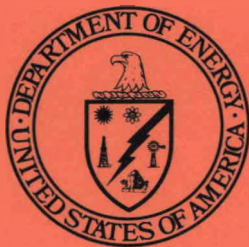


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Summaries of Physical Research in the Geosciences

Published: December 1989



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

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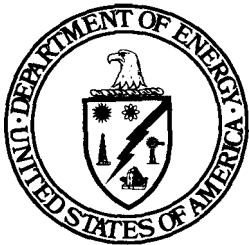
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FOREWORD

The Department of Energy supports research in the geosciences in order to provide a sound foundation of fundamental knowledge in those areas of the geosciences 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 Geoscience 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 extraction and utilization of such resources 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 Geoscience 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.

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 analogues. 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; correlate geophysical data with laboratory-determined properties; and the use of the drill hole as an experimental facility 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 distribution, and characteristics of solar radiation of the earth, including the long-term effects of solar radiation on the climate.

PART I

ON-SITE

$\frac{1}{2}$

1

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], C. P. Ervin [Northern Illinois University], and J. Sexton [Southern Illinois University]*)

This program involves the acquisition and interpretation of geophysical data over the midcontinent rift system. The objectives of the work are to determine the stratigraphy and structural evolution of the midcontinent rift system and whether the geological processes that formed the rift system were compatible with the production and preservation of hydrocarbon deposits.

An initial data set was acquired during 1988, consisting of 1,042 line kms of marine-type seismic reflection, gravity, and magnetic profiles over Lake Superior. Seismic data were collected using a tuned array of airguns and 120 groups of receivers spaced at 25-meter intervals along a 3.0 km streamer that allowed 60-fold processing. Gravity and total magnetic intensity data were collected at 11 second intervals along the ship's track. The data profiles are oriented parallel and perpendicular to the strike of the rift and tie together profiles obtained by the GLIMPCE consortium in 1986.

A 342.8 km profile (LS-08) from Duluth to 22 km east of Isle Royale parallels the axis of the rift. This profile shows an accommodation zone in the center that is associated with a gravity low. This zone separates axially adjacent pull-apart basins and is composed of a massive block of Archean gneiss. Modest thrusting and ramping up to the west is indicated on the east flank of the block. Thrusting must have occurred after volcanism but before deposition of the Bayfield and Oronto sandstones, which unconformably overlie the truncated crest of the block and the eroded subcrops of lava flows. The proximity of the Grenville convergence zone in space and time may have caused the thrusting. If post-rift thrust of reverse faulting occurred parallel to strike (as well as across strike as previously reported), with thrusts generated by stress fields emanating from a convergent plate margin, then the rift may have become a secondary feature that was quenched by the prevailing Grenville tectonics. The unusually great vertical extent of the rift basin and its billion year preservation are probably related to its lateral immobilization at a relatively early stage of development.

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] and J. K. Bohlke*)

The objective of this program is to achieve a better understanding of the geochemical processes involved in fluid-rock interactions that occur in hydrothermal systems in the Earth's crust. Generic problems being addressed include: the sources of hydrothermal fluids and their dissolved components, the rates and mechanisms of hydrothermal processes, and the relation of hydrothermal systems to larger scale tectonomagmatic and climatic processes. These problems are approached through detailed elemental and isotopic analysis of the materials comprising natural hydrothermal systems.

The applications of uranium-series measurements in the determination of the rates and mechanisms of fluid-rock interaction and in the geochronology of active hydrothermal systems are being explored in this program. Recent work has shown that zeolites in altered rhyolite in Yellowstone drill cores are in ion exchange equilibrium with coexisting thermal water and the minimum water flux can be determined by measuring the *in situ* distribution coefficient for the Ra and the whole rock $^{226}\text{Ra}/^{230}\text{Th}$ activity ratio. Travertine deposits in northern Yellowstone Park are being dated to clarify the timing of the last glaciation and its effects upon the hydrology of the thermal aquifers and to derive long term carbonate precipitation rates.

Measurements of the stable isotopic ratios of dissolved elements in thermal waters are being used to help define hydrothermal flow paths and aquifer rock types in the Yellowstone hydrothermal system. Correlations between the isotopic ratios of dissolved S, Ra, and U have been established and are related to aquifer rock type. Measurements of B and Sr isotopic ratios are in progress.

Determination of halogens and noble gas isotopes within individual fluid inclusions from a variety of modern and ancient hydrothermal environments is being pursued, in collaboration with J. Reynolds and colleagues at the University of California (Berkeley). This work utilizes a sensitive laser microprobe noble gas mass spectrometer to perform analyses in neutron-irradiated samples. Results from several localities indicate the participation of meteoric water in systems that were previously believed to be strictly magmatic or metamorphic.

B. Deep Carbon Geochemistry (*T. Abrajano [708-972-4261] and B. D. Holt*)

It is generally accepted that most, if not all, presently known oil and gas deposits are derived ultimately from diagenetic to metagenic alteration of buried organic matter. Questions remain, however, regarding the mechanisms, rates, and conditions (pressure, temperature, time) under which oil and gas are evolved and transported from their source rocks. The objective of this

program is to define the limiting geological conditions under which hydrocarbons may be generated or transported. The current focus of the work is on the thermal and chemical interactions between magmatic intrusions and hydrocarbon-bearing rocks in deep sedimentary basins. Introduction of large quantities of magmatic heat into potential source rocks in developing sedimentary basins (e.g., in rift basins or in subduction-related basins of the circum-Pacific type) could cause formation of hydrocarbon deposits where conventional oil- and gas-forming processes would not produce such deposits.

Work to date has been focused on the chemical and isotopic structure of bitumen and kerogen (Types I-III) in sedimentary rocks from thermal aureoles of mafic intrusions. The elemental (combustion-manometry), molecular (IR, GC-MS), and isotopic compositions of the bulk organic matter and its molecular constituents are being examined to test proposed mechanisms of organic matter metamorphism. Complex isotopic variations were observed in the Animikie basin sediments affected by Proterozoic magmatism in the midcontinent rift. These data contrast with the general belief that increasing metamorphism of organic matter leads to a monotonic increase in $\delta^{13}\text{C}$ caused by liberation of CH_4 . Similar studies are in progress for samples from the Mesozoic basins of the eastern United States.

Methods were developed for isotopic characterization of separable kerogen fractions in variably metamorphosed sedimentary rocks. It was demonstrated for maceral separates from selected coal samples that the isotopic characteristics (C, H, N) of liptinite, vitrinite, and inertinite components are distinct, even for mature coals, although the differences between macerals decrease with increasing metamorphic grade. These results are useful for understanding the metagenic alteration of Type II and Type III kerogens. Isotopic analyses of aromatic and aliphatic components of bitumen, kerogen, and individual macerals are in progress to further elucidate the mechanisms of organic matter metamorphism.

Contractor: BROOKHAVEN NATIONAL LABORATORY
Upton, Long Island, New York 11973

Contract: 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]*)

A study of elemental (major, minor, and trace) distributions in high-sulfur coal from the Illinois basin, coals of variable rank from the San Juan and Raton fields in New Mexico, and anthracite from eastern Pennsylvania is being made on a microscopic and macroscopic scale. The geological processes important in the formation of the coal are inferred from the measurements on geological samples, from the study of appropriate samples prepared in the laboratory, and from correlation of the data with predictions of computer modeling.

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. McEvelly

A. Deep Electromagnetic Sounding of the Crust (*H. F. Morrison, N. E. Goldstein, and K. H. Lee [415-642-3804]*)

The objectives of our investigations are to develop and apply advanced techniques for carrying out deep electromagnetic (EM) soundings of the Earth's crust, to develop better numerical methods for data processing and interpretation, and to develop better geological models for conductivity anomalies in the crust. Accurate mapping of the electrical conductivity has immediate applications in mineral, geothermal, and hydrocarbon exploration; in reservoir characterization and production studies; and in ground water problems. One of our principal goals has been to improve imaging capabilities through the combination of larger sources in controlled-source EM, signal enhancement techniques, and better methods for data interpretation.

A paper entitled "A New Approach to Modeling Electromagnetic Responses" has been accepted for publication by *Geophysics* and will appear in the September 1989 issue. The paper describes the q-domain approach to modeling EM scattering in the Earth with 2-D examples. Our ultimate goal, however, is to extend the method to 3-D problems. For this purpose, a 3-D q-domain algorithm has been written and tested on the MFE CRAY computer for layered Earth models composed of one million nodal points. The numerical solution for a 1-D Earth, when transformed back to the time domain, agrees well with the standard analytical solution. The next step is to extend the algorithm to include models of arbitrary 3-D conductivity structures.

As a first step toward EM imaging we are now able to construct wave fields from time or frequency-domain data. The process requires accurate data over more than four decades of frequency.

B. Center for Computational Seismology (*T. V. McEvelly and E. Majer [415-486-6709]*)

Continuing base level support of CCS (Center for Computational Seismology) has provided a facility that has aided not only BES programs but other DOE, government, and private industry cooperative ventures. CCS has now been built up to the point where it can offer a wide variety of state-of-the-art software and hardware to carry out research at the highest level.

CCS computing power is centered around the CONVEX, a 64 bit Vector, UNIX (Bell Labs trademark) based machine that runs 4.2 BSD. Bench marks to date indicate that in straight scalar mode it is 6 to 8 times faster than our previous system, a VAX 11/780, and if the calculations vectorize, we have observed speed increases of up to 20 times. For some very specialized uses,

i.e., FFT's, the speed is the same as a CRAY-1. In addition to the new hardware installed, CCS will be running the Sierra SEIS seismic reflection processing package. This package is a complete processing package that replaces the DISCO package. The graphics system will be the NCAR package running on top of the ATC GKS package. The ARPANET address of the new machine is ccs.lbl.gov, with an ARPANET node number of 128.3.254.11. Those interested in the facilities should mail to elm at this address.

During the last year full use was made of the CONVEX C-1/XP computer, with down time averaging a few hours per month, excluding routine maintenance. An additional 4 gigabytes of disk space were added along with an additional 16 Mbytes of memory. Presently there are 55 users on CCS who are routinely processing data. Interested people should contact elm@ccs.lbl.gov for a list of these reports.

On the scientific front, CCS continued support of the Cajon Pass project, 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:

- 1) A facility to analyze seismic data for CSDP and thermal regimes programs as well as other BES projects at LBL and other national laboratories.
- 2) Development of seismic exploration and monitoring techniques for the geothermal industry.
- 3) Research in hydrofracture propagation and monitoring.
- 4) Fracture detection research using VSP/tomographic techniques.
- 5) Research in the implementation and use of relational databases for seismic data.
- 6) Data processing center for CALCRUST: a consortium of four universities to use seismic reflection methods for intermediate and deep crustal structural analysis.
- 7) A base of computational support for software and hardware development of field systems for seismic monitoring.

C. Microcrack Growth in Crystalline Rock (*L. R. Myer, N. G. W. Cook, and Z. Zheng [415-486-6456]*)

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

In previous years theoretical work resulted in new crack models, which were used to predict behavior of brittle rock under triaxial compression. In FY 1988, laboratory experiments aimed at obtaining quantitative data on microcrack growth in rock samples were completed. Cylindrical specimens of Indiana limestone were axially compressed under different confining stresses. The microstructures in the rock as they exist under load were preserved using the Wood's metal casting technique. Results showed that extensile microcracks in this Indiana limestone under differential compression were generated by many different mechanisms and were oriented subparallel to the direction of maximum compression. The density, length, and thickness of the microcracks decreased as the confining stress on the specimen increased. The average orientation of the microcracks, obtained with respect to the direction of the maximum compression, increased

with increasing confining stress. With zero or low confining stress, the microcracks were concentrated near the surfaces of the specimen. Under high confining stress, the microcracks were more homogeneously distributed. Macroscopic shear bands consisted of many approximately equally long extensile microcracks subparallel to the direction of maximum compression. Under uniaxial compression, the dilatation of the specimen was due to the opening of extensile microcracks. Under high confining stress, porosity and volume of the specimens were reduced by pore collapse, which more than offset the dilatation caused by the opening of microcracks.

To complement the experimental results, numerical models of crack generation and interaction were carried out. Results showed that the interaction of two nonco-planar extensile cracks generates a stress field similar to that around a single "virtual" crack, which runs through the centers of the two cracks. Such a stress field in turn causes new cracks to be generated at locations aligned with the virtual crack. Results from the numerical model also showed that the presence of free boundaries changes the stress distribution around microcracks when they are close to a free boundary. When a crack is closer to a free boundary than a critical distance, stresses tend to concentrate on the side of the crack that is closest to the boundary. As a result the track of new crack generation turns towards the boundary. This is probably the reason for the formation of the "dog bone" shape during failure under uniaxial compression.

D. Process Definition in Fractured Hydrocarbon Reservoirs (*L. R. Myer, N. G. W. Cook, J. S. Long, E. L. Majer, T. V. McEvilly, H. F. Morrison, and P. A. Witherspoon [415-486-6456]*)

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 fractures and fracture networks of heterogeneous geometry, and hardware development for seismic imaging.

In the laboratory, studies of the effects of thin liquid layers on transmission of seismic waves across a single fracture, measurements using liquids representing a range in viscosities, and chemical characteristics were completed. Specifically, three polar liquids, glycerol (1000 cp), honey (100,000 cp), and water (1 cp), and three nonpolar liquids, hexadecane (2.6 cp) and two silicone oils of different viscosities (100,000 cp and 10 cp), were used. To perform the measurements, two fused quartz cylindrical disks were separated from one another by three circular Mylar spacers 2 mm in diameter and 12.5 μm thick. The space between the quartz surfaces was filled with selected liquids. A uniaxial load was applied and at each loading interval, corresponding to different thicknesses of the liquid layer, measurements of the transmitted shear (S-) and compressional (P-) pulses were recorded for analysis.

Good P-wave transmission was observed at loads as low as 0.5 kN and was not significantly changed as a function of load. However, honey and glycerol were the only two liquids that showed a consistent increase in S-wave transmission with decreasing liquid film thickness before any contact between the solid surfaces occurred. Surprisingly, high viscosity silicone oil, although of the same viscosity as honey and higher than that of glycerol, showed much poorer

transmission over the full range of film thicknesses. We believe the differences arise due to the different chemical characteristics of the liquids and the way in which they interact with the silica surface. We ascribe the differences to slippage across the solid-liquid interfaces. Slippage appears to be prevented when the solid and the liquid surfaces have strong affinities for each other. In these experiments those liquids giving good transmission are polar and would probably be hydrogen bonded to the fused quartz. This is a common type of Lewis acid-base interaction. When the liquid is nonpolar, and Lewis acid-base association does not occur with the acidic silica, the interfacial coupling is weak, and there is slippage across the interface. Consequently shear pulse transmission may be curtailed at the solid-liquid interface, irrespective of the liquid viscosity and the film thickness.

In studies related to development of imaging methods, work continued in the area of diffraction tomography. The inversion scheme uses the scattered field from fractures in order to find the location and degree of fracturing. Using an image-source principle, the method was extended to account for a fractured medium bounded by one or two free surfaces. The results produced a clear and accurate image of the fractures with the correct velocity contrast. Averaging of images at different frequencies was done to improve the single frequency image. Results were encouraging even when the total field instead of the scattered field was used in the inversion. Further extension of the method to the 2.5 dimensional (2.5 D) problem was carried out. Inversion results of synthetic data from 2.5 D medium were in good agreement with the input fracture model. Currently, the method is being applied to field data from a test site where a fractured zone is located between two tunnels. The data were collected on the two tunnel surfaces and also in two boreholes connecting these tunnels, giving a complete coverage of the fracture zone. An inversion assuming a crosshole configuration was successfully carried out.

Work on the crosshole electromagnetic method was advanced considerably both theoretically and experimentally. The feasibility of applying the principles of seismic diffraction tomography to the inversion of low frequency electromagnetic crosshole data was examined theoretically. Using a hypothetical two-dimensional geometry, it was shown that for a conductivity contrast of at least two between a fracture zone and its surroundings, a thin fracture zone may be detected between drill holes that are 100 m distant from each other. The use of crosshole electromagnetic tomography for monitoring a typical enhanced oil recovery (EOR) process involving a steam or salt water drive was also investigated. Assuming placement of the transmitter solenoid (vertical magnetic dipole) in the injection hole, it was shown that measurements of the vertical magnetic field in an adjoining observation hole can be effectively interpreted to determine the position of the flood front. New computer programs that embodied the principles of tomographic inversion were written for the purpose of this study.

The experimental work consisted of two activities. The first of these involved the construction of a laboratory scale model for testing and verifying the new computer codes. A cylindrical conducting zone was made from sponged aluminum at a scale of 1:2000. The measurements were made at 3000 Hz and showed that the computer codes were satisfactory for any further theoretical work. In the second activity, a prototype frequency domain transmitter-receiver system was assembled and tested successfully in two shallow (30 m) wells separated by 80 m of 20 ohm-m materials. These tests provided the technical information needed to proceed with the assembly of the field equipment for the upcoming deep well experiments.

In order to incorporate geophysical data into hydrologic models, a hydrologic conditional simulation model for two-dimensional and three-dimensional systems was developed. A statistical technique called "simulated annealing" is employed to build a numerical model of fracture geometry, permeability, and storativity using the observed hydrologic response. Geological and geophysical information can be incorporated into the model. A steady state cross-hole well test version of the algorithm was used to build a three-dimensional model of the Stripa Mine site, incorporating geological and geophysical information. The model was used to predict hydrologic response at the site, and this prediction will be compared with the measured response. The effects of element orientation, convergence properties, and combined steady state and transient annealing are currently under investigation.

Additional theoretical studies of flow phenomenon in fractured rocks have continued, based on the hypothesis that flow and transport are controlled by the variability of fracture apertures in a single fracture. Initial calculations on the relative permeability to non-wetting and wetting phase flow in a single fracture have been completed. In the past year, the work has also expanded from the study of flow in a single fracture to studies of transport in a fractured rock mass consisting of a group of fractures in series.

Finally, development continued on a new downhole swept-frequency, resonant shear wave source designed to operate over a frequency range of 50 to 500 Hz. Vibrating motion is achieved by reaction of an electromagnetically driven piston against a pneumatic spring. To demonstrate the effect of operation at resonance on force output of the device, tests were conducted in which the source was bolted to a large block of concrete and the block was instrumented with accelerometers to monitor the motion induced by the source. Measurements were made at various gas pressures up to 6.8 MPa. At each gas pressure, frequencies were swept while keeping the input current constant. Frequency spectra were obtained from the accelerometer output and compared for off-resonance and resonance operating conditions. The spectral amplitude of the primary frequency was more than an order of magnitude higher for resonance operation as compared with off-resonance conditions.

E. Coupled THM Processes in Petroleum Reservoirs (*C. F. Tsang and J. Noorishad [415-486-5782]*)

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. Work is under way to improve the numerical solution approach used in the code. A Newton-Raphson linearization scheme has been implemented for the solution of the coupled equations in the ROCMAS code. We have developed the necessary algorithms for an incremental solution technique, which replaces the old direct iteration algorithms. The constitutive relations for ideal elasto-plastic fractures were updated to that of a dilating strain-softening material. We have completed the verification of mechanical, hydraulic, and coupled hydromechanical algorithms of the code. The coupled hydromechanical verification was achieved through the solution of a problem of excavating a deep cavity under the water table in a hypothetical geological setting using two different versions of the ROCMAS code. A fundamental difference between the two versions is the linearization scheme employed. One version uses a direct iteration scheme and the other uses the modified

Newton-Raphson method. Convergence of the results of the two solutions, in the presence of strong system nonlinearities and errors in the discretization, points to the soundness and strengths of the numerical approach used in ROCMAS. A significant finding, identified during the course of solution of the problem, was that high instantaneous fluid pressures that may lead to hydrofracturing could develop in the rock near an excavation face. Presently, we are in the process of testing the role of this phenomenon and its significance to hydromechanical processes.

F. Gravity Field Monitoring at Yellowstone (*T. V. McEvilly [415-486-7347]*)

The development of the continuous monitoring micro-gravity experiments for the Yellowstone caldera is continuing with deployment planned for late summer 1989. This project, which will use high precision gravimetry to study temporal changes at two sites in Yellowstone National Park, will allow real-time monitoring of data for coordination of analysis with investigators at the University of Utah, who are monitoring seismic activity. The components of the two gravity monitoring systems, including satellite transmitters, gravimeters, and microcomputers, have been prepared for field deployment. A portable laptop computer will be used for initial field startup and follow-up tests. The components have been tested for interfacing, control of communication, and data transfer. The microcomputer acts as a data acquisition and data processing system for the gravimeter and acts as controller and data source for the satellite transmitter. The data processing performed by the microcomputer, including analog-to-digital conversion, digital low-pass filtering, and data storage until each daily transmission, is software controlled. The development of the microcomputer software is the focus of current work in anticipation of field deployment. In parallel with this software development, we will monitor gravimeter output for signal drift. The gravimeter drift tests, which can be performed at the Berkeley Seismographic Station, are important for calibration of the two gravimeters since we will be analyzing signal differentials. These drift tests will begin with analog strip-chart recordings and will conclude with a full digital test of each system including satellite telemetry and return of data to LBL's computer system. The deployment of both solar-powered gravimeter stations will begin after completion of this testing.

G. High Resolution Mapping of the Electrical Conductivity of the Ground Using Controlled-Source Electromagnetic (CSEM) Methods: New Systems for Petroleum Exploration and Reservoir Characterization (*T. V. McEvilly [415-486-7347], H. F. Morrison, A. Becker, N. E. Goldstein, G. W. Hohmann, and K. H. Lee*)

This is a multi-year, multi-task project to develop and demonstrate high-resolution electromagnetic (EM) imaging techniques applicable to crosshole and surface-to-borehole surveys. Advances in instrumentation, data acquisition techniques, data processing, and numerical algorithms for interpretation indicate we can attain greater accuracy and resolution in subsurface conductivity mapping than possible before. The approach to improved EM imaging involves mapping subsurface conductivity in a fashion analogous to the successful practices long used in seismic applications for mapping velocity structures. Specifically, this research will concentrate on two inter-dependent aspects of the problem: 1) improved resolution through the use of new inversion methods for modeling the conductivity distribution and by a new direct imaging technique using a wave field transformation of the diffusive EM fields and 2) improved data quality and coverage through the use of new arrays, new signal enhancement techniques, and new instrumentation. This research will be conducted under three tasks, two relating to data

processing and interpretation and one devoted to scale model and field experiments that produce high quality data.

This three-year research program is a joint effort between the Lawrence Berkeley Laboratory, the University of California--Berkeley, and the University of Utah. In addition, this research includes close collaborative efforts with industry.

H. Advanced Geoscience Research Concepts (T. V. McEvilly [415-486-7347])

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.

In addition to these activities, this year two specific short-term projects were undertaken as scoping studies for potentially much larger research programs. The first project involves the application of nuclear magnetic resonance (NMR) and position electron tomography (PET) to imaging of two phase flow in fractured rock. The objective is to obtain a sequence of NMR images from dry to variably saturated samples of fractured tuff and granite. Similarly, PET images are obtained on the same rock samples with both external and injected positron emitters as tracers. These experiments are the first to apply PET to geological samples and the first to apply NMR in fractured rocks.

In the second project, laboratory experiments are being conducted to test the feasibility of *in situ* hydrogenation of heavy oil, a novel method for enhanced recovery of heavy oil. The experiments involve measurement of hydrogen consumption and viscosity reduction of hydrocarbons using samples saturated with heavy oil. Results will provide a semi-quantitative estimate of the extent to which hydrogenation reactions occurred during the experiments.

Contractor: LAWRENCE BERKELEY LABORATORY
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Contract: DE-AC03-76SF00098

Category: Geochemistry

Person in charge: T. V. McEvelly

A. Thermodynamics of High Temperature Brines (*K. S. Pitzer [415-642-3472]*)

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 the heat capacities and heats of mixing or dilution of solutions exceeding 300°C and pressures to 1 kbar. The database for the principal components of natural waters has now become adequate for the prediction of mineral solubilities in brines up to about 300°C. Such calculations, based on the activity and osmotic coefficient equations of this project, were made for a number of systems containing Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, OH⁻, SO₄²⁻, and H₂O. 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-H₂O. Parameters were fitted to the vapor-lined coexistence surface for temperatures of 600°C and compositions from pure H₂O 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. Thermodynamic Properties of Silicate Materials (*I. S. E. Carmichael, R. A. Lange, and D. A. Snyder [415-642-2577]*)

This project measures high temperature thermodynamic properties of silicate liquids as a function of composition to enable the relevant quantities to be estimated for complex natural liquids. The iron redox state in silicate liquids has a dramatic effect on their volume, or their density. Measurements of the effect of temperature and oxygen fugacity on the ferric/ferrous iron ratio in natural liquids and liquids in the systems Na₂O-FeO-Fe₂O₃-SiO₂ and CaO-FeO-Fe₂O₃-SiO₂ have been used in conjunction with measurements of acoustic velocities to derive the compressibilities of liquids containing substantial amounts of ferric iron. With these data, values of the partial molar compressibilities of Fe₂O₃ and FeO in silicate liquids at 1 bar have been obtained.

As the iron redox state has a significant effect on the Fe/Mg distribution between crystals and silicate liquids, many of the trace metals, such as Ni and Co, will also have their distribution between liquid and crystals governed by the redox state, or the oxygen fugacity, of the magma. As magmas may encompass up to eight orders of magnitude of oxygen fugacity, experiments are underway to determine the effect of this range.

C. Studies of the Interactions Between Mineral Surfaces and Ions in Solution (*D. L. Perry [415-486-4819]*)

Studies have been conducted on the surface/solution interface reaction between galena (PbS) and copper(II) and chromium(VI) aqueous solutions using fluorescence techniques in conjunction with a synchrotron radiation source. The experiments, conducted at 25°C and atmospheric pressure, were performed in order to gain a better understanding of the phenomenon of reductive chemisorption of a metal ion from solution. In this process, a metal ion in a higher oxidation state is removed from solution by a reducing substrate; the subsequent metal ion on the surface is then in a reduced (or lower) oxidation state.

Fluorescence microprobe data were taken in order to study the surface morphology of the adsorbed copper and chromium on the galena substrate. These data were compared to previously reported findings in which the surface morphology of the reacted galena was shown to be highly dependent on the chemical state of the initial, unreacted galena. With respect to the products formed upon reaction with the metal ions, the chemistry of the oxidized surface was markedly different from that of the unoxidized surface. The difference has been shown to be of both a chemical and morphological nature.

This work, a prelude to studying these same basic reaction systems at the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory, has extremely widespread applications to energy conservation in a number of geochemically related processes. These studies, encompassing variable experimental chemical parameters such as pH, ion concentrations, temperature, and pressure, will lead to a better understanding of mechanisms and reaction products in several of these reaction systems. These same reactions will be studied by complementary surface approaches such as x-ray photoelectron, Auger, and scanning electron microscopy; in the cases of x-ray photoelectron and Auger spectroscopy, the preliminary research being done presently will be continued at the Advanced Light Source.

D. Chemical Transport in Natural Systems (*C. L. Carnahan and J. S. Jacobsen [415-486-6770]*)

The objective of this research is to gain increased understanding of processes affecting the movement of chemically reactive solutes in ground water flow systems. Our approach has been to investigate these processes theoretically through conceptual, mathematical, and numerical models based rigorously on physical, chemical, and thermodynamic principles while using reported experimental data for model input, verification, and guidance. We have developed computer programs that solve the nonlinear, partial differential, and algebraic equations describing movement of dissolved chemicals in geological media. Because of the complexity of modeling coupled transport processes and chemical reactions, these developments have proceeded along two parallel courses; we are now in the process of extending and merging these courses.

One course of development has grown out of our advances in the theoretical treatment of coupled transport processes, based on the thermodynamics of irreversible processes. A computer program, TIP, has been constructed to solve the equations governing simultaneous flows of heat, volume, and solute mass driven by evolving gradients of temperature, hydraulic head, and composition. The program accounts for three direct transport processes (Fourier's law, Darcy's law, Fick's law) and seven coupled processes (chemical osmosis, thermal osmosis, thermal diffusion, ultrafiltration, thermal filtration, diffusion thermal effect, chemical cross-diffusion) known to be active in low permeability, permselective materials such as certain clays and shales. Our work provides a complete solution of the combined constitutive and balance equations for the coupled transport processes. It also accounts for chemical reactions such as complexation, ion exchange, and precipitation of stable phases, all under the assumption of local chemical equilibrium.

The other course of development has concentrated on chemical aspects of solute transport. A computer program, THCC, has been constructed to simulate movement of solutes in the presence of homogeneous and heterogeneous chemical reactions. The homogeneous reactions are complex formation, oxidation-reduction, and pH variation. The heterogeneous reactions are precipitation-dissolution of solids and surface oxidation-reduction. The program can simulate reactive chemical transport in environments having variable temperature, oxidation potential, and pH. The THCC program is providing considerable insight into the processes affecting subsurface movement of reactive chemicals. The experience we have gained during the development of the THCC program has proven very valuable to our work in extending the TIP program to include chemical reactions. Currently, the THCC program is being extended to include coupling between chemical reactions and fluid flow via porosity changes and reactive solute transport in unsaturated media.

These investigations are made possible by OBES support and free access to the NMFEEC CRAY X-MP computer. Our fundamental research has led to support by other DOE activities for application to their particular interests.

These studies are relevant to the understanding and quantitative description of a variety of energy-related phenomena including the production of geothermal energy, the formation of ore deposits, the chemical evolution of fluids in deep sedimentary basins, and the subsurface migration of toxic and radioactive wastes.

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

The overall objective 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 the 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. A secondary but major objective is to ascertain if a series of time markers of very high precision and accuracy (in the form of iridium and other geochemical anomalies) can be developed 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 Ma 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.

In collaboration with Anthony Hallam from the University of Birmingham in England and W. D. Goodfellow from the Canadian Geological Survey, we have found a multiple Ir anomaly association with the boundary between the Triassic and Jurassic geological periods in the Kendelbach section of the Osterhorn Mountains in Austria. This was about the time of one of the five greatest extinctions of species that have occurred in the last 600 m.y. A huge crater in Canada (Manicouagan), which is considered to have been produced by the impact of an asteroid or comet, is also from this time period and has an estimated age of ~210 m.y.

In the boundary clay two and probably four Ir peaks with abundances of 42-49 parts-per-trillion (ppt) abundance have been observed superimposed on a background of 34 ppt. Because there are no detectable variations in major or selected trace element abundances (as measured by Goodfellow) corresponding to those found for the Ir, many explanations for the origin of Ir anomalies can be eliminated. An impact origin is the most viable hypothesis but the possibility of concentration of background Ir by organic phases not yet observed must still be investigated.

It has been previously suggested by other scientists that the Late Triassic extinctions resulted from the impact of a large asteroid or comet (bolide). If the Ir anomalies that we see in the Kendelbach section can be shown to be distributed worldwide (and not due to concentration of background Ir by organic phases), it will provide a strong argument for such an impact being the cause of the Ir anomalies and provide strong support for the theory that impacts of large comets on the Earth lead to extinctions.

In collaboration with Russian laser spectroscopists from the USSR Institute of Spectroscopy near Moscow, we have demonstrated that precise measurements of Rh, Ir, and Ru can distinguish stony meteorites from crustal or mantle-derived rocks. Cretaceous-Tertiary boundary rocks were found in such measurements to be indistinguishable from stony meteorites, as were ~3.5 billion year old rocks from several spherule beds in South Africa. Although we consider that previous chemical and geological data had established the impact relationship of the K-T rocks satisfactorily, there has been considerable questioning of this deduction in the literature and in scientific meetings. The present measurements give strong additional confirmation of the impact origin of these sediments.

We have found an Ir anomaly in rocks 35-39 Ma from a deep sea core taken off of Antarctica (ODP 698B). These data extend the Ir anomaly, found in Late Eocene rocks, from 36° to 64° south latitude. If this Late Eocene Ir anomaly is due to the fallout of Ir-rich dust resulting from an asteroid or comet impact on the Earth (as we have suggested), the Ir should be distributed worldwide. The present data provide the confirmation necessary in the southern hemisphere for this worldwide distribution.

F. Nonisothermal Reservoir Dynamics (*I. Javandel and P. Witherspoon [415-486-6106]*)

This project encompasses a wide range of fundamental studies of fluid, heat, and solute transport in rocks. These studies are relevant to geological disposal of nuclear waste, chemical transport in ground water systems, gas phase transport in the unsaturated zone, underground energy storage, geothermal energy, and other energy-related problems. The goal is to better understand various

physical and chemical transport processes in porous or fractured porous media and their effects through theoretical considerations, mathematical modeling, and laboratory investigations.

During the past year, the emphasis of the project was placed on the gas phase transport of various volatile organic compounds in the unsaturated zone. A manuscript entitled "Density Driven of Gas in the Unsaturated Zone Due to the Evaporation of Volatile Organic Compounds" was prepared and submitted to the Journal of Water Resources Research. This manuscript presents a theoretical investigation of factors affecting the gas phase transport of evaporating organic liquids in the unsaturated zone. When a volatile organic liquid is released in the subsurface environment, contaminants could migrate downward towards the water table through gas phase transport. This may lead to the contamination of ground water located at much lower elevation than the actual position of the liquid waste. The significant findings reported in this paper were that the density driven advection of the gas phase becomes very important when the permeability of the medium and the vapor pressure of the organic substances are large and the tendency of partitioning of the organic vapor into water and solids in the vadose zone is relatively small.

G. Center for Isotope Geochemistry (*D. J. DePaolo [415-486-4975]*)

Understanding of fundamental 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 direct observations of natural systems. In many cases, the complexity of processes precludes satisfactory predictions from first principles; so a phenomenological approach is an important complement to theoretical and laboratory studies of the underlying physics and chemistry. Isotopic geochemical measurements are a powerful means of characterizing natural systems; they provide the capability of verifying models in the field, and therefore, represent an important component of efforts to develop predictive capabilities.

The Center for Isotope Geochemistry has been established at Berkeley to provide a state-of-the-art isotopic measurements facility focused on geoscience problems. The aims of the center are to 1) make available to the DOE geoscience community a resource for high quality isotopic measurements, 2) facilitate the integration of isotope phenomenology into ongoing geoscience research, 3) develop new techniques for sampling and analyzing Earth materials, and 4) foster development of dynamical process models coupling isotopic ratios to physicochemical processes.

Efforts in the first year of operation have been directed at 1) developing methods for sampling and analysis of rock material to a spatial resolution of 50 μm , 2) developing the Sr isotope stratigraphic correlation method for application to paleo-climate dynamics and sedimentary basin evolution, and 3) measurement of high P, T, mineral-fluid partition coefficients for important parent and daughter elements.

Contractor: LAWRENCE BERKELEY LABORATORY
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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]*)

Emphasis is on the study of rock-fluid interactions in hydrothermal systems, with recent focus on the Long Valley caldera. There is strong collaboration with colleagues at Los Alamos National Laboratory and at the U.S. Geological Survey. Isotope ratios in rock matrix and fracture-lining minerals are combined with ratios in fluids samples at depth and from springs, and with alteration mineralogy of drill core and cuttings to determine the isotope signatures of these interactions. Oxygen, hydrogen, carbon, and strontium isotope ratios trace the paths of hydrothermal fluids from precipitation in recharge areas, through the hydrothermal system to surface manifestations. A strontium-isotope gradient in fracture-filling calcite and a systematic variation in Sr-isotopic ratios in thermal waters support the concept of upward flow of the hydrothermal system in the caldera's west moat and subsequent eastward movement of this water in the caldera fill. Alteration-mineral assemblages in cores from DOE, industry, and municipally drilled holes show clay-mineral transitions that are consistent areally in the western part of the caldera, indicating the widespread effects of the hydrothermal system. Investigation of rock-fluid interactions in precaldera basement rocks should be augmented within the next few years by core, cuttings, and fluid from DOE's magma energy hole, expected to be spudded in the summer of 1989.

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

The objective of this work is a tabulation of critically evaluated thermodynamic property values for minerals, gases, and aqueous species. The property values covered are Gibbs free energy of formation, enthalpy of formation, entropy, and heat capacity. The tabulated data are consistent with the CODATA Key Values and reproduce selected experimental values within the uncertainty of the measurements. A second important objective of this work is development of software, which permits the thermodynamic data to be used for solubility and other calculations by the Stanford University versions of the MINEQL (now HYDRAQL) code. This latter work is in collaboration with Dr. Malcolm Siegel, Sandia National Laboratories, Albuquerque.

The work with Sandia has been mainly for use in the performance assessment of nuclear waste repositories. One result of this collaboration is a comprehensive thermodynamic database for the actinides plutonium, americium, thorium, and uranium. This database includes: 1) chelates of metals with EDTA, citric acid, thenoyltrifluoroacetone and oxine; and 2) specific ionic interaction coefficients that permit solubility calculations up to 4 m concentrations.

C. Geophysical Measurements Facility (*T. V. McEvilly and H. F. Morrison [415-486-7347]*)

The Geophysical Measurements Facility (GMF) operates at LBL to maximize the use of field instrumentation through a facility that maintains the equipment in a field-ready state. Through shared equipment and properly maintained instrumentation, overall field costs are minimized. GMF is not intended to serve only LBL programs. It is meant to be used by all agencies participating in DOE programs. For example, Sandia has placed a portable drill rig at GMF.

The list of equipment at GMF is too long to detail here, but in general it includes a variety of field equipment for seismic (two ASP automated network processors, digital recorders, two seismic vibrators, analog and digital radio telemetry systems, VSP recording and processing system, acoustic emission system) and electrical methods (controlled source EM, DC resistivity, SQUID magnetometers). There is also a large variety of general field and test equipment (meters, scopes, etc.) at GMF. The most recent additions are a complete VSP recording and in-field processing system and two complete well logging vehicles, donated by Dresser-Atlas. One truck is outfitted with 5,000 m of new high temperature (300°C) 7-conductor cable. The other truck has a split reel with 900 m of 7-conductor cable on one side and room on the other half for any specialized cable. These logging trucks will be used in a variety of experiments this year, including a joint study of hydrofracture monitoring with Chevron, the Cajon Pass CSDP VSP survey, borehole S-wave tomography surveys at the Yucca Mountain waste repository site, a near-field explosion source function and anisotropy measurement at NTS, and cross-well EM experiments at oil company test sites. The facility also supplies vibrator and recording system operation and maintenance for the Parkfield earthquake prediction project. The basic GMF funding supports the facility to house, maintain, and upgrade the variety of equipment, while specific projects fund the actual deployments. In 1988, GMF moved into new facilities that expand the shop and fabrication capabilities and provide space for large-scale block testing. GMF is now serving many DOE programs, including BES, geothermal, waste isolation, and CSDP, and it has reached the goal of providing a state-of-the-art pool of field-ready equipment for a diverse clientele of investigators.

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Category: Geology, Geophysics, and Earth Dynamics

Person in Charge: L. W. Younker

A. Rheology of Partially Molten and Melt-free Crustal Rocks (*F. J. Ryerson [415-422-6170], W. B. Durham and B. Bonner*)

Our goal is to determine the rheological properties (creep and attenuation) of a variety of representative crustal lithologies under conditions of elevated pressure and temperature. The effects of grain boundary melts and fluids on rheological properties will also be investigated. The data will be used to constrain the processes of 1) ascent of granitic diapirs through the crust, 2) segregation of granitic magma from crystals, and 3) inversion of lower crustal seismic data.

Granite magmatism is a major process in determining the constitution of the continental crust. Granite plutons from the cores of most mountain belts and the ascent of granitic magma from either the upper mantle or lower crust into the upper crust are the primary mechanisms by which heat-producing elements are redistributed. Lower crustal granitoid anatexis has been suggested as a process leading to lower crustal dehydration and resulting in the formation of granulite facies terrains exposed in Archean cratons. Granite magmatism is also responsible for the transport of heat to the upper crust, as in the emplacement of epizonal plutons. Epizonal plutons drive the convection of meteoric water, which in turn is responsible for the petrogenesis of associated ore deposits and possible geothermal resources.

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. How are granitic magmas segregated and how efficient is the segregation process? How do granitic magmas or magma-crystal mushes rise through the crust and at what rate? By what processes do high-viscosity melts or crystal-charged melts differentiate? How is the final emplacement depth determined and how are the mechanics of final emplacement related to those of ascent? 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.

Many details relative to the physical processes involved in granitic magmatism remain problematical, controversial, or difficult to quantify due to the lack of relevant rheological data. In order to produce the necessary data we are performing low-stress creep and low-frequency attenuation experiments on synthetic samples representative of lower crustal rocks, e.g. clinopyroxenite, feldspar-rich rocks, and quartzites plus granitic melts.

We have received a spray dryer that will allow us to prepare very fine-grained (1 micron) synthetic samples. The powders will be made from solutions in which all of the chemical constituents are in solution. The fine-grained, homogeneous materials will allow us to focus on the effects of grain boundary processes during plastic deformation. Initial experiments will be performed on quartz-melt aggregates in the $\text{Na}_2\text{-K}_2\text{O-CaO-SiO}_2$ system. Once these experiments are completed, Al_2O_3 will be added to the system to produce haplo-granitic melt compositions.

The experiments are performed in the context of solid phase contiguity, the fraction of internal surface area as solid-solid grain contacts. An anhydrous sample has a contiguity of 1.0. Contiguity is a function of the wetting angle between the solid and liquid grains (determined by the relative surface energies) and the melt fraction. Hence, for a given assemblage of solids, the contiguity can be controlled through variations in melt composition. Rheological data can be then interpreted in the framework of contiguity and the rheological properties of the melt and solids.

The past year has been largely devoted to development of the deformation apparatus. A 10 Kb gas deformation apparatus has been refurbished. The gas pumping system has been revised and a load cell/end plug with o-ring, brass mitre ring pressure seal fitted to the vessel. A number of prototype furnaces have been designed and fabricated, and a power control system has also been completed.

B. Diffusion in Silicate Materials (*F. J. Ryerson [415-422-6170] and W. B. Durham*)

This project focuses on the experimental determination of transport and trace element partitioning in rock-forming minerals and melts and the application of these data to geochemical and geophysical problems. The project has also included one "natural experiment" in which a well constrained (by drilling) thermal episode has been used to measure low temperature diffusion of Ar in microcline.

Oxygen Diffusion in Olivine. Olivine is the major mineral constituent of the upper mantle; therefore, its mechanical properties will have a strong influence upon the nature of mantle convection and diapirism. As such, the last few decades have seen numerous experimental studies of deformation in olivine. Extrapolation of deformation behavior obtained at laboratory strain rates to geologically relevant strain rates is dependent upon our understanding of the deformation mechanism. The point-defect chemistry of the mineral as well as the formation of kinks and jogs on dislocations will play a major role in controlling deformation kinetics. The nature and concentration of point-defects and of dislocation kinks and jogs will, in turn, be determined by T, P and the thermodynamic activities of the various chemical constituents, e.g., $f(\text{O}_2)$, $a(\text{SiO}_2)$, $a(\text{MgO})$, etc. Point defect chemistry will also control diffusive processes in olivine, so that diffusive phenomena and deformation behavior may be strongly linked.

We have investigated the diffusion of oxygen in San Carlos olivine under conditions of controlled oxygen fugacity and enstatite activity. Experiments are conducted using mixtures of 99% ^{18}O -enriched CO/CO_2 gas and mineral buffers to insure the proper oxygen fugacity and enstatite activity. Depth profiles are obtained by a nuclear reaction technique employing a H_2^+ primary beam to eliminate channeling effects. Analysis of oxygen profiles has also been undertaken using the LLNL ion microprobe. Preliminary results are consistent with the results obtained from nuclear reaction methods.

The positive dependence of oxygen diffusivity on oxygen partial pressure (fugacity) indicates that oxygen diffusion is not controlled by a vacancy mechanism in olivine. Also, the activation energy for oxygen diffusion is significantly less than that for creep. This argues that if oxygen diffusion in olivine plays a part in determining creep kinetics in olivine, it must be coupled with an additional process, e.g., the formation of jogs or kinks on dislocation lines.

We have rejected arguments calling for the diffusion of oxygen interstitials due to the radius of the anion with respect to the close-packed olivine structure. Instead we draw attention to the similarity between the activation energies and fO_2 exponents for the diffusion of oxygen and the diffusion of cations in olivine. The similarity suggests that oxygen may be diffusing by a correlated mechanism coupled to the concentration of the majority cation vacancy. The presence of an adjacent vacancy perturbs the electronic structure of the oxygen bonds increasing the mobility of the oxygen anion.

Diffusive Argon Loss for Microclines Within the Contact Aureole of the Obsidian Dome Conduit, Long Valley Caldera: Thermal Constraints on Emplacement. In work conducted in collaboration with T. Mark Harrison (SUNY-Albany) we have analyzed the isotopic composition of microclines from the conduit/vent structure beneath Obsidian dome. Argon age spectra from microclines heated during the emplacement of the conduit/vent structure display a progressive loss of radiogenic ^{40}Ar with decreasing distance from the conduit-country rock contact. However, the loss is not monotonic, showing occasional reversals in trend. We have recently employed a new method of analyzing argon age spectra that allows the effects of variable diffusion domains to these data to be considered. When the effects of variable diffusion domain size are taken into account, the trends become much better behaved, displaying a regular, monotonic decrease in argon loss away from the boundary. However, the fractional losses are higher than one would predict from the conductively cooled intrusion (975°) in country rock with an ambient temperature of 30°C and constant over the sample area. The most likely process by which to obtain such high and homogeneous temperatures is by advection of heat by "intrusive tephra" and volatiles during the explosive eruptive phase of the intrusion. This model is consistent with the Eichelberger model for the formation of the vent structure.

C. Electrical Conductivity, Temperature, and Radiative Transport in the Earth (T. J. Shankland, L. M. Hirsch, and A. G. Duba [415-422-7306])

Both electrical and optical research efforts help determine temperature distributions in the crust and upper mantle. The thermoelectric effect and electrical conductivity in the mantle minerals olivine and pyroxene are being measured as a function of temperature, orientation, oxygen fugacity, and iron content. The results apply to inference of upper mantle temperatures from electrical data. We have achieved a breakthrough by calculating equilibrium thermodynamic concentrations of point defects in periclase, MgO containing FeO; this is a test case for more complex materials. 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. Unlike previous schematic representations our calculations demonstrate that changes in fO_2 dependence of conduction occur slowly over several orders of magnitude; higher temperature not only causes increased defect

concentration but can also alter the fO_2 at which transitions between conduction mechanisms occur, an important factor in determining conduction mechanisms. We can show that addition of Fe increases total defect content, and this result is experimentally consistent with olivine conductivity. Thus, using synthetic olivine crystals grown by LLNL, we have achieved two firsts: 1) Measurement of conductivity in an olivine single crystal having a composition outside the usual range of fayalite content of 8% for mantle olivines (or nearly zero for synthetic forsterite, which we have previously shown to behave electrically quite differently from more iron-rich specimens). 2) Observation that single crystal conductivity increases with iron content for fayalite contents in the range 8 to 15%; previous observations of this effect were clouded by the fact that they were made on sintered polycrystalline material having a substantial grain contribution. These results unequivocally tie olivine conductivity to the presence of iron.

D. Attenuation and Dispersion in Partially Saturated Rocks (*J. G. Berryman [415-423-2905] and B. P. Bonner*)

The objective of this project is to combine theory and experiment to analyze attenuation and dispersion of waves in partially or 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 that simulate explosion induced high amplitude wave propagations, which are used to investigate nuclear test containment and for the evaluation of 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. With a series of low frequency experiments, we demonstrated that traditional audio and ultrasonic frequency experimental methods overestimate attenuation at high strain amplitudes as a result of fatigue damage induced by periodic loading. Quantitative comparison with theory must account for these effects. The magnitude of the attenuation at low strain amplitudes depends on volatile content at low saturations, in agreement with accepted high frequency results. We discussed these nonlinear effects at the fall meeting of the American Geophysical Union and explored seismic implications in a presentation to the DOE/LLNL symposium on explosion source phenomenology. 2) Waves that travel at the interface between a fluid and saturated porous medium are sensitive to the unique coupled properties of the saturated solid. Working with our colleagues in the Ultrasonics Group, Department of Welding Engineering, Ohio State, we have focused on measurements of the normal modes that occur in thin plates, first described by Lamb. Lamb modes associated with the Biot slow wave have been observed in man-made porous media. Theoretical estimates of the slow wave speeds based on independent estimates of tortuosity have been made for comparison with direct acoustic measurements. 3) Extending previous analysis of waves incident from a fluid on a saturated porous medium at normal incidence at LLNL, our colleagues at Ohio State have examined the case of oblique incidence and have computed complete reflection and transmission coefficients for a single interface and a porous layer. These results will be useful both for experimental design and for analyzing more complex geometries.

E. Surface Wave Method for Determining Earthquake Mechanisms with Applications to Regional Stress Field Studies (*H. J. Patton [415-422-0720] and G. Zandt*)

The primary purpose of this study is to use surface-wave data to obtain source mechanisms and depths for earthquakes in the western United States. This study focuses on earthquakes occurring in the Basin and Range province and the less-well-studied areas of northern California such as the Cascades, the Sierran batholith, and areas adjacent to the Mendocino fracture zone. Our objective is to map in detail the regional stress field of these areas in order to gain a better understanding of continental rifting in the Basin and Range and of the role of plate boundary processes in controlling the style of deformation in extensional areas today. We have also accrued a considerable amount of information about the propagation speeds and attenuation rates of surface waves in western United States. This information has been used for structural interpretations, and we have developed broad-scale models for the three-dimensional velocity structure and for the Q structure of western United States. Both the structure and the information on the regional stress will be brought to bear on the problem of lithospheric extension, and the findings should be beneficial for assessments of geothermal potential and for tectonic stress constraints needed in models of convective hydrothermal systems.

The state of stress on the San Andreas fault system has been the recent subject of several important studies that have shown the maximum compressive stress is oriented close to normal to the fault trace in central and southern California. This fault-normal compression is at odds with the predictions from classical shear faulting theory and appears to support the contention that the fault has low shear strength. Fault creep in central California can also be cited as evidence that the fault is quite weak. Our work is providing observational constraints on the regional stress field with which to test the claims that the fault may be weak on other segments of the San Andreas fault system. If there are significant variations of the shear strength along different fault segments, this will have important implications for understanding the mechanical behavior of the fault system as a whole.

In the past year we have made considerable progress in developing an observational database of stress measurements in our study areas. The method employed in this study involves the linear inversion of surface-wave amplitudes for the elements of the seismic moment tensor, and we have successfully applied this technique to earthquakes with magnitudes as low as 3.5.

F. Thermal Stress Microfracturing of Crystalline and Sedimentary Rock (*B. P. Bonner [415-422-7080] 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. Present work includes acoustic emission, compressional and shear velocity and attenuation, precision compressibility

measurements, and direct observations with the scanning electron microscope. We have published a summary paper reporting results for Westerly, Illinois, Climax, and Stripa granites in the *Journal of Geophysical Research*.

A principal conclusion of our previous work is that acoustic emission in Westerly granite occurs as clusters of events normally distributed about a single temperature and that these peaks are suppressed by confining pressure. We are investigating the origins of these distinct clusters by extending our capabilities to examine the frequency content of the AE to see if the events differ systematically in energy release rate or in source dimension. Since the initial crack distribution for Illinois granite is quite different than for Westerly, acoustic emission experiments for Illinois are underway to test the generality of our results. Shear attenuation measurements for Sierra White granite show that the nonlinear component of low frequency seismic attenuation is a sensitive indicator of changes in crack density and might be useful for monitoring thermal fracturing.

G. Quantitative Image Analysis to Determine Rock Properties (*J. G. Berryman [415-423-2905] and S. C. Blair*)

The objective of this new 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 weapon testing, seismic verification, radioactive waste isolation, and deep drilling are all beneficiaries of this research.

Progress this year has been concentrated on moving image processing software from a mainframe based imaging system to a desktop color graphics workstation based system. Codes originally written in Fortran have been rewritten in C and upgraded to take advantage of graphics hardware and software available on the workstations. This phase of the work has been completed. In addition, some new capabilities for display and visualization of three-point correlation functions have been added to our suite of codes. Hardcopy of the rock images and the two- and three-point correlation functions are now easily accomplished using the photographic equipment attached to the workstation system. A new digitizer has also been purchased, so that our analog SEM images of rocks may be conveniently digitized in a form readily available to the workstations. Installation of the digitizer has also been completed.

H. Maximum Resolution Seismic Image of the Long Valley Resurgent Dome (*L. W. Younker [415-422-0720] and G. Zandt*)

The continental crust is the most important portion of the solid Earth in terms of potential impact on society. A major impediment in the study of the crust has always been the difficulty in

observing and sampling the depth dimension. In this study, we outline the development of a high resolution "Seismic Transmission Imaging" (STI) method on a scale that will be complementary to continental drilling in probing the upper crust. Although much of the theoretical developments will be applicable to any scale, we propose to concentrate on problems dealing with an overall scale length of ~10 kilometers. Our objective is to achieve a spatial resolution on the order of several hundred meters within a volume defined by an area of ~100 km² to depths of ~5-7 km. Some recent theoretical developments and approaches by Berryman and others promise to dramatically improve seismic transmission imaging capabilities in high wave-speed contract media. A major thrust of this work will be to adapt their techniques to our scale and test the new methods on existing data; however, a fully three-dimensional, spatially unaliased field experiment for the volcano-scale problem has not been performed. Such a data set is critical for the achievement of the "Maximum Resolution Seismic Image" (MaRSI) for the upper crust. Therefore, we have designed a fully three-dimensional, unaliased seismic transmission imaging experiment for the resurgent dome at Long Valley, California, and a program of research to obtain and interpret the maximum resolution images. The resurgent dome will be the site of a DOE-funded scientific deep ~6 km drill hole -- well "51-20." The borehole well-log data will be invaluable for the interpretation of the seismic images, and conversely, the seismic images of the upper crust around the borehole can be used to extend laterally the interpretation of the borehole data.

I. Nonlinear Sources for Seismic Imaging (*L. W. Younker [415-422-0720] and B. P. Bonner*)

This study is directed at developing a driver to produce collimated, low-frequency acoustic beams by nonlinear interaction of two high-frequency primary beams and to send them through rock bodies on a scale of meters. The lower frequency beam has the narrow width of the generating beams, but it can travel much farther because of lower attenuation; hence, it would be highly suitable for tomography. Such a narrow beam would permit examination of acoustic interfaces and monitoring fluid location and migration in hydrocarbon reservoirs and in waste repositories.

This study will increase the physical scale of previous laboratory experiments and we will follow these by field experiments. Although the ultimate purpose of this research is to develop nonlinear drivers for elastic wave imaging in the Earth, essential steps toward this goal include studying the source of nonlinearity and studying the effects of pore fluids on elastic and anelastic properties, including the seismic quality factor Q. Of basic interest in rock physics is the investigation of nonlinear properties of rocks and frequency dependence of elastic properties. This work augments existing BES-funded nonlinear elastic wave experiments.

J. Advanced Concepts (*L. W. Younker [415-422-0720]*)

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 assessing feasibility of research tasks. This past year, work on a variety of projects related to understanding fault heterogeneities and source parameters associated with the rupture of large earthquakes has been undertaken.

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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 and D. G. Miller [415-422-8074]*)

Transport of dissolved chemical species is important in a wide variety of aqueous geochemical phenomena. Examples include isolation of radioactive and chemical wastes, diagenesis and ore formation, and crystal growth and dissolution kinetics for certain types of minerals. Fickian diffusion coefficients are required to understand and model these processes. Activity coefficients are required for all chemical equilibrium calculations involving aqueous solutions, such as calculation of solubility products, Gibbs energies of formation for solid phases, vapor pressures of water above aqueous solutions, and stability constants. We have, therefore, been making a variety of experimental measurements to provide some of these required data: 1) We have measured diffusion coefficients for aqueous solutions at 25°C using optical interferometry. Systems studied include most of the major and minor brine salts (except K_2SO_4 and alkali metal carbonates) and mixtures of NaCl with $SrCl_2$ and with $MgCl_2$. 2) We have been measuring osmotic/activity coefficients for a variety of aqueous electrolytes and their mixtures up to saturation or supersaturation at 25°C including systems for which diffusion coefficients were measured. 3) Solubilities were measured for a number of these electrolytes using the isopiestic method. 4) We also measured densities of solutions used in the diffusion experiments.

This year we completed our extensive series of diffusion and density measurements for aqueous NaCl- $MgCl_2$ mixtures. This was done in collaboration with Dr. Luigi Paduano of the University of Naples, Italy and with Professor John Albright and his students from Texas Christian University and is part of an international collaboration to thoroughly characterize this system. We will analyze data being measured at other laboratories (in the U.S.A., Australia, Canada, Germany, Argentina), which includes electrical conductances, viscosities, tracer diffusion coefficients, thermal diffusion coefficients, and transference numbers. Analysis of the 7 compositions (out of 15) having complete sets of transport data has yielded preliminary values of the generalized transport coefficients 1_{ij} of irreversible thermodynamics. These are the quantities to be compared with statistical mechanical models of electrolyte mixtures. In addition, a preliminary comparison of these ternary 1_{ij} with a "mixture rule" that uses the binary 1_{ij} from NaCl- H_2O and $MgCl-H_2O$ shows fairly good agreement. This implies reasonably good estimates of ternary properties from binary data.

Other studies include an analysis of the equal eigenvalue case in 3- and 4-component diffusion and derivation of relationships among mixture rules for electrical conductance. We have completed isopiestic measurements for aqueous $NaHSO_4$ and $NaHSO_4-Na_2HSO_4$. This system

exhibits considerable deviations from ideal mixing rules due to HSO_4 formation. Previous activity data were restricted to lower molalities.

B. Compositional Kinetic Model of Petroleum Formation (*A. K. Burnham [415-422-7304], 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-equilibrium calculations, and geological modeling to achieve that objective. We test chemical kinetic models of varying complexity in an effort to outline the tradeoffs between simplicity and completeness. During the past year, we placed a special emphasis on deriving chemical kinetics for thermal indicators used to constrain geothermal models and on incorporating into our detailed chemical kinetic model the equations necessary to calculate source rock compaction and oil expulsion.

A crucial aspect in modeling petroleum generation is deriving a thermal history for all sedimentary layers at locations throughout the basin. Vitrinite reflectance is the most common indicator used to constrain geothermal histories. However, there is a long-standing disagreement in the literature on how vitrinite reflectance depends on time and temperature. We developed an improved method for calculating vitrinite reflectance from thermal histories. Our model reproduces changes in vitrinite composition (and hence its reflectance) for both geological and laboratory maturation. The model assumes that maturation proceeds by four independent reactions eliminating water, carbon dioxide, oil, and methane from the vitrinite structure. Each reaction is described by a distribution of activation energies. We then derived improved correlations between composition and reflectance. Combining these two aspects enables us to calculate reflectance for maturation at time scales from hours to millions of years. Model calculations agree with published data from laboratory experiments in sealed vessels and geological data from volcanic intrusions, geothermal areas, and normally subsiding basins.

Once a thermal history for each sedimentary layer has been calculated and checked, it can be used to calculate the timing of oil generation in various parts of the basin. The most crucial question is not when oil is generated, but when it is expelled from the source rock so that it can migrate to a trap. While in the source rock, oil is continually cracked to lower-molecular-weight oil and gas, so the delay between generation and expulsion has a large impact on the oil/gas ratio expected in a given trap. To model this process, we added equations for calculating oil and gas volumes to our chemical kinetic model. We allowed the source rock to be an open, closed, or leaky system. For the leaky system, we assumed that the equilibrium porosity decreases exponentially with the difference between the lithostatic pressure and the excess pore pressure (in excess of hydrostatic). We assumed that the rate of expulsion was proportional to the effective hydraulic conductivity estimated from the porosity. We added a pressure relief valve so that the pore pressure could not exceed lithostatic pressure. Activation of this valve simulates the process of natural hydrofracturing. We have used this model to estimate the efficiency of petroleum expulsion under various conditions, including variation organic concentration and heating rate. We also calculated the expected boiling point distribution of the expelled oil.

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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], P. W. Kasameyer, and R. L. Newmark*) (*Cooperative program with 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 the results of two shallow drilling projects, the Shallow Salton Sea drilling project and the Inyo domes drilling project, with other geological and geophysical data.

1) Salton Sea Geothermal Field

Recent geophysical data interpretations using rather simple three-dimensional prismatic gravity and magnetics models have improved our understanding of igneous intrusion geometry at the Salton Sea geothermal field. Aeromagnetic data analysis has established estimates of the dimensions, locations, and orientations of the igneous intrusions in addition to estimates of the bulk apparent magnetic susceptibility and total volume of intrusives. These intrusive boundaries are consistent with microseismicity patterns. Gravity and aeromagnetic data analysis have established that there is insufficient mass of intrusives in the sediment pile to account for the observed gravity anomaly. Furthermore, these analyses indicate that the initial heat stored in this mass of intrusives is probably insufficient to account for the observed heat flow anomaly, suggesting that the principal heat source may be deep.

2) Inyo Domes, Long Valley California

One of the most intriguing results from the Inyo drilling program 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 magma types in the finely porphyritic series and the coarsely porphyritic magma type. There may be a fourth independent magmatic component if chemical differences between Inyo eruptives and juvenile material identified in the breccia pipe beneath South Inyo crater are not due to post-emplacement alteration of the latter. Such chemical complexity in a system only 0.5 km³ in erupted volume is surprising.

In work completed this year, 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 and J. G. Berryman [415-423-2905]*)

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.

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. Two main approaches are being considered: 1) electrical impedance tomography (EIT) and 2) seismic tomography. EIT 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. Seismic tomography uses compressional and shear (elastic) waves to estimate the wave speed and attenuation distributions in the Earth. Seismic tomography has the advantage that low frequency sound waves travel very large distances through the Earth while still providing measurable signals; the disadvantage of seismic tomography is that the paths traveled by the waves depend strongly on the velocity contrasts between the source and receiver--thus, again more sophisticated reconstruction algorithms are needed for seismic tomography than are generally needed for the shorter range application to which HFEM tomography is well suited.

Continuing work on the EIT system has included studies involving the existing equipment using circular arrays of electrodes and some preliminary work on rectangular arrays in our experimental water tank. Our work on circular arrays has focused on determining the source of error at high electrolyte resistivities. Experimental studies of rectangular arrays have also been carried out to determine the feasibility of EIT measurements. For this work, a large water tank of approximately 3.6 m in diameter and 2.6 m in depth is being used. Work has also been completed this year to move our reconstruction algorithms and graphics capabilities to a UNIX based, SUN workstation environment. Reconstructions and real time display of the conductivities are now possible on this system and hardware is available to produce hardcopy, such as photographs or laser printer quality images, of the reconstructed conductivity distributions.

Recent progress on seismic tomography has included the development of new reconstruction algorithms based explicitly on Fermat's principle of least travel time and new, simplified ray-

tracing methods. Codes based on these algorithms have been developed for application to borehole-to-borehole problems and have been tested extensively on synthetic data. These codes have also been upgraded to include sophisticated graphics output available on desktop color graphics workstations, including all possible view angles as input to the reconstruction codes. Algorithms are currently working using modified ridge regression methods and singular value decomposition methods to stabilize the reconstructions. A new approach that makes explicit use of the Fermat feasibility boundary and the number of feasibility violations along ray paths to determine the optimum correction step at each iteration of the reconstruction method has been developed this year. This new approach yields stable and reasonably accurate reconstructions even for media with high contrast anomalies where standard methods tend to diverge. These techniques have also been used to invert real seismic and real electromagnetic cross borehole data and the results are just as stable as for the synthetic data.

C. Katmai Resistivity Studies (*P. W. Kasameyer [415-422-6487] and J. J. Sweeney*)

During the second half of FY89, we will participate in scientific activities at Katmai. Electrical soundings and cross sections will be measured at a number of locations within the area to be drilled. During FY90, these data will be interpreted to determine the variations in the depth to the water table, and those results will be communicated to the Katmai working group. In addition, during FY90 and later, we will use observations of the present thermal and physical state of the Katmai system, plus evidence about temperatures and fluid flow in the past obtained from geochemical studies as constraints to model the thermal and chemical evolution of the cooling system. These processes include the initiation and migration of a shallow young hydrothermal system; the cooling, compaction welding, and fracturing the eruptive products in the ash-flow and vent regions; and the cooling and degassing of shallow intrusions.

D. CSD Review Group (*L. W. Younker [415-422-0720]*)

The twelve-person group reviews on-going, planned, and proposed CSD 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
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Contract: W-7405-ENG-36

Category: Geology, Geophysics, and Earth Dynamics

Person in Charge: C. W. Myers

A. Electrical Conductivity, Temperature, and Radiative Transport in the Earth
(T. J. Shankland [505-667-4907] 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. The thermoelectric effect and electrical conductivity in the mantle minerals olivine and pyroxene are being measured as a function of temperature, orientation, oxygen fugacity, and iron content. The results apply to inference of upper mantle temperatures from electrical data. We have achieved a breakthrough by calculating equilibrium thermodynamic concentrations of point defects in periclase, MgO containing FeO; this is a test case for more complex minerals. 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. Unlike previous schematic representations our calculations demonstrate that changes in fO_2 dependence of conduction occur slowly over several orders of magnitude; higher temperature not only causes increased defect concentration but can also alter the fO_2 at which transitions between conduction mechanisms occur, an important factor in determining conduction mechanisms. We can show that addition of Fe increases total defect content and this result is experimentally consistent with olivine conductivity. Thus, using synthetic olivine crystals grown by LLNL, we have achieved two firsts: 1) Measurement of conductivity in an olivine single crystal having a composition outside the usual range of fayalite content of 8% for mantle olivines (or nearly zero for synthetic forsterite, which we had previously shown to behave electrically quite differently from more iron-rich specimens). 2) Observation that single crystal conductivity increases with iron content for fayalite contents in the range 8 to 15%; previous observations of this effect were clouded by the fact that they were made on sintered polycrystalline material having a substantial grain boundary contribution. These results unequivocally tie olivine conductivity to the presence of iron.

B. Nonlinear Generation of Acoustic Beams *(P. A. Johnson [505-667-8936], T. J. Shankland and J. N. Albright)*

We are using the nonlinear elastic properties of rocks to generate low-frequency, long-wavelength acoustic beams 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 lower frequency beam has the narrow width of the generating beams, but it can travel much farther because of lower attenuation. Such a narrow beam would permit

examination of acoustic interfaces from mine interiors and wellbores without the ambiguities of conventional seismology that use undirected sources. Should beam formation prove possible, there would be numerous applications to problems such as mapping fractures; the boundaries of ore and coal bodies; burn fronts in underground retorts; and fluid locations in oil, gas, and geothermal reservoirs. We successfully extended methods developed earlier in crystalline rocks (basalt and granite) to Berea sandstone, a standard model material for reservoir rocks, and it is noteworthy that the nonlinear difference-frequency signal was cleaner and stronger than in the crystalline rocks. Our first necessary step was to unequivocally prove that nonlinear interaction takes place in the sample rather than in the measurement apparatus; we swept the frequencies of the two driving beams that intersect at prescribed angles in order to verify that the angular selection rules for nonlinear interaction were observed. A second successful result was measuring the travel time of pulsed beams to be the sum of P-wave travel time to the interaction region plus S-wave travel time to the detection transducer. Measuring travel times is essential to practical application. Along the way we used our digital signal recording and subtraction method to also obtain travel-time measurements in granite.

C. Three-Dimensional Magnetotelluric Inversion (*B. J. Travis [505-667-1254]*)

The experimental state of the art for electrical geophysical methods is undergoing a rapid evolution due largely to the digital revolution. Our interpretation capabilities with electromagnetic data, however, are lagging behind, presenting a major obstacle to the wider application of electromagnetic principles in geophysics. For two- and especially for three-dimensional situations, even the simplest electrical techniques like magnetotellurics (MT) pose problems, and it can be frustratingly difficult to model and invert such data. Controlled source and time domain analysis are even more challenging.

To break this interpretational and modeling blockade, we are developing a model for MT data analysis based on new computational methods and conceptual approaches. Our computational approach is two-fold: adaptive finite elements (AFE) for optimal accuracy and ease of simulation design and incomplete factorization methods for highly efficient solution of the sparse matrix systems resulting from use of AFE. In AFE, computational nodes are positioned automatically where electromagnetic gradients are large and are spread out in shallow gradient areas. This is especially powerful for inverse problems in which the location of structures is not known beforehand. A new (to the MT field) conceptual approach to inversion is the use of regularization. Regularization remedies the instability problem inherent in inversion by imposing conditions on the smoothness of the sought-for solution--only the smoothest structure is admissible. Regularization is easily combined with the AFE methodology. Automatic mesh generation complements the two-dimensional and three-dimensional models and is virtually essential for complex geological simulations.

We plan to apply our new two-dimensional and three-dimensional models to the interpretation of data from the EMSLAB project and to sea floor mid-ocean ridge controlled source electromagnetic data.

D. Nonlinear Sources for Seismic Imaging (*T. J. Shankland [505-667-4907]*)

The purpose of this study is to develop a driver to produce collimated, low-frequency acoustic beams by nonlinear interaction of two high-frequency primary beams and to send them through rock bodies on a scale of meters. The lower frequency beam has the narrow width of the generating beams, but it can travel much farther because of lower attenuation; hence, it would be highly suitable for tomography. Such a narrow beam would permit examination of acoustic interfaces and monitoring fluid location and migration in hydrocarbon reservoirs and in waste repositories.

This study will increase the physical scale of previous laboratory experiments and we will follow these by field experiments. Although the ultimate purpose of the proposed research is to develop nonlinear drivers for elastic wave imaging in the Earth, essential steps toward this goal include studying the source of nonlinearity and studying the effects of pore fluids on elastic and anelastic properties, including the seismic quality factor Q . Of basic interest in rock physics is the investigation of nonlinear properties of rocks and frequency dependence of elastic properties. This work augments existing BES-funded nonlinear elastic wave experiments.

E. Imaging of Reservoirs and Fracture Systems Using Microearthquakes Induced by Hydraulic Injections (*M. Fehler [505-667-4318] and L. House*)

This new method for analysis of data obtained from microearthquakes induced by hydraulic fracturing will provide considerable information about the fracture system and reservoir in the vicinity of the fracture system. The method will exploit both arrival time and full waveform information from the induced microearthquakes and will yield a three-dimensional velocity tomogram of the fractured volume. In addition, the method will yield locations of prominent scatterers in the vicinity of the fractured volume. Both pieces of information will be of considerable benefit for understanding of the reservoir rock mass. Use of microearthquakes has the following advantages over artificial sources: 1) microearthquakes occur throughout a volume of rock, which allows better spatial resolution compared to that obtainable using only sources in boreholes or on the surface; 2) microearthquakes are very energetic sources, allowing identification of finer variations in velocity structure; and 3) microearthquakes excite considerably greater shear wave energy than do artificial sources, allowing better delineation of fractures both saturated and dry. While the methods will be developed and applied to microearthquake data from hydraulic injections done in crystalline rock, they should be directly applicable to the sedimentary rock environment and, therefore, should be of considerable interest to the oil and gas industry.

F. Advanced Concepts (*C. W. Myers [505-667-3644]*)

Advanced concepts research in geosciences involved five projects in FY89. Each of these projects was designed as a limited-term exploratory effort.

Definition of Solution Speciation in Geochemical Systems Using Spectroscopic Techniques. We have been able to define the complexation of Au and Fe with chloride at levels relevant to transport in geochemical ore-forming systems using resonance Raman spectroscopy. We have defined the speciation of Hg with chloride showing at low levels of concentration species

dominance changes radically with only small temperature changes (ambient to 90°C). Of course, these experimental observations impact the predictive modeling and precipitation reactions relevant to cooling discharges from hydrothermal systems.

Fiber Optics Geotechnical Instrumentation. Borehole strain meters are being fabricated for testing in the field at the Nevada Test Site. The borehole strain meters will be operated alongside seismometers and other geophysical instrumentation in underground locations where weapons test and tunneling operations will generate rock strains over an extreme band of frequencies and amplitudes. The performance of the borehole strain meters constructed with fiber optics sensors can then be compared with the seismometers and other geophysical instruments.

Thermal Spallation Drilling Research. The current spallation lance design and ignition system have proven to be completely reliable and have demonstrated that a small capacity burner can be used for spallation drilling tests. Sandstone samples were readily spallable with this equipment using test conditions similar to those used in the successful granite spallation tests. Rhyolitic ash flow tuff appeared to spall almost as easily as granite, and a potash (langbeinite) spalled readily when exposed to a low-temperature, water quenched flame. The langbeinite experiment appears to verify the hypothesis that reduction of flame temperature allows spallation to proceed in rock types with low-temperature brittle-to-ductile transformation points.

Sensitivity Analysis of 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. These include Gradient Enhancement, Latin Hypercube, Monte Carlo, Maximal Entropy, and Minimum-Variance methods. The goal is to systematically estimate uncertainties in geochemical calculations that are automatic, rigorous, usable for interpretation or experimental results, and able to enhance experimental efforts.

Description of the Lattice Gas Application to Porous Flow Problems. We are currently collaborating with the center for nonlinear studies at Los Alamos to apply cellular automation techniques to a variety of geosphere fluid mechanics problems. The strength of the method in these applications is that the full Navier-Stokes equations are solvable in an arbitrarily complex geometry. Our initial efforts have concentrated on flow through porous media. These simulations are of two-dimensional flow in fractally generated porous media and in geometries digitized from laboratory micromodels. Excellent agreement has been achieved in matching laboratory measured permeabilities in these micromodels. The technique has been extended to two immiscible components (e.g., mixtures like oil and water.) We are currently extending the method to three dimensions and improving the efficiency of the multi-component code.

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Contract: W-7405-ENG-36

Category: Geochemistry

Person in Charge: R. W. Charles

A. Raman Spectroscopy of Aqueous Solution Species (*D. R. Janecky [505-665-0253], C. D. Tait, and P. S. Z. Rogers*)

Chemical speciation in aqueous hydrothermal fluids is being determined directly using laser Raman techniques. Both spontaneous and resonance Raman are being used to study molecular complexes of metals with halide and organic ligands. A high temperature and pressure cell has been constructed and tested, which is capable of handling brine solutions. This information is important if thermodynamic data are to be properly interpreted and the subsequent data used in geochemical modeling efforts.

The current focus is on halide and organic acid complexation/interaction with dissolved metals and silicate. Zinc-halide systems have been used to initially calibrate and test the equipment. The effect of temperature and pressure on the complex equilibria has been examined and the results are being prepared for publication. The effects of addition of acetate and other relevant organic acids to these systems have been demonstrated to be significant at ambient conditions. Complexation studies of dissolved silica by oxalate, citrate, and phthalate at neutral pH have been expanded to include acetate and salicylic acids. We are now involved in quantifying the characteristics of complexation as a function of pH, pressure, and temperature. Additional organic anions are also being investigated for each system, as well as potential mixed ligand complexation for other metal ions such as Fe. Where possible, we are applying both spontaneous and resonance Raman techniques to maximize the concentration range that can be investigated from molal to millimolar concentrations of total dissolved metals. This work has important implications for mineral dissolution, ground water and geothermal transport, and precipitation, as well as for fossil fuel/reservoir interactions.

B. Thermodynamic Properties of Aqueous Solutions at High Temperatures and Pressures (*P. S. Z. Rogers [505-667-1765]*)

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 types 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-Na₂SO₄-H₂O, NaOH-H₂O, and Na₂CO₃-NaHCO₃-NaCl-H₂O to 39 MPa and 598 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 H₂O. The ultimate goal of this work is to provide data to 673 K in order to study the behavior of electrolyte solutions in the region very near the critical point of water.

C. Rock-Water Interactions and Element Migration (*D. R. Janecky [505-665-0253], R. W. Charles, P. S. Z. Rogers, 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 drilled by the Continental Scientific Drilling Project, primarily Valles caldera and Salton Sea. 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 are providing unique insights into which major minerals contain minor and trace elements (<1 weight % to ppb levels) and how different assemblages of minerals change the distribution of these elements. Our high temperature downhole fluid sampler is being used to collect solutions that can be compared to the analytical results and phase equilibria calculations, primarily from Valles caldera holes this year. Experimental systems are being applied to saline brine reactions, both to provide high quality data to test and enhance computational models and to characterize reaction path processes for analogues to natural rocks. The individual systems are anhydrite + brine and kspars + epidote + hematite + magnetite + brine as analogues of concentrated aquifers found in the Imperial Valley. Experimental hydrothermal systems are also being used to examine the kinetics of reactions using stable isotopic tracers ²⁹Si and ³⁰Si. 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 into large geochemical models and databases.

D. Dynamics of Rock Varnish Formation (*R. Raymond, Jr. [505-667-4580], 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, 3) the effect of different substrates on varnish formation, and 4) the relative effects of local and regional geology on varnish composition.

Interpretation of analytical data will result in a means by which to calculate or refine empirically derived rock-varnish cation-ratio curves for geomorphic surfaces. Such quantitative rock varnish dating curves will make it possible to decipher 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.

E. ^{238}U - ^{230}Th Disequilibrium Measurements in Geologic Systems Using Solid Source Mass Spectrometry (*M. T. Murrell [505-667-0967], S. J. Goldstein, D. R. Janecky, and R. E. Perrin*)

Detailed geochronology is critical to understanding both the mechanisms and frequency of dynamic geologic processes. The geochronology of the last million years takes on a special significance with the need to address questions regarding geologic hazards or the influence of man on the environment. Unfortunately, there are too few techniques for dating events on this timescale. We have developed a mass spectrometric technique for the measurement of ^{238}U - ^{230}Th disequilibrium in young (<350 ky) geologic samples and have recently applied this technique to obtain the first high precision measurements on ^{238}U - ^{230}Th disequilibrium in volcanic rocks.

Our initial work has been with fresh, axial MORB samples from the Juan de Fuca and Gorda Ridges. We have found distinct excesses of ^{230}Th relative to ^{238}U in these samples. These excesses are typically 14% but range up to 40%. (Precision and reproducibility for these data are 0.5 to 1% for 1 gram samples.) Low boron concentrations and $(^{234}\text{U})/(^{238}\text{U}) = 1$ for the samples verify the absence of detectable sea water contamination. From these results we infer that primary magmatic processes are the source of the measured ^{230}Th excesses and that Th is more

incompatible than U during partial melting of the MORB source. The $^{230}\text{Th}/^{232}\text{Th}$ ratios for the Juan de Fuca Ridge samples appear to be the highest yet measured for uncontaminated MORB. From these data we infer that these basalts formed from a rather uniform source that is highly depleted in Th with $\text{Th}/\text{U} = 2.2$. The uniformity of the $^{230}\text{Th}/^{232}\text{Th}$ ratios suggests that dating of off-axis samples with this technique is feasible.

F. Geochemistry of Technetium (*D. B. Curtis [505-667-4498], J. Fabryka-Martin, N. C. Schroeder, and D. J. Rokop*)

Technetium is a transient element in nature: it exists as a single radioactive isotope, ^{99}Tc , formed by the natural fission of uranium. The radionuclide decays with a half-life 2.13×10^5 years, short relative to the age of the Earth but long relative to human experience. Technetium is an ultra-trace element occurring in natural materials at concentrations less than 10^{-12} g/g. The magnitude of technetium abundances in natural materials is a function of its production rate and its chemical behavior in response to naturally occurring processes.

An understanding of the geochemistry of this rare, radioactive element has practical relevance with regard to the successful interment of high level nuclear waste in the geological environment. Such understanding also serves as the basis for using this radionuclide as a tracer and a chronometer in the study of physical and chemical processes in the subsurface. This research is characterizing the geochemical controls on the production, retention, and dispersion of technetium. A Monte Carlo model that calculates the neutron induced production in complex materials has been used to calculate the abundances of technetium in uraniumiferous static aqueous systems. The calculated values range over a factor of 2, from 1.6×10^{-12} $^{99}\text{Tc}/\text{U}$ (produced mostly by spontaneous fission of ^{238}U) to about 2.8×10^{-12} $^{99}\text{Tc}/\text{U}$ (produced in roughly equal proportions by spontaneous fission and neutron induced fission). The model calculations predict a strong correlation between the abundance of ^{99}Tc , fission product ^{129}I , and neutron-capture product ^{239}Pu . The ^{99}Tc abundance and the correlation between ^{99}Tc and ^{239}Pu predicted by the model are in disagreement with measurements of these properties in a sample from the uranium deposit at Koongarra, Northern Territory, Australia. At this early time, however, it is uncertain whether the disparity indicates chemical fractionation between the elements, or whether it is merely manifestation of inaccuracies in the model predictions or the measured abundances.

G. A Search for Evidence of Large Comet or Asteroid Impacts at Extinction Boundaries (*C. J. Orth [505-667-4785] 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. We have been collaborating with over 40 universities, museums, and geological surveys from around the globe. Neutron activation and radiochemical methods are used to measure abundances for more than 40 elements including the platinum group.

We have continued our measurements on the 92-Ma Late Cenomanian extinction (marine invertebrates) interval, where last year we reported finding two closely spaced Ir anomalies in

marine rock sequences in the western interior of North America. The Ir (also Sc, Ti, V, Cr, Co, Ni, Pt, and Au) peaks are strong in northern New Mexico and Colorado, but weaken to the north, being barely detectable in Manitoba. Sedimentary sequences in Texas (closer to the proto-Caribbean), England, Germany, France, and Italy were studied this year. A section near Van Horn, Texas, provided data for the Middle Cenomanian into the late Early Turonian, an interval of about three million years. Only at the extinction horizons in the Late Cenomanian did we observe the Ir and other trace element anomalies. We also found the anomalies, although weaker than in most of the North American sections, in the England and Germany sections, but not in France and Italy. Samples from these last two countries were taken from shallow marine carbonate sequences, where tidal and wave action might have erased the geochemical signals. We cannot entirely preclude impact sources for the two Ir anomalies, but our abundance patterns are better described by those from ocean ridge basalts suggesting broad distribution of ocean ridge material in the Late Cenomanian ocean. These geochemical anomalies are providing widespread to possibly global stratigraphic time markers in the geologic record.

H. Trace Element Geochemistry of Volcanic Gases and Particles from Basaltic Volcanoes and Geothermal Fluids (*D. L. Finnegan [505-667-6548] and T. L. Miller*) (Concluded January 1, 1989)

Field studies have been performed at the Hawaiian volcanoes Mauna Loa and Kilauea to better our understanding of the trace metal chemistry in volcanic gases and particles. The major goals of the project were to determine the characteristic trace element contents of volcanic fumes from Hawaiian eruptions, to evaluate the variations in the trace element composition of aerosols through eruption cycles, and to determine the speciation of highly enriched metals directly upon release from the magma. This information would be used to examine the geochemical mechanisms of trace element enrichment in volcanic fumes and to investigate the potential for using selected trace elements in the fumes as predictors of volcanic activity. Thus far the first two goals have been achieved and several trace elements have been identified as possible indicators of changes in volcanic activity. The most promising use for these trace metals would be for eruption prediction at silicic volcanoes, which usually have increased gas emissions and phreatic outbursts before major eruptions.

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Contract: W-7405-ENG-36

Category: Energy Resource Recognition, Evaluation, and Utilization

Person in Charge: C. W. Myers

A. Search for Magma Chambers and Structures Beneath the Northern Jemez Volcanic Field: An Integrated Geological, Geophysical, and Petrochemical Study (*K. H. Olsen [505-667-1007] and W. S. Baldrige*)

The Jemez volcanic field of northern New Mexico, which includes one of the world's largest and youngest calderas, is a complex volcanic field with a history of eruptions from more than 14 Ma to 130,000 years ago. Volcanism is broadly coincident with reactivation of the Rio Grande rift, with Basin and Range extensional deformation, and with regional basaltic activity. Recent seismic tomography experiments by us have delineated a large (greater than 15 km diameter by 15 km deep) pluton at shallow crustal depths beneath the Valles and Toledo calderas, which were the sites of two cataclysmic Bandelier ash flow eruptions 1.45 and 1.12 Ma. The Bandelier pluton includes the magma chambers that were the sources for the ignimbrite eruptions; these are large enough and young enough that they may still contain pockets of residual magma. The objective of this study is to closely integrate geophysical and geological/petrological techniques in an area immediately northeast of the Valles caldera where a long record of volcanic history of the Jemez is preserved.

Our work is directed toward a better understanding of the evolution of a complex intermediate-to-silicic volcanic field, of processes leading to formation of major calderas, and of the present structure of the volcanic field. By focusing on this region we will: 1) search for upper crustal magma chambers and/or plutons associated with a young andesite/dacite dome and flow field and with a group of young rhyolite domes, 2) quantify the thermal and composition-volume-structural development of the (composite) pluton underlying the Jemez volcanic field, and 3) correlate geophysical data (including density and seismic velocities) with petrographic studies to facilitate interpretation of subsurface geophysical data and to develop a detailed model of the structure and evolution of the magma chambers underlying this major silicic volcanic field.

B. Caldera Processes: Hydrothermal Dynamics and Ore Deposition in the Sulphur Springs Vapor Dominated Zone, Valles Caldera Magma-Hydrothermal System (Hole VC-2A) (*F. E. Goff [505-667-8060] and J. N. Gardner*)

Valles caldera has been a high-priority site since the earliest days of the Continental Scientific Drilling Program. Because of the size, youth, and excellent preservation of this caldera complex, its high-temperature hydrothermal system, and the available database, Valles caldera has appealed to both the thermal regimes and mineral deposits communities as an ideal laboratory for the study of magmatic processes, active hydrothermal systems, and recently ore deposit mechanisms. Two

core holes have been designed for study of the active hydrothermal system at Sulphur Springs: VC-2A was completed in September 1986 to a depth of 528 m and bottom-hole temperature of 212°C; VC-2B was completed in October 1988 to a depth of 1.762 km and bottom hole temperature of 295°C.

After conducting about 25 flow tests on the 490 m deep, 210°C flow zone in VC-2A, the chemistry and isotopic composition has been well characterized. Fluids are of the neutral-chloride type with about 3000 mg/kg Cl, 2 mg/kg As, 27 mg/kg Li, 26 mg/kg B, and 5 ppb Mo. Thus, VC-2A fluid is slightly more concentrated than Redondo Creek reservoir fluids 4 km east of Sulphur Springs. A complete total flow composition (fluid plus gas) has been calculated. The fluid has about 0.5 T.U., implying a water age >1000 years. Stable isotopes indicate an oxygen-18 shift of 4‰ and a deuterium shift of 15‰ heavier than local meteoric water. The oxygen shift is caused by high temperature isotopic exchange of water and rock. The deuterium shift has been noticed in a few other Valles fluids and its cause is still under investigation. Pressure, temperature, and flow rate data from the flow tests have not been analyzed.

A suite of six K/Ar dates was obtained on hydrothermal illites in the core hole. The dates indicate that hydrothermal activity began ≥ 0.83 Ma in the Sulphur Springs area and that the shallow, sub ore grade molybdenite deposit formed about 0.66 Ma. Stable isotopic analysis of the whole rock core and mineral separates indicates that the initial hydrothermal activity was dominated by water of local meteoric origin, just as hydrothermal activity is today.

Detailed fluid inclusion work on vein minerals and secondary quartz overgrowths on phenocrysts in the intracaldera tuffs indicates that the liquid dominated zone extended to about 100 m above present ground surface when the Sulphur Springs hydrothermal system originally formed. Thus, about 100 m of erosion has occurred at Sulphur Springs since ≥ 0.83 Ma. The fluid inclusions also indicate that the present vapor zone formed rapidly to a depth of about 240 m. Evidence from other studies in Valles caldera indicate that the vapor zone formed about 0.5 Ma when the southwest caldera wall was breached and intracaldera lakes were rapidly drained. The fluid inclusion evident from VC-2A supports this theory.

Remedial action was performed on VC-2A to correct imperfections in the original cement job in the 98 m casing. A braden head squeeze successfully corrected the problem, the cellar around the well head was filled with gravel, and VC-2A was formally released to the landowner in November 1988. A data report on VC-1 and VC-2A was published without interpretation that catalogues all geochemical, hydrogeochemical, geophysical, and physical property data obtained on this project.

C. Valles Caldera 2B: Caldera Processes, Hydrothermal Dynamics, and Mineralization, Sulphur Springs, Valles Caldera Magma-Hydrothermal System, New Mexico (*J. N. Gardner [505-667-1799] 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. Overall core recovery was 99.2%. VC-2B is possibly the deepest, hottest, continuously cored hole in North America. The project is jointly managed by Los Alamos National Laboratory, University of Utah Research Institute, and Sandia National Laboratories.

The stratigraphic sequence in VC-2B is: 0-174 m landslide, debris flows, volcanoclastic sandstones, accretionary lapilli tuffs, and a possible intermediate composition, subvolcanic intrusion; 174-366 m Tshirege member tuffs; 366-372 m volcanoclastic sandstone; 372-599 m Otowi member tuffs; 599-742 m lower tuffs; 742-798 m Santa Fe group sandstone and Cochiti formation debris flows; 798-1558 m Paleozoic sedimentary rocks; and 1558-1762 m (T.D.), quartz monzonite.

Lithologies in caldera-fill indicate the drill site may be proximal to ignimbrite vents and that an intracaldera lake with temperatures approaching boiling formed soon after the caldera itself. Structural correlations between VC-2B and the 528-m deep companion hole VC-2A indicate the earlier Toledo caldera (1.45 Ma; Otowi member tuffs) and even older Lower Tuffs caldera experienced no structural resurgence similar to the Valles caldera. All 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. The hydrothermal system penetrated by these bores consists of a shallow vapor-rich cap, which has evolved 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 suggests chloride-rich geothermal fluids were entering the bore and mixing with the drilling fluids in the fractured lower Paleozoic and Precambrian sections. To date, one fluid sample from a fracture zone at 1.752 km has been successfully obtained with a newly developed high temperature downhole sampling tool. Flow tests and sampling of fluids from this zone at the well head are in progress.

D. Operation of a Sample Management System for the CSDP (*S. J. Goff [505-667-7200] and R. Dayvault [UNC, Grand Junction]*)

The Curation Office, managed from Los Alamos, operates a core curation facility 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 7,200 square feet of space in Building 7 at the DOE Grand Junction facility. 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 many boxes of core at once. 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. Presently archived at the repository are approximately 40,000 feet of drill core from the various CSDP and related drilling projects. The Curation Office has also 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.

E. Scientific Assembly of the International Association of Volcanism and Chemistry of the Earth's Interior (IAVCEI) (*W. S. Baldrige [505-667-8477], G. Heiken, and K. Wohletz*)

The IAVCEI General Assembly, which is held every four years, was hosted this year by the United States. The theme of continental magmatism drew a record number of participants (800) and record number of papers (650) for IAVCEI. Meeting participants came from 35 countries. Another theme was volcanism in the Americas; through active advertising and a large program of financial aid, many participants came from throughout Latin America and presented their research for the first time at an international meeting. The abstracts volume and an 800-page field guide to volcanic terranes of the western United States were prepared for the meeting and published by the New Mexico Bureau of Mines and Mineral Resources, Socorro, NM.

There were several field trips associated with the assembly, including pre- and post-assembly field trips of 5 to 10 days each, covering volcanic terranes throughout the western United States. One day field trips, which were held at mid-week, were a great success, not only for the geologic information presented but because it gave meeting participants a chance to become well acquainted with those from many parts of the world.

The main purpose of the meeting, which was to create an environment where a lot of new information was to be exchanged, was a great success. New friends and collaborators were made, an enormous amount of research data presented, and a new sense of purpose created for the volcanological community--especially with regard to applications of the science to the problems of volcanic hazards, volcanogenic mineral resources, and volcanic energy resources.

F. Development of Database Management Systems (*N. Marusak [505-667-5698]*)

Continued efforts were made to address the database needs, implementation, and protocol for the Department of Energy/Office of Basic Energy Science (DOE/OBES) and the Deep Observation Sampling of the Earth's Crust (DOSECC) community. The concept of a central facility at one location is probably not the best solution for CSDP needs at this time. The cost, start-up time, and continued support is excessive for the needs. Because many organizations have some type of system in place and because the scientific goals from each location are so different, it is reasonable to consider a distributed database management system. This type of data management system allows for data to be stored locally under local control. Local storage decreases response times and communications cost and increases data availability. At the same time it can help integrate heterogeneous computing environments. This approach can recognize existing database management systems and at the same time unify data distribution.

Contractor: LOS ALAMOS NATIONAL LABORATORY
University of California
Los Alamos, New Mexico 8754

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. There are four goals of this research: to understand the flow of plasma energy in the near-Earth space environment from a small scale point of view, to understand the plasma physics of the solar wind-magnetosphere interaction, to understand the acceleration processes that produce energetic particles in the magnetosphere, and to understand astrophysical plasma physics problems that have implications for solar-terrestrial plasmas. 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]*)

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 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 and ionosphere.

Our most important accomplishment of 1988 has been our further description of the solar wind's interaction with newly created ions in the distant environment of comets. Our computer simulations have yielded scalings that now accurately predict the magnetic fluctuation amplitudes observed at both the proton cyclotron and water-group ion cyclotron frequencies near Comet Giacobini-Zinner. Our simulations have also established good agreement with cometary observations in demonstrating strong pitch angle scattering of cometary ions and magnetic fluctuation spectra that peak at the water-group ion cyclotron frequency.

B. Solar Wind-Magnetospheric Interaction (*J. Birn [505-667-9232] 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 electrodynamic 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 and appropriate scientific satellites) and by the development and use of theoretical models of the structure and dynamics of the magnetosphere.

Our most important achievements in 1988 were made in the analysis of auroral images taken from outer space and in the continued modeling of three-dimensional structures in the magnetosphere. We have examined auroral images taken with the University of Iowa auroral imaging experiment on satellite DE-1. In collaboration with our Iowa colleagues, 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." And, we have used our three-dimensional quasi-static theory to construct quantitative models of the magnetotail under quiet conditions. These models have demonstrated the singular role of the plasma sheet boundary layer as a carrier of field-aligned electric currents and of the low-latitude magnetopause boundary region as a potential region of interaction with the solar wind.

C. Energetic Particle Acceleration (*T. E. Cayton [505-667-2582]*)

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. Although the primary effort of this research involves the analysis of energetic particle data from Los Alamos spacecraft, we also make extensive use of theoretical ideas drawn from various magnetospheric models.

Our most important result of 1988 has been the observation that energetic electrons in the Earth's outer magnetosphere can be resolved into two distinct Maxwellian components that are each fully parameterized by a density and a temperature. The more dense, lower temperature "soft" electrons show a strong correlation with substorm activity, whereas the more tenuous, hotter "hard" component shows much less response to substorms and, in particular, is characterized by a temperature that shows very little change on an hourly time scale.

D. Radiation from Space and Astrophysical Plasmas (*G. Gisler [505-667-1375]*)

In this study we seek to understand how relativistic charged particles originate in both astrophysical and Solar System plasmas and then how these energetic particles couple with background thermal plasma and electromagnetic radiation. We have been studying the generation of intense charged particle beams from conducting accretion disks around black holes or neutron stars. These magnetically confined beams, accompanied by an intense Poynting flux, may be responsible for the jets observed in extragalactic radio sources. In 1988 we have begun examining pair production in neutron star magnetospheres to further elucidate the physics involved in jet formation. Intensive modifications to our computer models are being done to accommodate this new physics. In a different project, a study of the Fermi process of particle acceleration in the context of the Earth's bow shock is now underway. It turns out that the geometry of a "Fermi trap" is a crucial determinant of the energy spectrum of particles exiting the trap. This study should result in testable predictions for distribution functions of electrons at the Earth's bow shock. It will also provide an important benchmark against which ideas for particle acceleration in more exotic astrophysical contexts can be measured.

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] and G. K. Jacobs*)

This study addresses the development of advanced acoustic methods as applied to energy technology through underground imaging of geologic media using elastic waves. This work combines complementary research in seismic imaging and geochemistry to investigate the spatial configuration of magmatic and hydrothermal systems. We propose to acquire experimental data for a well-defined object in the field and to use those data to develop and test inversion algorithms that may be used for imaging a variety of geologic systems. The object of this experiment is an artificial lava lake that will be formed by the melting of rock and soil, and subsequently allowed to solidify, during the forthcoming *In Situ* Vitrification (ISV) demonstration at the Oak Ridge National Laboratory. The dimensions of the artificial lava lake will be several meters on a side and approximately 2.5 m deep. We propose to produce a sequence of images of the parent material before it is melted, at several stages as melting proceeds, and at intervals during crystallization. Temperatures during melting and crystallization will be monitored using a combination of optic fiber thermometry and high-temperature thermocouples. The vapor released during the melting period will be collected in an off-gas processing trailer as part of the ISV demonstration. These vapors and the particulates carried along will be analyzed and correlated with geophysical, thermal, and petrologic characteristics. Following the ISV experiment the vitreous mass will be core drilled and partially excavated to facilitate geochemical and petrologic characterization that will provide information for comparison with the seismic images.

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

Contract: DE-ACO5-84OR21400

Category: Geochemistry

Person in Charge: R. E. Mesmer

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

The solubility of gibbsite - $\text{Al}(\text{OH})_3$ - in NaCl brines is being studied in order to determine the stoichiometries and stability ranges of species intermediate between Al^{3+} and $\text{Al}(\text{OH})_4^-$, the dominant aluminum ions in highly acid and basic solutions, respectively. Such data are badly needed in order to model diagenesis and hydrothermal alteration in fluid/rock systems at near neutral pHs. Our initial experiments at 50°C and 0.1 molal ionic strength (NaCl media) have been complicated by interaction of aluminum ions with the pH buffers used in the experiments. As discussed elsewhere in this section, we have determined that Al^{3+} forms complexes with acetate ions that are strong enough to dominate the aluminum speciation in some natural oil-field brines. In addition, we have discovered that certain polyhydroxyl compounds (including Bis-tris, another of the buffers employed in our early experiments) form exceedingly strong complexes with $\text{Al}(\text{OH})_4^-$. This may have significant implications in environmental and biological sciences. Experiments are now under way in which the pH is buffered in the range of 4 to 7 by Tris buffer, an organic compound that we have established does not complex significantly with any aluminum species. Preliminary results indicate that the solubility minimum of gibbsite as a function of pH occurs at approximately 10^{-8} molal total aluminum (0.3 ppb) at a pH of 5.5 at 50°C, 0.1 molal ionic strength. In order to produce quantitative results at such low levels a new ion chromatographic aluminum analysis technique was developed. In order to determine the hydrolysis species by independent means, these solubility measurements are being complemented by potentiometric titrations of Al^{3+} solutions using our hydrogen-electrode EMF cell.

B. Experimental Studies of Aluminum Acetate Complexing in Hydrothermal Fluids and the Implications for Aluminum Mobility and Secondary Permeability During Diagenesis (*S. E. Drummond [615-576-4600], D. A. Palmer, and D. J. Wesolowski*)

EMF experiments designed to measure the thermodynamic stability of aluminum acetate complexes in 0.10 m NaCl media from 50° to 150° were largely completed in FY 1988. In a parallel study, similar experiments with acetate-free solutions were carried out to account for the hydrolysis of Al^{3+} . In addition, experimental studies of the solubility of gibbsite at 50°C in 0.10 m NaCl media were conducted over a range of acetate concentrations. The recent interpretation of these results clearly indicates the presence of both the $\text{AlCH}_3\text{COO}^{2+}$ and $\text{Al}(\text{CH}_3\text{COO})_2^+$ species. Formation quotients for the reaction $\text{Al}^{3+} + n\text{CH}_3\text{COO}^- \rightleftharpoons \text{Al}(\text{CH}_3\text{COO})_n^{3-n}$ vary from about 1.0×10^2 to 2.5×10^4 between 50° and 150°, respectively, for $n=1$, and from 2.0×10^3 to 1.0×10^8 between 50° and 150° for $n=2$. The coordination of Al^{3+} with acetate is considerably

stronger and more temperature dependent than for either Fe^{2+} or Zn^{2+} . Speciation calculations for a matrix of applicable pH, $[\text{CH}_3\text{COO}^-]$, and temperature conditions reveal the potential role of acetate in mobilizing aluminum in basinal brines. For a typical pH of 5.5 the acetate complexes are dominant over the free and hydrolyzed aluminum at total acetate concentrations ($[\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{COOH}]$) of 0.003, 0.01, and 0.03 m at 50°, 100°, and 150°C, respectively. The ratio of acetate/(hydroxy + free) aluminum species maximizes at pH ~4.5. In solutions with a total acetate concentration of 0.1 m this ratio can be as high as 8.3 at 50°C, 68 at 100°C, and 900 at 150°C. Alternatively, a basinal fluid at 100°C with 0.1 m total acetate can typically transport the same amount of aluminum as an acetate-free solution with either ten times more acid or fifty times more volume. These results demonstrate that acetate complexes are a major factor in the large-scale migration of aluminum and authigenic alumino-silicate mineralization in sedimentary basins. More work at other ionic strengths and temperatures is needed to understand the chemical and physical conditions most conducive to the generation of permeable conduits in reservoirs.

C. Zinc Acetate Complexing in Hydrothermal Solutions to 300°C (*S. E. Drummond [615-576-4600] and T. H. Giordano [New Mexico State University]*)

The hydrogen electrode EMF cell was used in more than 50 experiments to investigate the coordination of acetate with Zn^{2+} from 50° to 300°C and over a range of ionic strengths (0.03-1.0 m) and acetate concentrations (0.001-0.1 m). For the reactions $\text{Zn}^{2+} + n\text{CH}_3\text{COO}^- \rightleftharpoons \text{Zn}(\text{CH}_3\text{COO})_n^{2-n}$ the formation constants ($I = 0$) vary from 10^2 ($n=1$) and 3.5×10^2 ($n=2$) at 50°C to 2.0×10^5 ($n=1$) and 7.0×10^7 ($n=2$) at 300°C. The $\text{Zn}(\text{CH}_3\text{COO})_3^-$ species was observed at the conditions with the highest acetate concentrations and temperatures. These data demonstrate that the acetate complexes of zinc are stronger than those of ferrous iron but weaker than aluminum acetate complexes. In typical basinal brines, the principal competition for Zn^{2+} will be between the Cl^- and CH_3COO^- ligands. A discrepancy among various sources for the stability constants for the zinc chloride complexes makes any comparison with the zinc acetate complexes uncertain. However, on the basis of the best available data it appears that the zinc acetate complexes will play a substantial role in the aqueous transport of zinc with chloride/acetate ratios less than about ten. Although more reliable evaluation of the importance of the zinc acetate complexes awaits further experimental work on the zinc chloride complexes, it is now evident that the acetate complexes of zinc and other transition metals must be accounted for to model the transport capacity of sedimentary basin brines, which often have acetate concentrations exceeding 0.01 m.

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

Equilibrium constants have been determined for the principal reactions that control the solubility of dolomite and calcite in hydrothermal solutions: $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$ and $1/2\text{CaMg}(\text{CO}_3)_2 + \text{CO}_2 + \text{H}_2 \rightleftharpoons 1/2\text{Ca}^{2+} + 1/2\text{Mg}^{2+} + 2\text{HCO}_3^-$ at temperatures of 50°, 100°, 150°, 200°, and 300°C and pressures of 300, 800, and 1300 bars. A co-solubility approach was selected, wherein equal molar proportions of calcite and dolomite were reacted with aqueous solutions with CO_2 concentrations varying from 0.04 to 2.3 m and ionic strengths less than 0.03. Run durations ranged from a few days to as much as 41 days. The equilibrium constants for both calcite and dolomite exhibit systematic retrograde behavior with non-zero heat capacities for the reactions. Reversals in the log K values were determined by ramping up and down pressure at a fixed temperature. Extrapolation of log K values for calcite to low pressure conditions agree with

known calcite data. At 300 bars, log K values for calcite decrease from -4.86 at 100°C to -9.93 at 300°C, whereas log K's for dolomite decrease from -5.20 to -10.44 over the same temperature interval. An increase in pressure results in an increase in the solubility, and this effect becomes more pronounced with increasing temperature. An increase of 1000 bars leads to an increase in solubility of calcite or dolomite by factors of 10 at 100°C and 100 at 300°C. This nonlinear behavior can best be normalized by a function that relates the log K values with the log density of water. Strict adherence of all the data to one simple function indicates that the data are precise to ± 0.02 log K units for each solubility reaction. Data of this kind are essential for an understanding of the conditions that stabilize various carbonate phases (e.g., dolomite, siderite) and control permeability in diagenetic or geothermal systems via reactions such as the dolomitization of calcite ($2\text{CaCO}_3 + \text{Mg}^{2+} \rightleftharpoons \text{Ca}^{2+} + \text{CaMg}(\text{CO}_3)_2$), which yields a 14.2% volume reduction.

E. Oxygen and Hydrogen Isotope Systematics of Brines (*D. J. Wesolowski [615-574-6903] and D. R. Cole*)

The activity coefficients of oxygen and hydrogen isotopes in natural brines differ substantially from unity as a function of salinity, composition, and temperature. In order to model the paleotemperatures, water/rock ratios, fluid sources, and flow patterns in geothermal systems and sedimentary basins, a quantitative understanding of this subtle phenomenon is needed. The system NaCl-H₂O has been studied at 100°C and seven salinities ranging from 0 to 5.5 molal NaCl. The D/H ratio of water vapor is 27 permil lower than that of coexisting pure liquid water at 100°C. As the salt content of the liquid phase increases, this difference rises rapidly to a maximum of 38 to 40 permil at 0.5 molal NaCl and then decreases nearly linearly to approximately 20 permil at 5.5 molal. Presumably, the fractionation would become progressively smaller at higher salinities. These results are in excellent agreement with recent data reported in the Ph.D. thesis of K. Kazahaya at the Tokyo Institute of Technology. Preliminary results at 70°C indicate that the vapor-brine D/H fractionations differ significantly from our previous 100°C results for similar ionic strength solutions. At all NaCl molalities investigated at 70°C, the $\delta D_{\text{Vapor}} - \delta D_{\text{Brine}}$ fractionations are less negative than the $\delta D_{\text{Vapor}} - \delta D_{\text{Pure H}_2\text{O}}$ fractionation of -41 permil. For example, the $\delta D_{\text{Vapor}} - \delta D_{\text{Brine}}$ values average approximately -30, -34, -36, -32, and -28 permil at 0.3, 0.5, 1, 3, and 4.9 m NaCl, respectively. These results are preliminary and require further confirmation with more experiments. At 100°C, the vapor-brine D/H fractionations are more negative (e.g., -35 to -39 permil at 1 m NaCl) than the vapor-pure water D/H fractionation (-27 permil) for NaCl molalities up to about 3.3. Above 3.3 m, the vapor-brine D/H values are less negative (e.g., -26 to -23 at 3.5 m NaCl) than the pure water system. The size and unexpected complexity of the salt effect at these conditions make it important to investigate this phenomenon in greater detail. Similar large effects are anticipated in systems with other important natural salts and mixtures thereof. These results suggest a small but fundamental change in the nature of bonding or the ratios of "free" versus "hydrated" water molecules in brines as temperature increases. The effects observed can lead to gross changes in the interpretation of isotopic data from natural systems. For instance, the kaolinite-pure water D/H fractionation changes by only 5 permil as temperature increases from 70 to 100°C. Our results indicate that if the water contains 1 molal dissolved NaCl, this change in the fractionation increases to 15 permil. Thus, the isotopic compositions of pore fluids in a subsiding sedimentary basin will experience major deviations from model prediction if the salinity effect is ignored or unquantified. This can result in erroneous interpretations of porosity-permeability evolution and fluid migration pathways in sedimentary basins and geothermal systems.

F. Isotopic Exchange in the System: $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$ (D. R. Cole [615-574-5473], T. Burch and A. C. Lasaga [Yale University])

The purpose of this study was to determine rates of isotopic exchange for carbon and oxygen as a function of temperature, pressure, and mole fraction of CO_2 and H_2O . Conventional hydrothermal techniques were used (cold seal apparatus, Pt capsules) and all phases were analyzed for their isotopic composition. The calcite was also examined by SEM. Experimental conditions are varied between 300°C , 0.25 kbar and 700°C , 3.0 kbar with mole% $\text{CO}_2 = 0.0, 2.0, 4.0, 5.0, 11.0, 18.0,$ and 100.0 . By combining the isotopic data with a detailed SEM examination, it is possible to delineate exchange mechanisms of solution-precipitation, recrystallization, and diffusion, which are all participating to some extent over the range of experimental conditions. Unique to this study is the comparison of carbon and oxygen exchange rates, analysis of all phases in the reaction, and use of $\text{Ag}_2\text{C}_2\text{O}_4$ as an isotopic source for carbon and oxygen. One of the goals of this study was to use the experimentally determined rates in numerical models of fluid flow in contact metamorphism and sedimentary basins. Preliminary results show a rapid initial surface exchange and the rates for carbon isotopic exchange are approximately one order of magnitude greater at 700°C , 1.0 kbar than 300°C , 0.25 kbar with maxima between mole% $\text{CO}_2 = 4.0$ and 11.0 . Slightly more rapid rates of $^{13}\text{C}/^{12}\text{C}$ exchange were observed in systems where $\text{CO}_2/\text{H}_2\text{O}$ ratios were high. More rapid grain growth (Ostwald ripening) and oxygen isotopic exchange occurs in the calcite- H_2O systems. Even the calcite- CO_2 (H_2O absent) experiments exhibit measurable exchange rates due to a coupled surface sorption/diffusion mechanism.

G. Temperature-Salinity-Stable Isotope Trends in Boiling Fossil Geothermal Systems (D. R. Cole [615-574-5473], B. Smith [LBL], and T. Albison [Catorce, Ltd.]

The relationships between the temperature, salinity, depth, and $\delta^{18}\text{O}$ in quartz and calcite have been determined for samples from Real de Catorce, Colorado, Sombrerete, and Zacualpan. At Catorce, the $\delta^{18}\text{O}$ values of quartz range from 14.5 to 18.5 permil and display an increase with increasing salinity and decreasing depth to the surface. This trend is consistent with a mineralizing fluid undergoing ^{18}O enrichment due to vapor phase separation during ascent to the surface. The fluid inclusion evidence for Catorce supports this contention. An opposite trend is observed at Colorado, where the quartz $\delta^{18}\text{O}$ values tend to increase with decreasing salinity and temperature (less pronounced). This trend could result from the mixing of ascending mineralized fluids with either a boiled ground water or with condensed acid--volatiles low in NaCl but enriched in ^{18}O due to low-temperature alteration in upper portions of the system. Although boiling occurred high in the Sombrerete system, $\delta^{18}\text{O}$ -temperature-salinity-depth trends of the type observed at Colorado or Catorce are not observed. Random distributions are more common at Sombrerete. Boiling appears to correlate with high vertical thermal gradients (75 to $120^\circ\text{C}/\text{km}$), more restricted vertical mineralized intervals ($200\text{-}500$ m), and increased $\delta^{18}\text{O}$ enrichment in quartz with decreasing depth due to isotopic fractionation during vapor-phase separation. Absence of boiling coincides with small vertical thermal gradients ($<10^\circ\text{C}/\text{km}$), greater vertical extent of mineralization (>100 m), greater depth to the ore horizon, and general lack of correlation between $\delta^{18}\text{O}$ in quartz and either depth, salinity, or temperature. Understanding the time-temperature-salinity-isotope relationships in fossil hydrothermal systems yields insight into the physical chemical consequences of fluid/rock interaction, boiling, and

mixing in active geothermal systems even though the hydrothermal evolutionary cycle is still in progress.

H. Methane Generation, Migration, and Accumulation in the Appalachian Overthrust Belt (*D. J. Wesolowski [615-574-6903] and D. L. Hall [Virginia Polytechnic Institute]*)

The potential for hydrocarbon accumulations related to thrust belt emplacement and metamorphism are the primary subjects of this research. The Ducktown massive sulfide deposits in southeastern Tennessee are hosted by amphibolite-facies metamorphic rocks of the Blue Ridge thrust sheet. Despite the high metamorphic grade of these deposits, many of the silicate minerals contain abundant low-temperature fluid inclusions, which consist of essentially pure, high density methane. In order to determine the origin of this methane, which has also been observed in fluid inclusions in late-stage veins elsewhere in the thrust sheet, Donald Hull, a Ph.D. candidate at VPI, is conducting stable carbon and oxygen isotope studies of the Ducktown ores in our laboratories. Results to date indicate that the methane is unrelated to the formation or metamorphism of the ores and their host rocks. The P-T conditions of trapping of the methane as well as its occurrence in secondary fluid inclusions and quartz veins is consistent with an origin related to the latest Alleghanian brittle emplacement of the Blue Ridge thrust sheet over essentially unmetamorphosed platform sediments of the eastern U.S. continental margin. Equivalent units exposed to the northwest in the Valley and Ridge Province are known oil and gas producers. This work is related to the COSPLUM project which proposes to drill through the Blue Ridge thrust sheet in order to directly assess the hydrocarbon potential of overthrust platform sediments to the southeast of the Ducktown deposits.

I. Sulfur Diffusion in Silicate Melts (*D. R. Cole [615-574-5473], M. T. Naney, and E. M. Ripley [Indiana University]*)

Nearly 200 experiments have been conducted (900 to 1350°C, 1 atm, variable oxygen fugacity) to determine the sulfur diffusivities in three compositionally different silicate melts: low Fe²⁺/Fe³⁺ basalt (McCoy Canyon), and Fe-deficient high-silica Na-Ca rich glass. Diffusion coefficients estimated from concentration-time plots for basalt and troctolite are remarkably similar despite their compositional differences. Values for log D (apparent diffusion coefficient, cm²sec⁻¹) range from about -6.7 and -7.3 at 1200°C to -6.3 and -6.6 at 1300°C for troctolite and basalt, respectively. In general, reducing experimental conditions (QFM or below) resulted in slightly higher diffusion coefficients. This is true for both high- and low-silica melts. This redox trend may be due to the fact that all three starting compositions are more oxidized than the experimental conditions ultimately imposed on them via the CO₂/CO gas mixtures. The high-silica Na-Ca rich melts exhibit apparent diffusion coefficients approximately one order of magnitude less than the basalt (e.g., log D values of -8.7 at 1150°C, -8.0 at 1250°C, and -7.5 cm²sec⁻¹ at 1350°C for fO₂ conditions defined by the NNO buffer). Diffusion coefficients calculated from electron microprobe profile data obtained on quenched high-silica glass spheres are in moderately good agreement with log D values estimated from the concentration versus time plots. The activation energies for diffusion vary between 40-50 and 55-65 kcal/mole for the low- and high-silica melts, respectively. These ranges are similar to those reported for sulfur diffusion in Ca-silicate and Ca-Al-silicate melts and those predicted by the Stokes-Einstein relation. A detailed examination of the sulfur K α wavelength shifts by electron microprobe analysis of quenched glass indicates that the bulk of the sulfur occurs as sulfate rather than sulfide. The

presence of sulfur as sulfate has been corroborated by using FTIR spectroscopy where we observed an absorption doublet at roughly 615 and 650 cm^{-1} in both high- and low-silica glasses. This doublet is not common in sulfur-deficient glasses and mimics doublets observed in many sulfate phases, particularly CaSO_4 . Preliminary ESCA examination of our starting Na-Ca high-silica glass indicates that the sulfur appears to be bonded predominantly with Ca in the glass.

J. Magma Mixing and Textural Development of Rhyolites from the Inyo Volcanic Chain, Eastern California (*M. T. Naney [615-576-2049] and R. G. Gibson [ORAU Postdoctoral Research Associate, presently at AMOCO Production Co.]*)

Mineralogical analysis of silicic lavas from the Inyo volcanic chain supports the hypothesis that magma mixing was the primary process responsible for the bimodal mineral chemistry and banded texture of these rocks. Surface and drill hole samples were subdivided into three groups 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, which contain oligoclase and alkali feldspar phenocrysts, Fe-Rich ferromagnesian silicates, and no ilmenite; (III) banded samples from the early Dome tephra, the conduit beneath Obsidian dome, and the body of the Glass Creek, South Deadman, and Obsidian domes. Banding is defined either by variations in glass color and chemistry or variable microlite abundance. Compositions of all minerals in group 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 group I samples occur in brown glass or microlite-rich bands whereas grains with compositions like their counterparts in group II occur in microlite-poor bands of colorless glass. The observed features of the group III samples are explained by 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 ($T = 775^\circ\text{C}$, $\log f\text{O}_2 = -15.0$, $f\text{H}_2\text{O}$ bars) and dacitic ($T = 870^\circ\text{C}$, $\log f\text{O}_2 = -11.9$, $f\text{H}_2\text{O} = 100\text{-}600$ 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 group III samples formed either 1) as samples of the comingled magmas were immediately vented to the surface and quenched, preserving bands of two distinct glass compositions or 2) as bands of hotter dacitic magma precipitated microlites when cooled by the rhyolitic magma.

K. Crustal Stability of C-O-H Fluids (*J. G. Blencoe [615-574-7041] and S. E. Drummond*)

Work has commenced on measuring the P-V-T properties of pure gases (CH_4 , CO_2 , and H_2) and selected gas mixtures (e.g., $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CH}_4\text{-CO}_2$) in the C-O-H system at 100 - 4000 bars, 50 - 550°C. Initial experimentation has focused on determining the stability and precision of the vibrating tube densimeter. Results obtained during a two-month-long run indicate that: 1) frequency measurements are sensitive to pressure and temperature variations as small as 0.1 bars and 0.01°C; 2) the performance of the experimental apparatus is not significantly degraded by small changes in local magnetic field, diurnal variations in room temperature, and short-term instabilities in line voltage; and 3) extreme precautions are required to prevent external vibration from adversely affecting the operation of the densimeter. We conclude from the results that "noise" in frequency data is 1 ppm or less, and that overall precision of the data is close to 2 ppm, which corresponds to approximately 100 ppm precision in density.

Contractor: PACIFIC NORTHWEST LABORATORY
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Contract: DE-ACO6-76RLO 1830

Category: Geochemistry

Person in Charge: J. C. Laul

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

The major objectives of this research program are to gain a quantitative understanding of chemical migration over a range of temperatures in diverse geological media and geothermal systems (water/rock interaction). The study includes the understanding of dispersing solutions into country rocks, partitioning of elements between minerals and solutions derived from granite and pegmatite, and composition and evolution of the solutions. Earlier chemical studies in pegmatites were limited to chemical migration on a smaller scale. Now the study of granite-pegmatite/wall rock interactions is extended to investigate chemical migration to a much larger scale (~km scale). The overall aim is to understand the chemical fractionation and migration processes in the pegmatite-granite/wall rock interactions. 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. This study focuses 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.

For geothermal systems, the proposed site is Valles caldera VC-2A and VC-2B holes in New Mexico. The emphasis is on natural radionuclides of ^{238}U and ^{232}Th series and the REE in thermal fluids and cores. This 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), mixing of ground waters, and source of region geochemistry. In the unsaturated zone, retardation properties of radionuclides, hydraulic conductivity, and diffusivity data can be obtained experimentally by the unsaturated flow apparatus, to develop and validate transport models. The natural radionuclide data in cores can provide information on the past migration or leaching of elements up to a period of about one million years.

The granite/pegmatite study is in collaboration with J. J. Papike, South Dakota School of Mines, Rapid City, South Dakota, who is responsible for geologic, petrographic, and petrologic systematics. Our focus will be on the chemical systematics on some 40 elements by x-ray fluorescence, instrumental and radiochemical neutron activation analysis, and inductively coupled plasma-mass spectrometry.

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Contract: DE-AC06-76RLO 1830

Category: Energy Resource Recognition, Evaluation, and Utilization

Person in Charge: E. W. Kleckner

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

Since 1976, we have been conducting research in areas of remote sensing, image processing, and computer graphics. The goal of this task is to develop advanced, interactive computer techniques for processing, analyzing, and displaying combinations of remote sensing and geosciences data so scientists can interpret complex data combinations, involving resource discovery, energy development, environmental conservation, and national security. Beginning in 1985, task emphasis was placed on procuring, installing, and developing a second-generation interactive, image-processing, and data-integration system for analysis of geoscience data sets. The new system incorporates selected knowledge representation techniques with conventional image-processing/data integration functions.

Three-dimensional data sets consisting of arrays of data points in space are becoming increasingly available at high resolution. Examples are three-dimensional seismic reflection data, computer tomography, and output from three-dimensional simulation models. These data sets may contain from 10^6 to 10^8 data values, and thus are of the same order of size as multispectral Landsat data sets. In the past year we have extended our work with two-dimensional data sets to the more general problem of visualization of three-dimensional data that may be time dependent, adding a fourth dimension. We have developed a workstation-based interactive program for rendering three-dimensional data. Menus allow the user to select from a variety of rendering and visualization techniques, including color-coding, constant surface calculation, stream lines, and animation. Stereo views may be selected and viewed as composite anaglyph images or left, right color stereo pairs. Several options exist for producing and storing sequences of images that may be previewed on the workstation prior to transfer to video tape. Single images or stereo pairs can be viewed quickly, at low resolution, for selection of image content, rendering method, and view point and can then be produced at high resolution. Hard copy can be produced at resolutions up to 4,000 x 4,000 pixels.

We are exploring the application of these visualization techniques to geoscience data sets through two examples. The first example data set comes from a high-resolution (10^6 nodes), three-dimensional porous media flow model. In this case, we are looking for effective ways to present the relationship between the conductivity and pressure fields in a heterogeneous medium. Stereo streamline plots overlaid on equal pressure surfaces and animation with time-varying cutting planes or pressure thresholds are methods we have found to be promising. For the second example, we are focusing on 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. Currently, we are evaluating techniques for displaying geologic cross sections in the context of the other data sets. One approach is through animation, where the apparent view point moves from one point of interest to another and geologic cross sections can, in effect, be lifted out of the surface for detailed viewing.

B. Remote Geologic Analysis (*M. G. Foley [509-376-8635], D. E. Beaver, P. G. Heasler, and K. A. Hoover*)

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., valley, drainage networks and divides, scarps, dip slopes, and terraces) the three-dimensional orientation 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, ground-water potentiometric surfaces, and hydrogeochemical contour maps. Since 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.

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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 database 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 day-lighting. However, the primary emphasis of the insolation task 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], D. W. Slater, B. A. LeBaron, and N. R. Larson*)

The Rattlesnake Mountain Observatory data set of direct solar measurements (1977-1987) 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 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 1 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 1989 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 database 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 study with the University of Michigan is underway that will use 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.

Construction of a new solid state, intensified imager for use in extremely low light level conditions received major emphasis. The sensor element is a charge coupled device (CCD) consisting of an array of 384 x 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: W. C. Luth

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

Because many energy facilities, including power plants and waste repositories, are of necessity located in tectonically unstable areas, it is of critical importance to develop a physical understanding of the processes responsible for the instabilities. The most promising avenue at present is therefore to examine, by appropriate observational and theoretical methods, the mechanisms responsible for the accumulation and release of deformation, strain, and stress in the Earth. The overall objective is thus to develop physical models to explain geodetic strain changes observed at the Earth's surface over a period of years and to interpret these data using the predictions of the models. Laboratory data obtained from experiments involving frictional sliding of rocks can also be used as a guide to the appropriate physics to use in constructing the models. Emphasis during the past year has been on constructing and examining the consequences of thermodynamical theories for localized nonlinear deformation in otherwise linearly elastic solids. Using the principle of minimum Helmholtz free energy, a nonclassical nucleation theory was constructed to explain cracking in solids. Minimizing the free energy functional with respect to the offset field along the fault or crack leads to a set of Euler-Lagrange equations, which can be solved for the equilibrium offset distribution. Numerical solution of these equations yields the interesting result that the nucleation process for cracks generally involves the formation of an associated region outside the crack, which looks very much like the fracture process zone observed in laboratory studies, and which has heretofore been substantially unexplained. Its presence is thus inferred to be a direct consequence of the long-range nature of the elastic interactions between dislocations. This result was first obtained recently in condensed matter physics in studies involving nucleation phenomena in nature.

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 that 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 have been obtained for Tennessee marble, which undergoes a transition from brittle to ductile behavior at higher pressures, thus extending the damage surface concept beyond the brittle materials where it was

initially observed. In the ductile regime, the damage surfaces are basically pressure-independent. At lower pressures, in the brittle regime, damage is pressure-dependent. Pressure independence of damage has implications for theories of localization and failure in ductile rock.

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

Knowledge of *in situ* stress is becoming increasingly important in current trends toward a multidisciplinary approach to reservoir characterization and in the development and completion of oil, gas, and geothermal reservoirs. Anelastic strain recovery (ASR) measurements of oriented core is a technique which can, in some cases, provide important information on the stress state of a reservoir. A basic assumption of the ASR method of stress determination is that the recovery behavior of the core is related only to the present *in situ* stress state and does not involve the deformation history of the rock. In more complex geologic environments recovery may also be a function of a deformation fabric or residual strains stored in the rock. Application of the ASR method to stress measurements in complex geologic environments requires that we understand the deformation mechanisms involved in the recovery process. Time-dependent microcrack growth has been suggested as a possible mechanism for the strain recovery process. This hypothesis contends that a core will expand the most by microcracks opening in the direction of maximum strain relief. To test this hypothesis, acoustic emissions and compressional wave velocity measurements were monitored during anelastic strain recovery measurements on sandstone, siltstone, and chalk cores immediately after the cores were retrieved from 2.7 to 3.2 km deep boreholes. Strain recovery occurred in all of the cores and acoustic emissions were always detected during recovery. The acoustic emission rate decreased exponentially with time, similar to the strain relaxation behavior of the cores, and acoustic emission activity ceased when strain relaxation no longer occurred. The cumulative number of acoustic emission events was linear with volume expansion of the cores. No significant decrease in velocity occurred during strain relaxation monitored 6-52 hours after the cores were cut, because the strains were small (less than 300 microstrains). However, laboratory measurements of compressional velocity on relaxed, air dried cores show a well-defined anisotropy in low porosity cores, which had a strong preferred orientation of the principal recovery strains. The slowest velocity was a direction of maximum expansion. The field and laboratory results suggest that a statistically aligned microcrack population evolves during strain relaxation, with microcracks opening more in the direction of maximum strain recovery. It is proposed that the degree of anisotropy is dependent on the relative difference in the magnitude of the *in situ* principal stresses and corresponding strain relaxation, as well as the degree of heterogeneity of the rock. In high porosity rocks, the fractional increase in porosity due to relaxation microcracks is much smaller. Therefore, differential expansion of a core, due to opening of relaxation microcracks with preferred orientations, does not produce a measurable anisotropy.

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, in turn, a possible way to estimate the hydraulic properties both quickly and inexpensively. This work focuses on the

physics of transport of fluid and electric current through fractures and the scale dependence of these properties and has three main components: 1) 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, 2) 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, 3) evaluation of the results of numerical simulations with the goal of reducing the description of the transport properties of fractures to a minimum number of free parameters. In support of the laboratory studies, a surface profiler and a rock core permeability system have been built. Numerical simulations of conduction of fluid and electricity through a fracture were evaluated in terms of the equivalent channel model, effective medium theory, and real-space renormalization transformations. Effective medium theory was found to give an excellent approximation to both the hydraulic and electrical conductivities over a wide range of separations of the fracture surfaces. The success of this theory is significant. When effective medium theory is combined with an analysis for the contact of two mirror-image fractal surfaces under shear offset, the result gives the explicit general dependence of both the hydraulic and electrical conductivities of a single fracture on surface roughness, sample size, and shear and normal displacements across the fracture.

E. Reservoir Characterization: Reef Type Reservoirs (*V. L. Dugan [505-844-8735], G. J. Elbring, and W. C. Luth*)

A suite of crosshole seismic data sets will be collected across a reef-type oil and gas reservoir in northern Michigan. These data will include directly generated, rather than converted, compressional (P), vertically-polarized shear (SV), and horizontally-polarized shear (SH) wave data sets. Sandia's primary task for FY89 and FY90 will be the development of the existing downhole SV source for the expected borehole conditions and the machining and field testing of a new downhole SH source. Collection of the crosshole SV and SH wave data sets will be done jointly by Sandia and MIT near the close of FY90.

Data reduction and interpretation of these data sets will begin shortly after the data are collected. Collection of the crosshole P-wave data is scheduled for late in FY92 with data reduction and interpretation to follow. Interpretation of these data sets, primarily using tomography methods under development at MIT, will provide not only improved spatial resolution over surface seismic methods but also better information on the properties (e.g. anisotropy, fluid contacts) of the reservoir itself through the comparison of the data from the three different wave types.

F. Advanced Concepts (*W. C. Luth [505-844-3690]*)

Research conducted in 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.

Chemical Kinetics and Fluid Transport in Mineral Dissolution/Precipitation
(*M. E. Thompson and W. H. Casey*)

The transport of solutions through fractured and porous rock is common in many low to moderate temperature processes relevant to hydrocarbon resources, chemical and nuclear waste disposal,

and geothermal energy extraction. Mineral dissolution/precipitation processes in these solutions are controlled by both chemical kinetics and the dynamics of the flow field. A combination of experiments and computer modeling will be used to determine dissolution/precipitation rates as a function of flow conditions and solution parameters. The primary geometry to be investigated is that of an open two-dimensional fracture. The model and experiments will then be extended to flow through a bounded porous channel. The initial experiments will focus on dissolution/precipitation of calcite, which is likely to be surface reaction controlled at low temperature and transport controlled at higher temperature. Current efforts are focused on the development and testing of a series of computer codes for solution of two-phase moving boundary problems in both one- and two-dimensions. The codes are capable of incorporating thermal and mass diffusion in each of the phases as well as complex boundary conditions at the interface. Results indicate that the invariant imbedding techniques are well suited for modeling mineral dissolution and growth in natural systems.

Organic-Inorganic Diagenesis, Piceance Creek Basin (*L. J. Crossey [University of New Mexico] and C. L. Stein*)

Diagenetic reactions play a major role in the redistribution of porosity within sand/shale sequences undergoing progressive burial. A major goal of this study is to assess the hypothesis that porosity evolution of sandstones in the Mesaverde formation has been influenced by the catagenesis of adjacent organic-rich material. Thirty pairs of samples have been collected from core obtained in several sedimentary environments represented in the Mesaverde formation of the Piceance Creek basin. Sample selection criteria included published environmental designators for the Mesaverde formation and specific spatial relationships between sandstone lithologies and finer-grained material relatively rich in organic matter. Petrographic analysis of the sample pairs is currently in progress. Techniques being applied include cathodoluminescence, scanning electron microscopy, and electron microbeam analysis. Analytically determined hydrogen indices are being acquired to evaluate the sources of the organic matter and the degree of thermal exposure during burial.

NMR Spectroscopic Analysis of Experimentally Shocked Quartz (*R. T. Cygan*)

The purpose of this study is to measure changes in quartz disorder and diaplectic glass formation as a function of shock pressure and to determine the existence of minor high-pressure crystalline phases (coesite and stishovite). Nuclear magnetic resonance (NMR) is being used to investigate synthetic quartz recovered from experimental shocking in the Sandia "Bear" explosive loading facility. The solid state NMR experiments measure radiofrequency emissions from ^{29}Si nuclei that have been excited to higher-energy states by electromagnetic pulses while the sample is located in a very strong magnetic field. Magic-angle sample spinning (MASS) reduces part of the peak broadening usually associated with solid samples. Chemical and structural information (coordination, bond length, and bond angle distribution) can be obtained from the spectral characteristics, thereby providing a quantitative measure of shock-induced chemical changes. Our results to date suggest that the MASS-NMR technique can be used as a shock pressure and temperature gauge for quartz-containing rocks subjected to natural impact or nuclear explosion shocks.

Contractor: SANDIA NATIONAL LABORATORIES
Albuquerque, New Mexico 87185

Contract: DE-AC04-76DP00789

Category: Geochemistry

Person in Charge: W. C. Luth

A. Magmatic Volatiles (*T. M. Gerlach, J. C. Eichelberger, H. R. Westrich, and H. W. Stockman [505-844-5929]*)

This project is intended to provide understanding of the role of volatiles in shallow magmas of volcanic environments. The research is focused on determining the *in situ* volatile contents of shallow magmas, the mechanisms and rates of their exsolution, trace metal transport in volcanic gases, and the chemical and isotopic trends that characterize escaping gases at various stages of the degassing process. Investigations include development of on-site fumarole data acquisition capabilities, laboratory techniques to measure the chemical and isotopic compositions of volatiles in natural glasses and glass inclusions, experimental procedures to examine the kinetics of vapor exsolution (i.e., bubble nucleation and growth), low pressure bubble resorption and crystal growth in silicate melts at elevated pressures, and models for the mechanics of eruptive vesiculation and outgassing. One of the long range goals of the work is to understand the physiochemical processes controlling volcanic eruptions. Recent work has focused on problems of bubble resorption in obsidian at low pressures, bubble nucleation and growth rates in hydrous rhyolites at elevated pressures, the isotopic composition of carbon in Kilauea basalts, pre-eruptive volatile contents of rhyolitic magmas, and degassing of volatiles during magma ascent and eruption.

B. Organic and Inorganic Diagenetic Process (*H. Casey, H. R. Westrich, R. T. Cygan, [505]846-0196*)

The chemical composition and evolution of solutions in the Earth's crust involves reactions related to the formation, alteration, or dissolution of common, rock-forming silicate minerals such as feldspar and quartz. The overall goal of this project is to understand the dissolution mechanism(s) of silicate minerals in aqueous solutions. Part of the research consists of a series of carefully controlled experiments designed to measure the dissolution kinetics of quartz and plagioclase feldspar over a wide range of P-T-X conditions, using apparatus ranging from a room temperature, shaking-bath to a hydrothermal, rotating-disc autoclave. The remainder of the research involves careful post-reaction characterization of single crystals of quartz or plagioclase feldspar by a variety of analytical techniques, including methods for surface analysis, bulk chemistry and crystalline structure, and optical spectroscopy. When coupled with careful experimental control of pertinent physiochemical parameters, these analytical techniques can be used to determine the dissolution mechanism and provide the basis of a theoretical model for experimental testing. Recent work has focused on the hydrolysis of plagioclase feldspars at low temperatures (<45°C) in solutions of a wide pH range (1-13), hydrothermal dissolution of quartz and mica at 400 bars at temperatures of 200-450°C, and low temperature hydrolysis of other minerals such as diopside (magnesium silicate) and pyrite (iron sulfide).

Contractor: SANDIA NATIONAL LABORATORIES
Albuquerque, New Mexico 87185

Contract: DE-AC04-76DP00789

Category: Energy Resource Recognition, Evaluation, and Utilization

Person in Charge: W. C. Luth

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

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 field testing of thermopile heat flux sensors, oriented fluid flow sensors, and downhole fluid samplers. 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 partially field tested. These sources provide control of energy content and frequency of the downhole seismic signal. These instruments are being used in both hole-to-hole and hole-to-surface seismic experiments. In addition to the instrumentation and field experiments, some effort is being applied to research on methods to interpret the data. Current research is concentrated in these areas: 1) a third generation downhole, controlled, seismic shear-wave source is being field tested, 2) a second generation Darcy velocimeter for porous geologic media has been fabricated and bench tested and is being prepared for the first field test, 3) a new type of geologic heat flow sensor that is capable of making triaxial heat and fluid flow measurements is currently undergoing long-term field tests, 4) a fluid sampler has been developed for obtaining downhole samples of fluids and gases in hot thermal wells, and 5) a high temperature (800°C) thermal probe and associated cable and handling equipment have been developed for logging high temperature holes.

B. Inyo Domes Research Drilling Project (*J. C. Eichelberger, H. R. Westrich, and H. W. Stockman [505-846-0398]*)

Research drilling was conducted at the Inyo domes chain in order to provide new information about the behavior of silicic magma as it intrudes the upper crust. The approach was to sample the intrusive structures beneath a very young and well understood volcanic system. Such information is fundamental to determining the causes of eruptive phenomena and the development of igneous-related geothermal systems. It is also applicable to the problem of man-made perturbations of crustal regimes. The Inyo domes chain was chosen for this first drilling investigation of young igneous intrusions because it is the youngest rhyolitic system in coterminous United States. As a consequence of its 600-year age, the geologic record of the Inyo eruption is well-preserved and chemical alteration of the system, particularly of the volatile-bearing glasses, is minimized. Recognition that the 10-km-long line of vents was simultaneously active led to the hypothesis that the eruption was fed from a dike at shallow depth. The line of

vents runs northward from the west moat of Long Valley caldera out into the Sierra block. Holes were slanted under the vent line both inside and outside the caldera to test the dike hypothesis and to evaluate the effects of intra- and extra-caldera environments upon magmatic behavior. Differences evident at the surface are the development of large lava domes outside the caldera and large phreatic craters and normal faults inside the caldera, along the Inyo trend. Four holes were cored to an aggregate depth of 2.2 km. They confirmed the existence of a dike-like structure beneath the trend but revealed unexpected chemical complexity inconsistent with a single, simple dike. The holes also provided evidence for an origin of obsidian flows by degassing and collapse of magmatic foam, indicated a strong control of degassing upon subsequent crystallization, supported the concept that interaction of magma with ground water in the caldera fill led to the crater eruptions at the southern end of the chain, tightly constrained the western structural boundary of Long Valley caldera, and showed that igneous chemical zonations can develop by viscosity segregation during flow. Inyo drilling was from 1983 to 1987. Documentation of results was largely completed in 1989.

C. Katmai Research Drilling Project (*J. C. Eichelberger, C. R. Carrigan, S. Ballard [505-846-0398]*)

The Katmai project continues the line of investigation begun at Inyo domes, but in an igneous system so young that it is still hot and so large that important fumarolic transport of metals occurred. The target for drilling is the vent and ash-flow sheet of the 1912 eruption on the Alaska Peninsula, by far the largest eruption of this century. The holes are intended to provide complete sections through the 200-m-thick ash-flow sheet (the Valley of Ten Thousand Smokes) and the tephra filling the 2-km-diameter vent and to recover samples of the vent wall, late shallow intrusions, and deep intrusive equivalents of the pyroclastic eruptives. The objectives are to determine the behavior of magma during a major explosive eruption, to understand the source and mechanism of fumarolic transport of metals, and to measure the rate at which the system is cooling. The simplicity of the Katmai eruption makes it ideal for achieving these objectives. Results may find application in problems of assessing volcanic hazards, utilization of ore deposits and geothermal systems, and predicting the thermal consequences of radioactive waste disposal. Presently, the character of the 1912 vent is known primarily through interpretation of a concentric fracture system at the eruptive center. A multi-institutional field effort in 1989 seeks to define the subsurface vent structure through coordinated geophysical investigations.

D. Geoscience Research Drilling Office (R. K. Traeger [505-844-2155] and P. Lysne)

The GRDO is responsible for implementing the OBES/Geoscience efforts in the Continental Scientific Drilling Program. This implementation involves budgetary and field responsibility for the drilling operation and it often involves a continuing effort for sometime after the drilling itself. In the past year, the GRDO supported the VC-2B operations (see detail in other portions of this report). In this program, the GRDO designed the hole and it contracted for the drilling and other site-related services. It also provided downhole logging services to support the scientific and drilling activities. Other GRDO activities in the year involved a cost analysis of the Katmai project. The GRDO also maintains an instrumentation capability to support the drilling efforts, and this year saw an improvement in our high-temperature measurement capabilities. Personnel in the GRDO are also working on the calibration of neutron porosity tools in support of the VC-2B effort.

PART II
OFF-SITE

67/68

Grantee: UNIVERSITY OF ALASKA
Geophysical Institute
Fairbanks, Alaska 99775-0800

Grant: DE-FG06-88ER13530

Title: Magnetic Field Reconnection and Plasma Processes
in the Magnetosphere

Person in Charge: L. C. Lee and S.-I. Akasofu (907-474-7410)

Our proposed project is to study the basic plasma processes associated with magnetic reconnection in the Earth's magnetosphere. The three-dimensional (3-D) reconnection processes are emphasized. The results from this magnetosphere study are also applicable to plasma research in the other fields such as thermonuclear fusion research, solar physics, and astrophysics.

To explain the satellite observations of flux transfer events (FTEs), we have proposed a multiple X line reconnection (MXR) model for the dayside magnetopause. The same reconnection process may also explain the occurrence of geomagnetic substorms. The multiple X line reconnection is intrinsically a time-dependent process, featuring impulsive and intermittent magnetic reconnection. The study of driven magnetic reconnection process was further extended in the past year by our 3-D MHD simulations and 2-1/2-D electromagnetic particle simulations.

It is observed in the 3-D MHD simulations that magnetic reconnections may take place along the multiple X lines, resulting in the formation of helical magnetic flux tubes, confirming our theoretical model of multiple X line reconnection in the real 3-D environment. The geometry of the reconnected field lines revealed in the 3-D simulations is found to be much more complicated than anticipated. Strong plasma flows along the flux tubes are another feature observed in the simulations. The results suggested that the 3-D reconnections differ significantly from the 2-D reconnections. In the particle simulations, both the time-dependent MXR, characterized by the repeated formation and convection of magnetic islands, and the quasisteady single X line reconnection (SXR) can be observed depending on the driven boundary conditions. Energetic particles, bursty high-speed plasma flows, intense plasma waves, and particle heat fluxes are found to be generated during the driven reconnection process. The power spectra of electric and magnetic fluctuations are found to be comparable to those observed during FTEs at the dayside magnetopause. The preliminary simulation results obtained with an asymmetric current sheet configuration show resemblance of the layered structure associated with FTEs.

In addition, we also studied the characteristics of slow shocks, which have been observed by ISEE-3 satellite. The slow shocks are formed as a consequence of magnetic reconnection in the magnetotail. Our MHD simulations show that the properties of slow shocks vary as a function of the distance from the reconnection line (X line). Slow shocks in most regions of the magnetotail are found to be non switch-off shocks. Our 1-D particle simulations indicate that only switch-off shocks exhibit large-amplitude rotational wave trains, while non switch-off shocks do not. The present results can explain the lack of large-amplitude rotational wave trains at slow shock in the deep magnetotail. The lack of rotational wave trains in slow shocks observed by ISEE-3 also indicates that slow shocks in most regions of the magnetotail are non switch-off shocks.

Grantee: AMERICAN GEOPHYSICAL UNION
2000 Florida Avenue, N.W.
Washington, DC 20009

Grant: DE-FG05-89ER14010

Title: A.G.U. Chapman Conference on the Causes and Consequences
of Long-Term Sea Level Change (1-100 m.y.)

Person in Charge: A. F. Spilhaus, Jr. and B. Weaver (202-462-6900)

We are convening an American Geophysical Union Chapman Conference on long-term sea level changes with regard to measurement, causes, and consequences of sea level change. Chapman Conferences are topical meetings designed to permit organized and in-depth exploration of specialized subjects in a manner seldom possible at larger meetings. They encourage disciplinary and interdisciplinary focus on special problems and provide timely encouragement to the development of newly emerging research fields and problem areas. They generally draw around 125 participants, which facilitates informal discussions and subsequent further communication. Chapman Conferences promote communication and interaction between participants who are often in related but separate fields. The series was inaugurated in 1976 in honor of Sydney Chapman (1888-1970).

Grantee: UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

Grant: DE-FG02-88ER13670

Title: Solar Variability Observed Through Changes
in Solar Figure and Diameter

Person in Charge: H. A. Hill (602-621-6782)

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 constant. This approach to studying luminosity changes offers a viable alternative to the difficult task of obtaining reliable radiometric data over a period of decades. The primary observations are time series of diameter measurements lasting up to 12 hours per day. These observations are capable of detecting fractional changes in a solar diameter that are accurate to parts per million over climatically significant time periods. New observations were obtained in 1988 and 1989.

The 1973, 1979, 1981, 1983, 1984, 1986, 1987, and 1988 observations have been analyzed for changes in the limb darkening function. These variations reflect changes in the temperature gradient at the bottom of the solar atmosphere. Significant changes were detected; they correlated with changes in satellite observations of total irradiance. The correlations allow for a calibration of changes in the limb darkening function in terms of changes in total irradiance. Using this calibration and the referenced changes in the limb darkening function, it is inferred that the solar constant may have decreased a few tenths of a percent over the last 16 years; the time scale for these changes is considerably longer than the 11-year solar cycle.

Further work on gravity modes of the Sun has produced additional evidence of mode coupling in the solar interior. The total number of identified modes of this type increased more than fivefold. Mode coupling is relevant to an understanding of luminosity variations because it indicates that these modes may alter the neutrino and fusion energy production rates in the core of the Sun.

In another development, apparent changes in the equilibrium conditions of the solar convection zone were detected. These changes occurred over a six-year period and were inferred from changes in the frequencies of long period solar oscillations. Evidence of these oscillations was found in the solar diameter observations. Changes in the convection zone may also correlate with luminosity changes.

Grantee: BROWN UNIVERSITY
Department of Geological Science
Providence, Rhode Island 02912

Grant: DE-FG02-88ER13665

Title: Thermal Regimes of Major Volcanic Centers:
Magnetotelluric Constraints

Person in Charge: J. G. Hermance (401-863-3830)

Our research employs natural electromagnetic methods and other geophysical techniques to study major volcano-tectonic centers such as the Long Valley/Mono craters volcanic complex, the Cascades volcanic belt, and the Rio Grande rift. Because the electrical resistivity is so sensitive to the presence and composition of fluids in rocks, this work places fundamental constraints on the role that fluids play in (a) the transport of mass and energy in the deep crust and upper mantle, (b) the creation and maintenance of magma/hydrothermal reservoirs, (c) the transport of minerals in the crust, and (d) the emplacement of ore deposits. In addition, since we have worked in several of the intermontane sedimentary basins of the western US, as well as in the Triassic Hartford basin in the Connecticut valley, there is an application of these studies to developing exploration strategies for delineating structures related to hydrocarbon reserves.

One of the principal tectonic elements in the Long Valley volcanic complex is a deep, basin-like caldera bounded by steeply dipping normal faults having characteristic offsets of several kms that appear to control recent patterns of seismicity and volcanism. We found that the major boundary faults in the northwest sector of the caldera were buried beneath intracaldera fill several kilometers inside the physiographic boundary of the caldera. Moreover, from a closely spaced profile of MT sites in the south moat, we now have clear evidence for a zone of high conductivity at depths of 5 - 8 km beneath the caldera.

Employing a new generalized 2-D electromagnetic inverse algorithm, the recent interpretation of magnetic variation data from the Oregon Cascades revealed several sedimentary structures of interest, as well as an intra-crustal conductor at a depth of approximately 15 km beneath the Basin and Range province at the east end of our profile. This feature extends laterally to the west beneath the High Cascades, terminating below the older Cascades Range. It appears that modern Basin and Range structure is being imprinted on pre-existing Cascades structure.

During 1988 we undertook a new research initiative in the Rio Grande rift near Socorro, NM, where seismic anomalies and recent uplift suggest the presence of a lens of magma at mid levels in the crust. A sequence of wide-band (10 - 4000s), remote-referenced magnetic variation measurements along an E-W profile centered on this anomaly revealed the following features: first, a concentrated zone of high conductivity at shallow to mid levels in the crust, which appears to be associated with a zone of microseismicity; second, a conductor in the deep crust subtending the area on the east end of the profile, which bears a striking similarity to features seen elsewhere along the rift; third, a resistivity structure beneath the western end of our profile, which has properties remarkably similar to those reported for the Colorado Plateau.

Grantee: CALIFORNIA INSTITUTE OF TECHNOLOGY
Seismological Laboratory, Division of
Geological and Planetary Sciences
Pasadena, California 91125

Grant: DG-03-87ER13422

Title: *In situ* Stress in Deep Boreholes

Person in Charge: T. J. Ahrens (818-356-6906)

This research is concerned with the development of a new method of measuring *in situ* stress in deep, fluid-filled boreholes. All six components of the *in situ* stress tensor are obtained with this method, which does not assume that the principal stresses are oriented horizontally and vertically. Interference holography is used to measure the displacements of the borehole wall that occur when small, stress-relieving sideholes are drilled. Holograms taken through the clear filtered borehole fluid at a given depth are analyzed to yield the stress tensor. This method will have application in the oil and gas industry, as knowledge of the *in situ* stress is vital to effective hydraulic fracture simulation. Other applications include geothermal resource exploitation and monitoring of underground mines and structures, including radioactive and chemical waste isolation facilities.

During the last year most of our experimental effort has gone into the rigorous testing of the now-completed 6-in. holographic stressmeter apparatus. This 475-lb. instrument, consisting of computer controlled mechanical, optical, electronic, and hydraulic components, is capable of measuring the state of stress from uncased, fluid-filled boreholes at depths of several kilometers. This instrument can be deployed in boreholes having a diameter of 6 to 7 in., a substantial reduction in size over the only previous holographic stressmeter, which required a hole diameter of 12 in. or more and could only be used in dry boreholes. Other important features of this instrument are gas pressurization that maintains the optical and electronic cavities of the instrument at pressures equal to the ambient pressure in the borehole, a mudcake removal and water flushing system to make the fluid optically clear, a television system for monitoring the progress of the experiment, and the ability to measure the *in situ* elastic modulus as a function of depth by an indentation technique.

The analysis of the holographic data requires a knowledge of the displacement field that is produced by the drilling of the stress-relief sidehole on the borehole wall. Previous work has used a two-dimensional thin-plate model. Two-dimensional finite element calculations suggested that this approach may be inadequate, especially in the region immediately surrounding the stress relief hole. Moreover, work with the 12-in. version of the stressmeter has resulted in some holograms, from regions of low borehole wall stress, that had been impossible to model with the simple plate theory. Therefore, following the approach of Youngdahl and Sternberg, we developed and implemented a model for analysis that considers a cylindrical hole in an elastic, isotropic half-space. The numerical solution shows the existence of the three-dimensional stress boundary layer near the edges of the hole in the related problem of a plate of finite thickness, as the ratio of the thickness of the plate to the diameter of the hole increases. This model was used to analyze the holograms obtained from field deployment of the 12-in. stressmeter. The new model, while it gave generally the same values of the *in situ* stresses, significantly reduced the errors associated with those values and greatly improved and facilitated the analysis of the holographic data.

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)

Infrared spectroscopic studies have shown that "water" dissolves in silicate melts and glasses both as molecules of water and as hydroxyl groups. The fact that water dissolves in amorphous silicates as at least two distinct species raises interesting issues in isotopic geochemistry. For example, is there a hydrogen isotopic fractionation between the molecular water and hydroxyl groups in glasses and melts? If so, is it temperature or composition dependent? The answers to these and related questions would contribute to our understanding of the basic physical chemistry of hydrogen in silicate melts and glasses, could be applied to geothermometry of volcanic glasses, and would provide data essential to understanding the evolution of volcanic systems and their associated hydrothermal circulation systems. These results could also be valuable in applications of glass technology to development of nuclear waste disposal strategies.

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 H₂O) and hydrous vapor. Knowledge of these fractionations is critical to understanding the behavior of hydrogen isotopes during igneous processes.

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

We are also studying the concentrations of water and carbon dioxide in glass inclusions in phenocrysts from the Bishop tuff. The eruption of the Bishop tuff magma about 700,000 years ago led to the formation of Long Valley caldera in central California. We have discovered that water and carbon dioxide contents in these inclusions are inversely correlated. Moreover, the inclusions from the Plinian deposits, which are believed to have sampled the coolest, earliest erupted, and shallowest portion of the magma chamber, are generally richer in water and poorer in carbon dioxide than the inclusions from the later ash-flow deposits from the hotter, last erupted, and deeper portions of the magma. Crystallization of a vapor-saturated magma, in which the water-rich, carbon dioxide-rich 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.

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)

Studies in this laboratory have shown that, using improved sensitivity, it is possible to measure, by thermal ionization mass spectrometry, $\sim 5 \times 10^9$ atoms of ^{234}U or ^{230}Th to better than 5%. These new techniques for U and Th isotope ratios with 10^9 atoms have greatly improved the precision of the data and allow the application of the U-Th disequilibrium systematics to many investigations for which the α -counting techniques lack sensitivity. We are applying these techniques to the dating of corals in areas of neotectonic activity and have initiated applications to the study of deep, high pressure aquifers. A study of recent, well-documented corals from Vanuatu has been published that a) provides dates consistent with the proposed co-seismic emergence of adjacent corals and b) permits an estimate of a seismic recurrence interval of 108 ± 4 yr for one island and of 236 ± 3 yr for a second island.

A study of U and Th in a suite of saline ground waters from central Missouri has attempted to establish the characteristic behavior and time scales of nuclide transport in sedimentary aquifers. Waters with salinities of 1 - 30‰ discharge from Mississippian carbonates and Ordovician carbonates and sandstones in the form of natural springs and artesian wells. The spring waters have not been exposed to sources of anthropogenic contamination (e.g., drilling fluids, well casings). The more saline samples have higher $^{234}\text{U}/^{238}\text{U}$ activity ratios and lower $\delta^{18}\text{O}$ and δD values. These results preclude an ancient sea water source for the salinity in the waters and are consistent with a hydrologic model involving relatively old, far-traveled saline water and leaching of ^{234}U from α -recoil-damaged sites in aquifer minerals. Th measurements show that sorption processes involving colloids and mineral grain surfaces in the aquifer dominate in controlling Th concentrations in the waters. A model involving the derivation of the excess ^{230}Th through the *in situ* decay of ^{234}U gives maximum average residence times of 30 - 580 yr for Th in solution.

In cooperation with the Materials Science and Chemistry Divisions at the Argonne National Laboratory, we have initiated a study of the resonance photo-ionization of Os and Re for trace *in situ* analyses. A pulsed primary Ar^+ ion beam provides sputtered atoms for resonance ionization. This allows a close match in duty cycle between the pulsed primary beam and the laser pulses. A photo-ionization scheme has been developed that allows the detection of Os with a 10^{-2} efficiency, which represents at least two orders of magnitude of improvement over other techniques. The resulting sensitivity for *in situ* analyses of Os is 4 parts per billion. These developments will now be applied to the measurement of the concentration and distribution of Pt-group elements and of Os isotope ratios in natural samples.

Grantee: UNIVERSITY OF CALIFORNIA
Department of Geology and Geophysics
Berkeley, California 94720

Grant: DE-FG03-88ER13419

Title: Diffusion/Dispersion Transport of Chemically
Reacting Species

Person in Charge: H. C. Helgeson (415-642-1251)

The project goal is the quantitative understanding of chemical mass transport attending fluid flow and water-rock interaction in geochemical processes. We have focused on development of comprehensive mass transport models and characterization of the thermodynamic and transport properties of hydrothermal fluids. Recent research has focused on thermodynamic description of two geochemical systems: 1) concentrated aqueous electrolyte solutions at supercritical conditions and 2) the major organic compounds found in petroleum at temperatures to 350°C.

Calculation of accurate mineral solubilities in hydrothermal solutions requires knowledge of the thermodynamic properties of the predominant aqueous complexes. The solute in many hydrothermal brines consists primarily of alkali metal halides. Activity coefficients of the neutral ion pairs of these halides are commonly assumed to be equal to one. However, analysis of literature conductance data for dilute NaCl, NaBr, NaI, HCl, and HBr solutions suggests that the activity coefficients of neutral ion pairs in hydrothermal solutions may vary significantly from unity. The conductance data were used to generate revised dissociation constants for neutral 1:1 complexes (K_1), limiting equivalent conductances, and Setchénow coefficients. The behavior of the computed Setchénow coefficients and of $\log K_1$ suggests that neutral ion pairs may not be as abundant in concentrated supercritical electrolyte solutions as is commonly thought.

Molal stepwise dissociation constants for triple ions (K_2) of 14 alkali metal halides (e.g., Na_2Cl^+) were computed for temperatures from 400° to 800°C at pressures from 500 to 4000 bars with the aid of electrostatic theory. Species distributions calculated with these values, $\log K_1$ values, and activity coefficients for relevant species taken from the literature indicate that triple ions predominate in low-pressure supercritical aqueous solutions at total concentrations ≥ 1.0 m. Supercritical aqueous solutions of the alkali metal halides thus are apparently dominated successively by single ions, neutral ion pairs, and triple ions with increasing solute concentration. As a consequence, polynuclear complexes, such as KNaCl^+ , MgKCl_2^+ , ZnNaCl_2^+ , FeKCl_2^+ , etc. may have a significant effect on the solubilities of minerals in concentrated hydrothermal brines for many geochemical processes.

Preliminary calculations indicate that the thermodynamic properties of organic compounds at elevated temperatures can be used to characterize the interaction of petroleum with minerals and oil field brines. These properties have been computed for selected normal, branched and cyclic alkanes, alkenes, aromatics, naphthalenes, alcohols, ketones, organic sulfides, and amino and carboxylic acids. The results have been used to predict the aqueous solubilities of organic species in petroleum at temperatures prevailing in hydrocarbon reservoirs. The importance of oxidation-reduction reactions among hydrocarbons and aqueous species is being assessed for processes responsible for the origin, transport, and deposition of oil and gas in hydrocarbon reservoirs.

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

Grant: DE-FG03-88ER13667

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

Person in Charge: J. H. Reynolds (415-642-4863; 642-2260)

The RARGA laboratory studies noble gas systematics in fluid reservoirs. Although we continue to work on active hydrothermal systems, we recently concentrated on CH₄, CO₂, or H₂ natural gas reservoirs within the continental regime. Of interest is the source and subsequent migration of various noble gas components (e.g., mantle, crustal, etc.) sampled in the present-day integrated gas trap. It is well documented that many CO₂ wells contain excess ³He (R/Ra >1.0; Ra is the ³He/⁴He ratio in air), anomalous neon, and excess ¹²⁹Xe, all of which combine to indicate a MORB source. In CH₄-rich fields, the ³He/⁴He ratios typically are low (R/Ra <0.1) and consistent with a radiogenic or crustal origin. Just as many fields, however, have ³He/⁴He ratios >0.1 Ra and therefore outside the canonical range for average crustal radiogenic helium. If the mantle is providing high ratios, then in Alberta, Texas, and Oklahoma migration has sometimes spanned large distances. By combining noble gas data with Li, U, Th, and K in source and reservoir rocks, the potential for enhanced local ³He production in Li-rich environments and noble gas elemental fractionation during migration from source to reservoir (e.g., ⁴⁰Ar*/⁴He and ¹³⁶Xe*/⁴He not consistent with local K/U+Th ratios) can be evaluated. Natural gases from both Alberta and the Tucumari basin in SE New Mexico contain isotopically similar nucleogenic neon (α -capture reactions with nuclei of oxygen and fluorine). A source F/O ratio significantly greater than average crust is required. The identification of a well-defined crustal (nucleogenic) neon component will be a useful tool in tagging crust-derived gases in reservoirs where the two-isotope helium system is ambiguous. Isotopically, crustal neon is significantly different from mantle neon.

Our group studies fluid inclusions in metamorphic minerals using a sensitive mass spectrometer coupled with a laser microprobe. The objective is to develop a new technique for analysis of the chemical and noble gas content of microscopic inclusions of fluid in ancient hydrothermal systems. Present scope of the work involves: 1) Reduction of the blank in a noble gas mass spectrometer to a level low enough to analyze individual and small groups of fluid inclusion in synthetic and natural samples. 2) Preparation of synthetic fluid inclusions by fracturing pure quartz, immersing it in a standard salt solution in a sealed platinum vessel, and heating the vessel under pressure until fractures "anneal," thereby trapping small amounts of the solutions along the fractures. Such quartz cylinders are then cut and polished following the same procedure used for natural samples and their composition checked by petrographic techniques. Synthetic samples are neutron-irradiated along with natural specimens and neutron flux monitors. 3) Establishing the detection limit for Ar, Kr, and Xe plus I, Br, and Cl from these synthetic fluid inclusions. Early results indicate that we can detect and measure Cl, Br, and I (from ³⁸Ar, ⁸²Kr, and ¹²⁸Xe produced by neutron irradiation), as well as naturally occurring isotopes of Ar, Kr, and Xe, in 5 x 10⁻¹¹ liters of 1 molal Cl solution, spiked with 76 ppm and 96 ppm of I and Br, respectively.

Grantee: UNIVERSITY OF CALIFORNIA, 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 (213-825-3880)

The region of concentration is the Sawyers Bar area of the so-called Western Triassic and Paleozoic Belt (WTrPZ). The mapped region constitutes the lithotectonic belt of rocks 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 2000-7500 feet. Much of the area is heavily vegetated and weathered, hampering the mapping effort. Most of the investigated tract consists of ophiolitic oceanic crust and calc-alkaline arc rocks of the WTrPZ belt, but the southeasternmost part contains subduction zone units of the Stuart Fork terrane. Nevadan age granodioritic stocks subsequently invaded the complex on both the west (English Peak pluton) and southeast (Russian Peak pluton).

The WTrPZ in this area consists of units of the North Fork and possibly, on the west, the Hayfork formations. More than 550 thin sections have been studied petrographically, and 160 rocks analyzed by XRF for major element concentrations. Mineral separations have been initiated with the hope of providing suitable materials for radiometric and $^{18}\text{O}/^{16}\text{O}$ 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 consisted of predominant oceanic tholeiites associated with minor siliceous and graywacke-type clastic sediments. Lithologic contrasts between the Stuart Fork and North Fork terranes are subtle but tectonically important. These two pre-existing complexes were brought together by convergent plate motion along the accreting North American continental margin after the Triassic subduction event reflected in the Stuart Fork formation and (early Mesozoic) deposition of the Western Triassic and Paleozoic belt rocks. The greenschist facies metamorphism, which affected both lithotectonic units, seems to have preceded the local development of contact aureoles that accompanied the Late Jurassic emplacement about 160 Ma of the calc-alkaline plutons of English Peak and slightly older Russian Peak.

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

Grantee: UNIVERSITY OF CALIFORNIA, 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 or -4501) and
A. E. Williams (714-787-4611 or -4501)

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 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. Additionally, fluid inclusions in active systems are relatively unmodified by later tectonic and metamorphic events that can complicate studies in fossil hydrothermal systems. 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 are conducting a calibration-oriented study of the gas contents of fluid inclusions in vein minerals from three active geothermal systems having diverse fluid chemistries: Salton Sea, Coso Hot Springs, and Valles caldera. We will determine the major inorganic and short-chain hydrocarbon gas contents of fluid inclusions in veins and pore cements by using quadrupole mass spectrometric monitoring during mechanical and thermal decrepitation.

In addition to checking the mass spectrometric data against analyses of fluids from geothermal wells, the technique will also be calibrated by analyzing synthetic fluid inclusion having compositions appropriate to both saline (Salton Sea) and dilute (Coso, Valles caldera) hydrothermal fluids. Finally, our results will be cross-checked by interlaboratory comparison with other researchers using mass spectrometric, Raman laser, and infrared analytical techniques.

Grantee: UNIVERSITY OF CALIFORNIA, SAN DIEGO
Institute of Geophysics & Planetary Physics
Scripps Institution of Oceanography
La Jolla, California 92093

Grant: DE-FG03-87ER13779

Title: Two-Dimensional Modeling and Inversion of
Electromagnetic Data

Person in Charge: A. D. Chave and S. C. Constable (619-534-2409)

It has become relatively routine to collect high quality magnetotelluric (MT) and DC resistivity data along traverses consisting of 20 to 50 stations, for the purposes of studying the electrical structure of the Earth from 10s of meters to 100s of kilometers deep. While many data sets of this kind are accumulating, our ability to model them is rudimentary. Two dimensional (2D) forward modeling schemes are available, but they are limited in speed and accuracy. Inverse modeling schemes are virtually nonexistent. The usual approach is to create a 2D model consisting of a few tens of conductivity regions and use trial and error or damped least squares to fit the data by adjusting the conductivities of the regions. Since the boundaries in the model are chosen *a priori*, one could argue that this approach does little to improve our understanding of the Earth.

This project is a collaboration between B. J. Travis of Los Alamos National Laboratory and the principal investigators to produce a fast and accurate 2D MT forward code based on the method of moving finite elements and a regularized 2D inversion scheme to use this code in an objective manner to model field MT data. Computer codes addressing both aspects of the project are in the final testing stages.

For the forward code, an automatic mesh generator constructs a general triangular finite element mesh for a given conductivity model. During the solution of the 2D MT forward problem the node positions move automatically and adaptively to minimize the functional from which the finite element equations are derived. The effect is that the nodes move into regions where the electromagnetic (EM) field gradients are largest, thereby improving the accuracy of the solution. The use of modern matrix solution methods speeds the execution of the code, which runs and resides on a Cray XMP, taking a few seconds for a typical solution. The partial derivatives of the surface MT responses with respect to the conductivities of the model are also computed by the fast and accurate adjoint methods.

For the interpretation of MT and resistivity data, we have produced a 2D regularized inversion scheme. The model is composed of a regular array of many hundreds of conductivity regions, all of which are allowed to vary. However, the "roughness" of the model is measured by a 2-norm of the first or second spatial derivative, in both vertical and horizontal directions. In the inversion this roughness is minimized subject to the requirement that the model fit the data to within a statistically reasonable tolerance. Thus the model contains just enough structure to fit the data, but no more. The roughness penalty increases exponentially with depth to match the natural loss of resolution inherent in EM methods. The program, which currently resides on a Cray, Macintosh, and Convex, works excellently on (noisy) synthetic MT responses, and we have had initial success at inverting a field data set.

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

Grant: DE-FG03-88ER13267

Title: Long Valley Caldera: Monitoring Studies of Gas
Composition and He, Ar, and Carbon Isotopes

Person in Charge: H. Craig and D. R. Hilton (619-534-3260)

We have now completed a three-year intensive monitoring program of fumarole and hot spring gas chemistry at Long Valley caldera in the Sierra Nevadas. The study was initiated in response to earlier findings at the isotope laboratory linking variations in helium isotope ratios ($^3\text{He}/^4\text{He}$) to the presence of magma-based hydrothermal activity in the western United States. More detailed work on the Long Valley hydrothermal system in the early/mid 1980s revealed that variations in $^3\text{He}/^4\text{He}$ also appeared to be correlated, albeit crudely, with the pattern of seismicity--and by inference, magma movement, in the caldera. In an attempt to establish what relationship, if any, exists between variations in $^3\text{He}/^4\text{He}$ and the timing, magnitude, and location of seismic events in the area, we have focused on 6 sites within the caldera and immediate vicinity and sampled them a total of 12 times during the period 1986-88. Our analytical effort has centered on helium isotope ratios ($^3\text{He}/^4\text{He}$), because of their extreme sensitivity for monitoring the balance between magmatic and crustal additions to the volatile inventory; however, in an attempt to evaluate other geochemical parameters, we have also analyzed for major gas chemistry (CO_2 , O_2 , N_2 , Ar), other trace gases (CH_4), and the isotopic composition of carbon (CO_2 and CH_4) and argon ($^{40}\text{Ar}/^{36}\text{Ar}$).

Emphasizing the helium isotope results, the first point we note is that the $^3\text{He}/^4\text{He}$ ratio (R) is significantly greater than the atmospheric value (R_A) for all sites within the caldera and as far north as Mono Lake. This shows that the helium is predominantly magmatic in origin, like the associated source of heat. Secondly, if we assume that the initial magmatic helium isotope ratio is equal to that found in MORB ($R/R_A = 8$) and that crustally derived radiogenic helium is characterized by $R/R_A = 0.05$, then the proportion of magmatic helium at Long Valley varies between 78% at the Little Hot Creek locality ($R/R_A = 6.3$) and 46% at Hot Bubbling Pool ($R/R_A = 3.7$). However, at these and other sites in the caldera, the proportion of the two end-member components has varied by as much as 15% in the last three years even though local seismicity has remained at a low level ($M < 3$ in the caldera) for the duration of this sampling period. Importantly, there appears to be systematic pattern to this variation in R/R_A : the highest R/R_A ratios invariably occur in the winter/early spring period, which coincides with the period when ground water recharge is inhibited. Then, concomitant with the initiation of snowmelt in spring/early summer, R/R_A ratios decrease, reflecting the addition of radiogenic (low R/R_A) helium to the magmatic component at this time. Because of the rapid response of the R/R_A ratio, we presume that the variation effect is due to dilution of the deep magmatic fluid with a much shallower crustal component in the local ground water. Thus, these temporal trends are consistent with a picture of seasonal control on the R/R_A ratio, determined largely by the recharge and mixing characteristics in the uppermost portions of the hydrothermal regime. This is a surprising but very important result, and it has allowed us to establish a baseline variation curve for helium isotopes in a hydrothermal system. Now for the first time, we are in a position to assess and perhaps distinguish clearly any correlations between gas chemistry and seismic activity in the caldera.

Grantee: UNIVERSITY OF CALIFORNIA, 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

Seismic methods of underground imaging have made great progress in recent years. Advances in data collection include multi-channel recording, expanding spread profile (ESP), and vertical seismic profile (VSP) techniques; computational advances include 3-D migration, slant-stack and dip-moveout processing, and full waveform inversions. Despite these improvements, current methods are still limited in some important aspects. Many limitations could be removed if anisotropy could be resolved and its effects incorporated in seismic image processing. Almost all seismic processing techniques assume the Earth is isotropic. There is increasing evidence that anisotropy is present in the upper crust, with a typical strength of 5 to 20%. Neglecting the effects of anisotropy can lead to inaccurate depth estimates to underground structures. Also, tests for rock or reflector composition based on Poisson's ratio or reflection amplitude vs. range can produce misleading results.

High resolution images from reflection seismology are possible only in areas in which seismic reflectors are present. Thus, relatively transparent regions in the crust are not well resolved, even though they may contain structures of interest. Many of these features, such as variations in porosity or permeability and cracks or fractures, are of particular relevance to questions involving hydrocarbon and geothermal reservoirs and waste storage problems. Unless these structures are characterized by a sufficiently large impedance contrast, they will not produce seismic reflections. Refraction seismology and/or tomographic techniques can resolve the large scale seismic properties of these transparent regions but with generally poor lateral resolution compared to reflection profiling.

Many of these difficulties could be removed if it were possible to resolve the anisotropic properties of the crust. Not only would reflectors be more accurately imaged, but the additional information contained in a full anisotropic description of the medium could be used to resolve some of the ambiguities often present in seismic interpretation. Isotropic models contain a maximum of three parameters as a function of position—the density and the P- and S-wave velocities of the material (density resolution is generally very limited). If anisotropy could be resolved, much additional information could be obtained since up to 21 parameters are required to describe fully the most general form of anisotropy. In the upper crust, the dominant mechanism causing anisotropy is likely to be preferred alignments of fractures and cracks. In this case, it may be possible to determine crack orientation, aspect ratio, and degree of fluid saturation by studying the nature of the observed anisotropy. This is true even within the transparent regions discussed above. We will study ways in which anisotropy could be incorporated into existing seismic processing techniques and will concentrate on resolving details of the crack-induced anisotropy typical of the upper few kilometers of the crust. We will apply these techniques to reflection and refraction data sets from the East Pacific Rise, which show evidence for both azimuthal and vertical anisotropy. These results will help in designing appropriate experiments to resolve details of crack and fracture structure in shallow crustal rocks.

Grantee: UNIVERSITY OF CALIFORNIA, SANTA BARBARA
Institution 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 (805-961-4880)

This multifaceted research program is in direct support of the Continental Drilling Scientific Program and is aimed at 1) measuring the transport properties of multiphase magmatic mixtures at elevated temperatures and at varying shear rate and 2) understanding dynamical processes related to caldera subsidence and magma withdrawal. The first part of this project consists of laboratory rheometry on magmas. Specifically, an experimental investigation of magmatic emulsions (melt plus vapor) and magmatic suspensions (melt plus crystals) will be used to test extant constitutive rheological models for relevance to geologic systems. A new apparatus, a constant torque viscometer, will be constructed in order to measure yield strengths directly. Magmatic mixtures will be tested at a variety of temperatures, shear rates, crystallinities, and voidages. The second part of this project is concerned with simulation studies of several dynamical processes relevant to silicic magmatic systems. The first goal in numerical modeling is to investigate the dynamics of caldera resurgence. This problem may provide valuable information on the size, depth, and behavior of near-surface magma chambers; the local thermal structure; and the thermal-mechanical interaction with the crust. The second goal of the numerical study is to model, by means of the finite element method, the rapid (catastrophic) removal of magma, treated as a non-Newtonian fluid, from a density and viscosity-stratified reservoir. The driving force for the magma withdrawal process will be catastrophic foundering of the roof of the magma reservoir (i.e., caldera collapse).

Grantee: UNIVERSITY OF COLORADO
Department of Geological Sciences
Boulder, Colorado 80309-0449

Grant: DE-FG02-88ER13804

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 dependence 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 additional 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 the attenuation. This information should 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. The reflection points for the laser beams are arranged to allow longitudinal as well as torsional measurements without changing the experimental setup. The interferometer has an ultimate sensitivity of 10^{-7} m 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
Department of Geology & Geological Engineering
Golden, Colorado 80401

Grant: DE-FG02-88ER13840

Title: Workshop on Deterministic Approaches to Stratigraphic Analysis

Person in Charge: T. A. Cross (303-273-3883)

About 70 participants attended an international workshop on Quantitative Dynamic Stratigraphy, cosponsored by AAPG, DOE, GRI, NSF, and USGS in February 1988 at Lost Valley Ranch near Denver, Colorado. The goals of this workshop were to: 1) summarize the state-of-the-art in quantitative approaches to stratigraphic analysis, 2) identify major areas in which empirical geological information is required for construction and verification of quantitative models, and 3) define research directions that will significantly enhance capabilities to predict temporal and spatial relations of facies elements, fluid movement, and diagenetic changes in subsurface strata.

Quantitative dynamic stratigraphy (QDS) is the application of mathematical/quantitative procedures to analysis of stratigraphic, geodynamic, and hydraulic attributes of sedimentary basins, treating them as features produced by the interactions of dynamic processes operating on physical configurations of the Earth at specific times and places. Although QDS normally requires the construction of computer models that attempt, through simplification of the real world, to represent processes in terms of natural laws and/or empirical generalizations, it is a philosophically much broader and coherent approach to analysis of sedimentary basins. QDS allows more complete and effective integration of knowledge from previously separate disciplines; it requires more accurate definition of the variables involved in and their operations upon (within specified boundary conditions) the geologic system being simulated; it assesses or measures the degree of confidence in descriptions and predictions made by models; it may lead to new intuition by revealing interdependencies and feedback mechanisms among process variables and responses that are otherwise obscure or unnoticed; through real-time graphic simulations, it allows users to visualize and more completely understand interactions among processes and the products produced by their interactions; and, it reduces time and effort constraints that manual manipulation of data impose on scientists such that more hypotheses may be developed and tested and more insights gained about complex geologic systems.

Workshop participants presented a variety of QDS models that ranged over 10 orders of magnitude in temporal and spatial scales and that had been applied to problems ranging from geodynamics of basin formation, to genesis and prediction of stratal architecture and lithofacies distributions, to methods for increasing temporal resolution of the stratigraphic record, and to fluid flow and rock/fluid interactions. The participants formed seven small working groups to address questions and make specific recommendations related to the workshop goals listed above. Their recommendations will be published in the book "Quantitative Dynamic Stratigraphy" in 1989.

Grantee: COLORADO SCHOOL OF MINES
Golden, Colorado 80401

Grant: DE-FG02-89ER14079

Title: Computational Methods for Improving the Resolution
of Subsurface Seismic Images

Person in Charge: K. L. Lamer (303-273-3428) and N. Bleistein

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 problem 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. Such models are simply implemented and permit fast numerical computations of seismic waves, but they also inhibit the representation and imaging of complex but common geologic structures, such as overhanging salt diapirs and inhomogeneous reservoirs.

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 seismic waves traveling horizontally through stratigraphic layers with a thickness less than the seismic wavelength. Exploration seismologists have only just begun to realize the implications of this problem in surface seismic experiments. The problem is even more significant 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.

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: J. Taber and K. Jacob (914-359-2900)

The geophysical processes of subduction and arc-magmatism are investigated by seismological methods to obtain a fundamental understanding of convergence at a plate margin and to assess seismic risk to future energy projects in an active fore-arc back-arc region. We conduct a broad seismotectonic study of much of the Aleutians, and in the Shumagin Islands we study in detail a 300-km-long arc segment by operating a digital seismic network. The results range in spatial dimensions from small scale details of the plate interface within the Shumagin seismic gap to updated probabilities of the occurrence of great earthquakes along the entire Aleutian arc, and in time from the earliest instrumentally recorded earthquakes to automatic processing of the most recent events. We study the entire range of scale lengths because of the interaction between different tectonic elements. Applications concern the geothermal energy potential of the Aleutian arc and seismic, volcanic, and tsunami hazards to off-shore oil lease sale areas. Technical objectives are the sensing of wide dynamic range ground motions of moderate and large earthquakes for engineering applications.

A simple kinetic model describing the flow of material down the Aleutian subduction zone shows that arc geometry and current convergent directions and rates can explain the distribution of seismicity and volcanism along the arc. Studies of the seismic source have begun to expand the frequency band over which seismic rupture can be analyzed. A comparison of short and long-period data from the 1986 Andreanoff Island earthquake ($M_s = 7.7$) raises fundamental questions about how decoupled in space and time can the radiation of high frequency energy be from the release of moment-rate producing slip during a dynamic rupture. The basic source parameters were modeled by inverting long-period P and SH waves while the high frequency characteristics were approximated by the superposition of many small earthquakes used as empirical Green's functions. Modeling of the earthquake source has also added insight into the mechanics of the transition from subduction zone to transform fault in the Gulf of Alaska region.

The relocation of large earthquakes from the turn of the century has helped refine estimates of recurrence intervals and added more evidence that arc segments can rupture individually in one earthquake cycle and together in a much larger earthquake in the next cycle. The Shumagin gap can be segmented into smaller sections based on historic earthquakes and on the distribution of microseismicity. The refinement of long term recurrence estimates along the arc resulted in the finding that the Shumagin Islands segment stands out as having the largest and best constrained probability of rupture (62 - 96% over the next 20 years). We have quantified the energetic nature of the 1986 Pavlof eruption using particle motion and spectral studies. From July - December 1988 nearly 300 earthquakes were located near Mt. Dutton Volcano, where preliminary analysis suggests that this activity is related to shallow dike emplacement and thus may have geothermal potential.

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

Grant: DE-FG02-88ER13287

Title: Energetics of Silicate Melts from Thermal
Diffusion Studies

Person in Charge: D. Walker and C. E. Lesher (914-359-2900)

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 $\text{Fe}_2\text{SiO}_4(\text{Fa})\text{-KAlSi}_2\text{O}_6(\text{Lc})\text{-SiO}_2(\text{Qt})$ 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 the coexistence of crystals with a multicomponent fluid has shown that there is a substantial potential for inducing chemical migration, even in the absence of convection. Laboratory observations of cumulate maturation under the influence of thermal diffusion have been applied to postcumulus evolution of magma bodies and the formation of cyclic evaporite deposits.

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

Grant: DE-FG02-89ER14080

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

Person in Charge: R. H. Wood (302-451-2941)

Measurements of the apparent molar heat capacity of aqueous solutions of H₂S, CO₂, and CH₄ are being made at twelve temperatures from 25° to 450°C and at pressure near 350 bar. Measurements of the apparent molar volume of aqueous solutions of H₂S, CO₂, and CH₄, 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 in a wide variety of geochemical processes and 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: GEO-CHEM RESEARCH ASSOCIATES
105 North Jefferson Street
Bloomington, Indiana 47401

Grant: DE-FG02-88ER13802

Title: Nonlinear Phenomena at Reaction Fronts in
Porous Media with Energy Applications

Person in Charge: P. J. Ortoleva (812-332-1086)

Reaction fronts in porous media play key roles in the genesis of ore deposits and petroleum reservoirs and in a variety of engineered geological systems relevant to energy exploitation. These fronts form when fluids are imposed on a medium containing minerals that react with the chemical species in the inlet fluid. Because the moving fronts involve zones sustained out of equilibrium by the continuous flow of the imposed fluid, we expect that a great variety of nonlinear, pattern-forming, and other localizing geochemical phenomena should accompany them. Our objective is to delineate and characterize these phenomena.

Diagenetic reaction fronts were shown to take on a variety of scalloped and branching tree structures not related to initial bedding. These patterns arise through the coupling of grain growth reaction and flow via Darcy's law. The results are of interest in predicting the spatial distribution of porosity and permeability and the meter to kilometer scale geometric arrangement of minerals in a sedimentary basin. Such phenomena can significantly affect the migration path for petroleum and the creation of good reservoir rock and the destruction of cap rock.

The coupling of mechanics and reaction via pressure solution was introduced into our reaction-transport models to explain the genesis of laminated, diagenetic petroleum traps that likely developed in very low flow environments. This may be critical in predicting conditions favorable for the genesis of deep oil and gas reserves.

Kerogen decomposition into petroleum was shown to lead to appreciable natural convection. As a result, petroleum migration can be self-induced and be in the form of regularly spaced rising plumes that even may oscillate in time. Furthermore, a model of natural fracking was developed that illustrates the possibility of oscillatory release of methane from kerogen-bearing shales or overpressurized zones in a subsiding basin.

Grantee: UNIVERSITY OF HAWAII AT MANOA
Hawaii Institute of Geophysics
Honolulu, Hawaii 96822

Grant: DE-FG03-88ER13418

Title: Physical Characterization of Magma Samples

Person in charge: M. H. Manghnani (808-948-7825)

The main objectives of this project are: 1) to employ ultrasonic interferometry techniques to measure velocity and attenuation in natural and synthetic silicate melts, in an effort 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 rocks (basalts and komatiites) and on selected synthetic samples in the systems diopside ($\text{CaMgSi}_2\text{O}_6$)-anorthite ($\text{CaAlSi}_2\text{O}_8$) and albite ($\text{NaAlSi}_3\text{O}_8$)-anorthite ($\text{CaAlSi}_2\text{O}_8$) anorthite ($\text{CaAlSi}_2\text{O}_8$)-diopside ($\text{CaMgSi}_2\text{O}_6$) and to $\sim 1600^\circ\text{C}$ 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 (viscosity, relaxation time, etc.) in terms of their composition and structure. We are now turning to employing the recently set-up Brillouin scattering system and diamond anvil to study the compressibility of silicate melts at high pressures. The ultrasonic and Brillouin scattering results, to be extended to high pressures in the future, will provide important thermodynamic parameters (e.g., compressibility) for these melts at high pressure. The electrical conductivity measurements on the Kilauea Iki basalts have now been completed. In progress are the measurements on the nepheline-sodium disilicate (NaAlSiO_4 - Na_2SiO_3) system to $\sim 1000^\circ\text{C}$ to determine the effect of partial melting (solidus = 768°C) on the electrical properties.

Grantee: UNIVERSITY OF HOUSTON
Department of Geosciences
Houston, Texas 77204-5503

Grant: DE-FG05-87ER13771

Title: Bacterially Induced Precipitation of CaCO₃:
An Example From Studies of Cyanobacterial Mats

Person in Charge: H. S. Chafetz (713-749-3744)

The primary purpose of this investigation is to evaluate the role of bacteria in the precipitation of calcium carbonate in modern cyanobacterial mats. It is our contention that bacteria are very important in establishing a microenvironment favorable for the precipitation of calcium carbonate and, consequently, the lithification of cyanobacterial mats. The ultimate goal of our research is to demonstrate that bacteria can play a significant role in causing the precipitation of calcium carbonate in many other geologically relevant realms and since bacteria are essentially ubiquitous in the Earth's crust, the physical, chemical, and biological conditions under which calcium carbonate can precipitate will have to be reevaluated.

In order to fully evaluate the role of bacteria in the lithification of cyanobacterial mats, three intimately related but separate approaches are being employed. Laboratory experiments are establishing the types of carbonate precipitate that are produced due to the influence of bacteria under controlled conditions. Modern cyanobacterial mats from carbonate producing areas are being studied to determine if bacterially induced precipitates of calcium carbonate can be recognized within these deposits. And lastly, ancient stromatolites are being studied to evaluate the role bacteria played in the lithification of these strata.

A variety of media and nutrients have been used to culture the bacteria and in each case calcium carbonate crystals formed in association with the bacteria. Identical conditions with sterile (no bacteria) samples did not produce any precipitate. Both aragonite and calcite have been produced and variations in the mineralogy, crystal habit, etc., have been related to conditions of the media. The shapes of the precipitates formed in the laboratory (e.g., dumbbells, hemispheres, and stellate accumulations) are either identical to, or closely resemble, shapes that have been observed in natural environments and which we and others have attributed to precipitation under bacterial influence.

Grantee: UNIVERSITY OF HOUSTON
Houston Petroleum Research Center
Houston, Texas 77204-5503

Grant: DE-FG05-89ER14058

Title: Crosshole Geotomography in a Partially Depleted Reservoir

Person in Charge: J. A. McDonald (713-749-7336)

This research is a collaborative effort between Exxon Company U.S.A., the University of Houston, and Southwest Research Institute (SwRI). Exxon is providing access to a partially depleted oil field, the Friendswood (Webster) field just south of Houston and is providing data from wells in the field. Under a subcontract from the University of Houston, Southwest Research Institute is carrying out the field measurements using a unique source. This source can generate seismic signals in the range 400 to 5000 Hz, which have been detected in hole-to-hole experiments at borehole separations of 300 ft. Seismic signals with spectral content up to 1500 Hz have been received by instruments in boreholes separated by over 1000 feet. The Friendswood (Webster) field has upwards of 400 holes drilled in an area of 2 miles by 3 miles. There are, thus, many combinations of holes that could be used for these experiments.

The University of Houston is planning the field experiments in conjunction with Exxon and Southwest Research Institute. We are examining the geological parameters of the Frio sands, which are in the interval 5400-6000 feet, and the fluids contained within them. The oil in these sands is trapped between an expanding gas cap and the water table. With the hole spacing available in the field it is expected that seismic signals with a spectral content up to 2000 Hz will be readily detectable. These higher frequencies will require a detector spacing of about 2 feet not to be spatially abased. With this resolution it is expected that the gas-oil and oil-water interfaces will be readily imaged. In addition, the locations of faults within the Frio sands are expected to be delineated. Preliminary field tests and instrument developments are being carried out in the first year of the project. A large scale cross-hole seismic data acquisition program will be undertaken in the second year of the project.

The University of Houston is responsible for developing the software, processing the seismic data, integrating the cross-hole data with other field data, and developing the geotomographs of the field.

The first problem to be solved is the choice and implementation of an algorithm or algorithms. The search for a solution will probably start with iterative approaches based on straight ray techniques that are, in themselves, clearly unsuitable. The ultimate aim of the processing is full waveform inversion and migration to interpret the geological and physical parameters of the rock matrix and fluids contained therein.

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

Grant No.: DE-FGO2-88ER13978

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

Person-in-charge: J. M. Hayes (812-335-5610), L. M. Pratt, and A. H. Knoll

Our work is focused on the relationship between organic geochemistry and depositional environment in the Nonesuch formation. Our principal objectives are to: 1) describe the distribution of fine-grained lithofacies; 2) determine organic-carbon, carbonate-carbon, and total-sulfur contents of these units; 3) characterize the extractable bitumen and conduct preliminary analyses of biomarkers; and 4) infer the depositional environment and biological affinities of organic matter preserved in the Nonesuch. In parallel, we are studying related problems in the Belt group (Montana) and the Shaler group (Victoria Island, Canadian Arctic).

We have undertaken numerous field trips to these units and, for the Nonesuch, have also sampled cores not previously examined. In the fine-grained portions of the Nonesuch, graded laminae (1 mm - 3 cm) are nearly ubiquitous. Organic matter and framboidal sulfides are concentrated in shaly portions. In some cases, preservation of intact bacterial or algal mats is implied by apparently fibrous fabrics, only some of which are found in shallow-water facies. Well-preserved mudcracks indicative of alternating wet/dry conditions have been observed. We have no explanation for the clean separation of interbedded coarse- and fine-grained units 1 to 25 m in thickness. Contacts appear planar. The depositional environment appears to have been moderately deep water but the sedimentary structures are not typical of either turbidite, delta-front, or prodeltaic deposits.

Organic carbon contents of unmineralized Nonesuch sediments (mostly from cores) range from 0 to 2.8 wt% C. Total sulfur contents are positively correlated, but the C/S ratio decreases for $C_{org} > 1\%$. Either 1) the type of organic carbon is different in samples with high C_{org} , or 2) inadequate supplies of reactive iron limited amounts of sulfur that could be immobilized as pyrite, or 3) supplies of sulfate were limited. The C/S relationship is similar to that observed in Cambrian, Ordovician, and Cretaceous epicontinental marine settings and very different from that found in potentially similar Triassic-Jurassic rift basins on the Atlantic margin. In contrast, the C/S relationship in Belt sediments is similar to that observed in modern lacustrine settings.

Gas chromatograms of bitumen from unmineralized Nonesuch core samples differ significantly from those of extracts and oils deriving from the White Pine mine. The smooth and extended distribution of normal alkanes and high concentrations of isoprenoids are indicative of moderate thermal maturity. Application of metastable-reaction monitoring MS/MS indicates the presence of steranes, hopanes, and methylcyclohexyl alkanes in bitumens from core samples. The triterpenoid biomarkers are similar to those observed in other Proterozoic strata, notably the Walcott member of the Chuar group, Arizona, and the Barney Creek formation of the McArthur group, Australia.

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

Grant: DE-FG02-89ER14074

Title: HRTEM/AEM Study of Trace Metal Behavior, Sheet Silicate Reactions, and Fluid/Solid Mass Balances in Porphyry Copper Hydrothermal Systems

Person in Charge: D. R. Veblen (301-338-8487)

This project concerns high-resolution and analytical transmission electron microscopy (HRTEM and AEM) to study several geochemically important aspects of the hydrothermal systems associated with porphyry copper deposits: 1) the geochemical behavior of trace and minor metals (copper); 2) the alteration reactions in the silicates and the identification of the sequence of alteration products; and 3) the chemical consequences of the observed reaction mechanisms and phase chemistries for the composition of the hydrothermal fluid. Results of a reconnaissance study involving rocks from two porphyry copper deposits indicate that the above objectives are attainable. In addition, preliminary results for these two deposits show that: 1) the previously unidentified high-Cu sheet silicate associated with biotite and chlorite in these hydrothermal systems is consistent with hydrobiotite as defined by Brindley et al. (1983); 2) anomalous Cu is not present in solid solution, but rather as discrete, submicroscopic crystals of native copper concentrated in the hydrobiotite; and 3) the observed mechanism of biotite-chlorite reaction is one that can release large amounts of hydrogen to the fluid, providing a mechanism for reducing pH during progressive alteration.

We intend to enlarge the present study substantially to test the generality of our observations, to model quantitatively the mass balances among solids and fluids during alteration, and to constrain the conditions under which Cu enrichment and alteration reactions take place. We have assembled and intend to study a comprehensive and well-constrained suite of specimens from a variety of hydrothermal deposits. Their examination is essential for rigorous interpretation of our present results.

Grantee: LOUISIANA STATE UNIVERSITY
Diagenesis Group/Basic Research Institute
Baton Rouge, Louisiana 70803-4101

Grant: DE-FG05-88ER13748

Title: Ammonium Silicate Diagenesis and Its Influence
on the Interpretation of Fixed-Ammonium
Anomalies as an Exploration Tool

Person in Charge: R. E. Ferrell, Jr. 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 proximity. This research consists of field investigations of the interaction between N produced from hydrocarbons and clay minerals during diagenesis. Ammonium (NH_4^+) substitutes for K^+ in clay minerals at diagenetic temperatures. Experimental NH_4 -fixation is a second aspect of the project, intended to determine the physico-chemical and conditions optimal for NH_4 -fixation in various clay minerals.

Work in progress has shown that high fixed- NH_4 values are associated with mature hydrocarbons more than immature hydrocarbons and that there is a two-fold increase in NH_4 substitution in clays from hydrocarbon reservoirs versus NH_4 in clays from mudstones surrounding the reservoirs. Nitrogen is steadily released as from organic compounds throughout the organic decay process, but apparently a large quantity is released during catagenesis and may substitute in authigenic silicates as NH_4^+ . If it can be shown that fixed- NH_4 concentrations are predominantly affected by NH_4^+ concentration, then the high fixed- NH_4 values observed near hydrocarbon reservoirs are a record of this stage of maturation. 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.

Samples have been obtained 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, and with depth in the Salton Sea area (SSSDP) where the geothermal gradient is also high. The effect of migrating hydrocarbons on fixed- NH_4 trends was examined in samples from Green Canyon, a modern oil seep in the Gulf of Mexico.

Experimental work in progress has determined that layer-charge is an important factor in the fixation of significant amounts of NH_4^+ and that a linear increase in fixed- NH_4 occurs over time provided there is a constant supply of NH_4^+ ions. Continuing experiments are designed to examine whether or not the process of NH_4^+ substitution (i.e., adsorption or recrystallization) is a limiting factor in NH_4 -fixation.

The completion of this research will lead to a better understanding of the nitrogen cycle in terms of organic/silicate interactions. The results may lead to the formulation of an improved technique for evaluating organic maturity levels in source rocks and thereby lead to increased success rates in the exploration for liquid and gaseous hydrocarbons.

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

Grant: DE-FG02-88ER13636

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

Person in Charge: M. N. Toksoz (617-253-7852) and C. H. A. Cheng

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.

The research undertaken in the past year consists of 1) theoretical modeling of seismic wave propagation in a borehole with a vertical or horizontal fracture, and the testing of the model using laboratory scale model experiments; 2) measurements 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; and 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-FG02-89ER14084

Title: Reservoir Characterization by Crosshole Seismic Imaging

Person in Charge: M. N. Toksoz (617-253-7852)

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 these boreholes must straddle the region of interest. This has been done to a limited extent with a P-wave source in one borehole, but the use of shear waves awaits the development of a strong downhole shear wave source. Such a source has recently been built by Sandia National Laboratories and its use will be the central focus of our research. In the first year the vertically polarized shear wave (SV) source will be used and the horizontally polarized (SH) shear wave source will be used in the second year. In the third year we will repeat the set of P-wave measurements made in 1989. This second set of P-wave data will highlight any time varying phenomena that are taking place in the reservoir.

Tomographic imaging algorithms already developed at the Earth Resources Laboratory will be used in the processing and interpretation portions of this work. Modeling will precede and guide all data collection efforts. The data already existing at the test site indicate certain formations to exhibit anisotropy and that certain interfaces are rough in nature; both effects will be modeled.

Grantee: UNIVERSITY OF MINNESOTA
Minnesota Supercomputer Institute and Department
of Geology
Minneapolis, Minnesota 55455

Grant: DE-FG02-89ER14051

Title: Experimental Investigations of Magma Rheology and Numerical
Simulations of Caldera Collapse and Magma Withdrawal

Person in Charge: D. A. Yuen (612-624-9801)

This multifaceted research program is in direct support of the Continental Drilling Scientific Program and is aimed at 1) measuring the transport properties of multiphase magmatic mixtures at elevated temperatures and at varying shear rate and 2) understanding dynamical processes related to caldera subsidence and magma withdrawal. The first part of this project consists of laboratory rheometry on magmas. Specifically, an experimental investigation of magmatic emulsions (melt plus vapor) and magmatic suspensions (melt plus crystals) will be used to test extant constitutive rheological models for relevance to geologic systems. A new apparatus, a constant torque viscometer, will be constructed in order to measure yield strengths directly. Magmatic mixtures will be tested at a variety of temperatures, shear rates, crystallinities, and voidages. The second part of this project is concerned with simulation studies of several dynamical processes relevant to silicic magmatic systems. The first goal in numerical modeling is to investigate the dynamics of caldera resurgence. This problem may provide valuable information on the size, depth, and behavior of near-surface magma chambers; the local thermal structure; and the thermal-mechanical interaction with the crust. The second goal of the numerical study is to model, by means of the finite element method, the rapid (catastrophic) removal of magma, treated as a non-Newtonian fluid, from a density and viscosity-stratified reservoir. The driving force for the magma withdrawal process will be catastrophic foundering of the roof of the magma reservoir (i.e., caldera collapse).

Grantee: NATIONAL ACADEMY OF SCIENCES
NATIONAL RESEARCH COUNCIL
Washington, D.C. 20418

Grant: DE-FG01-88ER12018

Title: Basic Energy Science Studies

Person in Charge: R. S. Long (202-334-2160)

A. Studies in Geophysics (*T. M. Usselman [202-334-3349]*)

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 sources, natural hazards, and environmental maintenance and 2) science-oriented studies such as geophysical data and impact of technology on geophysics. 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. About two studies are expected to be completed each year.

B. Studies in Seismology (*R. S. Long [202-334-2160]*)

The research objectives of the Committee on Seismology are to influence major trends in seismology and identify related developments in other fields, conduct studies for government agencies, provide advice on U.S. government-supported seismic facilities, maintain cognizance of and provide advice on international seismological activities including seismic verification of nuclear test ban treaties, and coordinate within the National Research Council (NRC) activities in engineering seismology, rock mechanics, geodesy, geodynamics, geology, and seismic verification of nuclear test ban treaties. The committee meets twice a year to discuss current topics of major importance relevant to seismology; review with government agency personnel, in particular, the actions that have resulted from recommendations of the committee and its panels, and take actions to assure a healthy science that is in a position to provide maximum benefits to the nation and to society. Panels are established to conduct ad hoc studies on topics specified by the committee. The report of the panel on seismic hazard analysis has been published. New panels concerned with 1) the feasibility of real-time earthquake warning and 2) the problems of regional seismic networks are preparing reports for publication.

C. U.S. Geodynamics Committee (*P. J. Hart [202-334-3368]*)

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 Transect 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 include: assessing the singular suitability of Katmai for a proposed scientific program involving drilling at Katmai; input to the International Decade for Natural Disaster Reduction (two panels of the USGC); preparation of an overview of the transect program; looking into the broad national effort in geomagnetic research; developing criteria for assessing priorities for facilities for earth materials research; 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.

D. Board on Earth Sciences and Resources (*R. S. Long [202-334-2160]*)

The Board on Earth Sciences and Resources is a new entity of the Commission on Physical Sciences, Mathematics, and Resources that has been established to replace two standing Boards, the Board on Earth Sciences and the Board on Mineral and Energy Resources. The new board will have as its goal a recognition of the intellectual excitement of the earth sciences and their clear and obvious links to applications such as resource recovery. The charge to the new board will encompass 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 will monitor the status of the earth sciences, assess the health of the disciplines, identify research opportunities, and will respond to specific agency requests for advice.

The Board has underway two major reports: a study on *Status and Research Opportunities in the Solid-Earth Sciences--A Critical Assessment*, and a study on *Undiscovered Domestic Oil and Gas Resource Estimates*. The board and its committees are preparing for two major international activities to be held in Washington, DC: the 28th International Geological Congress (1989) and the 26th International Geographical Congress (1992).

E. Panel on Volcanic Studies at Katmai (*D. P. Russ and R. S. Long [202-334-2160]*)

The National Academy of Sciences has organized an ad hoc Panel on Volcanic Studies at Katmai, for the period of February 1 - July 31, 1989.

The National Park Service has received notice that the Interagency Coordinating Group (ICG) for Continental Scientific Drilling will submit a proposal to drill holes for scientific research purposes at Katmai volcano in Katmai National Park. The National Park Service is sympathetic

to the aims of the research, but wants to determine whether Katmai is uniquely suited to the research. Accordingly, the Park Service has asked that the ICG support an independent assessment of this aspect and suggested the National Academy of Sciences as an appropriate organization for the study.

In response to the request from the Park Service, the National Academy of Sciences/National Research Council proposes to establish a Panel on Volcanic Studies at Katmai, under the aegis of the U.S. Geodynamics Committee. The proposed investigation at Katmai has been extensively reviewed for scientific merit by the three sponsoring and participating agencies. Thus, the scientific merit of the proposed drilling at Katmai is not at issue. The panel will review the proposal for scientific drilling at Katmai and prepare a short report addressing the specific question of the degree to which it is essential that the drilling be conducted at Katmai as opposed to volcanic areas elsewhere in the world.

In accordance with Academy policy, reports resulting from this effort shall be prepared in sufficient quantity to ensure the distribution to the sponsors, committee members, and to other relevant parties. Reports may be made available to the public without restrictions.

Grantee: NATIONAL ACADEMY OF SCIENCES
NATIONAL RESEARCH COUNCIL
Washington, D.C. 20418

Grant: DE-FG05-88ER13815

Title: Support of the Numerical Data Advisory Board

Person in Charge: G. C. Carter (202-334-2755)

This board is supported by several federal agencies including the DOE. Within DOE/ER/BES, support is garnered from Geosciences, Engineering, Chemical Sciences, and Carbon Dioxide Research. The objective of the board is "improvement in quality, reliability, accessibility, dissemination, informed utilization, and management of scientific data to meet the present and future needs of the scientific and technological communities." Committees of the board include the U.S. National Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (ICSU), the Committee on Fundamental Constants and Basic Standards, the Committee on Very Large Databases, and the Committee on Line Spectra of the Elements - Atomic Spectroscopy. Another unit under NDAB, the Panel on Basic Nuclear Data Compilations, is funded by another office of the DOE. The two most recent reports issued by the board are, "Data Needs for High-Tech Materials," and "Automated Database Needs for the Computerized Instruments Industry," National Academy Press, 1989, available from NDAB. The board's program is increasingly dealing with environmental data issues and the ICSU's International Geosphere-Biosphere Program.

Grantee: NATIONAL SCIENCE FOUNDATION
Division of Earth Sciences
Washington, DC 20550

Grant: DE-AI05-87ER13813

Title: U.S. Support for the 28th International Geological Congress (IGC)

Person in Charge: T. O. Wright (C. L. Drake at IGC) (202-357-7915)

The 28th International Geological Congress (IGC) will be held in the United States (Washington Convention Center, Washington, DC) in July of 1989 in collaboration with, and under sponsorship of the International Union of Geological Sciences (IUGS). This is the oldest international scientific congress meeting on a continually scheduled basis. It last met in the U.S. in 1933. The 28th International Geological Congress is co-hosted by the U.S. Geological Survey and U.S. National Academy of Sciences in cooperation with major U.S. earth science societies, industry organizations, and U.S. governmental units, on behalf of the entire U.S. earth science community.

The technical program will offer numerous symposia utilizing displays of regional maps and data from all over the world. The program will include about 4000 oral presentations, about 100 field trips, and especially prepared exhibits. Participation in IGC is to be fostered by special sessions on projects of such major importance as the International Geological Correlation Program and the International Lithosphere Program. Poster presentations and field trips to local attractions such as museums, government agencies, and industrial and geological sites will be featured. Short courses and workshops will rely heavily on the use of microcomputer hardware and software.

In conjunction with the Congress, the IUGS will hold meetings of its executive committee and council, bringing together top scientists from more than 95 member countries. In addition, representatives from most of the IUGS's ten constituent international scientific commissions and 22 affiliated organizations will convene.

The Department of Energy has a fundamental interest in the successful outcome of the 28th International Geological Congress as it has program efforts in geosciences, in one form or other, occurring in all its mission arms. Many of its related activities are impacted strongly by geological data and analysis.

The National Science Foundation will assemble and be responsible for dispersion of funds from the federal agencies to the IGC. These funds will be used for printing of the Second and Third Circular Program, volumes of abstracts, and related documents and brochures, for postage and shipping, for travel by non-Federal 28th International Geologic Congress officers, and for audiovisual equipment at the meeting.

Grantee: NATIONAL SCIENCE FOUNDATION
1800 G Street, NW
Washington, D.C. 20550

Grant: DE-AI01-88ER60574

Title: Partial Support for the National Academy of Sciences/
National Research Council on Global Change

Person-in-charge: R. Correll (202-357-9715)

The National Academy of Sciences/National Research Council has established a Committee on Global Change to serve as the USA representative to the International Geosphere-Biosphere Program (IGBP). The committee provides guidance on plans and interagency activities related to the IGBP and the NASA-sponsored Earth Systems Science Committee (ESSC). The Committee serves as a focus for developing new initiatives for the IGBP and serves as the primary channel of communication, coordination, and advice between the USA scientific community, federal agencies, and international nongovernmental planning and coordinating bodies. Under the auspices of NAS/NRC, the Committee provides scientific guidance and leadership to the government on important national and international and multidisciplinary problems involving the Earth system (ocean, biota, space, solid earth). The NSF is requesting that six agencies (including the NSF) support this action through the NSF Directorate for Geosciences.

DOE supplies 16% of the total cost with the Geosciences Program funding 1/8 of that. The Carbon Dioxide Research Division handles relations with the NSF.

Grantee: NATIONAL SCIENCE FOUNDATION
1800 G Street, NW
Washington, D.C. 20550

Grant: DE-FG05-89ER14007

Title: Conference on the Continental Lithosphere

Person-in-charge: L. E. Johnson (202-357-7971)

The Conference on the Continental Lithosphere will produce a science plan for a coherent national Continental Lithosphere Program, including objectives and priorities for coordinated, broadly-based scientific research of the continental lithosphere; its structure, composition, origin, and dynamic evolution. A principal result of the Conference will be a report to the sponsors that will include:

- Rationale for an integrated continental lithosphere program;
- Present status of continental lithosphere projects;
- Short- and long-term scientific objectives, goals, and priorities;
- Options for management and implementation of projects under the program;
- Scientific, economic, technological, and social benefits to be realized; and
- Recommended course for interaction with the international scientific community.

It is intended that the resulting report will generate support for the national Continental Lithosphere Program, provide a long-term prioritized science plan for the sponsoring agencies, establish a position paper for the U.S. program to be used for international coordination, and serve as a reference for presentations by agencies and the scientific community during congressional deliberations.

Grantee: CITY UNIVERSITY OF NEW YORK, BROOKLYN COLLEGE
Department of Geology
Brooklyn, New York 11210

Grant: DE-FG02-88ER13692

Title: Deep Burial Diagenesis of Carbonate Reservoirs

Person in Charge: G. M. Friedman (518-273-3249)

A continuing decrease in hydrocarbon reserves has prompted investigation of ways of increasing hydrocarbon recovery, both from existing fields and from new discoveries. The three major sedimentary rock types, carbonates, sandstones, and shales, occur in roughly equal proportions. However, carbonates dominate in terms of hydrocarbon production. Further, carbonate reservoirs are more complex and are subject to two important diagenetic processes that hardly affect sandstone reservoirs: dissolution and dolomitization. Heterogeneity of carbonate reservoirs occurs on a variety of scales and has a profound effect on hydrocarbon recovery. Accordingly, this project was initiated to address the question of how carbonate reservoirs change during burial and how these changes affect reservoir characteristics and quality.

This research program emphasizes the evolution of rock textures, mineralogy, chemistry, and porosity with depth. Specific research topics investigated include the differential behavior of dolostones and limestones under progressive burial; the morphology, topology, and capillary-pressure characteristics of rock-pore systems of deeply buried carbonates; and the development of predictive models of reservoir performance based on petrophysical characteristics. These last two points are critical to the accurate evaluation of reservoirs for enhanced recovery schemes.

Three Paleozoic carbonate reservoir units are being studied and compared: the Early Ordovician Ellenburger dolomite, Delaware basin, Texas and New Mexico; the Late Ordovician Red River formation, Williston basin, Montana; and the Late Ordovician to Early Devonian Hunton group, Anadarko basin, Texas and Oklahoma. Samples have been collected ranging from 5,000 to 30,000 feet of burial (1.5 to 9.1 km). Sequential samples of all carbonate lithologies were selected downhole to study changes in rock texture and mineralogy in relation to primary lithology, burial depth, and diagenetic history.

A new outgrowth of the ongoing petrophysical studies is documentation of the utility of well cuttings for capillary-pressure analyses. Previous work at our laboratory and elsewhere had suggested that such an approach might be feasible and further experiments are ongoing to test this hypothesis. Because well cuttings are much more readily available and cheaper to collect than other kinds of rock samples from boreholes, the potential applications of this method are far-reaching.

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

Grant: DE-FG02-88ER13961

Title: Evaporites as a Source for Oil

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

Evaporites forming in modern settings contain and are associated with vast amounts of organic material produced by cyanobacteria and halophylic bacteria. Similarly, evaporitic sediments that have been buried to depths of 1-2 kilometers also contain intercalated calcareous-sapropelic layers having a total organic content up to 18%, primarily derived from similar bacterial sources. At fairly shallow depths (ca. 0.5 km) some of the immature organic material is already able to migrate from the source rocks. Ancient, deeply buried evaporites on the other hand have almost no organic content and only small wisps of organic matter are associated with these sediments. The disposition of this voluminous evaporitic organic matter is virtually unknown. We know only that the organics develop with evaporitic deposition, are present in comparatively young sediments, and are not common in the ancient deeply buried rocks. Where do they go and what becomes of them?

While biomarkers, typical of clastic and carbonate depositional settings, are fairly well known, those markers that typify evaporitic settings and their maturation products are not well known. We are studying the deposition of evaporites, through early diagenesis, and on to deep burial (through the oil window) in order to identify the relationship between these sedimentary facies and the characteristic suite of organic components, their chemical components, and pathways of maturation. The initial set of samples, from the Bresse basin of France (Oligocene), is taken from the basin center facies. These facies are comparatively lean in organic content, but were chosen because they are basin central and least likely to have contamination from outside of the basin. Other samples presently under investigation are the evaporitive Upper Miocene (Messinian), organic-rich marls from the Apennines and the Cattolica basin of Italy.

Our initial results suggest the following observations in the evaporitive organics: there is a low pristane to phytane ratio and an abundance of docosane, squalane, gammacerane, and a series of extended hopanes (C_{30-35+}), while the aromatic fraction is largely composed of organic sulfur compounds. It is known that the original depositional environments produce large quantities of cyanobacteria in the first stages of hypersalinity, and then, halophylic bacteria predominate in the more saline portions of the water bodies. The bottom sediments of saline water bodies (in the upper meter of accumulation) commonly are host to thiobacillus and methanogenic bacteria, all of which produce characteristic compounds that are recognizable in the Oligocene and Miocene organics studied to this point.

Grantee: STATE UNIVERSITY OF NEW YORK
Albany, New York 12222

Grant: DE-FG02-88ER13722

Title: Energy Related Studies Utilizing Microcline Thermochronology

Person in Charge: T. M. Harrison (518-442-4469)

$^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum analyses on detrital K-feldspars and muscovites from the Salton Sea geothermal field, southern California, yield constraints on the heating duration as well as provenance ages for the sandstones. Core and cuttings have been collected from six wells, which span a present temperature range of $\sim 150 - 275^\circ\text{C}$. Fine-grained ($\sim 120 \mu\text{m}$) K-feldspar aggregates were analyzed from the State 2-14, Landers #1, and Dearborn Farms #1 wells, while single crystals ranging from ~ 150 to $750 \mu\text{m}$ have been analyzed from the Magmamax #2, Elmore #3, and Sinclair #3 wells. The single crystals define three provenance populations of ~ 25 , 70 and >800 Ma, with the smallest crystals generally being Proterozoic. Heating the single crystals in a low Ar blank furnace allows calculation of diffusion coefficients necessary to assess the argon retentivity of the samples. None of the single crystals analyzed reveal recent argon loss. Considering that many of these crystals are presently at $\sim 250^\circ\text{C}$ and using the kinetic parameters, these samples could not have been at this temperature for more than 1000 years as recent argon loss would be easily detected. The 250° and 286°C samples from the State 2-14 well reveal recent argon loss. These results indicate that the State 2-14 area may have experienced a longer heating duration ($\sim 1000 - 10,000$ years) relative to the other areas of the field analyzed. This is interesting because the highest geothermal gradients are observed at the Elmore #3 site and thus it has been inferred to coincide with the longest heating duration.

K-feldspars from accretionary prism sediments located on the central California coast have been analyzed to assess the heating related to Tertiary ridge subduction. Sediments from the Cambria, Pfeiffer Beach, and Pt. San Luis slabs have been sampled and reveal generally flat age spectra indicating provenance cooling ages ranging from ~ 75 to 92 Ma. These ages are expected as the provenance is likely the adjacent Salinian block. The Arrhenius relations for the K-feldspars are very similar and yield activation energies of ~ 33 kcal/mol and frequency factors of $\sim 750/\text{sec}$ for the small domain size. Several of the samples yield apparent age gradients over the first 10% of ^{39}Ar released and have minima less than 65 Ma. This age gradient is thought to represent heating of the deepest samples in the section due to ridge subduction at ~ 25 Ma. For a heating duration of 1 Ma, the observed argon loss would suggest a maximum paleotemperature of $\sim 150^\circ\text{C}$. A new theoretical analysis of K-feldspar age spectra and associated Arrhenius data suggests that many samples contain a distribution of diffusion domain sizes. We have confirmed this prediction by performing many non-conventional Ar extraction experiments involving isothermal heating, short and long duration heating (50 sec to 2 days), and cycled heating/cooling. The appropriate domain distribution can be chosen through fits to both the age spectrum and Arrhenius plot, which allows unique selection. This approach, together with cycled heating/cooling experiments, optimizes the thermochronological information obtainable from $^{40}\text{Ar}/^{39}\text{Ar}$ analyses of K-feldspar. Small (μg), single crystal analyses indicate the domains are an intrinsic property of K-feldspar not separable at the μm scale, thus requiring these deconvolution techniques. Thus, a single feldspar can reveal a segment of a cooling history, rather than a single datum.

Grantee: STATE UNIVERSITY OF NEW YORK AT PLATTSBURGH
Center for Earth & Environmental Science
Plattsburgh, New York 12901

Grant: DE-FG02-87ER13747

Title: Depositional and Diagenetic History of the Edgecliff Reefs
(Middle Devonian Formation of New York and Ontario)

Person in Charge: T. H. Wolosz (518-564-4031)

An understanding of the biological and physical environmental factors that controlled the growth of ancient reefs is critical to the successful prediction of the subsurface location of these potential hydrocarbon reservoirs. Reefs of the Eifelian Edgecliff member of the Onondaga formation have been studied along the Onondaga outcrop belt from south of Albany to Buffalo. These reefs exhibit 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. "Mud mounds" dominated by small, delicate branching tabulate corals characterize deepest water conditions; while at shallower depths, increased levels of water turbulence led to the development of dense colonial rugosan mounds, which gave way to interlayered banks of crinoidal grainstone and colonial rugosan thickets under shallowest water conditions. Successional patterns in all eastern reefs indicate growth during a local regression.

The pattern of dominant coral faunas within these reefs has also confirmed the hypothesis that the succession of reef builders was turbulence controlled, with the following sequence of corals representing a gradient from lowest to highest turbulence conditions (roughly equivalent to a deep to shallow water trend): *Cladopora* > *Syringopora* > *Acinophyllum* > *Cylindrophyllum* > *Cyathocylindrium* > crinoidal sand banks with large favositid colonies.

Analysis of large central New York reefs (gas producing in the subsurface) using the above successional model indicates cycles of growth within these large structures attributable to relative sea-level fluctuations. These shallowing/deepening cycles are related to the interplay of central basin subsidence and early faulting or folding causing gentle uplift along the subsurface reef trend. This strongly supports the hypothesis that the location of the large subsurface reefs was tectonically controlled.

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

Grant: DE-FG02-88ER13416

Title: Geochemistry and Origin of Regional Dolomites

Person in Charge: G. N. Hanson (516-632-8200)

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 expanded our petrographic and geochemical studies into three separate 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; 2) the dolomites in the Western Canada Basin that occur in isolated Devonian carbonate build-ups occurring over a regional scale; and 3) the dolomites in Neogene carbonates formed in reefal and peri-reefal facies in tectonically active island settings in the Mediterranean, Spain, and in the Netherland Antilles. The Devonian dolostones are of interest as petroleum reservoirs.

Grantee: UNIVERSITY OF NORTH CAROLINA
Department of Geology
Chapel Hill, North Carolina 27514

Grant: DE-FG05-88ER13414

Title: Activity-Composition Relations in Silicate Melts

Person in Charge: A. F. Glazner (919-962-0689)

The purpose of this investigation is to gain insight into the relationship between the composition of magma and its thermochemical properties. These studies are useful for understanding the energy balance in a cooling magma body and for using samples of crystallized magma to infer the pressure and temperature conditions of crystallization. A secondary goal of the project has been to determine one-atmosphere phase relationships in mixed magmas.

Ongoing work on this project includes both experimental and theoretical studies of phase equilibria. We are currently determining the one-atmosphere phase equilibria of mafic volcanic rocks from the East African rift (Lake Turkana) and from the East Pacific rise. These studies complement our previous work on mixtures of alkali basalt and rhyolite from California and greatly extend the database of compositions of coexisting crystals and silicate liquids. Doping experiments on alkali basalts from Lake Turkana indicate that addition of minor components such as TiO_2 and P_2O_5 can greatly affect phase relations. We will extend these studies to other components (notably, K_2O) in order to quantify these effects and, if possible, develop a projection scheme for basalts that is immune to bulk-composition variations. Studies of three basalts (alkalic, transitional, and tholeiitic) from the East Pacific rise clarify the relationships between these three coexisting magma types and yield insight into the origin of high-alumina basalts. During this study we unexpectedly found extreme compositional zoning in a single pillow.

Additional experiments have been aimed at determining what happens when granitic minerals (quartz, alkali feldspar, and plagioclase) are immersed in basaltic liquid. Results indicate that alkali feldspar dissolves rapidly (thus accounting for the relative lack of sanidine xenocrysts in basalts), whereas quartz and plagioclase react with the liquid to form protective shells. Liquid halos around both plagioclase and quartz exhibit pronounced uphill diffusion of alkalis; this leads to abnormally high K_2O contents in the cores of partially digested plagioclase crystals.

Theoretical studies have concentrated on developing an algorithm for determining the enthalpy of a mixed magma. Preliminary calculations in hydrous systems indicate that mixing of anhydrous basalt with water-saturated rhyolite should lead to significant precipitation of crystals.

Grantee: OHIO STATE UNIVERSITY
Department of Welding Engineering
Columbus, Ohio 43210

Grant: DE-FG02-88ER13749

Title: Investigations of Ultrasonic Surface Wave Interaction
with Porous Saturated Rocks

Person in Charge: L. Adler (614-292-1974)

This research work investigates the interaction of ultrasonic waves (including bulk waves, surface waves, and generalized Lamb waves) with fluid-saturated porous solids. The effort of the research should find applications in the geophysical evaluation of porous fluid bearing rocks where such parameters as porosity, tortuosity, permeability, surface flow impedance, saturation level or composition, and elastic properties of the skeleton frame and the saturated frame are of importance.

With the development of the theoretical treatment for reflection and transmission of fast, slow, and shear waves at a fluid/fluid-saturated porous medium interface, an alternate case concerning interactions of bulk waves with a plane interface separating two fluid-saturated porous media has been studied. The theoretical analysis includes developing property boundary equations and derivation of energy transmission and reflection coefficients for fast, slow, and shear waves through the interface. We have shown that the surface flow impedance imposed previously for characterizing pore boundary conditions is a vector instead of a scalar quantity, and usually, only the normal component of the impedance vector plays a significant role in the analysis of reflection and transmission coefficients. Numerical calculations for energy transmission and reflection coefficients have been made for a case where the interface is formed by two porous media consisting of fused glass beads and fused lead beads with different porosities. Our analysis is focused on the effect of pore interface conditions (determined by the value of the normal component of flow impedance vector). Predictions show in either fast or shear wave incidence the reflected and transmitted fast and shear waves behave with no evident difference at a sealed or an open pore interface, while the reflected or transmitted slow wave is affected strongly by the pore interface conditions. Numerical results show the amount of energy allocated from the fast or shear incident wave to the reflected and transmitted slow waves is negligible. For a normally incident slow wave with an open pore interface, about 88% energy is converted to the transmitted slow wave and 0.5% to the reflected slow wave while, with a sealed pore interface, a complete reflection occurs for the slow wave.

The investigation of generalized leaky Lamb wave interaction with a fluid-saturated porous plate has been conducted theoretically and experimentally. According to Biot's theory, numerical results of reflected and transmitted spectra through a thin porous plate immersed in a liquid has been achieved. Ultrasonic measurement of reflected signal spectra from porous plate at different angle has been performed to obtain phase velocity of various Lamb modes as function of product of frequency and thickness. Experimental results show that the measured lowest Lamb mode in a porous plate is attributed to the slow wave. At small incident angle, the horizontal axis of the asymptotic phase velocity of the measured lowest Lamb mode is in coincidence with half of the slow wave velocity. The good agreement between experimental results and theoretical predictions shows that the Lamb wave technique provides a new approach for detecting slow wave in porous media.

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)

The major objectives of this research are designed to study the origin and migration pathways of oils in the Anadarko basin, Oklahoma. Despite the large quantities of oil and gas produced from this basin, uncertainty remains concerning the source(s) of the major oil accumulations. 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. Additional emphasis has also been placed on understanding various effects, such as biodegradation, that alter the composition of the crude oils.

The work has diversified into a number of different areas. The major subdivisions are: specific oil/source rock correlations in well defined areas of the basin, use of hydrocarbon and porphyrin biomarkers to further our understanding of the origin of oil seeps occurring in the Ordovician Oil Creek sandstone, and a study of the effects of biodegradation on biomarkers and asphaltenes in various oil seeps and biodegraded oils. Samples of the major suspected source rocks, namely the Woodford shale, have been collected both from outcrops and cores. The aim of this part of the study is to evaluate the Woodford shale as a source for the oils. Collection of outcrop samples of the Woodford shale has also provided us with an indication of the effects of weathering on this shale, an important part of any geochemical study and an essential part of the process in selecting rocks for further evaluation. The shales, and also asphaltenes from the oils, are being characterized by pyrolysis-gas chromatography-mass spectrometry using a PYRAN pyrolysis system.

Early studies were concerned with oils from the Pauls Valley area of the Anadarko basin. Recently in collaboration with the USGS, Denver, we have expanded our oil study into the northern part of the basin to examine oils from regions near the Oklahoma/Kansas border. These oils are also apparently sourced from the Woodford shale in the southern part of the basin. Hence these samples are providing us with the opportunity to study long distance migration effects. Techniques are also being developed to examine hydrocarbons and organosulphur compounds produced from source rocks and asphaltenes by microscale pyrolysis.

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)

Precambrian rocks have long been of interest with respect to the chemical and tectonic evolution of the Earth's crust and their frequent association with economic mineral deposits. More recently, with the paleontologic documentation of biological remnants, research has also focused on the evolution of the Earth's biosphere and the attendant consequences for the nature of the hydrosphere and lithosphere. Although it has been suggested that organic carbon levels in Proterozoic sediments are in many cases equivalent to corresponding Phanerozoic lithofacies, very few systematic attempts at evaluating the petroleum source rock potential of Precambrian organic-rich rocks have been undertaken, particularly in North America. This deficiency is primarily attributed to the fact that the distribution of Precambrian rocks in the subsurface is poorly understood. Also, it is generally assumed that rocks of such extreme antiquity, commonly found in association with intrusives, must be metamorphosed. The perceived unlikelihood that oil and gas, if generated and migrated, could have been preserved through ensuing, disruptive tectonic episodes is yet another reason for the limited commercial exploration in these regimes.

Despite these formidable complications, extensive organic geochemical studies of Precambrian rocks are being undertaken by researchers on other continents, particularly in Australia, with some surprising results. However, work on North American Precambrian rocks that has been done or is in progress is apparently restricted to either detailed organic geochemical studies on solvent extracts from one or more samples from a single locality or routine screening work on somewhat more substantial sample sets. These studies have produced mixed results. Given their limited scope, it is clear that further attention is necessary to fully appreciate the nature of these rocks. Research in this direction may help in recognizing previously overlooked potential petroleum frontiers and, as an important secondary benefit, would provide a database from which the role of organic material in ore forming processes could be further clarified. Additional implications include the geochemical elucidation of Precambrian biotic and depositional systems and their possible applications to biostratigraphy and modeling of more recent analogs.

This study entails the collection and analysis of Middle and Late Proterozoic fine-grained, clastic rocks from several areas in the United States. The goals of this study are: 1) identification of source rocks by quantification and characterization of constituent organic matter; 2) evaluation of the possibility of previous or current hydrocarbon generation using general stratigraphic, geochemical, and tectonic information; 3) use of organic geochemical and petrographic data to characterize the depositional settings; and 4) interpretation of secular trends (e.g. $\delta^{13}\text{C}$) within specific depositional settings. Preliminary results demonstrate the feasibility of realizing these objectives.

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)

We are developing and applying some statistical techniques to improve the collection and analysis of wide band magnetotelluric data. The principal goal of the research is to develop fully automatic single station and remote reference impedance estimation schemes that are robust, unbiased, and statistically efficient. In particular, we are pursuing some extensions of the standard regression M-estimates (which we have previously applied to this problem) to allow for non-stationary and non-Gaussian noise in both electric and magnetic field channels measured at one or more simultaneous stations. A second goal is to develop formal, reliable procedures for estimating an undistorted 2-D strike direction and to develop statistics for assessing the validity of the 2-D assumption that are not affected by static surface distortion. The research is "data driven" -- we are basing our development primarily on "what works" for a set of 200 wide band MT data sets, rather than on strictly theoretical considerations.

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

Grant: DE-FG02-88ER13437

Title: Silicate Thermochemistry

Person in Charge: A. Navrotsky (609-452-4674)

A study was performed to examine the effects of the charge coupled substitution $\text{Si}^{4+} = \text{T}^3 + \text{Na}^{1+}$ ($\text{T} = \text{Al}, \text{B}, \text{Fe}, \text{and Ga}$) on the overall stabilization of framework silicate glasses in the systems $x\text{NaTO}_2-(1-x)\text{SiO}_2$. Enthalpies of solution in molten $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 973 K were determined for $x \leq 0.5$. The heats of solution in each of these systems become increasingly endothermic with increasing x and exhibit a maximum near $x = 0.5$ reflecting an exothermic ΔH of mixing. In the glassy systems $\text{M}_{1/n}\text{AlO}_2\text{-SiO}_2$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{and Pb}$), the enthalpy of stabilization was found to scale inversely with the field strength (Z/R) of the non-framework cation, M. This implies that the stability of the aluminosilicate framework in these systems is controlled by the strength of the M-O bond and the concomitant weakening of the T-O-T angle. In the present study, ΔH_{stab} does not scale with the strength of the T-O bonds. Instead it appears that the stability of the aluminosilicate framework is controlled by the range of T-O-T bond angles permitted by the substitution of T^{3+} for Si^{4+} . The substitution of Al, Fe, Ga, and B for Si changes to varying degrees the range of bond angles that are energetically favorable. As this range decreases, the stability of the glass decreases.

A technique has been developed for solution calorimetry of oxides of highly charged cations in molten $2\text{PbO}\cdot\text{B}_2\text{O}_3$. It is used to obtain enthalpies of vitrification of crystalline $\text{K}_2(\text{Ti,Zr})\text{Si}_4\text{O}_9$. Transposed-temperature-drop calorimetry experiments are being performed upon a glass that undergoes rapid glass-glass phase separation at 1173 K. These experiments indicate that it is possible to directly measure the enthalpies of unmixing of immiscible liquids and glasses. Thermodynamic mixing properties of glasses of the system $\text{K}_2\text{O-SiO}_2\text{-La}_2\text{O}_3$ are being measured.

Investigation continues of the structural and thermodynamic effects of aluminum substitution on tri-octahedral Fe-free micas. Nine synthetic samples along the join from $\text{K}_{0.94}(\text{Mg}_{2.93}\text{Al}_{0.04})(\text{Al}_{0.94}\text{Si}_{3.06})\text{O}_{10}(\text{OH})_2$ to $\text{K}_{0.90}(\text{Mg}_{2.08}\text{Al}_{0.92}) - (\text{Al}_{1.83}\text{Si}_{2.17})\text{O}_{10}(\text{OH})_2$ have been studied. Microprobe and thermogravimetric analyses of synthetic materials were completed. The five Si-rich samples had constant weight up to 1003 K, then they lost ~4.3 wt% H_2O due to mica dehydroxylation. Weight loss occurred in two steps, probably due to a difference in -OH sites and related to the Al content of the octahedral sheet. The Al-rich samples showed a gradual weight loss of up to 1.8 wt% in the 473 - 1003 K range that was temperature dependent and time independent. They lost 3.9 - 4.1 wt% H_2O in the 1003 - 1423 K range due to mica dehydroxylation. Lattice parameter refinements have been completed. Calorimetric study to determine enthalpies of mixing is planned for later this spring. A series of amphiboles is also under study.

Our data and models for glasses are correlated to the structure and physical properties of silicate melts and have potential applications in such diverse fields as geochemistry, magma energy generation, ceramic science, nuclear waste disposal, and reactor safety. The work on hydrous phases is applicable to sedimentary petrology, diagenesis, metamorphism, and nuclear waste storage.

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

Grant: DE-FG02-89ER14078

Title: Studies on the Use of Non-Conventional Imaging Methods
With Narrow- and Wide-Angle Crustal Seismic Data

Person in Charge: R. A. Phinney (609-452-4101)

The increasing availability of crustal seismic data with enough closely spaced channels to suppress aliasing and enough offset coverage to approach the near- and post-critical regime now raises the question of developing methods for converting these new data into subsurface images and for extracting velocity information. Existing methods that can, in principle, be used as steps in the processing include: migration of shot gathers, coherency enhancement of shot gathers before stack, migration of multiple common offset sections, iterative modeling and ray tracing, and so forth. The goal of the proposed research is to sort through these possibilities and several others that we believe have promise to develop a more or less standard set of protocols that will produce the needed image and velocity models. Since much of the newer data is low-fold explosion data, this research will be directed toward direct processing of shot gathers, rather than working with the CDP approach.

The specific avenues to be followed include:

- Multi-model scans of migration of limited aperture shot gathers
- Interactive studies of velocity inversion by focusing
- Use of coherency picking to close the loop on the migration/modeling process
- Procedures for velocity and imaging work on the near-surface refraction data
- Information extraction from conventional refraction spreads
- Rapid finite difference modeling of refraction data

We will treat near-vertical reflection data merely as a subset of the more general collection that runs from zero to post-critical offsets.

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)

Fluid transport through a fracture network in rock depends strongly on the nature of connections between fracture segments and between individual fractures. We are developing three-dimensional models for natural fracture connectivity and to analyze the mechanisms responsible for the linkage (or lack thereof) of single fractures and fracture sets. The models will be based on detailed field mapping and observations from both massive and layered sedimentary rocks, typical of producing reservoirs. The mechanisms responsible for connectivity will be determined using continuum and fracture mechanics principles applied to the fracture process, including initiation, propagation, interaction, and termination of fractures under natural loading conditions. By identifying these mechanisms we will relate the degree of connectivity to the geometry, state of stress, and material properties of the reservoir rocks and, in turn, be in a position to evaluate the influence of these factors on fracture permeability in oil and gas reservoirs. The results of our research will be complimentary to and help to constrain geophysical imaging techniques and geostatistical models of fractured reservoirs.

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 (605-394-6152)

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. During 1988-89 we continued to attack these problems through studies in the granite-pegmatite systems of the Black Hills, South Dakota.

Mineral chemistry, major element chemistry, and trace element modeling of the Harney Peak granite (Black Hills, South Dakota) suggest that 75% to 80% fractional crystallization was the dominant mechanism in producing evolved tourmaline-bearing granite (high B, Li, Rb, Cs, Be, Nb) from a biotite-muscovite granite. To evaluate the petrogenetic evolutionary relations between the granite and the surrounding rare-element pegmatite field, over 500 K-feldspars (Kf) were analyzed from 60 unzoned to complexly zoned pegmatites. Pegmatites with Kf relatively high in Ba (>140 ppm) and relatively low in Rb (<1000 ppm) and Cs (<30 ppm) are distributed in regions of high pegmatite density (>200 pegmatites/sq. mile), where highly evolved pegmatites with Kf enriched in Rb (>4000 ppm) and Cs (>500 ppm) are distributed in regions of low pegmatite density (<100 pegmatites/sq. mile). In addition, distinct swarms of pegmatites can be distinguished based on feldspar chemistry and associated mineral assemblages. The extent of pegmatite evolution as reflected in the Kf documents the relation between the degree of fractionation and internal zoning characteristics. With increasing degrees of fractionation as reflected in the decrease in K/Rb in the Kf, the segregation of alkali elements (Rb, Cs, K) from Na appears to have been more efficient. This may be the direct impact of changes in volatile content, volatile composition, and melt structure during granitic melt evolution. In general, the Kf chemical data are consistent with a model in which the pegmatites represent a continuation of the fractionation processes postulated for the central granite. However, local unsystematic enrichments or depletions in bulk pegmatite (Li, Rb, Cs, F, B) or Kf (e.g., anomalously high Cs with low Rb; low Rb in Li-enriched pegmatites) chemistry suggest petrogenetic "branches" in the granite fractionation process or variations in local partial melting processes.

Grantee: UNIVERSITY OF SOUTHERN CALIFORNIA
Department of Geological Sciences
Los Angeles, California 90089-0740

Grant: DE-FG03-88ER13807

Title: Continental Scientific Drilling Program:
The Seismology of Continental Thermal Regimes

Person in Charge: K. Aki (213-743-3510)

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 completed the investigation of the Earth's structure under the Valles caldera using teleseismic P waves. We found an extremely low Q (high absorptive) body, which we attributed to the hydrothermal system, underlain by a low velocity body, which we attributed to the magma body. We continued the studies on the seismic inverse problem for magma chamber delineation and on the seismogram synthesis using ray methods, Gaussian beam method, and boundary integral method. We also progressed in theoretical studies on long-period events and volcanic tremor.

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 regime 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. We are also developing a high-temperature borehole seismometer by the use of fiber optics.

Grantee: STANFORD UNIVERSITY
Geophysics Department
Stanford, California 94305-2215

Grant: DE-FG03-88ER13601

Title: Porosity with Fluids: Origin and Effects on
Physical Properties of Crustal Rocks

Person in Charge: A. M. Nur (415-723-9526)

Our studies in rock physics focus on problems related to the characterization of reservoirs and the crust and to the exploration for and production from hydrocarbon reservoirs. Fast Montoto thinning image processing has been used to explore how pore geometry and connectivity are related to porosity and permeability. A microgeometry model for sand, shale, and shaley sand has been developed to explain and predict the dependence of sonic velocity, porosity, and permeability on clay content and compaction. Ultrasonic data have been examined to estimate velocity dispersion in saturated sandstones.

Pore connectivity. Fast Montoto thinning was used to analyze thin sections of Fontainebleau sandstone. Thinning transforms the digitized pore space into a network and the data are coded into a matrix of lengths, apertures, and connections. These results provide means to understand variations in porosity and permeability between rock samples. In time, they may serve as the bases for network models of pore microstructure with predictive value, when calibrated to bulk rock measurements.

Permeability in sand/clay mixtures. We have developed a model for the effect of clay content (c) in unconsolidated sand/clay mixtures on velocity, porosity, and permeability. Our model predicts a minimum in porosity and a corresponding maximum in velocity, when the clay content in the mixtures is sufficient to fill the sand pore space completely ($c = \phi_{sand}$). We have modeled permeability using the Carmen-Kozeny relation, taking care to account for the influence of clay content on porosity, tortuosity, and specific surface area. Permeability decreases drastically with increasing clay content in sands and shaley sands ($0 < c < \phi_{sand}$) but is almost insensitive to clay content in sandy shales and shales ($\phi_{sand} < c < 1$). In combination with well-log and seismic data, our model provides the basis to obtain spatial estimates of porosity, permeability, and shaliness from seismic data.

Velocity dispersion in sandstones. Biot-Gassmann theory was used to examine velocity dispersion in a suite of 69 sandstones. Biot velocity dispersion (BVD), the velocity difference between the high- and low-frequency limits of Biot theory, was low (<1.5%) and found to increase with porosity, cementation, and differential pressure and to decrease with clay content. Apparent velocity dispersion (AVD) is defined as the difference between ultrasonic (1 MHz) measurements and the Biot low-frequency limit. Non-Biot velocity dispersion (NBVD) is the difference between AVD and BVD. It had a relatively large range (1-9%) and, in contrast to Biot dispersion, decreased with porosity, cementation, and differential pressure and increased with clay content. Non-Biot mechanisms control velocity dispersion in these sandstones. We believe the "local flow" mechanism to be dominant and modulated by the effects of clay, cementation, compaction, and differential stress. Our results suggest that ultrasonic measurements may be used to infer velocity dispersion at the frequencies of seismic (10-100 Hz) and logging (10-20 kHz) methods.

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

Grant: DE-FG03-88ER13319

Title: Structure and Emplacement of the Magmatic Intrusion
Beneath the Valley of Ten Thousand Smokes

Person in Charge: D. D. Pollard (415-723-4679)

The goal of this project is to provide constraints on the subsurface geometry of the vent, feeder conduit(s), and possible intrusive bodies in the Novarupta basin, Valley of Ten Thousand Smokes (VTTS), Katmai National Park, Alaska. If the proposed Katmai drilling project is funded and receives Park Service permits for drilling, 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. While we cannot guarantee unique solutions for the subsurface geometry, we expect our results to provide important constraints on the shape of the vent and the origin of the surficial fractures. 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: 1) complete a detailed topographic-structural map of surface fractures including spatial distribution and relative displacements, 2) carry out numerical and physical model studies that relate surface fractures to major subsurface structures, and 3) interpret the origin of surface fractures in light of these model studies.

A detailed fracture map of the Novarupta basin was checked and updated. Topographic profiles were surveyed to assist in identifying structures and the magnitude of associated displacement. The mapping and topographic profiling of fractures in the basin has revealed four regions and styles of deformation: 1) translational block slides and slope-parallel opening fractures (gulls) on the flanks of Trident and Broken Mountain, 2) arcuate grabens between Broken Mountain and Trident, 3) opening fractures on the flanks of Trident and near Novarupta dome, and 4) grabens on the crest of the Turtle. The different styles of deformation in different areas of the vent suggest that the topography of the original depositional surface was important in determining the style of surface fracturing. Other factors controlling surface deformation could be distance from the vent, existence and movement of underlying faults, and dilation of subsurface magma bodies.

Because much of the material in the vent region is poorly consolidated, the present profiles of fissures and fault scarps do not represent the original geometry and therefore hamper measurement of relative offsets and dips of the fracture walls. In an effort to obtain estimates of the original geometry of the fractures in the vent region, more than 7000 photographs from the National Geographic Society expeditions to the VTTS, led by Robert F. Griggs in 1916-1919, have been examined. It is clear from many of the photographs that scarps with a current maximum slope of $<40^\circ$ may have had initial slopes approaching vertical. We plan to reoccupy as many of these photographic sites as possible, to obtain estimates of the amount of scarp degradation at those localities.

Grantee: STANFORD UNIVERSITY
Department of Geology
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)

Fluid transport through a fracture network in rock depends strongly on the nature of connections between fracture segments and between individual fractures. We are developing three-dimensional models for natural fracture connectivity and to analyze the mechanisms responsible for the linkage (or lack thereof) of single fractures and fracture sets. The models will be based on detailed field mapping and observations from both massive and layered sedimentary rocks, typical of producing reservoirs. The mechanisms responsible for connectivity will be determined using continuum and fracture mechanics principles applied to the fracture process, including initiation, propagation, interaction, and termination of fractures under natural loading conditions. By identifying these mechanisms we will relate the degree of connectivity to the geometry, state of stress, and material properties of the reservoir rocks and, in turn, be in a position to evaluate the influence of these factors on fracture permeability in oil and gas reservoirs. The results of our research will be complimentary to and help to constrain geophysical imaging techniques and geostatistical models of fractured reservoirs.

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)

The Mission Canyon formation in southwestern Montana and its stratigraphic equivalents in east-central Idaho were deposited during apparent collision of the western continental margin of North America with an inferred 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. Detailed sedimentologic studies have led to a better understanding of the evolution of the platform margin-to-basin transition. An integrated petrographic 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.

To date, third-to-fifth order scale (10^6 to 10^4 yr) cyclic sedimentary sequences have been documented in shallow platform to deep basin environments. The third order cycles can be correlated across the platform and into the Antler foredeep. This study has documented how sedimentation in ancient slope and basinal environments responds to relative sea level fluctuations on a shallow carbonate platform that supplied most of the sediment to these environments. Measured thicknesses for individual beds also are being used in a regional study of platform and basin subsidence in Montana and Idaho. Stratigraphic data from Upper Devonian through upper Mississippian rocks are being included in the subsidence analysis. This subsidence analysis should provide important information concerning the tectonic driving mechanisms for subsidence during foundering of a former passive margin and its transition into a convergent margin.

Several regional petrographic geochemical trends have been observed in the Mission Canyon formation. Near paleostrandline positions, discrete freshwater lenses apparently developed after aggradation and subaerial exposure of each third order depositional sequence. On basinward parts of the Mission Canyon platform, diagenetic trends indicate that the short lived freshwater lenses related to the third order cycles did not extend to the outer platform. Instead, extensive meteoric diagenesis is related to regional subaerial exposure of the entire platform during post-Mission Canyon time. Another important aspect of research on 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. Cation exchange columns are being constructed so that Sr and REE can be separated from diagenetic carbonates; Sr and Nd isotopic compositions will be analyzed using isotope dilution techniques. These data should provide important information concerning the systematics of Sr and REE behavior during carbonate diagenesis.

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)

The anisotropic deformation of foliated and lineated rocks at elevated temperatures and pressures is under investigation to predict the mechanical response of rocks surrounding buried magma chambers to the stress fields generated by deep drilling. Our approach is to perform triaxial extension and compression tests at temperatures and pressures representative of the borehole environment on samples cored along six selected orientations and to fit the data to an orthorhombic yield criterion. We are investigating Four-Mile gneiss (a strongly layered gneiss with well defined lineation), a biotite-rich schist, and Westerly granite (using a block oriented with respect to the granite's rift, grain, and hardway). Progress has been made in three areas: the experimental determination of strength anisotropies for the three starting materials, theoretical treatment and modeling of the results, and characterization of fabrics surrounding magma bodies resulting from their diapiric emplacement into shallow portions of the Earth's crust. Some results to date follow.

Extension and compression experiments defining the inelastic behavior of Four-Mile gneiss have been completed; nearly 80 oriented samples have been tested at temperatures ranging from 25° to 800°C, confining pressures of 0 to 400 MPa, and strain rates of 10^{-4} to 10^{-6} s⁻¹. A rate-independent constitutive relationship for Four-Mile gneiss may be justified by negligible variations in strength with strain rate and weak dependencies upon temperature.

Thirteen successful experiments have been performed on samples of biotite schist at temperatures ranging from 25° to 400°C and confining pressures of 50 to 300 MPa at a strain rate of 10^{-5} /s. Remarkably, the schist chosen exhibits very weak anisotropy as compared with the gneiss and previous results for phyllite. The temperature dependence of strength resembles that of biotite single crystals, reflecting the predominance of basal dislocation glide; however, biotite schist strengths exhibit a weak, though measurable, dependence upon confining pressure, suggesting that dilatant brittle mechanisms are operative as well.

Room temperature compression experiments of oriented samples of Westerly granite have been initiated. Strengths of Westerly granite at failure are comparable to those measured for gneiss samples in the strongest orientation.

The foliation development within the metamorphic and deformation aureoles of a granite stock exposed in the Kern Mountains of Nevada has been investigated and compared with models of forceful magma emplacement. The deformation aureole is narrow relative to the pluton's size with foliations extending ~400 m into the country rocks, compared with a mean pluton radius of 5 km. Combined with appropriate intrusion modeling, these results will help assess the extent and nature of deformation-induced fabrics that may be expected surrounding buried magma bodies.

Grantee: UNIVERSITY OF TULSA
Tulsa, Oklahoma 74104

Grant: DE-FG05-88ER13417

Title: Stability of Natural Gas in the Deep Subsurface

Person in Charge: C. Barker and N. Takach (918-631-3014)

Fluid inclusions offer one of the best ways of obtaining samples of the gases present during mineral formation. They are not inherently limited by either depth or age and the gases in the inclusion are protected from contamination. Unfortunately because of their small size, and the possibility of multiple populations, they pose a severe analytical challenge. We have continued to develop our computer-driven, dual mass spectrometer system for analyzing the bursts of gas released from individual rupturing inclusion. The digitized output from the mass spectrometer is transferred for off-line processing. Cracking patterns for individual compounds (e.g., water 18-17-16 amu) show good reproducibility unless the inclusions are very small (when noise becomes a problem) or very large (when the analog-to-digital interface saturates). The graphics package permits display of any subset of inclusions so that size extremes can be eliminated easily. Program development in the last year has included the possibility of examining burst shape (in terms of amu versus time) for any burst. This has been very useful for deciding whether unusual data are valid or spurious.

System capabilities have been evaluated by running a wide range of minerals representing many different environments. The method works well except for minerals that decompose before inclusions rupture (e.g., gypsum) and minerals with inclusions containing crude oil since they do not over pressure enough to induce rupture. The experimental system has been used to analyze gases in quartz samples from subduction complexes in the Aleutians, Barbados, and the Olympic Peninsula. Although most are water-rich many show methane-rich inclusions, and in a few cases methane appears to be the sole content with even water being absent. Minor amounts of carbon dioxide and carbon monoxide have also been observed but there are no sulfur gases or higher hydrocarbons in any of the samples studied.

Inclusion in bedded and domal salts (Palo Duro basin and Gulf Coast, respectively) have been analyzed. Water dominates but trace to major quantities of methane also occur. Higher hydrocarbons were observed only in the bedded salts and are absent in the domal salt. This is consistent with the deep, high temperature origin of the domal salt because higher hydrocarbons would have been thermally cracked. Minor carbon dioxide, hydrogen chloride, and traces of sulfur compounds occurred in some inclusions.

Gases in melt inclusions can be analyzed but much higher temperatures are needed to rupture these inclusions. We now have the capability to heat samples to 1600°C and have demonstrated the feasibility of the method with melt inclusions in plagioclase phenocrysts from mid-ocean ridge basalts. Compositions vary but sulfur dioxide is often a major component along with carbon dioxide.

We have continued to support the analytical work with the thermodynamic calculations of deep gas compositions. The program finds the minimum free energy in multi-component (up to 70), multi-phase (up to 30) systems for subsurface conditions down to 40,000 feet.

Grantee: U.S. GEOLOGICAL SURVEY
905 National Center
Reston, Virginia 22092

Grant: DE-FG05-88ER13981

Title: Workshop on "Crustal Dynamics: Chaotic Behavior
and Fractal Structures"

Person in Charge: R. L. Wesson (703-648-6714)

This workshop was funded jointly by the National Science Foundation, National Aeronautics and Space Administration, and the Department of Energy and supported operationally by the U.S. Geological Survey (USGS) and was held February 12-15, 1989 at the Asilomar Conference Center in Pacific Grove, California. The workshop brought together earth scientists, physicists, and mathematicians to discuss new approaches to problem-related earthquakes and crustal dynamics.

During the last decade, our understanding of dynamical systems has undergone a revolution. We now realize that, contrary to previous assumptions, even simple nonlinear systems can exhibit very complicated behavior. Our understanding of this "deterministic chaos" offers the hope of improved short-term predictive ability but at the same time implies that long-term prediction of chaotic behavior is a practical impossibility.

One of the most tantalizing possibilities raised by new ideas on nonlinear dynamics is that they may be applicable to earthquakes. Only a few earth scientists are now working in this area, because few seismologists are yet knowledgeable about nonlinear dynamics and few dynamicists know much about earthquakes. Therefore, the workshop began with reviews. Earth scientists explained our current understanding of earthquakes and tectonic processes, while physicists and mathematicians introduced such subjects as fractals, the phase transition analogy, and condensed-matter physics. The bulk of the workshop consisted of detailed presentations based on recent work and was organized into sessions on nucleation, dynamics and chaos, fractals and scaling, and the renormalization group.

In addition to the technical sessions, workshop participants were treated to a field trip to the nearby Calaveras and San Andreas faults. This trip provided graphic evidence of the complexity of seismic processes and highlighted the central question of whether this complexity might be understandable in terms of simple underlying mechanisms.

The effectiveness of the workshop in stimulating interdisciplinary communication far exceeded the hopes of the organizers and augurs well for new and creative approaches to understanding the dynamics of the Earth. Many of the participants expressed hope that there will be follow-up meetings over the next few years to follow developments in the field as they occur.

A report on the workshop is in preparation for submission to EOS. In addition, a News and Views article about it appeared in *Nature*.

Grantee: UNIVERSITY OF UTAH RESEARCH INSTITUTE
Earth Science Laboratory
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 Magma-Hydrothermal System

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

VC-2B was drilled in the Sulphur Springs area of the Valles caldera late in 1988. The principal objective in completing the core hole was penetration through the the active, high-temperature, Sulphur Springs hydrothermal system in order to obtain otherwise unavailable measurements of temperatures, pressures, and fluid compositions throughout much of the system's full vertical extent in an instant of geologic time. These measurements should improve our ability to model both active geothermal systems and analogous ancient systems, which formed a variety of epithermal ore deposits.

VC-2B was completed late in 1988, with core recovery approaching 100%. The hole penetrated not only through an upper-level, high-temperature hydrothermal system, circulating principally in the Valles intracaldera ignimbrite sequence, but also possibly a deep system, with much different fluid composition and temperatures, principally in fractured Precambrian quartz monzonite. The two systems appear to be separated by a thick, impermeable, Paleozoic sedimentary sequence. Preliminary fluid-inclusion evidence from primary inclusions believed to have been trapped in the contemporary Valles hydrothermal system indicates that whereas high-level fluids are very dilute, deep ones may be much more saline (up to at least 2.9 equiv. wt.% NaCl). Thus, VC-2B may have penetrated "stacked" hydrothermal cells separated by an essentially conductive thermal regime in the Paleozoic sequence.

The core hole also encountered a wide variety of metallic sulfides and sulfosalts, although not the deep molybdenite accumulation originally envisioned. Those found above about 800 m are typical of many epithermal ore deposits (e.g., pyrrargyrite); these are zoned above a base-metal sulfide suite comprising principally chalcocite, chalcopyrite, bornite(?), sphalerite, and galena.

Grantee: UNIVERSITY OF UTAH RESEARCH INSTITUTE
Earth Science Laboratory
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 (801-524-3422)

We are conducting a tensor, controlled-source audiomagnetotelluric (CSAMT) survey at the Sulphur Springs area of the Valles caldera geothermal system. The survey will support scientific interpretation of CSDP hole VC-2A drilled in the fall of 1986 and hole VC-2B completed recently. 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, will be concentrated over the Sulphur Springs area but some will be taken as much as 2-3 km away for control. The frequency range of the data spans 4.1 Khz down to 1.0 Hz, allowing tight control of near-surface structure but also providing information on structure to depths approaching 2 km. The tensor nature of the data proposed is very desirable to strengthen the interpretation and take advantage of the precise and versatile 2-D and 3-D magnetotelluric modeling techniques developed at ESL/UURI.

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

The purpose of this project is to study the relationship between hydrothermally induced mobility of uranium and lead isotopes and the chemical and mechanical properties of small populations of zircons ($ZrSiO_4$). Our experiments utilized both natural and synthetic zircons as starting materials. During the first year of this project, we refined techniques for growing zircons in tungstate and molybdate fluxes. Variations in the size and morphology of the synthetic zircons are demonstrably related to both cooling rates and the addition of minor amounts of rare earths and other elements to the starting mixtures.

The hydrothermal stability of the U-Pb isotopic system of natural non-metamict zircons has been investigated at varying pressure and temperature conditions utilizing two fluid compositions, 2M NaCl and 2% HNO_3 . Experiments were conducted at 4 and 6 kilobars, at 300° and 600°C, and for durations of 24, 200, and 720 hours. A large fraction (~30 - 40%) of uranium (assumed to be bonded in the mineral structure) was removed from the zircon during the runs made with 2M NaCl, while the zircons treated with the HNO_3 solution lost less than 10% uranium at the same run conditions. We are currently investigating the relationship between crystallinity and chemistry of zircons, development of microfractures and the loss of uranium and lead from the experimental charge.

Preliminary SEM imaging of the run products indicates that microfractures are, to some extent, crystallographically controlled. Microprobe analyses suggest that trace constituents (other than uranium and lead), such as Hf, Y, and P, appear to be unaffected by the experimental solutions. Microfracture growth and nucleation mechanisms are being investigated using theoretical models. From these studies, we are developing models that relate the timing of microfracturing to changes in the surface/volume ratio and the transport of uranium and lead out of zircons.

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

Grant: DE-FG05-89ER14065

Title: PVTX Properties of Fluid Systems: NaCl-CaCl₂-H₂O

Person in Charge: R. J. Bodnar (703-961-7455)

Most geologic processes in the Earth's crust take place in the presence of one or more fluid phases, and the compositions of these fluids vary from one environment to another. In order to derive thermodynamic properties of geologic fluids and fluid-melt systems and to interpret microthermometric data from fluid inclusions trapped in these environments, an experimental database on the PVTX properties of geologically important fluid systems must be established. Until recently, derivations of thermodynamic properties of geologic fluids and interpretations of fluid inclusion volumetric properties and phase equilibria have generally been based upon the PVTX properties of simple unary and binary subsets of the larger system NaCl-KCl-CaCl₂-MgCl₂-H₂O-CO₂-CH₄. These simple systems often do not adequately describe observed phase behavior in fluid inclusions, nor do they provide representative models for many of the more complex fluids found in nature.

We have begun a research program to determine accurately and completely the PVTX properties of geologically important fluid systems over the complete range of temperature, pressure, and composition conditions commonly encountered in the Earth's crust. These data have been and will continue to be gathered in a systematic manner, starting with relatively simple binary systems and progressing to more complex higher order systems. We have completed our studies of the NaCl-H₂O and the NaCl-KCl-H₂O system. Work on the NaCl-H₂O-CO₂ system is nearly completed. We have recently begun reconnaissance investigations of the CaCl₂-NaCl-H₂O system. We plan to complete our study of phase equilibria and volumetric properties of the NaCl-CaCl₂-H₂O system.

Information obtained in this study will add to our knowledge of the physical and chemical properties of geologic fluids found at crustal P-T conditions. As such, our results will broaden our understanding of many important fluid-related geochemical processes of interest to geoscientists.

Grantee: UNIVERSITY OF WASHINGTON
Geophysics Program
Seattle, Washington 98195

Grant: DE-FG06-86ER13472

Title: Two- and Three-Dimensional Magnetotelluric Inversion

Person in Charge: J. R. Booker (206-543-8020)

We have developed an efficient iterative inversion method applicable to both two-dimensional (2-D) and three-dimensional (3-D) magnetotelluric data. The method approximates horizontal derivative terms with their values calculated from the fields of the previous iteration. The equations at each horizontal coordinate become uncoupled and 1-D with an added term containing the effects of the horizontal derivatives. At each iteration this allows separate inversions for the conductivity profile beneath each measurement site. Resultant profiles are interpolated to form a new multi-dimensional model for which the fields are calculated. Residuals to this new model are used in the next iteration. The method is very fast, as partial derivatives are calculated for 1-D problems only and computation time grows only linearly with the number of sites of data inverted. Preliminary tests with 2-D data show very promising results. Some problems remain in application of the algorithm to real 2-D data. We are attempting to resolve these questions and to extend the method to 3-D.

Grantee: UNIVERSITY OF WASHINGTON
Geophysics Program
Seattle, Washington 98195

Grant: DE-FG06-88ER13979

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

Person in Charge: S. D. Malone (206-543-8020)

Geothermal ground noise and volcanic tremor are sustained, low level, quasi-periodic vibrations of the ground often observed in geothermal areas and at active volcanoes. It has been suggested that geothermal ground noise and shallow volcanic tremor may be caused by vigorous boiling within hydrothermal systems. The physical model for such a seismic source consists of multiple distributed monopole (volume) sources of compressional wave energy radiating discrete pulses randomly with time. Each monopole source corresponds to a single vapor bubble surrounded by liquid; the acoustic energy liberated during formation or collapse of the bubble takes the form of a sharp pressure pulse, and is considered to be the direct source of seismic energy in such a model. The amplitude and frequency content of the observed seismic signal are functions of the acoustic power spectrum of boiling, as well as the impulse response functions of the conduits in which boiling occurs, the material through which seismic energy passes in traveling to the receiver, and 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 acoustic power spectrum of boiling (the "source" spectrum in the above model). We simulate boiling in the lab by injecting high pressure steam from a boiler into a pressure vessel that is filled with water. The water pressure fluctuations that result from the repeated formation and collapse of steam bubbles at the steam inlet vents are recorded by a hydrophone whose output is digitized at 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, $<139^\circ\text{C}$, 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 experimental variables. Besides the overall shape of the boiling power spectrum, we are investigating the absolute spectral levels in frequency bands typical of geothermal ground noise and volcanic tremor (0.5 - 10 Hz) and the ratio of acoustic power liberated to total available power. The values of these parameters are critical to hydrothermal boiling's ability to generate ground motion amplitudes in accordance with observation. If it can be shown that the range of observed ground noise/tremor amplitudes can be accounted for by hydrothermal boiling at reasonable heat transfer rates, this knowledge would be invaluable to designers of seismic monitoring experiments related to geothermal resource exploration/evaluation and volcanic eruption prediction.

Grantee: WASHINGTON STATE UNIVERSITY
Geology Department
Pullman, Washington 99164-2812

Grant: DE-FG06-87ER13796

Title: Geological Spatial Analysis

Person in Charge: R. Thiessen (509-335-4947), J. Eliason, and K. Johnson

Geologic spatial analysis (GSA) research is focused on three-dimensional analysis of regions using geologic data sets that can be referenced by latitude, longitude, and elevation/depth. These databases include digital elevation models of topography, lineaments from a variety of imagery, earthquake foci, fractures identified on acoustic images, faults and joints observed in the field, and geochemical, gravity, magnetics, and borehole data. The GSA techniques determine the location and orientation of structural features in three-dimensional space to develop a regional geologic model. This concept is based on classic structural analysis techniques that are more concerned with mapped patterns of lithologies and/or orientation of structures, and not their location in three-dimensions. These relationships are essential for exploration and development of energy resources, assessment of seismic risk, analysis of hydrologic systems, and regional geologic research.

The objective of this research program is to develop and test a package of quantitative GSA computer programs that will enable scientists to determine the three-dimensional structural relationships of a region. Development and testing of the GSA programs are being done with data from field studies to verify the GSA techniques. The GSA topographic analysis concept is based on the geologic observation that planes of weakness, such as faults, fractures, and bedding planes, localize erosion and are often followed by topographic lows. The digital analysis technique involves looking for topographic lows in a digital elevation model, fitting vectors to these lows, and finding those vectors that are coplanar and are likely to be controlled by a geologic structure. Two separate approaches for determination of alignments of seismic foci are currently being developed. The first fits vectors between sets of seismic foci and uses the coplanar algorithm to determine which foci are coplanar. The second method runs a series of three-dimensional counting boxes over the earthquakes. Boxes that contain a higher number of foci may represent seismically active fault planes. A comprehensive lineament analysis system developed at WSU includes the unique capability of comparing multiple sets of lineaments. Average traces are calculated for lineaments that have been identified a larger number of times and are therefore more reproducible. Current work includes registering the lineaments and mapped faults to digital elevation models in order to provide them with the three-dimensionality required by the GSA coplanar routines.

The major goals of the GSA project are the ultimate integration of a series of different databases into one analysis sequence, producing a comprehensive three-dimensional structural model. The GSA routines will define the three-dimensional location and orientation of geologic structures based upon a plethora of data types. An interactive model of the structures will then allow the user to examine various aspects and parameters of the geologic system in the study area.

Grantee: UNIVERSITY OF WISCONSIN
Department of Geology and Geophysics
Madison, Wisconsin 53706

Grant: DE-FG02-88ER13184

Title: Thermal Stress Microfracturing of Crystalline and Sedimentary Rock

Person in Charge: H. F. Wang (608-262-5932)

Slow uniform heating of crustal rocks is both a pervasive geologic process and an anticipated by-product of radioactive waste disposal. Such heating generates microcracks that alter the strength, elastic moduli, and transport properties of the rock. The ability to predict rock response to temperatures of up to 300° or 400°C under pressures of 6 to 60 MPa would be a major asset in the selection and remote monitoring of a high level nuclear waste repository.

A numerical model was used to simulate coincident grain boundary cracking due to slow thermal cycling in granite under confining pressure. The model consists of an array of four hexagonal grains embedded in an infinite medium with homogeneous and isotropic elastic and thermal expansion properties. Elastic moduli within the four grain array are assumed to be identical to those of the matrix, but each grain is allowed to have its own independently oriented, anisotropic thermal expansion tensor. The model I stress intensity factor can be calculated for an initial flaw of assumed length, originating at either triple junction and lying along the central facet.

The primary goal of the numerical modeling is to predict experimentally observed acoustic emission data during thermal cycling of Westerly granite to 300°C under 7, 28, and 55 MPa confining pressure. The numerical model performed well, yielding very good fits to the acoustic emission data for the three pressures. In particular, the model was able to match the acceleration of acoustic emission events above 200°C in the 7 MPa experiment, with reasonable values of model parameters, which included the temperature and pressure dependence of Young's modulus and the distribution of initial crack lengths. The model also provided a reasonable explanation for crack density trends found in thermally cycled Westerly and Illinois granites. Mode I cracking is favored along feldspar-feldspar facets in heating and along quartz-quartz facets in cooling. In heating, the relatively small volumetric expansion of feldspar grains along the facet face and the relatively large thermal expansion of quartz grains along either edge of the facet favor cracking. In cooling, the large volumetric contraction of quartz grains along the facet face and the relatively small contraction of feldspar grains along the facet edges favor cracking.

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 Ocean Sediments

Person in Charge: J. K. Whelan (617-548-1400, ext. 2819)

The objective of this program is to develop a better understanding of the processes of hydrocarbon generation and migration in coastal and offshore sedimentary basins as an aid in predicting favorable exploration areas for oil and gas.

Pyrolysis T_{max} determinations of methane were carried out by the new technique of the thermogravimetric Fourier transform infrared spectroscopy. Measurements on whole rocks from one Alaskan North Slope well and two sets of kerogens from the Gulf Coast show that the technique can provide maturation data through both the oil and gas windows for whole rocks and kerogens (maximum maturity of samples still showing methane peak measured to date is $R_o = 3.8\%$).

Preliminary analyses of bitumen extract profiles were carried out on the Alaskan North Slope Lisburne well containing high maturity interbedded carbonate and siliceous sediments, which will provide a standard high maturity source rock reference for these two marine formations, which run over most of the North Slope. Thin sections of cores from the Pebble Shale, Kingak, Shublik, and Lisburne formations were also examined from Alaskan North Slope Ikpikpuk well. The Shublik slides appear to be showing petroleum expulsion from fine-grained rocks lending support to the idea that the pyrobitumen found in this formation represents unexpelled source rock bitumen rather than residual and thermally altered carrier bed bitumen. Also, detailed C_{15+} profiles for the Gulf Coast East Cameron well were obtained after downhole vitrinite reflectance profiles showed an excellent continuous maturation profile through the Miocene section. This well can serve as a standard for the response of a variety of measurements of both source and maturation characteristics for the Tertiary section of the Louisiana Gulf Coast. A debate currently rages about whether this type of sediment is a major source for oil in the deeper water sections of the Gulf--the other leading contender being a deep marine Cretaceous source. The biomarker steranes and hopanes were very weak for the well, so that the chemical ionization technique developed last year was applied for their measurement. Additional calibrations of the technique this year showed that the results are extremely reproducible over a long period of time and that it is capable of producing reproducible sterane maturation R/S ratios on sediments where more conventional MS measurements fail.

Collaborative work was carried out with Mark Richardson and Mike Arthur from the University of Rhode Island in analysis of biomarkers from evaporitic sequences in cores from Gulf of Suez wells. A complex series of alkyl thiophenes were found adjacent to halites, while hopanes and alkylbenzenes were associated with anhydrites. This information can be applied together with the work on the E. Cameron well in evaluating the potential importance of deep Cretaceous marine versus Tertiary oil sources in the Gulf of Mexico since a carbonate-dominated salt basin underlies much of the Louisiana Gulf Coast.

Grantee: UNIVERSITY OF WYOMING
Department of Geology and Geophysics
Laramie, Wyoming 82071

Grant: DE-FG02-88ER13805

Title: Techniques for the Delineation of Liquid Hydrocarbon
Resources Using Maturation and Enhanced Reservoir
Porosity Models

Person in Charge: R. C. Surdam and H. P. Heasler (307-766-3386)

This project involves the modeling of Cretaceous reservoir and source rocks in the Bighorn Basin, northern Wyoming, to better delineate these prolific liquid hydrocarbon targets.

Maturation models of the Cretaceous source rocks are being developed in order to estimate the timing of liquid hydrocarbon generation and the timing of diagenetically significant mono- and difunctional acid generation. The maturation models incorporate the temporal variation of regional heat flow, sediment thermal properties, burial history of the sediments, and chemical kinetic properties of the hydrocarbon source rock. Diagenetic models are being developed in order to quantitatively estimate diagenetically enhanced reservoir porosity. Factors considered in the diagenetic model include the depositional character of the reservoir rock, early and late diagenesis of the reservoir rock, and the timing of intense diagenesis in relation to hydrocarbon expulsion from oil source rocks.

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

<u>ON-SITE</u>	<u>FY 1979</u>	<u>FY 1980</u>	<u>FY 1981</u>	<u>FY 1982</u>	<u>FY 1983</u>	<u>FY 1984</u>	<u>FY 1985</u>	<u>FY 1986</u>	<u>FY 1987</u>	<u>FY 1988</u>	<u>FY 1989</u>
ANL	\$ 140	\$ 240	\$ 310	\$ 330	\$ 330	\$ 360	\$ 360	\$ 355	\$ 340	\$ 335	\$ 440
BNL	—	—	—	—	—	—	—	—	—	50	90
LANL	1,084	1,420	1,500	1,375	1,684	2,343	2,289	2,263	2,603	2,868	2,638
LBL	735	995	1,075	1,180	1,405	1,485	1,596	1,632	2,162	2,100	2,265
LLNL	630	910	1,060	1,110	1,280	1,815	1,898	1,521	1,837	1,732	2,121
ORNL	240	280	380	430	430	470	480	492	690	785	944
PNL	450	565	580	520	520	578	595	605	725	850	848
SNL/A	800	1,165	1,310	1,546	1,682	2,087	1,861	2,256	2,462	2,711	2,213
<u>ON-SITE TOTALS</u>	\$4,079	\$5,575	\$ 6,215	\$ 6,491	\$ 7,331	\$ 9,138	\$ 9,079	\$ 9,350	\$10,819	\$11,431	\$11,559
<u>TOTAL OFF-SITE</u>	\$1,895	\$2,509	\$ 3,030	\$ 3,141	\$ 4,523	\$ 3,309	\$ 4,260	\$ 3,507	\$ 4,453	\$ 4,868	\$ 5,595
<u>TOTAL OPERATING</u>	\$5,974	\$8,084	\$ 9,245	\$ 9,632	\$11,854	\$12,447	\$13,346	\$12,857	\$15,272	\$16,299	\$17,497
<u>TOTAL EQUIPMENT</u>	\$ 355	\$ 560	\$ 923	\$ 900	\$ 890	\$ 960	\$ 1,100	\$ 1,094	\$ 1,150	\$ 1,150	\$ 1,150
<u>TOTAL GEOSCIENCES</u>	\$6,329	\$8,644	\$10,168	\$10,532	\$12,744	\$13,407	\$14,446	\$13,951	\$16,422	\$17,449	\$18,647

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

<u>INSTITUTION (PI)</u>	<u>FY 1979</u>	<u>FY 1980</u>	<u>FY 1981</u>	<u>FY 1982</u>	<u>FY 1983</u>	<u>FY 1984</u>	<u>FY 1985</u>	<u>FY 1986</u>	<u>FY 1987</u>	<u>FY 1988</u>	<u>FY 1989</u>
U/ALASKA (LEE)	\$ 85	\$ 84	\$ 108	\$ 113	\$ 117	\$ 120	\$ 126	\$ 126	\$ 128	\$ 140	\$ 143
U/ALASKA (PULPAU)	113	87	70	—	—	—	—	—	—	—	—
AM GEOPHYS UNION (SPILHAUS)	—	—	—	—	—	—	—	—	—	—	5
U/ARIZONA (HILL)	—	91	96	99	101	90	121	—	101	103	121
U/ARIZONA (NORTON)	—	—	66	60	48	—	—	—	—	—	—
*ARIZONA STATE (FINK)	—	—	—	—	—	—	22	23	11	—	—
ARIZONA STATE (NAVROTSKY)	—	35	62	66	123	—	—	—	—	—	—
ASPEN INSTITUTE (ROBERTS)	57	71	—	—	—	—	—	—	—	—	—
BECHTEL (HARPER)	—	—	—	—	—	—	—	25	—	—	—
*BROWN U (HERMANC)	95	140	164	165	333	—	166	—	150	150	—
*CAL TECH (AHRENS)	—	—	—	—	72	81	160	—	150	100	—
CAL TECH (STOLPER)	—	—	—	—	—	—	50	98	—	78	82
CAL TECH (WASSERBURG)	—	—	—	—	—	—	—	—	—	200	250
U/CALIFORNIA-B (HELGESON)	—	—	—	—	204	—	120	120	135	116	121
U/CALIFORNIA-B (REYNOLDS)	127	168	144	150	165	196	233	200	200	210	236
U/CALIFORNIA-D (MacGREGOR)	61	23	—	—	—	—	—	—	—	—	—
U/CALIFORNIA-LA (ANDERSON)	—	—	—	—	—	60	74	—	23	—	—
U/CALIFORNIA-LA (BOEHLER)	—	—	46	NFX	60	66	75	—	—	—	—
U/CALIFORNIA-LA (KENNEDY)	72	72	—	—	—	—	—	—	—	—	—
U/CALIFORNIA-LA (ERNST)	—	—	—	—	—	—	—	—	64	69	—
U/CALIFORNIA-LA (HARRISON)	—	—	—	—	—	—	—	—	—	—	54
U/CALIFORNIA-LA (WARREN)	103	107	121	NFX	—	—	—	—	—	—	—
*U/CALIFORNIA-R (McKIBBEN)	—	—	—	—	—	—	50	—	40	—	77
U/CALIFORNIA-SD (CHAVE)	—	—	—	—	—	—	—	—	120	—	—
U/CALIFORNIA-SD (CRAIG)	—	—	—	—	—	35	41	41	42	35	—
U/CALIFORNIA-SD (HARDING)	—	—	—	—	—	—	—	—	—	—	63
U/CALIFORNIA-SB (SPERA)	—	—	—	—	—	—	—	—	—	—	64
U/CHICAGO (ANDERSON)	—	54	NFX	38	98	NFX	46	—	—	—	—
U/COLORADO-B (SPETZLER)	—	—	—	—	—	—	—	—	95	87	91
COLO SCH MINES (CROSS)	—	—	—	—	—	—	—	—	—	10	—
COLO SCH MINES (LARNER)	—	—	—	—	—	—	—	—	—	—	192
COLUMBIA U (ENGELDER)	100	140	150	156	289	—	150	75	—	—	—
COLUMBIA U (TABER)	274	312	318	318	337	359	360	360	360	360	290
COLUMBIA U (WALKER)	—	—	—	—	—	73	79	106	—	85	90
U/DELAWARE (WOOD)	—	—	—	—	—	—	—	—	—	—	62
DOSECC, INC (BARBER)	—	—	—	—	—	—	6	—	—	66	—
GEO CHEM RES ASSOC (ORTOLEVA)	—	—	—	—	—	—	—	—	50	100	—
HARVARD U (THOMPSON)	—	—	—	—	372	—	115	—	18	—	—
U/HAWAII (MANGHNANI)	—	—	—	88	96	99	200	—	100	100	—
U/HOUSTON (CHAFETZ)	—	—	—	—	—	—	—	—	69	—	—
U/HOUSTON (McDONALD)	—	—	—	—	—	—	—	—	—	—	273
HEADQUARTERS SERVICES	—	—	—	6	1	3	15	5	3	3	3
INDIANA (HAYES)	—	—	—	—	—	—	—	—	—	186	162

**GEOSCIENCES RESEARCH (ERDA/DOE)
HISTORICAL SUMMARY/OFF-SITE
(OPERATING FUNDS — THOUSANDS)
(CONTINUED)**

INSTITUTION (PI)	FY 1979	FY 1980	FY 1981	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989
JOHNS HOPKINS (VEBLEN)	\$ —	\$ —	\$ —	\$ —	\$ —	\$ —	\$ —	\$ —	\$ —	\$ —	\$ 63
LOUISIANA STATE (FERRELL)	—	—	—	—	—	—	—	—	60	59	64
U/MARYLAND (VALETTE-SILVER)	—	—	—	—	—	—	43	—	NFX	—	—
U/MINNESOTA (JOHNSON)	—	—	68	57	NFX	—	—	—	—	—	—
U/MINNESOTA (YUEN)	—	—	—	—	—	—	—	—	—	—	48
MIT (AKI)	142	152	160	151	158	147	—	—	—	—	—
MIT (SIMMONS)	100	90	100	106	106	110	80	80	—	—	—
MIT (TOKSOZ)	—	—	—	—	—	—	—	142	—	113	370
*MICHIGAN STATE (VOGEL)	—	—	—	—	—	—	31	NFX	34	—	—
*MICHIGAN TECH (McDOWELL)	—	—	—	—	—	—	50	—	—	—	—
MONTANA TECH., BU. MINES & TECH. (BARTHOLOMEW)	—	—	—	—	—	—	—	—	—	8	—
NAS/NRC (CARTER)	—	—	—	—	—	—	—	—	—	—	3
NAS/NRC (HART)	44	116	168	282	—	200	187	124	202	132	—
NAS/NRC (LONG)	—	—	—	—	—	—	—	—	—	—	100
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	—	—	—	—	—
CUNY-B (FRIEDMAN)	—	—	—	—	—	—	95	86	100	50	—
CUNY-Q (E-SCHREIBER)	—	—	83	81	49	—	116	—	—	—	—
CUNY-Q (C-SCHREIBER)	—	—	—	—	—	—	—	—	—	101	105
SUNY-A (DEWEY)	—	—	86	—	—	—	—	—	—	—	—
SUNY-A (HARRISON)	—	—	—	39	136	—	58	60	54	52	—
SUNY-P (WOLOSZ)	—	—	—	—	—	—	—	—	72	—	56
SUNY-SB (HANSON)	—	—	—	—	112	118	120	120	128	128	120
SUNY-SB (PAPIKE)	51	59	65	—	—	—	—	—	—	—	—
U/N CAROLINA (GLAZNER)	—	—	—	—	—	—	38	39	—	35	—
OHIO STATE UNIV (ADLER)	—	—	—	—	—	—	—	—	50	52	55
U/OKLAHOMA (ENGEL)	—	—	—	—	—	—	—	—	—	—	112
*U/OKLAHOMA (PHILP)	—	—	—	—	—	—	—	28	—	—	—
U/OKLAHOMA (PHILP)	—	—	—	—	—	—	84	88	106	110	124
U/OREGON (WEILL)	—	—	—	—	103	94	—	—	—	—	—
OREGON STATE (EGBERT)	—	—	—	—	—	—	—	—	—	—	43
OREGON STATE (FEHLER)	—	—	—	38	—	—	—	—	—	—	—
PENN STATE (MARTIN)	—	62	83	NFX	—	—	—	—	—	—	—
PENN STATE (GIVEN)	—	—	—	—	—	100	—	NFX	—	—	—
PURDUE UNIV (AYDIN)	—	—	—	—	—	—	—	—	—	—	56
PURDUE UNIV (HINZE)	—	—	—	—	—	—	—	—	8	—	—
PRINCETON U (NAVROTSKY)	—	—	—	—	—	—	100	—	85	120	125
PRINCETON U (PHINNEY)	—	—	—	—	—	—	—	—	—	—	97
RPI (FRIEDMAN)	—	—	91	99	150	—	—	—	—	—	—
RICE (AVE LALLEMENT)	—	—	—	—	120	121	—	—	—	—	—

**GEOSCIENCES RESEARCH (ERDA/DOE)
HISTORICAL SUMMARY/OFF-SITE
(OPERATING FUNDS – THOUSANDS)
(CONTINUED)**

INSTITUTION (PI)	FY 1979	FY 1980	FY 1981	FY 1982	FY 1983	FY 1984	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989
S DAKOTA SCH M&T (PAPIKE)	\$ —	\$ —	\$ —	\$ 67	\$ 100	\$ 130	\$ 150	\$ 99	\$ 100	\$ 105	\$ 115
*U/S CALIFORNIA (AKI)	—	—	—	—	—	—	150	150	155	159	164
U/S FLORIDA (SACKETT)	—	—	34	—	—	—	—	—	—	—	—
SMU (BLACKWELL)	—	—	54	70	—	—	—	—	—	—	—
STANFORD U (LIOU)	—	—	—	34	45	NFX	—	—	—	—	—
STANFORD U (NUR)	147	140	140	125	160	172	172	165	165	170	175
STANFORD U (PARKS)	—	—	—	57	56	56	—	—	—	—	—
*STANFORD U (POLLARD)	—	—	—	—	—	—	39	42	44	70	152
U/ROCHESTER (GOVE)	—	—	—	—	—	—	—	—	8	—	—
*U/TEXAS-AR (SELF)	—	—	—	—	—	—	43	NFX	80	—	—
U/TEXAS-AU (BARKER)	—	—	—	—	54	—	—	—	—	—	—
TEXAS A&M (CARLSON)	—	—	—	—	—	—	—	98	—	—	—
TEXAS A&M (CARTER)	—	—	—	—	—	70	—	—	—	—	—
TEXAS A&M (DOROBK)	—	—	—	—	—	—	—	—	52	55	57
TEXAS A&M (FRIEDMAN)	63	208	202	200	201	93	100	194	—	—	—
TEXAS A&M (GILBERT)	—	—	—	—	—	—	—	98	88	101	10
TEXAS A&M (KRONENBERG)	—	—	—	—	—	—	—	—	117	156	197
U/TULSA (BARKER)	60	NFX	75	71	75	80	80	81	133	—	76
USGS (HAAS)	54	—	—	—	—	—	—	—	—	—	—
USGS (MORGAN)	—	—	—	—	—	—	—	—	35	—	—
USGS (RUSS)	—	—	—	—	—	—	—	—	—	—	12
USGS (WESSON)	—	—	—	—	—	—	—	—	—	6	—
*UURI (NEILSON)	—	—	—	—	—	—	—	114	—	—	—
*UURI (HULEN)	—	—	—	—	—	—	—	—	—	125	—
UURI (WANNAMAKER)	—	—	—	—	—	—	—	—	—	—	91
VPI & SU (BODNAR)	—	—	—	—	—	—	—	—	—	—	114
VPI & SU (SINHA)	—	—	—	—	—	—	—	—	—	82	60
U/WASHINGTON (BOOKER)	—	—	—	—	—	—	—	27	30	—	78
U/WASHINGTON (MALONE)	—	—	—	—	—	—	—	—	—	32	32
U/WISCONSIN (WANG)	—	57	38	—	—	48	52	97	84	87	92
U/WYOMING (SURDAM)	—	—	—	—	—	—	—	—	65	65	—
WASHINGTON STATE UNIV (THIESSEN)	—	—	—	—	—	—	—	—	103	—	—
WOODS HOLE (WHELAN/FARRINGTON)	—	—	—	—	—	—	223	223	226	238	220
WOODS HOLE (HUNT)	102	141	139	150	190	208	—	—	—	—	—
*WOODWARD-CLYDE (BURDICK)	—	—	—	100	100	100	40	—	—	—	—
XDATA (DINES)	—	—	—	54	66	—	—	—	—	—	—
YALE U (GORDON)	45	4	35	26	39	184	—	—	—	—	—
OTHER	—	96	64	—	—	—	—	—	—	254	341
OFF-SITE TOTALS:	\$1,895	\$2,509	\$3,030	\$3,141	\$4,523	\$3,309	\$4,260	\$3,507	\$4,453	\$4,868	\$5,595

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