	$4,868	$5,755	$5,683

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