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Summaries of Physical Research in the Geosciences

Published: December 1988



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

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Washington, D.C. 20545

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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

Contractor: ARGONNE NATIONAL LABORATORY
Argonne, Illinois 60439

Contract: 109 ENG 38

Category: Geochemistry

Person in Charge: F. A. Cafasso and N. C. Sturchio

A. Hydrothermal System Evolution (*N. C. Sturchio [312-972-3986], J. K. Bohlke, and C. M. Binz*)

The objective of this program is to contribute to a deeper understanding of the geochemical processes involved in fluid/rock interactions that occur in hydrothermal systems in the Earth's crust. Specific problems being addressed include: the sources of hydrothermal fluids and their dissolved components, the mechanisms by which dissolved components are enriched or depleted in these fluids, the effects of these fluids on the enveloping rocks, the rates of hydrothermal processes, and the relation of hydrothermal systems to large scale tectonomagmatic processes.

The applications of uranium-series measurements to geochronology and the rates of water-rock interaction in active hydrothermal systems are being explored in this program. Hot spring deposits and hydrothermal vein minerals are being dated from the silicic caldera complexes at Yellowstone, Valles, and Long Valley to help understand the geologic evolution of their hydrothermal systems. A study of the relation of $^{226}\text{Ra}/^{230}\text{Th}$ disequilibrium to zeolite-water ion exchange in Yellowstone drill cores Y-7 and Y-8 was completed. The apparent diffusivity of Ra through the rock matrix in the sampled environment was 10^{-12} to 10^{-10} cm^2/s , a value insufficient to produce the observed scale of disequilibrium by matrix diffusion; porous flow was required with a minimum average linear velocity on the order of 10^2 cm/s . For a 1% hydraulic gradient, local matrix permeabilities must have exceeded 10^{-10} cm^2 . Large volume water samples were recently collected from a variety of hot springs in Yellowstone National Park and analyzed for the isotopes of U, Th, and Ra so that the rates and mechanisms of redistribution of these elements may be better understood in conjunction with drill core studies.

The hydrothermal systems of active andesitic volcanoes in the Northern Andes are being studied in collaboration with Prof. S. Williams (Louisiana State U.) and several other colleagues from Colombia and Japan. The isotopic compositions of SO_2 in the volcanic gas plume and of SO_4 in the acid-sulfate-chloride hot springs of Nevado del Ruiz volcano (Colombia) have been determined. These data indicate that the SO_2 is of magmatic origin and that the acid-sulfate-chloride springs tap a perched reservoir produced by interaction of magmatic gases with ground water beneath the crater. Samples of thermal water and steam from several other volcanoes are being analyzed.

Fossil hydrothermal systems provide insights into environments presently inaccessible to direct observation in active hydrothermal systems. A regional study of the variation in ages, temperatures, and compositions of fluids in Cretaceous hydrothermal systems of the northern Sierra Nevada foothills is in progress. Fluid inclusions from hydrothermal veins are being studied to determine sources of fluids and dissolved components and the significance of fluid mixing and boiling processes in relation to mineral precipitation. In collaboration with Prof. J. Reynolds and others (U. California, Berkeley), we have tested a new laser microprobe mass spectrometer method for simultaneous analysis of halogens (Cl, Br, I) and noble gas isotopes (Ar, Kr, Xe) in irradiated fluid inclusions containing volumes as little as 10^{-9} liter. The Sierran fluid inclusions are similar in many respects to modern geothermal ground waters: low salinities (≤ 0.5 m TDS), atmospheric

isotope ratios of Kr and Xe, absolute ^{36}Ar concentrations near that of air-saturated surface water, Br/Cl ratios near that of sea water, and moderately elevated $^{40}\text{Ar}/^{36}\text{Ar}$. These features support the controversial hypothesis that CO_2 -rich fluids responsible for Sierran gold mineralization contained a large component of meteoric water and provide direct evidence for deep circulation of meteoric water in the Earth's crust. Samples of fluid inclusions from a variety of other modern and ancient hydrothermal environments are being analyzed for halogens and noble gas isotopes.

B. Actinide Geochemistry (*G. W. Reed, Jr. [312-972-3585] and S. Jovanovic*)

As an aftermath of the recognition of the Oklo natural reactor, other researchers conducted an extensive survey of the literature on uranium isotopic ratios in terrestrial uranium ores and found two modal values of the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio that exhibited a relative difference of 0.03%. In comparison, an enrichment of 0.18% ^{235}U relative to normal uranium was reported by others for two basaltic lavas. Recent measurements of uranium isotopic ratios in nanogram amounts of uranium from midocean ridge hydrothermal fluids give $^{235}\text{U}/^{238}\text{U}$ ratios equal, within error, to those of average sea water and normal uranium. The range of deviations from normal (-0.52% to +0.34%) reported reflects the uncertainty in the isotopic ratio measurement of such small amounts of uranium; deviations of the magnitude reported in ores and volcanic rocks (0.03% to 0.18%) would not be resolved.

An objective of this research is to extend and evaluate earlier work by others that indicated variations of the isotopic composition of uranium in volcanic rock samples. Such variations may provide important information on cosmochemical and geochemical processes over the time scale of the solar system. Precise measurements of the isotopic composition of uranium and plutonium (if present) are being made in several suites of volcanic rocks from Hat Creek (Oregon), Mt. St. Helens (Washington), and Auvergne (France). Large samples (hundreds of grams) are being processed to minimize reagent and environmental blank interference and to separate large amounts of uranium (tens of μg) for mass spectrometer measurements. The results obtained thus far appear to support the earlier findings of others. In all samples analyzed to date, relative enrichments of 0.2% to 5.94% ^{235}U have been measured, with an instrumental precision of $\pm 0.07\%$ (1σ). The two Auvergne samples gave the largest deviations (5.94% and 0.66%) from the normal isotopic ratio. Uranium blank levels determined during the analyses were $< 0.2\%$ and $< 3\%$ of the total recovered in parallel sample runs. The analyses are being repeated on carefully homogenized aliquants of the Auvergne samples, and the mass spectrometer has been upgraded for more precise analysis of smaller samples, in an attempt to understand these results. These data, if confirmed, will have important cosmochemical and geochemical implications; however, further work is required to clarify the source(s) of the isotopic variations observed.

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

Contract: AS-132-AAP

Category: Geochemistry

Person in Charge: K. W. Jones (516-282-4588)

A. Trace Element Microdistribution in Coal

Trace element concentrations, mineral speciations, and microdistributions will be determined in United Kingdom and North American coals using the x-ray microprobe at the National Synchrotron Light Source at Brookhaven National Laboratory. The coal research is part of an ongoing trace-element geoscience program coordinated by the Regional Center for Trace Element Geochemistry. The results of this geochemical study will aid the development of petrogenetic models for coal formation and lead to improved coal prospection protocols. Better understanding of coal formation processes has cross-cutting applications to other energy-related problems including oil and gas transport and concentration mechanisms.

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 (415-486-7347)

A. Deep Electromagnetic Sounding of the Crust (*H. F. Morrison, N. E. Goldstein, and K. H. Lee*)

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 conceptual models for the conductivity of the crust. One of our principal goals has been to image mid-crustal conductors. Because the magnetotelluric sounding technique suffers from a severe loss of resolution at low frequencies or large depths of investigations when near-surface inhomogeneities are present, we have been investigating spatial filtering techniques to suppress or eliminate the deleterious effects of near-surface geologic noise. Thus far, this study has concentrated on numerical simulations.

In the area of controlled-source EM, substantial progress has been made in q-domain modeling and data processing. The q-domain approach involves transforming the diffusive electromagnetic fields from a time-domain source into fictitious wave fields. Numerical calculations have been successfully carried out for a 2-D model, and the numerical solution agrees with those for the direct time-domain solution. Our ultimate goals are to extend q-domain analysis to 3-D models, not presently tractable by other means, and to EM imaging. As a first step toward imaging, we were able to construct wave fields from time-domain data.

B. Center for Computational Seismology (*T. V. McEvelly and E. Majer*)

The establishment and continuing base level support of CCS have 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.

During the last year the CONVEX C-1/XP computer was installed and tested at CCS. The CONVEX is a UNIX (Bell Labs trademark) based machine that runs 4.2 BSD. It is a 64 bit Vector machine. 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 SIERRASEIS 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. On the scientific front, CCS continued support of the Cajon Pass project in the interpretation of the VSP data, CALCRUST, and several projects for the DOE nuclear waste program. In these projects significant progress has been made in the areas of the application of

seismic tomography for the imaging of fractured rocks, and in using VSP data for the detection of anisotropy. Some examples of CCS's role in seismic research are:

- 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 data bases 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 J. M. Kemeny*)

We are continuing our investigation of the growth of microcracks in brittle rocks when subjected to compressive stresses up to and past the strength of the rock. We have extended the theoretical crack models that were previously developed in this task to include the time dependent effects of stress corrosion cracking. This results in stress strain curves due to triaxial compression that depend on the loading rate and also give creep vs. time behavior at a fixed value of triaxial stress. The results of the time dependent models are in close accord with published experimental data.

We have also begun some experimental investigations of microcrack growth in Indiana limestone and Berea sandstone. We have examined microcrack growth in uniaxially compressed cylindrical samples (1 in. diam. by 3 in. long), and hollow rock cylinders (1 in. inside diam., 3.5 in. outside diam., 6 in. long) subjected to internal and external pressure. Our procedure for studying stress induced microcracks in these experiments is to load the samples up to various points on the stress strain curve, and preserve the microcrack geometry at these loads with the injection of a low melting point liquid-metal alloy called Cerrosafe. The liquid metal pore fluid is kept at 5 MPa, which allows it to permeate openings down to the order of 0.1 microns in size. Samples are cooled prior to unloading and then sectioned and examined by both optical and scanning electron microscopy. In the Indiana limestone, we are able to look at the three dimensional pattern of microcrack development by etching the surface of the limestone sections with hydrochloric acid, which removes a thin layer of limestone but leaves behind a metal cast of the microcrack geometry. Results of the uniaxially compressed samples suggest that a variety of microscopic mechanisms produce extensile cracking parallel to the direction of maximum compression. The hollow-cylinder tests investigate the effects of stress gradients, as occur in drill holes and around underground openings. The hollow-cylinder tests have resulted in the formation of borehole breakouts and reveal that borehole breakouts evolve by the growth, interaction, and coalescence of extensile microcracks near the inner boundary, similar in many respects to the pattern of microcrack growth found in the uniaxially compressed samples.

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*)

The objective of this program is to address by an integrated interdisciplinary approach the problems associated with detecting and determining the physical properties of fracture systems and relating these measurements to fluid transport in fractured hydrocarbon reservoirs. The program consists of three elements. Studies in the first program element, theoretical and laboratory studies of basic physical processes and properties of fractures, was begun in FY 1986. In FY 1987, work

was initiated in the remaining two program elements: studies to develop integrated field applicable hydrologic, seismic, and electrical methods and studies to develop hardware.

Properties of Fractures. In continuing studies of the effects of single fractures on transmission of seismic waves, a laboratory investigation of the effect of viscous coupling in liquids in a fracture shear wave transmission was initiated. In these studies a fractured rock is idealized by a stack of seven quartz discs compressed uniaxially between seismic transducers. To eliminate effects of coupling at varying stress levels between the quartz discs and transducers, the top and bottom discs are glued to the transmitter and receiver, respectively. The planar surfaces are optically flat and covered with a film of gold approximately 100 Å thick. The surfaces of the discs were lapped to minimize asperity contact between surfaces separated by a film of water. X-ray profilometer measurements demonstrated that roughness was on the order of a few Angstroms. The stack of discs is assembled with a film of water in the interface between each pair of gold-covered surfaces. Since the gold coated surfaces are hydrophilic, it is possible to estimate by calculation the equilibrium thickness of the water. This equilibrium thickness is approached by viscous flow. The uniaxial load is held constant at step and compressional and shear waveforms collected as a function of each time. Initial experiments showed that the liquid layer, as expected, strongly enhanced the compressional wave amplitudes. The shear wave amplitudes also increased as axial stress increased. In comparison with the P-waves, the S-wave amplitude increased much more rapidly with load. However, it was observed that large perturbations resulted from minute changes in surface conditions, obscuring clear trends. Further tests will be performed.

Methods of Development. Work was initiated on two studies: 1) a theoretical investigation of diffraction tomographic techniques and 2) development of a cross-borehole audio frequency electromagnetic method. Diffraction tomography techniques are being developed to invert for the P-wave velocity distribution of a fractured region. Algorithms that carry out the inversion procedures have been developed, tested, and implemented. The inversion is two dimensional but can be extended to three dimensions. Locations of the sources and receivers can be arbitrary, provided they follow a straight line. The knowledge of a background velocity is necessary to obtain the scattered field from the total field recorded. Because of the Born (or Rytov) approximation involved in the theoretical development of the algorithms, deviations in velocity from a background velocity must be small, which is the only constraint on the medium. Dense raypaths and good angular coverage of the medium are necessary in order to achieve high resolution and accurate results. To test the inversion technique a data set was obtained from a crosshole seismic experiment in fractured rock. Little research has been done on utilizing a cross-borehole electromagnetic method. As a preliminary investigation, therefore, a literature review on the electrical and geometrical parameters of fracture zones was carried out. The general finding is that the fracture zones of interest are thin and water filled, which makes them more conductive than the surrounding rock. If one uses a low frequency electromagnetic method to map them, only the fracture conductance (thickness-conductivity product) will be of importance. The conductance usually ranges from 0.01 to 1.0 Siemens or higher, while the host rock usually has a resistivity of at least a few hundred ohm-m. In some cases, the fracture conductance cannot be estimated from the available information. The lateral extent of the fracture zones ranges from tens of meters to several hundred meters or more. Although their geometric form is usually not known with any accuracy, it can be assumed to be square for the simplicity needed in numerical modeling studies.

Hardware Development. Development continued of a new down-hole swept-frequency, resonant, shear-wave source designed to operate under 700 W of power over a frequency range of 50 to 500 Hz. Vibratory motion is achieved by the reaction of an electromagnetically driven piston against a pneumatic spring. The volume and pressure of the gas spring is varied so that the device operates at resonance at all frequencies. With initial component fabrication completed under other DOE programs, effort was concentrated on bench testing for preliminary performance evaluation. Initial tests were performed at moderate gas pressures of 200 psi and 500 psi. At each pressure the

frequency of the driving current was swept while holding the current magnitude constant. The internal pressure transducers were monitored to evaluate the effect of resonant operation on the cyclic pressure generated by the motion of the coil-piston assembly. The pressure transducer output is directly proportional to the force output of the device. The resonant frequency at 200 psi gas pressure was found to be 68 Hz while at 500 psi gas pressure it was 115 Hz. Using the pressure transducer output as a function of frequency, Q , calculated by the half-power method, was found to be about 7 at 68 Hz and 13 at 115 Hz.

E. Coupled THM Processes in Petroleum Reservoirs (*C. F. Tsang and J. Noorishad*)

Various aspects of petroleum reservoir engineering, such as isothermal and non-isothermal hydraulic fracturing and permeability variations near injection and production wells, involve coupled thermal-hydraulic-mechanical (THM) processes. The computer code ROCMAS was developed to address these coupled phenomena. 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. We also updated our fracture element to that of a dilating, strain-softening material. We have so far completed verification of the mechanical part of code by comparison with a geotechnical code and we have also verified uncoupled fluid flow algorithms. Presently, effort is directed towards a verification of the coupling terms and coupled effects in the new algorithms.

F. Advanced Geoscience Research Concepts (*T. V. McEvilly*)

This activity provides support to encourage the development of new ideas in the geosciences. In this respect, specific activities are of relatively short term. They often encompass the evaluation of the feasibility of performing contemplated research by preliminary modeling of a concept and scoping its experimental plan.

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Contract: DE-AC03-76SF00098

Category: Geochemistry

Person in charge: T. V. McEvilly (415-486-7347)

A. Thermodynamics of High Temperature Brines (*K. S. Pitzer*)

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 capacity and the density of solutions in the range 0 to 300°C and 0 to 1 kbar. Recently, heat capacity measurements on $\text{Na}_2\text{SO}_4(\text{aq})$ have been extended from 200 to 300°C. A comprehensive equation of state for $\text{Na}_2\text{SO}_4(\text{aq})$ has been prepared and applied to calculations of the solubility of various minerals containing Na_2SO_4 .

The data base 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^+ , Mg^{2+} , Ca^{2+} , Cl^- , OH^- , SO_4^{2-} , and H_2O . 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 standard-state thermodynamic properties of the geochemically important aqueous ions for the extended range, including supercritical conditions, to 1000°C and 5 kbar.

B. Thermodynamic Properties of Silicate Materials (*I. S. E. Carmichael, R. A. Lange, and D. A. Snyder*)

Experimental studies constraining the dependence of ferric/ferrous iron ratio in natural silicate melts on temperature, oxygen fugacity, and composition have been completed. Similar studies are under way in the $\text{Na}_2\text{O-SiO}_2\text{-FeO-O}_2$ and $\text{CaOSiO}_2\text{-FeO-O}_2$ systems. Our results suggest that these two systems behave substantially differently. At constant temperature and oxygen fugacity, the ferric/ferrous ratio of melts in the $\text{Na}_2\text{O-SiO}_2\text{-FeO-O}_2$ system is independent of $\text{Na}_2\text{O/SiO}_2$ ratio but is dependent on total iron content. In the $\text{CaO-SiO}_2\text{-FeO-O}_2$ system, on the other hand, ferric/ferrous ratios are independent of total iron content but increase with increasing CaO/SiO_2 .

We are currently constructing an apparatus that will, for the first time, allow the determination of acoustic velocities, and thus isothermal compressibilities, under an oxidizing atmosphere. This, along with our ferric/ferrous equilibrium experiments, will allow us to determine the effect of pressure on the partial molar volume of the ferric component in silicate melts.

In a related study, we are now assembling an internally heated high-pressure apparatus that will allow the determination of acoustic velocities, and thus isothermal compressibility, of silicate liquids at pressures up to 4 kbar. Also, during the past year, all remaining calibrations of the 2700 K drop calorimeter have been completed. Determination of the enthalpy of the calorimetry vessel as a function of temperature over its operating range has been accomplished. In addition, the high temperature optical pyrometer has been calibrated at the melting point of platinum. The apparatus is now ready for its first measurements of $\alpha\text{Al}_2\text{O}_3$.

C. Studies of the Interactions Between Mineral Surfaces and Ions in Solution (*D. L. Perry*)

Studies have been conducted on the interaction of aqueous ions with geologic cores using nuclear magnetic resonance imaging (NMRI) to follow both the reaction products and reaction kinetics. The reaction between NaF and Berea sandstone was studied under ambient temperature and pressure in an attempt to learn what amount of information could be obtained about basic reaction chemistry of this system as it relates to the reaction zone inside the core. The reaction of the fluoride ion with the Berea sandstone has been monitored with ^{19}F nuclear magnetic resonance, while the reaction zone in the unsaturated core has been imaged using ^1H (proton) nuclear magnetic resonance imaging. The results clearly showed heterogeneous reaction areas in which the fluoride ion had reacted with the sandstone, followed by dissociation of complex fluoride ions to form new Al-F complexes.

This is the first observation of an inorganic reaction zone in a geologic material using NMRI. It should have a significant impact on studies of hydrocarbon-related reactions in rock by following the proton images and spectra. Under ideal conditions, both the reaction products and reaction zones of hydrogen-containing compounds can be studied.

This work complements research involving the outer layer of geologic materials and the reactions, reaction mechanisms, and reactions that have been previously studied that relate to those outer layers. Such studies serve to give experimental evidence and models for theory involving basic solid state/solution chemical reactions.

D. Chemical Transport in Natural Systems (*C. L. Carnahan and J. S. Jacobsen*)

The objective of this research is to gain increased understanding of processes affecting the movement of chemically reactive solutes in ground water flow systems. This objective is being approached through theoretical analyses and mathematical descriptions that can be converted to numerical simulators. The simulators are used to perform numerical experiments that demonstrate the behavior of the systems being modeled under the influence of variations of system compositions, driving forces, and ambient conditions. The process simulators are based rigorously on thermodynamic, chemical, and physical principles governing the movement of fluids in the subsurface and chemical interactions among fluid components and reactive solids.

Two simulators have been prominent in recent research. One, called THCC, focuses on effects of varying temperature and oxidation potential on transport of chemically reactive solution species. During the past year, the THCC program has been used to study numerically the migration of uranium and the precipitation/dissolution of uranium-bearing minerals under conditions of varying temperature and oxidation potential. The other simulator, called TIP, focuses on transport processes active in low-permeability, permselective materials such as certain clays and shales. In addition to the direct processes described by the phenomenological laws of Fourier, Darcy, and Fick, the TIP program simulates coupled processes including chemical osmosis, thermal osmosis,

thermal diffusion, ultrafiltration (reverse osmosis), and coupled chemical diffusion. During the past year, chemical reactions (formation of complex ions and ion pairs in the aqueous phase and cation exchange) have been added to the TIP program. Both the THCC and TIP programs use a method of solution in which the numerical analogs of the partial differential equations of transport are solved simultaneously with the equations describing chemical changes. In the TIP program, the transport equations are those describing transport of heat, bulk fluid, and individual solution species in the possible presence of reactive minerals.

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

E. Thermodynamic Tables of Geochemical Materials (*S. L. Phillips*)

The principal result of this research is consistent, documented, reviewed, and evaluated thermodynamic property tables with intrinsic values for the following four properties: Gibbs free energy of formation, enthalpy of formation, entropy, and heat capacity. These quantities are tabulated at 25°C, zero ionic strength, and one atmosphere. An uncertainty is usually assigned to the property values. The computerized tabulation covers selected aqueous species, gases, simple solids such as oxides, and minerals. The actinide elements are emphasized. These tables are consistent with the CODATA Key Values, consistent with the fundamental relation $\Delta_r G^\circ = \Delta_r H^\circ - 298.15 \Delta_r S^\circ$, and consistently reproduce critically evaluated experimental measurements and other data to within the uncertainty of log K. Research is done to fill significant gaps by calculation of missing property values, and methods are developed for computerized management of the thermodynamic data base. The data base is available via telecommunication to LBL and in report form. A significant subset of this work is development of a data base for use in the performance assessment of nuclear waste repositories (LBL 22860).

F. Impacts and Mass Extinctions (*L. Alvarez, F. Asaro, H. V. Michel, W. Alvarez, and R. Muller [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 selected 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.

We have studied samples from an Ocean Drilling Program core (ODP Hole 689B Core 6H) taken from the Weddell Sea and covering 1 m.y. of deposition. This work is in collaboration with Dr. James Kennet of U.C. Santa Barbara. A multiple Ir anomaly was observed with our iridium coincidence spectrometer comprising about 8 peaks. All but one correlated with an iron-bearing phase (possibly clay) or a cobalt-rich phase (possibly manganese precipitates). These Ir peaks should be terrestrial in origin because of the large Fe or Co component relative to Ir. The single remaining Ir peak had an abundance of about 40 parts-per-trillion and an age of about 11.7 Ma

(the same age as previously for an Ir anomaly in a core from the Tasman Sea about 10,000 kilometers away, which was considered to likely have an impact origin). These data suggest an impact large enough to distribute Ir one fourth of the way around the world. With the previously known horizons of Ir-enriched rocks with ages of 67 and 35-37 Ma, the new horizon at about 11.7 Ma suggests a periodicity of 27 m.y. comparable to the 26 m.y. reported for minor and major mass extinctions and 28-30 m.y. reported for crater ages. The new data lend experimental support to those theories that hypothesize periodic impacts of comets on the Earth, one of which predicts a companion star (Nemesis) orbiting the Sun. Double measurements, spaced by at least one month, of the northern skies with a computerized telescope have shown (so far) that 300 selected stars cannot be Nemesis.

G. Reservoir Dynamics

a. Nonisothermal Reservoir Dynamics (*C. F. Tsang*)

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, 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. New measurement techniques to provide key data needed for these investigations are explored. In the first subtask, performed in cooperation with the Weizmann Institute of Science and Ben Gurion University in Israel, we are studying the thermohydraulics of unsaturated-soil heat-storage systems. A one-half scale field test is currently being constructed in Israel and carried out by Ben Gurion University and Weizmann Institute with their own funding sources. LBL will perform mathematical modeling to study thermohydraulics of the system and to understand the basic physical processes involved. A second subtask we are undertaking is the development of an integral finite difference model that is capable of simulating three-dimensional, three-phase flow with interphase mass transfer. All three phases (air, water, and a non-aqueous phase liquid or NAPL) flow in response to pressure and density gradients. The NAPL (e.g., hydrocarbon liquid in petroleum reservoirs) is assumed to consist of slightly soluble, volatile components that may be transferred to the other phases by assuming local phase equilibrium or by using empirical kinetic mass transfer expressions. Model development is near completion.

b. Isothermal Reservoir Dynamics Hydrodynamics of a Vertical Fracture (*T. N. Narasimhan*)

Investigation of Orthotropy and Anisotropy: Anisotropy is a general term denoting the dependence of flow parameters such as permeability on direction. Orthotropy and non-orthotropy, on the other hand, provide specialized information about the underlying geometric structure of the porous medium that dictate the exact directional dependence. A theoretical analysis of orthotropy and anisotropy has been carried out. A manuscript has been prepared for prospective publication and is under review.

Hydrothermal Convection in the Guyamas Basin: Heat flow and other data obtained under the auspices of the Deep Sea Drilling Project from the Guyamas basin in the Gulf of California were used as the basis for numerical simulation of hydrothermal convection. The work was carried out in collaboration with Andrew Fisher of the Rosenstiel School of Marine and Atmospheric Sciences, University of Miami.

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Contract: DE-AC03-76SF00098

Category: Energy Resource Recognition, Evaluation, and Utilization

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A. Hydrothermal Chemistry (*H. A. Wollenberg*)

Activities continued to be focused on the Long Valley caldera. In collaboration with the USGS and Los Alamos National Laboratory, isotopic signatures of rock-fluid interaction are being investigated. Oxygen, hydrogen, carbon, and strontium isotope ratios in water, rock-matrix, and fracture-filling minerals are compared and are combined with information on the alteration mineralogy of core and drill hole cuttings. To form a complete picture of the hydrothermal system, the path of fluids is being traced by use of these isotopes, investigating precipitation that recharges the ground water system, the eastward-flowing hydrothermal system, and the deeper portion of the system that circulates into Paleozoic metamorphic and Mesozoic plutonic rocks that underlie the caldera. Core and fluid from DOE hole RDO-8, drilled in the caldera's southwestern moat, and core from geothermal test holes drilled in 1987-88 by Mammoth Lakes are important sources of these data. Core from geothermal industry holes recently available through DOE's Curatorial Office and core, cuttings, and fluid from DOE's magma energy hole, to be drilled to ~6 km over the next four years, will also provide valuable material for these investigations.

B. Synthesis of Long Valley Geophysical Data (*N. E. Goldstein, T. V. McEvelly, H. F. Morrison, and H. A. Wollenberg*)

To help determine sites for future CSD drilling in the Long Valley caldera, including a deep hole to be drilled under the DOE Magma Energy Program, LBL coordinated and expedited the processing and interpretation of critical data sets in an effort that has involved the USGS, academic institutions, and the National Laboratories. The work resulted in a two-day symposium and the subsequent publication of a proceedings volume containing the major findings. One result of the symposium is a different perception of present-day magmatic conditions. There is much less evidence that a large, zoned magma chamber still exists at depths of less than 10-12 km. Magma at drillable depths, 5 to 6 km, is more likely to occur as small, isolated volumes of melt, each less than 2 km in horizontal dimension. There are correlative mid-crustal gravity and seismic anomalies beneath the western part of the caldera that may be related to magma in the roots of the volcano. The surface deformation in the decade 1975-1985 can be accounted for by an inflation of 0.20 to 0.30 km³ centered at a depth of approximately 8 km. Due to the inherent ambiguity of interpreting the shape of the inflation zone, the surface deformation is equally likely to have been caused by a series of dike injections as by the expansion of a single magma chamber. Since 1984, the rate of deformation has dropped to a uniform level roughly half the 1980-83 rate, and seismicity within the caldera has also decreased markedly.

C. Continental Scientific Drilling Review Group (*T. V. McEvelly and H. Wollenberg*)

The twelve-person group reviews on-going, planned, and proposed CSD projects, primarily in the thermal regimes sector, which are supported by the Department of Energy. Meetings were also

held with the Science Advisory Committee of DOSECC to cover topics of interest to both the thermal and non-thermal regimes sectors of the national CSD program. The Review Group is made up of scientists from Federal agencies, universities, industry, and DOE laboratories.

D. Fundamental Studies of Fluid Flow in Fractured Rock Masses under Stress

(Y. W. Tsang and L. Myer)

In this program, laboratory measurements are coupled with theoretical investigations to study fluid flow in fractured rocks. Our basic understanding of the flow phenomena in single fracture has been greatly advanced. Our laboratory and theoretical investigations have to: 1) refute the common view that a fracture under stress may be idealized as a pair of parallel plates; 2) establish a more realistic description of the fracture in terms of spatially correlated apertures of a range of values; 3) confirm the existence of flow channeling in the fracture; 4) develop the hypothesis that flow and transport are controlled by fracture aperture geometry; and 5) develop relationships between parameters in physical process to fracture geometry parameters. The focus of our work is to relate measurable parameters from physical processes to the (not so accessible) parameters of the fracture aperture. From our theoretical investigations on flow channeling, we showed that the mean residence time in tracer data may be related to the mean aperture of the statistically equivalent flow channels, and the dispersion of the tracer data is related to the standard deviation of the aperture density distribution of the flow channels. From mercury porosimetry measurements on a single fracture we found that the capillary curves derived from first and repeated mercury intrusion can respectively give information on aperture parameters that control the tracer transport and flow permeability. In particular, these measurements provided estimates of the cumulative distribution of aperture sizes over the area of the sample as well as the volume of void space isolated behind void constriction when the stress changed.

E. Geophysical Measurements Facility *(T. V. McEvilly and H. F. Morrison)*

The maintenance and field operation of numerous geophysical systems (e.g., P- and S-wave vibrators, a number of data acquisition systems, downhole fluid sampling tools, and two logging trucks) are conducted at the Geophysical Measurements Facility (GMF), which was recently moved to a new installation at LBL. In addition, two GMF technicians, each with extensive experience with LBL geophysical field programs, have received training to operate the specialized equipment. As an example, the technicians have attended exploration-industry courses in vibrator operation and maintenance and have since gained experience operating the systems for various projects. This arrangement provides the continuity of competent personnel necessary to carry out this type of work. The efficacy of the arrangement has been demonstrated by the use, at affordable 'as used' costs, of the vibrators and recording systems in a number of surveys, including Parkfield, Cajon Pass, The Geysers, and Long Valley, California.

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Category: Geology, Geophysics, and Earth Dynamics

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A. Rock Mechanics (*B. P. Bonner and W. B. Durham*)

Understanding fluid flow in jointed rock in the crust is fundamental to a wide range of problems such as hydrocarbon recovery, extraction of geothermal heat, mineralization of ore bodies, and waste isolation. The approach of the rock mechanics project to understanding fluid flow has been to relate the three-dimensional physical image of the joint to the measured hydraulic conductivity of the joint. Theoretically, the simplest joint is the space between two parallel smooth plates, where the hydraulic conductivity is proportional to the cube of the aperture (the "cube" law). Real joints in rocks are much more complex. Although many theoretical treatments of flow in joints exist, corroborative experimental work has not been done. Complete verification of theoretical models requires measurements of joint permeability as a function of aperture and characterization of joint topography. The specific goal of our project is to finally test the model of joint flow.

We have constructed a profilometer that digitizes the topography of joints in laboratory-sized specimens (maximum dimension approximately 200 mm). The instrument accurately measures surface profiles in three dimensions so that the two surfaces that form a joint can be directly compared to one another, thus providing an image of the joint space itself. (More typical profiling instruments have fine measurement resolution normal to a surface but are unable to index adjacent or mating profiles.) With this instrument we have measured for the first time the characteristic length above which the two surfaces of the joint are correlated and below which the surfaces are uncorrelated and the joint is fractal-like. We improved the hardware this year to increase reliability and measurement precision. We have modified signal processing software, originally developed for seismic applications, to handle the voluminous data that result from three-dimensional profiles.

During the past year we performed detailed and repeated profiles on joints in two rocks, a natural fracture in a tuff and a man-made tensile fracture in a gabbro. A complete set of laboratory measurements of aperture and permeability as a function of normal force across the joint was available for the gabbro, which allowed us for the first time to fully test theoretical models. Brown predicted that the cube law should break down at small apertures (of order of the joint roughness) based on an approximate analysis from lubrication theory using Reynolds' equations. Brown's model was the first to explicitly include joint roughness and not simply express roughness in terms of an effective aperture. Our measurements disagree with the model prediction. We found the cubic relationship between permeability and aperture still applied, even though the measured aperture (which decreased with increasing normal force) approached the measured surface roughness. Now that we are able to make measurements of joint roughness with such ease, the generality of this disagreement between theory and experiments should be tested for additional rocks on which permeability and aperture measurements have been made.

We have also continued collaboration this year with researchers outside LLNL who require the unique three-dimensional profiling capabilities of our instrument. T. Tullis and W. Power of Brown University are studying fault surfaces on the field and laboratory scales as part of a study of

earthquake dynamics. We are collaborating to determine the mating scale for fault surfaces that have been active in recent geologic time. With P. McWilliams (USBM, Spokane) and S. Miller (University of Idaho) we are profiling a common test sample to compare our technique to a stereographic technique they are developing.

B. Diffusion in Silicate Materials (*F. J. Ryerson 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. Oxygen diffusion in olivine has been measured in San Carlos olivine (Fo92) between 1000 and 1400°C for the [100] and [010] directions along the Ni-NiO and Fe-FeO buffers. The primary goal of this work is to constrain the mechanisms of plastic deformation in olivine and to further constrain its point defect chemistry. The data will also have application to the electrical conductivity of olivine and the rate of isotopic exchange between olivine and hydrothermal fluids.

To date, our data are most complete for the [100] direction, and the diffusion coefficient is given by Arrhenius relation modified for the effect of changing oxygen fugacity. These data are in the range previously determined for the diffusion of oxygen in endmember forsterite. Diffusivities for the [010] direction are slightly faster than those for [100]. The most striking feature of the data is the positive dependence of oxygen diffusion on oxygen fugacity. Point defect reactions in olivine indicate that the concentration of oxygen vacancies in olivine should either decrease or remain constant with oxygen fugacity dependent upon the charge neutrality condition and buffering oxides. The increase in oxygen diffusivities with oxygen fugacities argues against the diffusion of oxygen by a vacancy mechanism. The most likely alternative diffusion mechanism is an interstitial mechanism. However, the anionic radii of oxygen is extremely large relative to the radii of interstitial sites in the close-packed olivine structure. Hence, we would expect that the activation energy for interstitial diffusion of oxygen in olivine to be much higher than that measured in our experiments. An interstitial mechanism would also fail to explain the lack of fO_2 dependence for oxygen diffusion in forsterite. The similarity in both the fO_2 dependence and the activation energy for oxygen diffusion and cation diffusion in olivine suggests vacancies in which the presence of a cation vacancy weakens the bonding of the adjacent oxygen atom allowing it to migrate more easily. This "covacancy mechanism" has also been suggested to explain similar paradoxical oxygen diffusion phenomena in spinels.

The activation energy for creep in olivine is approximately twice that for oxygen diffusion measured here. Hence, creep in olivine cannot be controlled by the movement of a single oxygen point defect. A coupled process involving the diffusion-rate limited migration of jogs on dislocation lines or kinks on dislocation lines must be appealed to explain the disparity between diffusion activation energies measured for oxygen and silicon and creep in olivine.

Accessory Phase Parameters and Granite Petrogenesis. Accessory minerals in granites are known to concentrate trace elements and, of particular importance, the heat-producing elements U and Th. As such, the behavior of accessory minerals during granite petrogenesis will have a profound effect on the redistribution of heat-producing elements by this process. As outlined by Watson and Harrison and coworkers, accessory phase behavior is controlled by 1) the equilibrium saturation levels of essential structural constituents as a function of external conditions, 2) the dissolution rate of the accessory phase, and 3) the diffusion of trace elements in the accessory minerals. In the

previous year we further developed a saturation model for monazite in peraluminous magmas. This year's effort has concentrated on accessory phase behavior in metaluminous "granite" compositions. Experiments have been performed to determine the saturation values of sphene and allanite under a range of conditions appropriate to granite petrogenesis. The runs are currently being analyzed.

C. Electrical Conductivity, Temperature, and Radiative Transport in the Earth (*A. G. Duba; joint research with T. J. Shankland, LANL*)

Results of both the electrical and optical research efforts help determine temperature distributions in the crust and upper mantle. The thermoelectric effect S and electrical conductivity σ 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. Although there are seismic models to explain the low velocity zone (LVZ) as a solid-state phenomenon not requiring partial melting, the most well-constrained laboratory electrical measurements are more consistent with the partial melting hypothesis for the high conductivity layer (HCL) apparently associated with the LVZ. If the LVZ/HCL is not a partial melt layer, then mantle geotherms would be considerably lower than previously inferred. We are evaluating the constraints on temperature imposed by electrical studies.

We have analyzed electrical conductivity and thermoelectric results for olivine and forsterite in terms of detailed conduction mechanisms; both materials have mixed ionic and extrinsic electronic conduction between 1000 and 1500°C. Using the complete conductivity tensor as a function of temperature for San Carlos olivine, we calculated an average conductivity suitable for polycrystalline aggregates of olivine by means of several spatial averaging schemes: Hashin-Shtrikman, Maxwell-Waff, effective medium, geometric mean, and self-similar. These averaging methods all agree within 3% between 1100 and 1500°C; we believe the resulting conductivity-temperature curve to be the best obtained to date for the purpose of inferring upper mantle temperatures from conductivity profiles.

In addition, we measured the frequency dependence of the conductivity of a black shale from 5.4 km depth to a borehole near Muenster, West Germany. The conductivity at room temperature is about 1 S/m, three orders of magnitude greater than normal shales and equivalent to molten basalt, and is approximately independent of frequency between 10^{-4} and 10^5 Hz. Since such high conductivity could be typical of hydrocarbon reservoir source rocks, this suggests that electromagnetic studies could be important in future hydrocarbon exploration strategies.

D. Attenuation and Dispersion in Partially Saturated Rocks (*J. G. Berryman, B. P. Bonner, and S. C. Blair*)

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 will also impact code calculations for the Nuclear Test Containment Program and waveform analysis for the Seismic Verification Program. This project has continuing experimental and theoretical components: 1) Our recent experimental efforts have concentrated on verifying theoretical predications for wave propagation in fluid-bearing porous media. Recent theoretical analysis (done by Prof. M. Miksis of Northwestern in collaboration with us) predicts that contact line movement may contribute to observed attenuation in partially saturated rocks at low frequencies. We have constructed a torsional oscillator suitable for testing this suggestion. Acoustic

microscopy shows promise as a new tool to evaluate the morphology of porous rock. In order to test this premise, we are examining a set of matched petrographic thin and 100 micron sections of various rocks--including sandstones, tuffs, limestones, and crystalline rock. We are in the process of constructing optical mosaics to examine larger scale features. 2) We have also continued our collaboration with the Ultrasonics Group, Department of Welding Engineering, Ohio State University. Experimental techniques used ordinarily for non-destructive evaluation have proven useful for investigating saturated porous media. Our attention is directed mainly at the properties of waves that propagate in the vicinity of interfaces between fluids and saturated porous rock. We have investigated the acoustic properties of high porosity foams, since these exhibit extremes of porous media behavior. Biot's second (slow) compressional wave appears to dominate wave propagation in these materials, which are also strongly anisotropic. 3) Theoretical efforts have produced a generalization of Biot's theory to partially saturated media, and a paper describing this work was submitted for publication this year. The main features of the theory for saturated media still apply, but the velocities and attenuation depend on the relative distribution of the liquid and gas phases. A new explanation has been suggested for the excess wave attenuation observed for saturated media. More energy is dissipated in regions of high local permeability, but the bulk permeability is biased low by flow through relatively open paths. The spatial variation at the permeability must be taken into account in computing the constants appropriate for the theory. Image processing techniques developed at LLNL are being applied to computing local permeabilities.

E. Surface Wave Method for Determining Earthquake Mechanisms with Applications to Regional Stress Field Studies (*H. J. Patton and S. R. Taylor*)

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.

In 1987-1988 we have made considerable progress determining source mechanisms and depths for earthquakes in the study areas. Over twenty events have been processed to date and another twenty or so are slated to be analyzed in the coming months. We have found that the method employed in this study, which involves the linear inversion of surface-wave amplitudes for the elements of the seismic moment tensor, appears to be viable for earthquakes down to magnitude 3.5, and could possibly be used for smaller events if there are sufficient numbers of stations about 150-500 km of the source. This is quite encouraging since it goes beyond our expectations at the start of this project. We have several means of judging the internal consistency of our results, and these checks have been satisfactory. We have also engaged in a study to compare our measurements with those obtained by other seismic methods with the results of the comparison reported in the literature, and they were found to be quite satisfactory. We have reported our preliminary findings on the stress field at the 1988 spring meeting of the American Geophysical Union and will be reporting future progress at the fall meeting in San Francisco.

F. Advanced Concepts (*L. W. Younker*)

This project involves exploratory research in several geoscience-related areas. New topics are deleted 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 the programs and assessing feasibility of research tasks. Projects funded this past year were primarily aimed at enhancing our experimental and calculational capabilities. We investigated the feasibility of installing a multi-anvil sliding system into one of our existing high-pressure presses, thereby greatly increasing the pressure on relatively large volume samples. We also designed an apparatus to obtain infrared and optical spectra at high temperatures (to 1000°C) and high pressures (to 500 MPa). Finally, we developed computer codes for the interactive display of 3D seismic velocity models.

G. Thermal Stress Microfracturing of Crystalline and Sedimentary Rock (*B. P. Bonner and B. J. Wanamaker*)

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

Acoustic and seismic methods show promise for monitoring cracking in rock subjected to thermal stress, a suggestion primarily based on experiments performed at ultrasonic frequencies. We have now extended these measurements to the seismic frequency range. Shear modulus (G) and the attenuation in shear ($1/Q_s$) of Westerly RI granite at temperatures up to 300°C were measured at 10 Hz with a torsional oscillator producing peak strains of up to 3×10^{-5} . Experiments were performed in ambient atmosphere without confining pressure to maximize thermal cracking effects. Between 20 and 120°C, G increases and $1/Q_s$ decreases with temperature, probably as a result of crack closure or outgassing of volatiles. Above ~120°C, G decreases and $1/Q_s$ increases with temperature up to 20 and 40%, respectively, at 280°C. Separate experiments show that acoustic emissions begin at 75-85°C, suggesting that either 1) AE sources other than formation of new cracks, for example, sliding or preexisting cracks, or decrepitation of fluid inclusions, operate at low temperature or 2) a critical density of new microcracks is required to alter the bulk properties. Collaborative experiments for unconfined Westerly granite with Prof. R. Bodnar of VPI suggest that at low pressures, decrepitation of fluid inclusions may be an additional source of acoustic emission, although these effects are interrelated in that fluid inclusions also cause stress concentrations, which may nucleate cracking through geometrical effects alone.

Contractor: LAWRENCE LIVERMORE NATIONAL LABORATORY
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Contract: W-7405-ENG-48

Category: Geochemistry

Person in Charge: L. W. Younker (415-422-0720)

A. Thermodynamics, Kinetics, and Transport in Aqueous Electrolyte Solutions (J. A. Rard and D. G. Miller)

Transport of dissolved chemical species is important in a wide variety of geochemical phenomena. Geochemical applications include radioactive and chemical waste isolation, diagenesis, ore formation, and mineral crystal growth and dissolution kinetics under some conditions. Mutual diffusion coefficients are required to understand and model these processes. Activity coefficients are required for all chemical equilibrium problems involving aqueous solutions (solubility products, Gibbs energy of formation of hydrated solids, chemical speciation).

We have, therefore, been making experimental measurements to provide some of these necessary data: 1) We have measured diffusion coefficients using optical interferometry for aqueous solutions of most of the major and minor brine salts (except K_2SO_4 and carbonates) at $25^\circ C$, and have measured extensive data for several mixed electrolytes. Planned future work is to study K_2SO_4 and additional mixtures at $25^\circ C$, and to extend measurements to other temperatures where relatively little published data are available either for single salts or their mixtures. 2) We have been measuring activity/osmotic coefficients for a variety of electrolytes and their mixtures at $25^\circ C$ by using the isopiestic method, including those systems for which diffusion coefficients were measured. 3) We have been modeling the mixed electrolyte diffusion and activity data by using various approximation methods; so far the activity data have been more amenable to accurate modeling than have the diffusion data. 4) We have also measured density data for all of the mixed salt solutions used in diffusion experiments and for some of their single salts.

This year we completed the last set of diffusion experiments for aqueous $NaCl-SrCl_2$ at total molarities of 0.5, 1.0, 2.0, and $3.0 \text{ mol} \cdot \text{dm}^{-3}$ and molarity fractions of 1/3, 1/2, and 2/3. Two papers resulted from this study; one has been published and the other accepted for publication. We have also published a paper on diffusion of sodium and potassium bicarbonates in collaboration with colleagues at Texas Christian University. In addition, we have now completed an even more extensive set of measurements for aqueous $NaCl-MgCl_2$ at molarity fractions of 1/4, 1/2, 3/4, and for "traces" of $NaCl$ in $MgCl_2$ and of $MgCl_2$ in $NaCl$. This was done in collaboration with visitors from Texas Christian University and the University of Naples. One paper based on this study has been submitted for publication and several more will be written. We previously published our isopiestic data for this system.

Various properties of aqueous $NaCl-MgCl_2$ are of interest for modeling sea water and its evaporites. Our diffusion coefficients, activity coefficients, and densities are part of an international collaboration to fully characterize the transport and thermodynamic properties of one electrolyte mixture containing a higher valence salt. Data being measured at other laboratories (USA, Australia, Canada, Germany, Italy, Argentina) include electrical conductances, viscosities, tracer diffusion coefficients, thermal diffusion coefficients, and transference numbers. When these other measurements are complete we will calculate Onsager L_{ij} transport coefficients; they will then be used to test new statistical mechanical theories. We have also begun isopiestic measurements for aqueous $Na_2SO_4-H_2SO_4$ at $25^\circ C$ and are now about one half done. This system

shows considerable complexity owing to bisulfate formation. Previous activity measurements for it are for greatly restricted concentration regions.

A paper was prepared describing a new technique for extracting the diffusion coefficients for three- and four-component systems from Gouy fringe pattern data. This method will probably be the only practical one for four-component system and is similar to the method developed at LLNL for analyzing Rayleigh fringe pattern data.

B. Compositional Kinetic Model of Petroleum Formation (*A. K. Burnham, 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.

It is now well recognized that chemical kinetics of oil generation derived from laboratory experiments covering a time frame of minutes to weeks extrapolate qualitatively to a geological time of millions of years, but there are still major questions about how to derive kinetics for quantitative use in oil exploration. Related questions concern how sensitive the chemical kinetics are to the original depositional environment and if the variations are large enough that kinetics must be determined for each source rock. Last year we developed and reported a relatively simple technique for measuring oil generation kinetics from micropyrolysis. Supplemented with additional measurements during the past year, we have examined four lacustrine and eight marine source rocks and demonstrated that there are significant variations in the predicted oil generation temperatures of kerogens of the same general type. We also showed that other more complicated procedures are adversely affected by mass transport processes, which cause significant errors in the kinetic parameters. We have partially completed a comparison of various experimental procedures to determine the simplest, most reliable procedure for measuring oil generation kinetics.

The ultimate economic interest is in how much oil migrates to traps, so generation kinetics must be coupled to thermodynamic and transport properties to predict the timing of expulsion from the source rock. Depending on how efficient the expulsion is in various circumstances, variable amounts of oil may be cracked to gas before being expelled; this in turn affects the driving force for oil expulsion. Moreover, understanding the mass transport contribution to various laboratory experiments is essential for their proper interpretation. To address these issues, we have incorporated more rigorous phase equilibrium calculations using the Peng-Robinson formalism into our detail pyrolysis model. We have just started a comparison of model calculations with a variety of published experiments results. We have also begun reexamining published literature to improve our oil cracking kinetics.

Since there is no rigorous theoretical proof that a quantitative extrapolation of chemical kinetics to a geological timescale is valid, it must be demonstrated empirically by deriving thermal histories of thermal sediments from geological models and comparing the resulting predictions with geochemical evidence. Therefore, the verification of the chemical kinetic models depends on a good understanding of both the geologic thermal history as well as how oil migration influences the geochemical evidence. We have improved our geologic modeling capability by writing a computer program for backstripping and steady-state thermal modeling of a sedimentary column. Application to the Uinta basin showed that the simple geological model we used a few years ago is within the uncertainty of more sophisticated geological models. We have also analyzed several samples from that basin to improve the certainty of our previous demonstration that laboratory chemical kinetics extrapolate well to a geologic time scale.

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Contract: W-7405-ENG-48

Category: Energy Resource Recognition, Evaluation, and Utilization

Person in Charge: L. W. Younker (415-422-0720)

A. Continental Drilling Program Information and Data Management Unit (*G. Pawloski and P. W. Kasameyer*)

The Data Management project involves the assessment of the value of data management approaches for CSDP activities. Originally our efforts were to evaluate means to inform researchers about "holes of opportunity" where scientific projects could be added to planned drill holes. As CSDP has evolved to the point of funding the drilling and coring of research holes, our efforts evolved to the acquisition and testing of a site-specific data base installed on a commercially available well-log data management system at the SSSDP drill site. We had four purposes in constructing this data base: to handle pre-existing and new data as an integrated data set and provide quick interactive data viewing and analysis capability for researchers on the drill site; to provide the means to rapidly disseminate the data in usable form as the researchers analyzed their results; to have the data available for scientific analysis in an integrated system; and to determine the value of having such a data-handling system as part of a CSDP project.

We constructed the initial data set, with logs and picks from 17 wells in the Salton Sea geothermal field, and loaded the well logs and mud logs collected on site. We used the system to generate plots for the initial data report published by the USGS and have participated in the analysis of the data. We used our data management system in two research projects to analyze well-log data from State 2-14. We evaluated the changes in the well logs as the degree of metamorphism increased with depth. This work will lead to improved means to estimate the degree of alteration from logs before samples have been analyzed. From analyzing density and borehole gravity data, we learned that although State 2-14 is near the edge of the present thermal field it is surrounded to a distance greater than a kilometer by dense, altered rocks typically seen in thermal areas. This work indicates that areas to the east of State 2-14 may have been hotter in the past. In summary, the Data Management program has ensured that the logging data from the SSSDP well were available to scientists during the drilling, were archived in an accessible manner, and are being used to understand the hydrothermal system at the Salton Sea.

B. Viscosity and Electrical Conductivity of Rock Melts: Continental Scientific Drilling Program (*F. J. Ryerson and H. C. Weed*)

The work reported here is part of an ongoing study of the rheology of magmas at both super- and subliquidus conditions. We have concentrated our work on subliquidus phenomena in part due to the relative paucity of data but also due to the fact that a large fraction of igneous phenomena occur in melt-crystal systems as opposed to melt-only systems. Data from melt-crystal and melt-bubble systems are also necessary if rheological models (e.g., Einstein-Roscoe equation) are to be validated.

Last year we reported on a high-Al basalt from the Medicine Lake Highlands. This year we present results from an olivine andesite (Medicine Lake OPOA). The crystallization sequence for

OPOA has been previously determined by others. Flow curves of torque vs rotational speed were determined in a series of isothermal runs in a rotation cup viscometer of the Couette type in which torque and temperature were measured at the central bob. Oxygen fugacity was fixed at the QFM buffer. Experimental results in the temperature range 1356 to 1130°C are as follows. OPOA showed negligible yield strength from 1356 to 1169°C and a rapidly rising yield strength to 1130°C. The curvature of the flow curves was near zero above 1169°C and negative below, indicative of increasingly pseudoplastic behavior.

The range of viscosities at unit shear rate was from 40 to 3060 Pa•s for the highest and lowest temperatures, respectively. The Arrhenius plot is comprised of two branches intersection at ~1193°C. The upper temperature branch corresponds to flow in a single phase liquid in which the viscosity rises to 460 Pa•s at 1193°C yielding an activation energy of $58 \pm 2 \text{ kcal} \cdot \text{mol}^{-1}$. The low temperature branch corresponds to flow in a magmatic suspension with an apparent activation energy of $148 \pm 17 \text{ kcal} \cdot \text{mol}^{-1}$. Although some of the increase in activation energy with decreasing temperature must be attributed to changing melt composition, previous work by us has shown that the major effect is due to hydrodynamic interaction of solids. We propose that the non-Newtonian behavior in subliquidus magmas is due to reorientation of solids in the flow field and solid-solid interactions. The time dependent pseudoplasticity and yield strengths are produced by the relationship between solid phase contiguity (the fraction of solid internal surface area shared with other solids) and grain dispersive pressure due to shearing. Increased contiguity is related to increased apparent viscosities and yield strengths, while increased grain dispersive pressure due to shearing acts to diminish contiguity.

We began design and testing of two devices that will allow us to investigate the rheological properties of systems containing only small melt fractions. A 10 kbar gas deformation apparatus was refurbished and pressure tested to 5 kbar. The controlled clearance packings for the uniaxial compression ram were also successfully tested and the pressure intensifier rebuilt. Preliminary plans for a one-atmosphere controlled oxygen fugacity deformation apparatus were completed.

C. Shallow Hole Investigations of Long Valley, Valles, and Salton Sea Thermal Regimes (L. W. Younker, P. W. Kasameyer, and R. L. Newmark) (Cooperative program with SNL, LANL, and LBL)

Salton Sea Shallow Thermal Gradient Project. Analysis and interpretation of the high quality shallow thermal data recently acquired in the offshore part of the Salton Sea geothermal field and some new deep hole data in the onshore region are increasing our understanding of this important hydrothermal system. The Salton Sea thermal anomaly can be described as three nested thermal features superimposed on the regional Salton trough heat flux: a broad region of elevated conductive heat flow with constant temperature gradients of about 0.1°C/m, a central anomaly of high (0.4°C/m) near-surface gradients observed through a conductive thermal cap underlain by a nearly isothermal zone of hydrothermal circulation, and two local anomalies with shallow temperature gradients as high as 0.8°C/m superimposed on the central geothermal system.

These observations of the thermal anomaly provide important constraints for models of the circulation of the hydrothermal system. Thermal budgets based on a simple model for this hydrothermal system indicate that the heat influx rate for local "hot spots" in the region may be large enough to account for the rate of heat flux from the entire Salton trough. Simple models consisting of igneous bodies intruding into a circulating region, overlain by a conductive thermal cap, produce temperature profiles and surface thermal gradients for comparison with field observations. The size and depth of intrusive bodies are constrained by interpretation of the magnetic anomaly and by results of drilling and other observations in the geothermal field. Models consistent with the field observations place constraints on the relative ages of the thermal

sources. The broad anomaly can be produced by intrusions occurring on the order of 50-100,000 years ago at depths on the order of 2 km, which is consistent with models of the main magnetic anomaly. Models consistent with the field observations require additional shallow intrusions at a considerably younger age.

Inyo Domes Drilling Project. During the summer of 1987, a hole was cored along a slanted trajectory that passed directly beneath south Inyo crater in the western portion of Long Valley caldera. Objectives of the hole were to sample intrusive features formed during the 600-year-old Inyo volcanic event and to probe the western caldera moat. The hole was sited 213 m southwest of the phreatic crater, passed beneath its center at a depth of 570 m, and terminated 73 m northeast of the crater center at a depth of 817 m. Three breccia zones containing dense crystalline basalt and glassy vesicular rhyolite clasts were intersected at 11.4 - 9.7 m and 0.9 - 0.5 m southwest and 8.7 - 25.2 m northeast of the crater center. It is clear that the Inyo feeder is fragmental at a depth where outside the caldera it was found to be a 6-m-thick wholly intact intrusion. The observations support the hypothesis that the south Inyo crater event represents a silicic explosive eruption, quenched at an early stage of development. The silicic magma apparently exploited the path of an old moat basalt feeder. Basement, represented by Sierran roof pendant consisting of brecciated quartzite and metavolcanic rocks, was encountered at a depth of 779 m. The volcanic sequence is nearly 900 m thinner than that of a Unocal well 900 m to the southeast, due to the absence of precaldern lavas, the Bishop tuff, and 200 m of lowermost Early rhyolite. Apparently a major fault, likely the southern extension of the Hartley Springs fault, passes just east of Inyo-4 and forms part of the western structural boundary of the caldera, 4 km inboard of its topographic boundary.

D. Underground Imaging (*W. D. Daily and J. G. Berryman*)

The thrust 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 processes. The results of this project have been used by many DOE programs, including nuclear waste management and enhanced oil recovery. Other programs will benefit from our basic research in imaging structure and processes in the subsurface.

A vigorous program is in progress to continue development of electrical impedance tomography (EIT) for geophysical applications. We have developed a faster, more computationally efficient algorithm based on the iterative Newton-Raphson method. This algorithm has also been extended to make the finite element resistivity distribution piecewise continuous and allow for image reconstruction from the surface, between two boreholes, between two boreholes and the surface, and between one borehole and the surface. Also, various cases of geophysical interest have been investigated using finite element models. Computer models for data acquired on the surface only (the half plane model) were evaluated for imaging layers, dikes, and voids (water or air filled). Models for the case of measurements between two boreholes and the surface (three sided model) were evaluated for imaging a two layer model with a conducting anomaly at various locations in the lower layer. Experimental apparatus has been designed, built, and tested for doing laboratory scale model tests to compare with the computational modeling described above. The apparatus is capable of high speed data acquisition of low level voltages with an optimum signal to noise ratio. Model data are being taken for the borehole to borehole and surface to borehole cases. Also we are modeling the extreme cases where data are available only along one surface (such as tomography from surface resistivity surveys) and where data can be gathered from all sides of the target (such as imaging of core samples in the 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], 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. Although there are seismic models to explain the low velocity zone (LVZ) as a solid-state phenomenon not requiring partial melting, the most well-constrained laboratory electrical measurements are more consistent with the partial melting hypothesis for the high conductivity layer (HCL) apparently associated with the LVZ. If the LVZ/HCL is not a partial melt layer, then mantle geotherms would be considerably lower than previously inferred. We have analyzed electrical conductivity and thermoelectric results for olivine and forsterite in terms of detailed conduction mechanisms. Using the complete conductivity tensor as a function of temperature for San Carlos olivine we calculated an average conductivity suitable for polycrystalline aggregates of olivine. We believe the resulting conductivity-temperature curve to be the best obtained to date for the purpose of inferring upper mantle temperatures from conductivity profiles. In addition, we measured the frequency dependence of the conductivity of a black shale from 5.4 km depth to a borehole. The conductivity at room temperature is three orders of magnitude greater than normal shales and is approximately independent of frequency between 10^{-4} and 10^5 Hz. Since such high conductivity could be typical of hydrocarbon reservoir source rocks, this suggests that electromagnetic studies could be important in future hydrocarbon exploration strategies.

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. Of more interest to basic research in rock physics is the investigation of nonlinear properties of rocks and frequency dependence of elastic properties. In the laboratory, we have shown that the intensity of the difference beam is proportional to the product of intensities of the driving beams as predicted by theory. The definitive work has come from observations of the general case of two driving beams intersecting at arbitrary angles to produce a difference beam at a

still different angle. In this case we have been able to verify the selection rules that govern these angles when sample velocities and frequency ratios are specified.

C. Time-Dependent Deformation of Rock (*R. L. Kranz [505-667-4856] and J. D. Blacic*)

Assurance of long-term isolation of nuclear wastes in mined cavities in rock requires knowledge of the time-dependent strength and transport properties of these rocks, such as stress-aided corrosion, hydrolytic weakening, and stress and strain generation resulting from hydration or dehydration of susceptible minerals. The objectives of this research are: 1) to understand and evaluate the effects of water on time-dependent brittle rock deformation, including rock swelling and contraction, and 2) to evaluate changes in transport properties, such as permeability, that accompany this deformation. To accomplish these objectives, we perform creep and hydration experiments on repository host rock (from the proposed Yucca Mt., Nevada repository site) tuff under simulated *in situ* repository conditions. Experiments have demonstrated that increases in water content, internal pore pressure, or temperature accelerate the static fatigue of rock, lowering strength and time to failure under constant load. We have also demonstrated that the time-dependent adsorption of water by zeolite minerals in confined tuff can create large compressional internal stresses. We are now studying the reverse situation where dehydration causes extensional stresses, possibly resulting in microcrack generation, which would reflect on the transport properties.

D. 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.

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

Advanced concepts research in geosciences involved six projects in FY88. Each of these projects was designed as a limited-term exploratory effort.

Trace Noble Gas Signatures. The mass spectrometer system has been calibrated to increase the dynamic range. Progress to date includes measurement of helium-8 to helium-4 ratios of $1.3 \times 10^6 \pm 20\%$ in samples with only 6×10^6 atoms of helium-3. Additional calibrations have been performed for isotopes of neon, argon, and krypton. Current activity involves designing a high temperature low blank furnace.

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 location 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.

In Situ Thermal Spallability of Different Rocks. Near the end of this fiscal year we intend to complete small-scale experiments that will test the ability of shale, limestone, and sandstone to be excavated using thermal spallation.

Expert Systems. The Geologist's Assistant is an expert system being developed at Los Alamos. The system is being created by applying pattern matching techniques developed in speech recognition technology to geophysical log analysis or comparison. The Geologist's Assistant is designed to aid geoscientists with the analysis of geologic and geophysical data obtained from drilled holes at the Nevada Test Site. The goal of this analysis is to characterize the site and identify any potential geologic hazards that might be a threat to the containment of radioactivity during an underground nuclear test. As each new hole is drilled, thousands of measurements are made to characterize the geology beneath the surface. Measurements include electrical resistivity, density, gamma-ray emissions, and many other properties of the subsurface. Information about each site is stored in GEODES, a data base management system that was developed at Los Alamos to retain and retrieve all the accumulated data. The Geologist's Assistant has on-line access to the geologic and geophysical information stored in GEODES as required in order to analyze a site.

Interwell Survey for Fault Detection. Los Alamos has been requested by Amoco to test the Los Alamos acoustic receiver at the Mounds, Oklahoma field test site prior to an experiment in the Hastings, Texas oil field. At the time of this writing, preparations are underway for the test at Mounds. Advance geoscience concepts funds will be used to analyze data from the Mound's site and explore the feasibility of more in-depth research in this area.

Stable Isotopically Labeled Organic Tracers for Geological Processes. We have investigated the possibility of field testing biological workover using a reactive tracer. Our investigations show degradation of Leavy Acetic acid ($D_3^{13}C_2OOH$) is a likely tracer for this purpose. The heavy methane produced, $D_3^{13}CH$ (methane-20), can be detected to 1 part in 10^{11} normal methane if the microorganisms are present. A full proposal for further studies is submitted for funding in FY89.

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

Contract: W-7405-ENG-36

Category: Geochemistry

Person in Charge: R. W. Charles

A. Coal Maturation: Occurrence, Form, and Distribution of Inorganic Phases Within the Peat-to-Lignite Transition (*R. Raymond, Jr. [505-667-4580] and D. L. Bish*)

Peat, the precursor of coal, is composed predominantly of plant components and secondarily of mineral matter derived from various sources. To evaluate the occurrence of inorganic phases in a coal deposit, we must understand the mechanisms for their introduction into the original peat deposit and the physical and chemical conditions affecting the peat during its transformation into coal. The objectives of this research are: 1) to identify and correlate authigenic and detrital inorganic phases found in different peat types and compare these with those found in lignites; 2) to identify the processes that enhance and/or inhibit distribution and preservation of inorganic material in the initial coal-forming environment; and 3) to construct geochemical models for formation, preservation, alteration, and distribution of inorganics in peats and lignites.

To achieve the above objectives, we will investigate the occurrence of inorganics within peat and lignite deposits and the physical and chemical conditions affecting these deposits. Deposits will be chosen such that the most reasonable correlations can be made between the depositional environments of the peats and those of the lignites. We will characterize the modes of occurrence and content of biogenically and non-biogenically derived inorganic phases in the peats and lignites and then establish geochemical models for the alteration of those phases during the peat-to-lignite transition. These models should allow us to predict the occurrence and distribution of inorganics within various lignite and higher rank coal seams. Results to date suggest that: inorganic phase contents and major and trace element contents of peats relate directly to depositional and ecological settings rather than geographic provinces; sulfur occurrence in coals is attributable to sulfur availability during peat deposition and peatification, and alteration of mineralogic phases occurring in peat deposits can occur contemporaneously with peat deposition with no apparent additional alteration during later coalification.

B. Rock-Water Interactions and Element Migration (*R. W. Charles [505-667-4985], D. R. Janecky, T. M. Benjamin, and P. S. Z. Rogers*)

The emphasis of this project is experimental and computational modeling of rock-fluid reactions in hydrothermal systems applicable to environments of general interest for the discovery and recovery of energy whether geothermal or fossil. The major thrust at this time in the CSDP context consists of sample collection and experimental hydrothermal reactions investigating various natural hydrothermal systems. The discrimination of major, minor, and trace element (via nuclear microprobe) chemistry and associated phase equilibria during mobilization, transport, and deposition is the thrust. Experimental systems are used to develop models for element migration in strong brines using single minerals as well as rocks. The results will aid in developing a model relating portions of the various hydrothermal systems using the mineral assemblages defining the state of local equilibrium. Solubility (mass transport) models, reaction path calculations, and

coupled-flow and rock-water interaction calculations are upgraded as the experimental data are analyzed.

The modeling of natural systems has yielded important new results from CSDP wells. From the observed phase assemblages, we are able to define the state of equilibrium, very tightly constraining the pH and fO_2 of the naturally occurring phase assemblages. It is possible to define perturbations in the samples due to lost circulation materials, well liner dissolution, sample fractionation, and mixing with other natural flow-zones. Apparently, the zone is undersaturated to varying degrees with respect to Pb, Zn, and Ag sulfides and is probably a zone of transport rather than deposition.

The experimental program uses Au-Ti reaction cells to examine reaction pathways, mineral reaction rates, alteration mineralogy, solution composition, and effects of salinity, temperature, and pressure. Work is coordinated with the calorimetry and Raman projects. Experimental work at this time deals primarily with brine bearing natural systems. Our results are being incorporated into experiments dealing with more complex mineral systems similar to those found in Salton Sea: magnetite, hematite, epidote, kspat, and quartz; and pyrite, hematite, epidote, kspat, and quartz.

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

Knowledge of the thermodynamic properties of aqueous solutions is basic to an understanding of many geochemical systems. Hydrothermal alteration, element migration, and sedimentary diagenesis are a few examples of processes largely dependent on the properties of the associated aqueous fluid. Studies of these processes require information on the heat content and free energies of mixed electrolyte solutions over a wide range of composition and temperature.

The number of different electrolyte solutions of interest at high temperatures is large, so a method of obtaining thermodynamic properties from a minimum amount of experimental data is desirable. Heat-capacity measurements are ideal for this purpose because the heat-capacity data can be integrated as a function of temperature to determine solution enthalpies and total free energies. These thermodynamic properties can be used to provide an accurate model for electrolyte solutions at high temperatures and pressures. A high temperature/high pressure flow calorimeter has been constructed to measure the heat capacities of aqueous electrolyte solutions with an accuracy of better than .03%. Heat capacity data have been obtained for the systems $NaCl-Na_2SO_4-H_2O$, $NaOH-H_2O$, and $Na_2CO_3-NaHCO_3-NaCl-H_2O$ to 370 bar and 32°C. The ultimate goal is to provide data to 400°C in order to study the behavior of electrolyte solutions in the region very near the critical point of water.

D. Geochemistry of Technetium (*D. B. Curtis and D. J. Rokop [505-667-4498]*)

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 properties of

technetium. The experiments define the technetium production rate in different geological environments and the degree of fractionation between technetium and its parent uranium in different geochemical environments. A production rate of 10^{15} atoms of ^{99}Tc (mole U) $^{-1}\text{yr}^{-1}$ has been measured in buried uranium ore. This rate is a direct manifestation of the neutron flux produced *in situ* within the ore body. Water from the ore body contains a 10^{-17} moles Tc/ ℓ , reflecting dissolution of technetium bearing minerals and subsequent chemical controls on the aqueous concentration of this rare element.

E. Raman Spectroscopy of Aqueous Solution Species (*N. A. Marley, D. R. Janecky, and J. S. Gaffney [505-667-4498]*)

To further our understanding of chemical speciation in aqueous hydrothermal fluids, we have established a laser Raman facility to directly study molecular complexes in solution. A high temperature and pressure cell has been constructed for laser Raman spectroscopy, which is capable of handling brine solutions. Having demonstrated the power of the Raman system for zinc halide systems to 400°C and 1 kbar, we are now expanding this program to develop a fundamental understanding of the chemical and physical interactions between mineral and organic interfaces in aqueous solutions.

Zinc chloride and bromide solutions were studied to test the capabilities of the high temperature and pressure system. Ambient temperature and pressure studies initiated in FY 1987 have been extended to determine the behavior at higher temperatures and pressures. These systems were successfully studied over concentration ranges from one to five molar. Temperatures were varied from ambient to 400°C and pressures up to 1 kbar.

The possibility of organic acid complexation with silica at neutral pH has been proposed as the reason for increased ground water solubilities. We have initiated studies to determine if organosilica complexes can be detected directly using Raman techniques. Preliminary studies have been completed for oxalate, citrate, and phthalate solution reactions with silicic acid. Using difference spectra, clear evidence for the formation of an organosilica complex has been obtained. These studies indicate that the complex is an organosilica ester. Also, the polymaleic acid (PMA) is being studied as a model compound for humics, in a collaborative study with Florida State University (G. R. Choppin). Because many humic and fulvic acids are colored and fluoresce when excited by the argon ion laser, the use of dye lasers and longer excitation wavelengths will be investigated to study these important organics. Spectral studies of the conformational changes of PMA as a function of pH have indicated that internal hydrogen bonding is very important in these molecules. PMA also appears to strongly complex silica in solution. This work indicates that organic reactions with quartz may be important in reservoir and ground water situations.

F. Trace Element Geochemistry of Volcanic Gases and Particles from Basaltic Volcanoes and Geothermal Fluids (*B. Crowe and D. Finnegan [505-667-4498]*)

Laboratory and field studies are being performed to determine the trace element compositions of volcanic gases and particles of active volcanoes. We have sampled fumes from Mauna Loa and Kilauea volcanoes during active eruptions, both on the ground and from aircraft and at cooling vents following the eruptions. The major goals of the project are: 1) determine the characteristic trace element contents of volcanic fume associated with the eruption of Hawaiian magmas, 2) evaluate the variations in the trace element composition of aerosols through eruption cycles, and 3) determine the speciation of highly enriched metals directly upon release from the magma. This information will be used to examine the geochemical mechanisms of trace element enrichment in volcanic fume and to investigate the potential use of monitoring of selected trace elements in volcanic fume for the prediction of future volcanic eruptions. The most promising use of trace

metal monitoring for eruption prediction would be at silicic volcanoes, which commonly show a phase of increased gas emissions and phreatic outbursts prior to major eruptions.

G. A Search for Evidence of Large Comet or Asteroid Impacts at Extinction Boundaries (*C. J. Orth [505-667-4785] and M. Attrep, Jr.*)

There is considerable evidence that a large extraterrestrial body collided with Earth at the end of the Cretaceous Period, about 65 Ma, and that the impact probably led to the mass extinction that characterizes the Cretaceous-Tertiary (K-T) boundary. Although no distinctive crater has been identified, the occurrence of microspherules, shocked-mineral grains, and a strong Pt-group (Ir) anomaly at the boundary is consistent with the impact scenario. The objectives of this work are to search for evidence of large-body impacts and/or volcanism at the other extinction boundaries in the fossil record, to study the consequences of the local release of ultra-high amounts of energy, and to study the effects of "impact winter," nature's equivalent of "nuclear winter." Samples are collected with paleontological guidance; we have been collaborating with more than 60 stratigraphers and paleontologists from 36 universities, museums, and geological surveys from around the globe. We have found several Ir anomalies and it is necessary to measure abundances of many elements to understand the source of the excess Ir, which has generally proven to be derived from terrestrial processes. Recently, we found excess Ir, Sc, Ti, V, Cr, Co, Ni, Pt, and Au just below the 92-Ma Cenomanian-Turonian stage boundary at 15 widely separated localities in the western interior of North America. Currently, we are studying localities in Texas, England, and Spain to determine the source of the excess siderophile-like elements. We are also studying the 210-Ma Triassic-Jurassic boundary in Europe and North America. This boundary is important because the massive Manicouagan impact crater in Quebec has a similar age.

H. Development of a Borehole Hydrothermal Solution Sampler for High Temperatures, Brine Salinities, and Gas-Tight Operation (*R. Charles [505-667-4985], C. Navarro, and D. R. Janecky*)

Investigation of the composition of hydrothermal fluids has important applications to resource evaluation, both in energy and materials development. Studying fluid compositions can lead to understanding of the source and pathway of fluids and indicate geothermal energy potential, hydrocarbon resources, and metal deposit formation. Since most hydrothermal solutions do not appear at the Earth's surface, sampling fluids from boreholes is a necessary part of hydrothermal research efforts. Our objective is to develop a wireline-based tool for simultaneous collection of uncontaminated and unfractionated gases and fluids in the difficult environment encountered in CSDP boreholes. This sampler will be designed to function at temperatures up to 400°C, be of flow-through design, operate without electrical connections to the surface, and be of one liter volume. We have a prototype sampler constructed of titanium Beta-C that has been tested successfully in the field to 210°C. The sampler body and hardware will operate to 400°C. The sealing mechanisms are under construction to operate to 400°C.

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

Contract: W-7405-ENG-36

Category: Energy Resource Recognition, Evaluation, and Utilization

Person in Charge: 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 data base, 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 will be cored starting in July 1988.

Fluid inclusion studies of the sub-ore grade molybdenite deposit (≤ 0.6 wt-% MoS_2) from 25 to 125 m in VC-2A indicate that the molybdenum was deposited from dilute, Na-Cl hydrothermal

solutions (0.2 to 0.5 wt-% NaCl equivalent) at temperatures of 196 to 215°C. Because the deposit occurs in post-caldera ignimbrites, the molybdenum was formed in an early hydrothermal episode after caldera formation. It appears that molybdenum would form from present solutions at pH 6 to 7 and log fO₂ of -45 to -40. Also, a zone in VC-2A at 490 m having a temperature of 210°C was perforated and stimulated to flow superheated, neutral-chloride, hydrothermal fluid. Chemical geothermometers indicate subsurface equilibration temperatures of 280°C in the deeper reservoir. Flow tests indicate the 490-m zone has only limited fracture permeability, a problem encountered by geothermal wells throughout the Valles caldera. A wide variety of core studies have been completed to provide background data for other interested researchers on this CSDP 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, UURI*)

The third research core hole in Valles caldera and the tenth in the Department of Energy's series in the Continental Scientific Drilling Program, will be drilled in July-October, 1988. Valles caldera, which represents the culmination of over 13 million years of volcanism in the Jemez volcanic field, is renowned as an excellent model for resurgent cauldrons and for its high temperature geothermal systems. In 1988 Valles Caldera 2B (VC-2B) will penetrate vapor and liquid zones of the active Sulphur Springs geothermal system and will bottom at about 2 km and 300°C in Precambrian granitic rocks. The core hole will be sited near the junction of the caldera's resurgent dome and main ring fracture and will continuously sample Quaternary caldera-fill tuffs and sedimentary rocks, as well as older rocks, all of which will exhibit effects of young caldera-related hydrothermal activity and thermal metamorphism. The hole will be kept open for four years following drilling to allow researchers to conduct experiments, log, and/or sample fluids.

D. Natural Hydraulic Fracturing in Volcanoes (*G. Heiken [505-667-8477], K. Wohletz, and J. Eichelberger, SNL*)

Fractures containing juvenile magmatic pyroclasts were encountered during drilling into a 600-year-old feeder dike beneath the Inyo domes chain, California. Boreholes were cored through the 51-m diameter conduit of Obsidian dome, the largest of the Inyo domes, and through an unvented portion of the intrusion (dike) 1 km to the south. Pyroclast-bearing fractures were intersected in both holes; the fracture fillings consist of mineral clasts derived from the quartz monzonite, quartz monzonitic and basaltic lithic clasts, and juvenile glass pyroclasts. Angular mineral components are present in the same ratio as in the surrounding quartz monzonite country rock. The presence, orientation, and texture of fracture fillings strongly resemble those of propped, manmade hydrofractures. We interpret these fractures as naturally occurring hydrofractures. The apparently horizontal fracture orientations may have been controlled by perturbations of maximum principal stress by the dikes or by preexisting sheet fractures in the quartz monzonite country rock. Assumption of elastic moduli and fracturing properties for the Sierran basement rock allows calculation of fluid overpressures 5 to 9 MPa in excess of overburden stress. These overpressures are consistent with either vapor exsolution from decompressed magma or rapid heating of ground water. However, the textural and chemical similarity of the pyroclasts to phreatomagmatic tephra that appears late in the explosive eruption sequence suggests that heating of ground water by the dike/conduit caused the fracturing. Such fracturing around volcanic conduits may play an important role in the development of hydrothermal circulation.

Inyo 4, an 861-m-long hole, has been cored on a slanted trajectory that passed beneath south Inyo crater in the west moat of Long Valley caldera. Breccia zones that intrude caldera fill were intersected at depths of 500 m to 650 m consist of vesicular rhyolite and lithic clasts derived from

earlier rhyolitic lavas and an earlier basalt feeder dike. The vesicular rhyolite clasts match fresh pyroclasts in deposits of south Inyo crater. We are continuing the study of breccias and comparing them with surface phreatomagmatic pyroclastic deposits. The degree of wall rock fracturing adjacent to the complex dike system below south Inyo crater is being studied to determine the relationship to magmatic and phreatomagmatic eruption processes and to subsequent hydrothermal circulation in the fracture network.

E. Operation of a Sample Management System for the CSDP (*S. J. Goff [505-667-7200]*)

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 15,000 feet of drill core from various CSDP and related drilling projects. The Curation Office has also published Curatorial Policy Guidelines and Procedures for the Continental Scientific Drilling Program, which includes the Field Curation Manual for the Inyo domes, Salton Sea, Shady Rest, and Valles caldera drilling projects.

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

The 1989 Scientific Assembly of the International Association of Volcanism and Chemistry of the Earth's Interior (IAVCEI) will be partially supported by the DOE Office of Basic Energy Sciences. The meeting will be held in Santa Fe, New Mexico and emphasize volcanology and geochemistry-petrology. Numerous scientific sessions and symposia are planned as well as a field excursion into the nearby Jemez volcanic field, Valles caldera, and Taos plateau volcanic field. Several Los Alamos geoscientists are members of the organizing committee. Those interested in receiving future circulars regarding the meeting should contact IAVCEI/1989 c/o Protocol Office, Los Alamos National Laboratory, Mail Stop P366, Los Alamos, NM 87545, USA.

G. Development of Data Base Management Systems (*N. Marusak [505-667-5698]*)

Continued efforts were made to address the data base 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 data base 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 data base 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. Our goals are to understand: the flow of plasma energy in the near-Earth space environment from a small scale point of view, the plasma physics of the solar wind-magnetosphere interaction, the details of the acceleration processes affecting energetic particles in the magnetosphere, and certain 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.

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 1987 has been our description of the solar wind's interaction with newly created ions in the distant environment of comets. We have used computer simulations to show that there are two distinct categories of this interaction: water-group ions from the comet induce rapid instability growth to relatively large amplitude magnetic fluctuation levels, whereas cometary protons give rise to weaker fluctuations that grow much more slowly in time. The first comparisons with magnetic fluctuation data from comets Giacobini-Zinner and Halley show qualitative agreement between observed wave amplitudes and those predicted by our computer simulations.

B. Solar Wind-Magnetospheric Interaction (*J. Birn [505-667-9232] and E. W. Hones, Jr.*)

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 magneto-electrical 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 1987 were made in the study and explicit representation of fully three-dimensional structures of the magnetotail plasma sheet and plasmoids. We were able to solve the general three-dimensional magnetostatic tail equilibrium problem by reduction to ordinary differential equations, which can be solved by straightforward computational procedures. These solutions are of relevance not only for the average quiet structure of the magnetotail, but also form the basis for understanding particle motions in and the dynamic evolution of the magnetotail. We have also examined the topological

structure of a plasmoid without the usually assumed symmetries. This study has revealed a complicated filamentary structure and has led us to reconsider the concept of magnetic reconnection from a more general point of view. We have shown the crucial role of an electric field parallel to the magnetic field and its relation to magnetic helicity.

C. Energetic Particle Acceleration (*D. N. Baker and J. T. Gosling [505-667-5389]*)

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. Our studies examine energetic particle phenomena from a few keV to many MeV, and we have considered energetic particle processes in a variety of magnetospheric systems (Jupiter, Mercury, and Comet Giacobini-Zinner) as well as the terrestrial system. 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. An important result of 1987 has been the observation that highly relativistic electrons in the Earth's outer magnetosphere show a strong solar cycle dependence. We have found that fluxes of these 2 to 15 MeV electrons are observed to vary with the same period as the eleven-year sunspot cycle. Most of these electrons remain trapped in the magnetosphere, but some of them may precipitate in the auroral regions and penetrate down into the stratosphere. These electrons are particularly effective in the production of odd nitrogen and odd hydrogen species that, in turn, catalytically remove ozone from the atmosphere. The observed correlation between years of greatest ozone loss and largest relativistic electron fluxes suggests that this mechanism may play an important role in terrestrial ozone depletion, particularly the enhanced depletion levels recently observed in Antarctica.

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. In 1987 we used our particle computer models to demonstrate that electron-positron jets from electrically conducting accretion disks are strongly radiation-dominated. We also examined the collective acceleration of ions resulting from the propagation of such jets through a background plasma with a gradient and found that energetic ions are readily produced in these environments. In addition, we began a study of the fundamental physics of plasma expansions. In a hot expanding plasma, an electric field develops at the expansion front because of the higher mobility of the electrons. This electric field is known to accelerate the ions behind the electron front, in some cases up to the electron thermal velocity. We have examined ion acceleration in the case of diamagnetic plasma expansions, in which the expanding plasma does work against an external magnetic field, and have found that field-aligned ion beams are produced even when the external field is quite weak.

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Category: Geochemistry

Person in Charge: R. E. Mesmer

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

Experiments have been initiated to measure the equilibrium constants for the principal reactions that control the solubility of dolomite and calcite in hydrothermal solutions: $1/2\text{CaMg}(\text{CO}_3)_2 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons 1/2\text{Ca}^{2+} + 1/2\text{Mg}^{2+} + 2\text{HCO}_3^-$ and $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$. The experiments were carried out in gold-bag rocking autoclaves containing both calcite and dolomite at 100, 150, 200, 250, and 300°C and 300, 800, and 1300 bars. Approximately one gram of mixed calcite/dolomite (with a mean grain diameter of 18 μ for the mixture) was reacted with water ranging in mass from about 250 to 300 gms and CO_2 concentrations varying from 0.15 to 0.80 m. The measurements of calcite solubility are in good agreement with results in the literature. The dolomite solubility results represent the only reliable measure of this equilibrium at any condition and show that, in terms of the above reactions, dolomite is 2 to 3 times less soluble than calcite. The solubility of both phases increases by about a factor of 10 between 300 and 1300 bars. With these results it will be possible to delineate the conditions that favor enhanced secondary permeability in carbonate terranes during diagenesis.

B. Metal-Acetate Complexing in Hydrothermal Solutions (*S. E. Drummond [615-576-4600], D. J. Wesolowski, D. A. Palmer, and T. H. Giordano [New Mexico State University]*)

The hydrogen electrode emf cell was used to investigate the complexing of acetate with Fe^{2+} , Zn^{2+} , and Al^{3+} up to 300°C and over a range of ionic strengths and acetate concentrations. The mono-, di-, and triacetato complexes were observed for both iron and zinc. For iron, the log of the formation constants for conditions ranging from 50 to 300°C increased from 1.2 to 3.7 for the $\text{FeCH}_3\text{COO}^+$ complex and from 2.4 to 6.8 for the $\text{Fe}(\text{CH}_3\text{COO})_2$ complex. The $\text{Fe}(\text{CH}_3\text{COO})_3^-$ species was observed only at the highest ionic strength investigated (1.0 m) at 250 and 300°C, with log K of 3.8 and 4.7, respectively. The mono-, di-, and triacetato complexes of zinc are stronger than those for iron by factors of approximately 10, 40, and 50, respectively. Experiments in sodium chloride and a non-complexing medium (sodium trifluoromethane sulfonate) were compared to give a relative measure of the zinc acetate and zinc chloride complexes. These results show conclusively that, for zinc, the acetate complexes are stronger than the chloride complexes and that literature values for the formation constants for the ZnCl^+ species are seriously overestimated. Similar emf experiments were performed with aluminum-acetate solutions in 0.10 m NaCl medium from 50 to 150°C. The analysis of these data is at an early stage, but it appears that the aluminum-acetate complexes are the strongest of the metal-acetate complexes measured to date. This is substantiated by studies of gibbsite solubility over a range of acetate concentrations at 50°C. Although a complete assessment of the role of acetate complexes in the transportation of metals is premature without further studies of other metal-acetate complexes and the competing metal-chloride complexes, it is clear from the work to date that organic complexes must be considered prominently in models of permeability modification during diagenesis.

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

Aluminum ions in aqueous fluids hydrolyze extensively, resulting in profound pH-dependent effects on the stabilities and solubilities of important aluminosilicate phases such as clays, feldspars, micas, etc. This in turn has a major effect on the evolution of permeability and brine chemistry in geologic systems. We have begun studying the hydrolysis of aluminum in 0.1 molal NaCl solutions using the hydrogen-electrode emf cell. The logarithm of the equilibrium quotient for the reaction $\text{Al}^{3+} + \text{OH}^- \rightleftharpoons \text{Al}(\text{OH})^+$ varies from 8.30 at 50°C to 8.51 at 125°C. This is the first direct measurement of this hydrolysis constant at elevated temperatures. These results complement both the aluminum acetate complexing studies described above and a major project for DOE's Geothermal Technology Division to study the solubility of gibbsite - $\text{Al}(\text{OH})_3$ - in NaCl brines.

D. Hydrothermal Stability of Organic Acids (*S. E. Drummond [615-576-4600], D. A. Palmer, and J. Schleusener [Pennsylvania State University]*)

About 24 separate acetate decarboxylation experiments were completed during this period. The goal of these experiments was to study the catalytic effects of common minerals such as quartz, calcite, montmorillonite, and pyrite on the decarboxylation of acetic acid and acetate and the relationship between reaction rate and both the pH and the mineral surface area. The experiments were carried out in titanium autoclaves and gold-cell hydrothermal apparatus at temperatures between 330-360°C. The results demonstrate that the fate of acetate in hydrothermal systems is highly dependent on the temperature profile, mineralogy, and pH. Iron-bearing minerals are typically very effective catalysts for decarboxylation reactions. Activation parameters derived from the temperature dependence of the measured rate constants are consistent with the linear free energy relationship observed in previous studies. These findings warrant further study because of their importance to the overall understanding of the behavior of water-soluble organics in hydrothermal processes.

E. Stable Isotope Exchange Between Geothermal Minerals and Fluids (*D. R. Cole [615-574-5473] and D. J. Wesolowski*)

We have conducted partial isotope exchange experiments at 150 and 350°C for the following systems: Fe-rich chlorite - H_2O , biotite - H_2O , hematite - H_2O , scheelite - H_2O , and muscovite - H_2O . At 350°C, the bulk of the observed oxygen isotopic exchange in these mineral-fluid systems (5 to 10%) occurs during the first 6 to 8 days of reaction. The overall magnitude of exchange for all phases typically did not exceed 12% even after 20 weeks of reaction. Oxygen isotopic rate constants have been calculated from the initial recrystallization step. For example, values (logarithms in moles of $0 \text{ m}^{-2} \text{ sec}^{-1}$) range from -10.8 (150°C) to -9.46 (350°C) for hematite-water, -9.13 (350°C) for chlorite-water, -11.1 (150°C) for biotite-water, and -8.8 (350°C) for scheelite-water. These values are similar to others calculated for silicates and oxides that have been recrystallized during hydrothermal reactions. The equilibrium oxygen isotope fractionation between chlorite and H_2O is approximately 0.5‰ at 350°C. Preliminary hydrogen isotope fractionation data have also been obtained from chlorite- H_2O and biotite- H_2O experiments at 350°C. The extent of D/H exchange is on the order of 25% for durations of 8 to 10 weeks. The equilibrium hydrogen isotope fractionation between chlorite and H_2O is approximately -45‰ at 350°C.

F. Salinity Effects on Oxygen and Hydrogen Isotope Partitioning Between Geothermal Brines and Other Phases at Elevated Temperatures (*D. J. Wesolowski [615-574-6903] and D. R. Cole*)

The activity/concentration relationships of oxygen ($^{18}\text{O}/^{16}\text{O}$) and hydrogen (D/H) isotopes in water containing dissolved electrolytes must be quantitatively known in order to accurately model the exchange of these isotopes between the various reservoirs in geothermal systems, sedimentary basins, and other geologic settings. Such modeling has often been applied in determining paleotemperatures, water/rock ratios, fluid sources, and the extent of boiling. However, the effects of dissolved ions on the partitioning of oxygen and hydrogen isotopes between water and other phases has typically not been included in these models due to a lack of reliable data at elevated temperatures. We have initiated a detailed study of the partitioning of hydrogen and oxygen isotopes between water vapor and brines of fixed isotopic concentration in the system $\text{H}_2\text{O}-\text{Na}-\text{K}-\text{Mg}-\text{Ca}-\text{Cl}-\text{SO}_4$. These direct measurements of the "isotopic activity coefficients" of water in brines should resolve many of the uncertainties and ambiguities concerning the magnitudes and factors controlling these effects. The system $\text{NaCl}-\text{H}_2\text{O}$ has been studied at 100°C and seven salinities ranging from 0.3 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. 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 involving the other important natural salts and in mixtures of these salts.

G. Carbon Isotopic and Trace Element Indicators of Depositional Environments in the Early Permian, SW United States (*D. R. Cole [615-574-5473], T. H. Giordano, and G. Mack [New Mexico State University]*)

A reconnaissance trace element, mineralogic, and stable isotopic geochemical study of ancient pedogenic calcareous nodules from SW Colorado and SC New Mexico was initiated to: 1) delineate different depositional environments through geochemical signatures preserved in the nodules, 2) estimate fluid compositions responsible for deposition of the nodules, and 3) better refine interpretation of Early Permian climate in these areas of Colorado and New Mexico. Preliminary conclusions based on phase equilibria, trace element, and isotopic geochemistry are: 1) pore solutions responsible for caliche nodule formation are estimated to have an Eh of roughly -0.2 ± 0.05 and pH of between 7.5 and 8.0; 2) stable carbon isotopes of the nodules can be used to discriminate between tidal flat and fluvial depositional environments (The ranges in values for $\delta^{13}\text{C}(\text{PDB})$ and the environments they correspond to are -1.8 to -1.4‰ for tidal flat facies and -4.3 to -6.3‰ for fluvial facies.); and 3) Sr concentrations can also be used to distinguish environments. Concentrations of Sr (ppm) and the environments they represent are 400 to 1000, tidal flat; 300 to 400, fluvial; and 130 to 160, alluvial fan.

H. Temperature-Salinity-Stable Isotope Trends in Boiling Fossil Hydrothermal Systems (*D. R. Cole [615-574-5473] and B. Smith [LBL]*)

The occurrence and intensity of boiling in hydrothermal fluids, as recorded by the presence of vapor-dominated inclusions, appears to be a critical control for the deposition and distribution of metals in many central Mexican high-level Ag-Au and Ag-Pb-Zn systems (Colorado, Sombrerete, Catorce, Taxco, Frisco, and Zacualpan). Fluid inclusion homogenization temperatures for the

various mineralized zones fall within the 150 to 330°C range, with salinities generally below 6 wt.% NaCl. Evidence of boiling appears to correlate with marked vertical thermal gradients (7.5 to 12°C/100 m), more restricted ore intervals (200 - 450 m), and pronounced enrichment and greater variation in the $\delta^{18}\text{O}$ values of vein quartz (e.g., Catorce, +14 to +19‰). Absence of boiling coincides with lower vertical thermal gradients (less than 10°C/100 m), greater vertical extent of ore mineralization (≥ 600 m), less pronounced enrichment and narrower variations in $\delta^{18}\text{O}$ values of vein quartz (e.g., Taxco, +13.7 to +14.5‰). It appears that the boiling systems are characterized by more abrupt and better defined downward termination of ore; non-boiling systems exhibit gradual downward impoverishment of mineralization.

I. Fluid Flow and Methane Generation Associated with the Appalachian Overthrust Belt (*D. J. Wesolowski [615-574-6903], D. R. Cole, and M. S. Drummond [University of Alabama at Birmingham]*)

Over the past few years we have been studying the generation of fluids during metamorphism and thrusting and the fluid flow paths in the Appalachian overthrust belt. It is clear from these studies that: 1) C-O-H-S fluids are generated in large quantities and are able to migrate at great depths in the Earth's crust, even to the zone of partial melting; 2) that major tectonic features such as thrust faults and pervasive petrofabrics channelize the flow of these fluids and may play a more interactive role with the fluids; and 3) methane can be and is generated in a variety of settings in this terrain ranging from reactions involving graphite during peak metamorphism of the crystalline rocks to degeneration of organics in overthrust platform sediments. This research has led to our participation in two major, multi-institutional efforts. The Appalachian Deep Core Hole (ADCOH) project is the first U.S. ultradeep (>15 km) scientific drill hole, targeted to penetrate all of the major stacked thrust sheets of the Eastern overthrust belt and sample the Grenville basement beneath. The proposed COSPLUM (Crystalline Overthrust Structures in the Platform Localizing Unconventional Methane) project would drill a 3-km hole through the Blue Ridge thrust sheet into what is postulated to be a domal thrust duplex structure in the underlying sediments.

J. Chemistry, Mineralogy, and Textural Development of Silicic Magma in Volcanic and Sub-Volcanic Environments at the Inyo Domes and Inyo Craters, California (*M. T. Naney [615-576-2049] and R. G. Gibson*)

The objectives of this program are to: 1) ascertain the ability of glassy rhyolite to preserve the redox signature of a parent magma, 2) estimate the pre-eruption H_2O content of the Inyo domes/Inyo craters magma system, 3) place constraints on the conditions that produce microlite crystal growth in silicic magmas, and 4) aid the design of experimental studies that will clarify the conditions of hydrous phase stability and microlite crystallization in near-surface volcanic environments. Chemical and petrographic analysis of core materials obtained from the 1983 and 1984 drilling projects at Inyo domes, California made in collaboration with S. E. Swanson (University of Alaska) and H. R. Westrich (SNL) indicate that: 1) the bulk-rock $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratios of obsidian glasses are nearly constant, 2) hydrous ferromagnesian silicates are present as microphenocrysts, and 3) microlite crystal size distribution is nearly constant in the samples analyzed from all three core holes. These observations suggest respectively that: 1) the oxidation state of the magma system remained unchanged during the eruption process, 2) the dissolved H_2O content of the magma prior to eruption was significantly higher than is indicated by the H_2O content of flow obsidians, and 3) microlite crystallization was initiated in response to decompression during magma ascent. Research drilling at Inyo craters, California during the summer of 1987 afforded an opportunity to compare the chemistries, mineralogies, and textures of unvented (Inyo craters) and vented (Inyo domes) segments of the same rhyolite dike system.

Analysis of materials obtained from these projects yields information about the redox state of selected dike samples and glassy products recovered from core drilling.

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

We have conducted experiments (900 to 1350°C, 1 atm, variable oxygen fugacities) to determine the sulfur diffusivities in three compositionally different silicate melts: low Fe²⁺/Fe³⁺-low silica troctolite; high Fe²⁺/Fe³⁺ basalt (McCoy Canyon), and Fe-poor high silica Na-K rich glass. Diffusion coefficients estimated from concentration-time profiles for the basalt and troctolite are remarkably similar despite their differences in SiO₂ content and Fe²⁺/Fe³⁺. In the cases we investigated, reducing experimental conditions resulted in slightly higher diffusion coefficients. This is true for both high- and low-silica melts. The high-silica Na-K rich melts exhibit diffusion rates of about one order of magnitude less than the basalt or troctolite. The sulfur diffusivities we measured are comparable to those observed for other volatile species (e.g., O₂, CO₂) in basalts and high silica Na-K melts. The activation energies range between 40 and 60 kcal/mole and are similar to those reported for S-diffusion in Ca-silicate and Ca-Al-silicate melts and predicted by the Stokes-Einstein relation. An examination of the sulfur K_α wavelength shifts by electron microprobe analysis of quenched glasses indicates that the bulk of the sulfur occurs as sulfate rather than sulfide. Using FTIR spectroscopy, we observed an absorption doublet between ~615 and 650 cm⁻¹ in high-silica glasses that may be indicative of a sulfate-type species.

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

Efforts to locate reservoirs of natural gas would be aided by additional information on the stability of methane in the Earth's crust. To obtain such information, work has commenced on a new project designed to elucidate the thermodynamics of methane and other key gases (CO₂, H₂O, and H₂) in the C-O-H system at high pressures and temperatures. This research is focusing on 1) measuring the P-V-T properties of pure gases (CH₄, CO₂, and H₂) and selected gas mixtures (e.g., CO₂-H₂O, CH₄-H₂O, CH₄-CO₂) in the C-O-H system at 100 - 4000 bars, 50 - 550°C and 2) identifying the proportions of gas species in both graphite-saturated and graphite-unsaturated C-O-H gas mixtures at 1000 - 10,000 bars, 500 - 1100°C. Design and construction of the apparatus has been completed and testing of several key pieces of equipment is in progress.

P-V-T data on C-O-H gases and gas mixtures are collected using a vibrating tube apparatus that permits the densities of "unknown" C-O-H fluids to be measured with exceptional accuracy and precision relative to the densities of standard gases (H₂O, N₂, and Ar). A fluid-delivery system based on precise high-pressure positive displacement pumps has been developed to inject fluids alternately and isobarically into the vibrating tube densimeter. This capability eliminates the hysteresis and long-term drift associated with pressure excursions. For each fluid, data are taken under static (no flow) conditions after all environmental conditions and electronic signals have stabilized. Information on the proportions of gas species in C-O-H mixtures (P-T-X data) is obtained using a hydrogen-service internally heated pressure vessel (IHPV) equipped with a special motorized rapid-quench device. Liquid or gaseous C-O-H reactants of predetermined C:O ratio are sealed in platinum capsules for experimentation in the IHPV. The reactants are equilibrated at experimental P-T conditions with the hydrogen fugacity established by an Ar:H₂ pressure medium. Intracapsule reactions among gas species are terminated by allowing capsules to drop vertically from the hot zone of the furnace to a subjacent cold zone. Using this rapid-quench technique, the temperatures of capsules fall below 100°C within a few seconds. C-O-H gas samples obtained from P-T-X experiments will consist predominantly of CH₄, CO₂, H₂O, and H₂.

An analytical technique has been developed for analyzing micromolar quantities of these products. This technique involves: 1) cryogenically separating the individual gas species, 2) measuring the pressure of each gas ($\ll 1$ atm) in a thermostated chamber of fixed volume, and 3) using the ideal gas law to calculate the ratios of the gas species in the sample.

M. High-Temperature Hydrogen Permeation through Platinum at Elevated Pressure (*M. T. Naney [615-576-2049]*)

Hydrogen permeation rates through platinum have been measured at $P_{\text{tot}} = P_{\text{H}_2} = 250$ MPa and $T = 600, 800, 862, \text{ and } 1000^\circ\text{C}$. Thin-walled platinum tubing fitted with an internal support structure served as the permeation membrane. The membrane was installed in a hydrogen-service internally heated pressure vessel (IHPV). The vessel was pressurized with H_2 gas before heating the membrane to the experimental conditions. After pressurization the external surfaces of the membrane were in direct contact with high-pressure hydrogen gas, while the internal volume remained at atmospheric pressure. After heating the membrane to experimental conditions the pressure rise in the membrane due to H_2 permeation was monitored at frequent intervals (1 - 10 minutes). When the pressure inside the membrane reached that in the IHPV, osmotic equilibrium was attained and the permeation experiment was complete. The H_2 contained in the membrane/pressure transducer assembly was then allowed to expand into a high-pressure capillary tube of known volume while monitoring the pressure drop. This procedure permitted calculation of the volume of gas contained in the membrane/transducer assembly. From these measurements and the timed pressure-rise data, the mass of H_2 diffusing through the membrane over successive, short time periods was calculated. Corrections for the room-temperature compressibility of hydrogen were made using the available literature data. The measured permeation rates were used together with calculated fugacity coefficients to derive the permeation constant for successive small time intervals (10 - 60 minutes). Calculations for the 800°C data set, collected subsequent to a 1000°C experiment, consistently yield $\log k$ values of -10.6 ± 0.2 . This value is low in comparison to published values for $\log k$ at 800°C . Examination of the platinum membrane used in this study subsequent to experimentation showed that the membrane had experienced significant recrystallization and grain growth in the active tip area. In addition, the observed rate of permeation was significantly greater prior to cycling the membrane to 1000°C . Quantitative comparison of changes in permeation constant for platinum must await data reduction for the complete set of 250 MPa experiments. However, these preliminary calculations suggest that H_2 permeation through platinum is significantly influenced by the thermal history of the platinum membrane.

N. Rapid-Quench Sample Holder (*M. T. Naney [615-576-2049] and J. G. Blencoe*)

A rapid-quench sample holder is being developed for use in the 1000 MPa hydrogen-service internally heated pressure vessel (IHPV). This apparatus provides new and important capabilities for high pressure experimentation. The study of kinetic processes (e.g., reaction rates and crystal nucleation and growth rates) is improved because multiple samples of the same reactants are subjected to identical pressure-temperature conditions before being quenched at different times. The rapid-quench system allows quenching one of five identical samples from the furnace hot zone at any desired time. Therefore, kinetic studies are simplified because timed experiments that have previously required multiple cycles of loading and unloading the pressure vessel can be accommodated in a single experimental run. A critical component of the rapid-quench mechanism is the stepping motor used to sequentially rotate a drop tube under the five positions of the sample holder. This motor must be able to operate reliably in the high pressure H_2 -Ar mixtures used as pressurization media in the IHPV. Two motor designs have been tested at ambient temperature and pressures up to 400 MPa. The greatest success was achieved using a rotary solenoid switch that operated reliably during pressure cycling between 50 and 400 MPa. However, the design is modular and hence lends itself easily to incorporation of other motor designs.

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Contract: DE-ACO6-76RLO 1830

Category: Geochemistry

Person in Charge: J. C. Laul (509-376-3539)

A. Chemical Migration in Continental Crustal and Geothermal Systems

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), past migration of radionuclides in cores, and source region geochemistry and mixing of ground waters.

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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Category: Energy Resource Recognition, Evaluation, and Utilization

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A. Remote Sensing: Geoscience Data Analysis and Integration (*H. P. Foote 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.

During the past year the emphasis in the program has been adapting photogrammetric methods to an interactive workstation environment. The problem of digitally correlating stereo pairs was chosen as one of both practical and theoretical interest. This problem is the most difficult step in the process of deriving elevation from stereo aerial or satellite photography. We have largely automated the matching step; however, some operator interaction is still required in the final editing of the derived parallaxes. Now that stereo satellite imagery is available from the French SPOT remote sensing satellite in digital format, it is desirable to use computer processing to directly derive digital elevation maps (DEMs) from the stereo data. The traditional photogrammetric process begins with photographic transparencies and requires expensive high precision optical-mechanical equipment and a trained operator. This procedure has a long tradition and can produce quality map products; however, the necessary equipment and skilled operators are generally found only in large organizations devoted to map production. Our goal in this research is to begin with digital imagery, replace an optical analog computer with a digital computer, and produce digital map products, e.g. DEMs as output. This approach is being implemented on a workstation with strong graphic and computational capabilities. Various imaging geometries and correlation strategies can be addressed through software. Additionally, we are investigating the feasibility of knowledge based systems to allow the human operator to assume an oversight-monitoring role as opposed to an integral part of the hardware. We are currently running the KEE software tool for rule based system experiments.

In the area of scientific visualization we have been exploring techniques for viewing three dimensional data sets. The site we are focusing on is the Valles caldera in New Mexico, a Continental Scientific Drilling site where an extensive geologic and geophysical data base 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. Structural Geologic Research on Spatial Analysis Techniques (*M. G. Foley, D. E. Beaver, and M. A. Glennon*)

We have developed advanced digital analysis techniques for geoscientific research since the mid-1970s. Cooperative research with Washington State University from 1982 to present has resulted in the development of semi-automated quantitative methods for Remote Geologic Analysis (RGA). These methods are based on the unique digital analysis techniques developed by PNL to identify planar features manifested as linear valleys in topography. This digital Geological Spatial Analysis (GSA) finds the low points in digital elevation models (DEMs) of the topography, fits vectors to lineaments of such low points, and compares each vector with all others in the data set to identify those that are coplanar. We assume that the planes identified by coplanar vectors may be manifestations of fracture planes; we further assume that major fracture zones will be represented by a number of such planes and rank the quality of interpreted "fracture zones" on the basis of the number and density of two-vector planes comprising them. Such an analysis is reproducible and unbiased; it identifies potential fracture zones by three-dimensional location and attitude, a unique property of our analysis not found in conventional lineament analyses, which can identify only nearly vertical planar features. We have subsequently expanded and successfully tested GSA capability to deal with three-dimensional point data sets (e.g., seismic hypocenters).

We have designed and implemented a preliminary version of a software executive shell to manage remote geologic analysis software on an existing RGA workstation. GSA software has been optimized, verified, and subjected to peer review at a joint OBES-OAC workshop on remote geologic analysis held at PNL. We have performed comparative analysis of hand-digitized contour maps vs. USGS DEMs for Morgantown Energy Technology Center's (METC's) Study Area 1 in West Virginia and for the Nevada Test Site. Results of GSA application to METC Study Area 1 were studied in comparison with structural geologic and gas production data. Results were very promising, but the effort highlighted the need for the advanced RGA workstation capable of real-time 3D graphics. This workstation is being procured in FY 1988.

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Category: Solar, Solar-Terrestrial, and Atmospheric Interactions

Person in Charge: E. W. Kleckner [509-376-8425]

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

The insolation program relies on a data base of direct and diffuse solar radiation measurements made in visible and near-infrared spectral passbands. The research has two goals. One is to quantify the spectral characteristics of scattered and direct sunlight. This is germane to energy generating solar technologies, including photovoltaics and 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, 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 are in the process of making a wavelength-dependent inversion of this turbidity data to recover 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 1988 have been created and are available for research studies by outside users.

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

A study with the University of Michigan was initiated 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.

Design and 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 near operational status, with software required for data analysis being written currently.

Data analysis of measurements made by the MASP network during a recent chemical release experiment above Alaska has proven these data to be of considerable importance. A comparison of accelerations actually experienced by ionized barium released at approximately 1000-km altitude with those expected by modeling of the event has strongly suggested the presence of localized regions of electric fields parallel to the Earth's magnetic field. Further analysis is currently underway at NASA.

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]*)

The objective of the crustal strain program is to understand the physical mechanisms responsible for large-scale, long-term deformation and strain in the Earth. To accomplish this objective, it is necessary to construct physical models for the interpretation and analysis of geodetic data, and to a lesser degree, other data obtained from regions undergoing active tectonic deformation. In addition, physical models require an understanding of frictional instabilities in rocks, both in the laboratory and in the field. Hence, it has been necessary to seek a broad, fundamental theory to explain the phenomena associated with frictional sliding. A new approach has been adopted in which the principle of minimum free energy is used. Thus, a unification with fundamental laws of thermodynamics is accomplished. The result, while incorporating previously known models of friction, also leads to an entirely new viewpoint in which fault systems are viewed as systems in metastable equilibrium. An earthquake then represents the tendency for the system to return to a state of minimal free energy. With viable models and sufficient data, it is possible to understand the physical mechanisms responsible for long-term deformation in the Earth and to evaluate the susceptibility of a given region to tectonic instabilities such as earthquakes. Of particular interest are long-term, time-dependent strains obtained from an examination of historic triangulation and leveling, modern microgravity and trilateration surveys, and space-based measurements. Results to date have had considerable success in explaining crustal motions in the western United States, Japan, Alaska, and South America.

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, for both brittle and ductile stress regimes, extending the damage surface concept beyond the brittle materials where it was initially observed. Analysis of an experiment to locate AE events was completed showing good accuracy for the locations. The wave form acquisition system is being upgraded to increase speed and flexibility, with the ability to handle 24 channels and do tomography.

C. Determination of *In Situ* Stress in Geologic Structures (*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) of oriented core is an

evolving technique that 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 were monitored during strain relaxation measurements of siltstone and limestone cores, immediately after the cores were retrieved for 2.9 - 3.6 km deep boreholes in the North Sea. Acoustic emissions were always detected. The acoustic emission rate decreased exponentially with time, similar to the strain relaxation behavior of the core, and acoustic emissions ceased when strain relaxation no longer occurred. These field experiments indicate that microcracking is a mechanism for creep recovery of rock.

D. 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.

The Role of Crystal Defects in Mineral Dissolution Rates (*W. H. Casey and H. R. Westrich*)

Weathered minerals commonly contain an abundance of surface etch pits, which nucleate and grow at the surface outcrop of a lattice defect. We are examining the hypothesis that mineral dissolution rates are controlled by reaction at such surface dislocations. Experiments examining the role of lattice defects on the dissolution kinetics of rutile showed that bulk dislocation densities did not correlate with dissolution rates. These results are published in the June 1988 issue of *Geochimica Cosmochimica Acta*. To complement this research on rutile, we shocked labradorite feldspar at ~4 GPa to induce a high concentration of lattice defects. The samples were then thermally annealed to produce subsamples with a range of dislocation concentrations. The shocked feldspar, however, dissolved at nearly identical rates to unshocked material. Thus, bulk lattice defects do not strongly affect the rate of feldspar dissolution. Although bulk dislocations do not correlate with dissolution rates, it is clear from qualitative studies that lattice defects are important to the dissolution reaction. Experiments are, therefore, underway to examine the influence of aluminum impurities in quartz on the dissolution rate. The aluminum impurity is associated with a monovalent interstitial defect.

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 development of the numerical model and design of experiments.

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. This research is intended to compare the effects of different types of organic matter on diagenetic processes in immediately adjacent sandstones of the Piceance Creek basin. Core samples consisting of thirty pairs of sandstones and associated organic-rich layers were collected from various sedimentary environments. Organic-rich zones were specifically targeted in sampling. Petrographic studies, x-ray diffraction analysis of clay fractions, and organic analysis are in progress for each sample. The extremely close stratigraphic proximity of sandstone and organic matter suggests that local effects on sandstone pore fluid chemistry induced by the presence of organic matter will be reflected in the diagenetic mineralogy.

Paleomagnetic and Rock Magnetic Studies of the Inyo Dike (*J. W. Geissman [University of New Mexico] and J. C. Eichelberger*)

Measurement of rock magnetic properties offers the potential of interpreting both the flow regime and thermal history of igneous bodies. Because of its youth, relative simplicity, and continuously sampled sections, the Inyo domes system has been selected for an early test of the utility of this approach. Efforts have concentrated largely on continued acquisition and compilation of data from materials retrieved during drilling at Inyo domes. These investigations have demonstrated that rhyolitic magmas are distinguishable on the basis of rock magnetic properties. Remanence data from vertically oriented core through Obsidian dome are consistent with an age of approximately 500 years for the dome and support arguments that collapse of the vesiculated magma occurred during and after extrusion occurred at temperatures above approximated 600°C.

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 natural glasses and glass inclusions, experimental procedures to examine the kinetics of vapor exsolution and bubble 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 establish volatile budgets of volcanic systems. Such budgets are presently poorly defined and are needed as benchmarks for assessing the environmental impact of energy technologies relative to that of volcanism and for better definition of biogeochemical cycles. Recent work focused on these problems: 1) phase equilibria in volatile-containing rhyolitic systems; 2) bubble nucleation and growth rates in hydrous synthetic rhyolitic glasses at elevated pressures; 3) plutonic degassing of CO₂ from basalts at transitional and mid-oceanic spreading centers; 4) the isotopic composition of carbon in Kilauea basalts, and 5) the O₂ fugacity of Kilauea basalt from liquidus to solidus conditions.

B. Clay-Water Interactions (*J. L. Krumhansl [505-846-9614]*)

During the last year clay solubility measurements were expanded to include studies on (Mg-rich) saponite and (Fe-rich) nontronite in addition to the (Al-rich) montmorillonite already studied. The nontronite proved to be mineralogically unstable in the hydrothermal setting, but solubility data were obtained from the saponite at 200°C out to 345 days. Analytic techniques were developed that allow microscale chemical analyses obtained on a scanning electron microscope to be related to bulk clay mineral standard analyses obtained by d.c. plasma emission spectroscopy. A thermochemical data base was established to bridge the gap between the solubility data and the various theoretical formalisms used in predicting clay solubility products. Attempts will be made to evaluate a solubility product for nontronite, saponite data will be obtained at 300°C, and a comparison between theoretically predicted and actual solubility measurements will be published.

C. The Kinetics of Mica Dissolution (*W. H. Casey [505-846-00196]*)

The chemical composition and evolution of solutions in the Earth's crust involves reactions related to the formation, modification, or dissolution of phyllosilicate minerals such as micas. These reactions generally do not proceed to complete equilibrium but require time as a critical variable in their description. The goal of this study is a series of experiments designed to obtain the dissolution kinetics of muscovite over a range of conditions. Hydrothermal dissolution experiments are in their preliminary stages. Initial experiments in the rotating-disk autoclave indicate that small amounts of ferric iron poison the dissolution of aluminosilicate minerals. The

disk assembly that is used to isolate mica basal sheets in the autoclave was thus electroplated with nickel. This nickel surface does not oxidize in the chloride background electrolyte and should prevent the poisoning of the mica dissolution reaction. Effort has been expended to automate an ion chromatograph for analysis of alkalis, silica, and aluminum. This ion chromatography is needed to handle the large number of samples produced during dissolution experiments.

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, seismic, and electrical methods to locate and define subsurface anomalous thermal areas. Surface or near-surface thermal instrumentation includes development and field testing of thermopile heat flux, oriented convective heat flow sensors, and downhole fluid samplers. Seismic techniques involve use of surface geophones 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. This instrument will be used in both hole-to-hole and surface-to-hole seismic studies. In addition to the instrumentation per se, each of these studies involves research on methods to interpret the data. Current research is concentrated in these areas: 1) a downhole, controlled, seismic shear-wave source that has been developed and field tested provides control of energy content and frequency of the downhole seismic signal, 2) a new device has been developed that is capable of making triaxial heat flow measurements in a vertical borehole, 3) a downhole seismometer with extended temperature (250°C) capability has been designed and field tested, 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. Magmatic Emplacement (*C. R. Carrigan [505-846-3463]*)

Heat and mass transfer across magma-hydrothermal systems involves processes that can give rise to surface and borehole observables. Investigation of the modes of interaction between heat sources and hydrologic regimes provides a testable framework for the use of borehole and surface data as indicators of the past and present state of magma-hydrothermal systems. Quantitative models of magma-heat-source/host-regime interaction are being used to study those thermal, physical, and chemical couplings that affect the evolution of magmatic systems. For calderas, it is found that heat transfer will tend to be limited by the insulating host regime and that temperatures on the boundaries of convecting magma bodies will have magmatic values. Even though heat loss from magma is limited, calculations show that the convective vigor of the magma is significant. Regarding magma transport, boundary layer models for basaltic dikes predict that solidification will usually occur after only a few kilometers of flow. However, in andesites viscous heating can play a role in preventing solidification. It is also found that boundary layer models, which do not include effects of transcurrent aspects of dike flow, including two phase flow and surface roughness, will permit dikes to propagate much further through cooler host rock than is implied by even sophisticated boundary layer modeling. Boundary temperatures at contacts will have near magmatic values in basaltic magmas. In andesites, boundary temperatures can exceed input magma values owing to viscous heating. The pressure drops required to drive such flows are quite small (1-20 bars for a 2 km x 1 m dike).

C. 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, and tightly constrained the western structural boundary of Long Valley caldera. Inyo drilling was from 1983 to 1987. Investigations of the core were largely completed in 1988.

D. Katmai Research Drilling Project (*J. C. Eichelberger [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. Objectives of the project 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 - it was a single event in which magma erupted through uniform basement and the vent was not subsequently modified by collapse - 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. The project is now in its initial phase of surface studies for defining the vent.

E. Geoscience Research Drilling Office (*R. K. Traeger [505-846-6885]*)

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 Inyo IV operations (see detail in other portions of this report). In this program, the GRDO was the legal operator of 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 and VC-2B drilling projects. 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

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

Grant: DE-FG06-86ER13530

Title: Magnetic Field Annihilation in the Magnetosphere
and its Applications

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

It has been known that the ionized matter or plasma constitutes the major part of our universe. Due to its vast complexity, the matter in plasma state is much less well understood than the matter in the other three states--solid, liquid, and gas. Our proposed project is to study the basic plasma processes associated with the magnetic reconnection in the Earth's magnetosphere. The result from this magnetosphere study is applicable to plasma research in the other fields such as thermonuclear fusion research, solar physics, and astrophysics.

Based on the satellite data concerning the observed flux transfer events, we have proposed a multiple X line reconnection model for the dayside magnetopause in contrast to the classical single X line reconnection model. Due to magnetic reconnections at multiple sites in this model, the multiple X line reconnection exhibits impulsive and intermittent features.

In our earlier attempt, we have determined the criterion for the transition from multiple to the classical single X line reconnections. Under the space plasma conditions (i.e., large electrical conductivity and large scale), our recent global numerical simulation study indicated that dayside reconnection favors the multiple X line process. The magnetic islands generated can produce magnetic signatures similar to that of the observed flux transfer events. In three dimensional geometry, the reconnection line is bound to be of finite length. We found that the Kelvin-Helmholtz instabilities are likely to initiate reconnection at certain points, leading to the patchy reconnection.

In addition, the dayside field-aligned electrical current system associated with the dayside multiple X line reconnection may play an important role in the generation of the observed dayside auroras. We proposed that there would exist two types of field-aligned current systems with different north-south symmetry and that these field-aligned currents would induce a localized convection pattern in the ionosphere. Finally, the correlation of some of the Earth's cusp-region ultra low frequency geomagnetic pulsations and the dayside flux transfer events has motivated us to study the possibility that the dayside magnetic reconnection can be an energy source for the generation of these pulsations. Our study showed that the impulsive and intermittent multiple X line reconnection can indeed produce the geomagnetic pulsations in the frequency range 1 - 19 mHz.

In the past year, we also proposed a mechanism for the generation of plasmoid and kink waves in the distant magnetotail and in the heliospheric current sheet. This mechanism is associated with the streaming sausage and kink modes in the presence of a super-Alfvénic shear flow.

Grantee: UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

Grant: DE-FG02-87ER13670

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 employ long-term changes in the figure and diameter of the Sun as an indirect diagnostic of changes in the solar constant. This indirect diagnostic of changes in luminosity offers a viable alternative to the difficult task of obtaining reproducible radiometric data over the period of years to decades necessary for a significant study of solar luminosity changes. The primary observations are diameter measurements of approximately 9 hr observing runs per day. These observations are capable of detecting a fractional change in a solar diameter of one part in 10^5 to 10^6 over climatically significant time periods. Solar diameter and/or differential radius observations have been made in 1973, 1975, 1978, 1979, 1981, 1983, 1986, 1987, and 1988. Analysis for long term changes in the shape of the limb darkening function has begun. Preliminary results based on the 1986 and 1987 observations show both linear and periodic variations. A linear variation cannot be understood as a terrestrial atmospheric phenomenon.

The ratio between the fractional change in luminosity to normalized change in differential radius has been inferred to be ≈ 5 from work on gravity modes by comparing diameter observations with satellite observations of total irradiance. For a ratio of 5, we find: $\langle d(\ln L)/dt \rangle \approx (3.5 \pm 3.1) \times 10^{-5}$ per year for 1986 and 1987. This is consistent with the satellite total irradiance observations that indicate the solar luminosity was nearly constant in 1986 and early 1987 while starting to increase late in 1987. The results indicate the potential of diameter observations as a probe of the solar luminosity variability.

A major breakthrough has been made in the development of a technique to analyze total irradiance observations for evidence of gravity modes. The new technique renders the satellite observations far more valuable in the study of solar variability and in particular solar gravity modes. Since gravity modes are known to have very long coherence times, the discovery of gravity signals in total irradiance observations has very important implications for anticipation of future changes in the luminosity. Further work on the gravity modes has produced additional evidence of mode coupling in the solar interior. Mode coupling is of interest to understanding luminosity variations because it indicates that these modes may alter the neutrino and fusion energy production rates in the core of the Sun.

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

Grant: DE-FG02-87ER13665

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 the dynamical processes and thermal regimes of major volcanic centers such as the Long Valley/Mono Craters volcanic complex, the Cascades volcanic belt, and one of the most seismo-volcanically active areas of the Rio Grande rift, the Socorro anomaly. This work addresses questions regarding geothermal energy, chemical transport of minerals in the crust, emplacement of economic ore deposits, and optimal siting of scientific drill holes. In addition, since much of our work is performed in the intermontane sedimentary basins of the western U.S., 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 kilometers 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; this is compatible with recent drilling at Inyo domes where basement was encountered at unexpectedly shallow depths. Moreover, we now have clear evidence, confirmed by limited drilling data, for a buried uplift on the basement surface beneath the resurgent dome.

Employing a new generalized 2-D 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 that involved a wide-band (10-4000s) sequence of remote-referenced magnetic variation measurements along an E-W profile centered on Socorro, NM. The reason for selecting this particular location is that although most workers readily accept the seismic evidence for a lens of magma beneath the Socorro area, many do not accept the possibility that this magmatic intrusion is, in fact, spread under a much larger region than presently delineated using seismic methods alone. Our experiment is intended to assess if the Socorro magma body is electrically anomalous and, if so, whether it is physically contiguous with conductivity anomalies seen elsewhere along the rift.

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

Grant: DE-FG03-87ER13422

Title: *In situ* Stress in Deep Boreholes

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

This research project is concerned with development of a new method of measuring via interference holography *in situ* stress in deep fluid filled boreholes. By drilling a series of small sideholes in the main borehole and taking interference holograms through the clear filtered bore fluid, the complete *in situ* stress tensor is obtained. We expect this method will have application in the oil and gas industry in the future, as knowledge of the *in situ* stress is vital to effective hydraulic fracture simulation. Other applications of *in situ* stress measurements and data include geothermal resource exploitation and design and monitoring underground mines and structures, including radioactive and chemical waste isolation facilities. We expect to deploy this instrument in scientific boreholes to study the stress regimes associated with a series of tectonic and geothermal related issues.

During the last year most of our experimental effort has gone into completing construction of the 6-in. holographic stressmeter apparatus. This 475-lb. instrument consisting of computer controlled mechanical, electronic, optical, and hydraulic components is new and is capable of measuring all six components of the *in situ* stress tensor from uncased fluid filled boreholes to depths of several kilometers. This has never been done before. Important features of the 6-in. instrument are onboard gas pressurization that maintains the optical cavity used for holographic recording at pressures equal to the mud pressure in the hole; mud-cake removal and water flushing system; an optical television system for monitoring the borehole wall through filtered, optically clear, borehole fluid; and the ability to measure *in situ* elastic modulus as a function of depth by the indentation technique. In addition to completion of construction and testing of the 6-in. holographic stressmeter, with partial support by DOE, we refurbished a Schlumberger type 7600 logging truck. A water pumping and filtering system, power supplies, and cable tensioning transducing system have been purchased and were installed. We have also constructed an 11-m-high portable tower for lowering the stressmeter into boreholes. One of the last items we are just completing before going into the field has been an 11-m-long instrument casing to be lowered in boreholes prior to deploying.

During the previous year, we conducted finite element analysis of the deformation around the side test holes in the holographic stressmeter to determine the precision that could be obtained with this instrument using the two-dimensional plate model approximation. The finite element results demonstrate that the two-dimensional plate model provides a reasonable approximation to the real rock displacement at radii of greater than $1.3a$, where a is the radius of the sidehole. Because the vertical displacements near the edge of the borehole are not taken into account in this model, the value of the *in situ* stress inferred by comparison calculated to observe interference patterns will tend to give us *in situ* stress values that are systematically too high by 10 to 30%. To overcome this problem, we have calculated the three-dimensional problem of the surface displacements resulting from the drilling of a deep hole in a prestressed half-space. This is exactly the problem we need to solve within the approximation that the radius of the access drillhole is much greater than the sidehole radius and that the depth of the sidehole drilled is much greater than its radius.

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

Grant: DE-FG03-85ER13445

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 the various hydrogen-bearing species dissolved in silicate melts and glasses. During the current grant period, we have conducted 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.

A series of experiments was performed to determine the hydrogen isotope fractionation factors between water vapor and "water" dissolved in natural synthetic glasses and melts. These experiments were conducted at 635, 750, and 850°C. At the vapor pressures of the experiments (0.6 - 2.6 atm), the dissolved water in the glasses (<0.2 wt.% H₂O) is entirely in the form of hydroxyl groups, as verified through infrared spectra. The solubility of water in the glasses varies linearly as a function of the square root of pressure and is dependent on temperature and composition. Infrared measurements of water concentration profiles and isotopic reversal experiments indicate that equilibrium was attained during the 140 - 3000 hour runs.

The fractionation of hydrogen isotopes between the vapor and dissolved water in the glasses was measured by determining the D/H ratios of the coexisting phases. Little temperature dependence was observed for D/H fractionation between the vapor and the OH in the glass or melt over the studied temperature range. This fractionation is substantially greater than that observed for most hydrous minerals at these temperatures. The measured fractionation factors for D/H in vapor relative to dissolved hydroxyl in rhyolitic glasses are similar to values previously estimated from a suite of obsidians from Mono craters, California, and can be used to interpret hydrogen isotope ratios of these and other igneous rocks related by degassing processes.

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 have applied 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: a) provides dates that are 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. The effective rates of (episodic) seismic uplift were also determined.

We have initiated a study of U and Th in a suite of saline ground waters from central Missouri in order 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. These subsurface waters have not been exposed to sources of anthropogenic contamination (e.g., drilling fluids, well casings). Our previous study of the H, O, Sr, and Nd isotopes in these ground waters indicates that the saline samples evolved by dissolution of halite by meteoric water in a large-scale (~ 1000 km) flow system and that subsequent mixing with local dilute recharge produced the spectrum of water compositions. 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 seawater source for the salinity in the waters and are consistent with a hydrologic model involving relatively old, far-travelled saline water and leaching of ^{234}U from α -recoil-damaged sites in aquifer minerals, and precipitation of ^{230}Th and ^{232}Th on a time scale of ~ 500 yr.

Experimental studies of the diffusion and partitioning of Ru, Ir, Pt, and V in Ni-Fe alloys have been performed. We have determined the diffusion coefficient of Ru in Ni between 1270 and 870 K and the partitioning behavior of Pt, Ir, and V between coexisting phases in the Ni-Fe-Ru-O system. We have also conducted preliminary studies of phase equilibria in the Ni-Fe-Os-Re system and of Re and Os solubility in silicate melts as a function of oxygen fugacity. These data have been used to develop a new model for the origin of metal, magnetite, and sulfide opaque assemblages in refractory inclusions and chondrules in carbonaceous chondrites. We have shown that opaque assemblages do not preserve an independent history of the primitive solar nebula but formed by exsolution, oxidation, and sulfidization at low temperatures (≤ 800 K) in the cooling nebula or in the planetary environments.

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

Grant: DE-FG03-85ER13419

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

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

Water-rock interaction plays an important role in many geochemical processes. Comprehensive transport models incorporating coupled fluid flow and chemical reactions are required, together with knowledge of the physics and chemistry of minerals and aqueous solutions at temperatures and pressures characteristic of the Earth's crust, to better understand and predict the consequences of these processes. The focus of this project over the past year has been on development and refinement of predictive algorithms describing the thermodynamic and transport properties of aqueous species as functions of temperature, pressure, and composition.

Tracer diffusion coefficients were calculated from the limiting equivalent conductances of ions using the Nernst-Einstein equation. Corresponding states algorithms were developed to predict as a function of temperature and pressure the limiting equivalent conductances of many electrolytes of geologic interest for which no high pressure/temperature experimental data are available. Combining these estimates with equations describing the transference numbers of NaCl permits prediction of the limiting equivalent conductances of ions, and therefore, tracer diffusion coefficients to 1000°C and 5 kb. Values of these coefficients were computed for 30 monovalent anions, monovalent cations, and divalent cations of geologic interest at high temperatures and pressures. The limiting equivalent conductances were also used together with corresponding values of the viscosity of H₂O to compute the Stokes' law radii, apparent solvation numbers, Walden products, and residual friction coefficients of these same ionic species.

Dissociation constants from 400 to 800°C at 500 to 4000 bars were calculated for 14 aqueous alkali metal halides from experimental conductance measurements reported in the literature using the Shedlovsky equation and the law of mass action, together with independently calculated limiting equivalent conductances for the electrolytes generated from equations described above. The requisite activity coefficients were calculated for neutral and charged species from the Setchenow and extended Debye-Hückel equations, respectively. Where direct comparison can be made, dissociation constants generated in the present study fall within estimated uncertainties of corresponding values previously reported.

In addition, effort was devoted to the characterization of the effective electrostatic radii of aqueous species (r_{ej}) at supercritical conditions. Values of (r_{ej}) were determined by regression of experimental dissociation constants of NaCl^o with the revised HKF equation of state. Equations describing the behavior of (r_{ej}) with changing temperature and pressure have been incorporated into a revised version of the computer code SUPCRT, which permits the calculation of the standard partial molal thermodynamic properties of aqueous species to 1000°C and 5 kb. Research plans call for the use of the thermodynamic and transport properties in comprehensive mathematical models to compute aqueous mass transfer coupled to water-rock interaction in hydrothermal systems.

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

Grant: DE-FG03-87ER13667

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

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

The RARGA laboratory for analysis of noble gases in terrestrial fluids was deployed in Los Alamos County, New Mexico from January through November 1987. Samples from New Mexico geothermal and gas fields were collected and analyzed, plus samples from potential geothermal production sites in Honduras. Additionally analyzed for argon and heavier gases were meteoric waters from the Great Artesian basin, Australia collected by T. Torgersen.

$^3\text{He}/^4\text{He}$ ratios in New Mexico samples correlate with tectonic province. Samples collected within the Basin and Range, including the Rio Grande rift, have R/Ra values >0.5 up to 5.0 in Valles caldera. The high values indicate that these reservoirs, associated with extensional, crustal-thinning tectonics, contain significant contributions from a mantle source. Outside the Basin and Range, in both the Colorado Plateau and Great Plains provinces, the R/Ra values varied in the range 0.02-0.30. Colorado Plateau samples were consistently higher (0.15-0.30) than those of the Great Plains (0.02-0.15). Low values indicate relatively more radiogenic or crustal gases. Methane from the Great Plains province contains a neon component isotopically similar to that found in an earlier study of natural gases from Alberta, Canada, requiring a source with a fluorine-to-oxygen ratio significantly greater than average crustal values. Like the Basin and Range province of New Mexico, the tectonic forces of Honduras are extensional. Geothermal waters issuing from faults associated with pull-apart basins all contain a significant mantle helium component with R/Ra values varying from 1.0 up to 6.5.

Ground-water samples of known hydrologic age from the Great Artesian basin, Australia contain significant excesses of ^{40}Ar . The accumulation rates in the aquifer cannot be supplied by *in situ* production or by dissolution of aquifer minerals but require a crustal flux equivalent to whole crustal production. These data supply the first direct measure of ^{40}Ar crustal degassing flux and supplement similar inferences from analyses (elsewhere) of helium from the same samples.

Our group continues to study metamorphic minerals and associated fluid inclusions using a sensitive mass spectrometer coupled with a laser microprobe. In some metamorphic rocks individual crystals are surprisingly heterogeneous in noble gas content, on a ≤ 1 mm scale. Garnet and quartz crystals from Sri Lanka, Scotland, and New England have trapped argon with $^{40}\text{Ar}/^{36}\text{Ar}$ ratios much greater than the modern atmospheric value, as well as radiogenic and atmospheric argon.

We have also analyzed Ar, Kr, and Xe extracted from small groups of fluid inclusions in neutron-irradiated quartz samples from mineralized veins of the Mother Lode, Sierra Nevada and thereby determined the concentrations of I, Br, Cl, Ca, and K present. Similarly, we measured trapped Ar, Kr, and Xe. We conclude that the fluids in quartz veins associated with gold mineralization are most similar to "metamorphic spring waters," fluids that derive from a relatively shallow level in the Earth's crust.

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

Grant: DE-FG03-87ER13803

Title: To Complete the Thermodynamic Functions of Five
Minerals Up to 1500 K and Up to Compressions of
 $V/V_0 = 0.7$

Person in Charge: O. L. Anderson (213-825-3880)

Two papers were submitted for publication, which give the details of the thermodynamic functions (graphs and tables for two minerals Mg_2SiO_4 and MgO). A paper on the thermodynamic functions of Al_2O_3 is now being prepared. Another paper on the thermodynamic functions of $NaCl$ and KCl is being written.

For the three hard minerals, the data are now extended to 2000 K, all at various compressions up to $V/V_0 = 0.7$. For $NaCl$ and KCl , the temperature range will be 300 K - 1500 K.

We have found that the thermodynamic functions are slightly sensitive to the parameter $(dK_T/dP)_T$ versus T , which is not well known. We have found a pronounced correlation between the uncertainty in the thermal expansivity and the uncertainty in entropy. The thermodynamic functions in the $T - V/V_0$ field are entropy, internal energy, and the Helmholtz free energy. The thermodynamic functions in the $T - P$ field are entropy, enthalpy, and the Gibbs free energy.

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

Grant: DE-FG03-87ER13806

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

Person in Charge: W. G. Ernst (213-825-3880)

The area of particular concentration is the Sawyers Bar area of the so-called Western Triassic and Paleozoic Belt (WTrPZ). The mapped region constitutes the southern portion of the Marble Mountain Wilderness, 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 calc-alkaline arc rocks of the WTrPZ belt, but the southeasternmost part contains subduction zone units of the Stuart Fork formation. Neva-den 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 400 thin sections have been studied petrographically, and 100+ 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 will commence this fall. On the southeast, above a subhorizontal to east-dipping thrust fault, 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 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. It is expected that the stable isotope and major element analyses of coexisting minerals now to be initiated, employing suitable thermobarometers, will allow the thermal history of this volcanogenic arc to be deciphered. Most of the data gathering will be concluded by the end of the second year of the project.

Grantee: UNIVERSITY OF CALIFORNIA, RIVERSIDE
Institute of Geophysics and Planetary Physics
Riverside, California 92521

Grant: DE-FG03-87ER13408

Title: Sulfide-Oxide-Silicate Phase Equilibria and
Associated Fluid Inclusion Properties in the
Salton Sea Geothermal System, California

Person in Charge: M. A. McKibben (714-787-3444 or -4501)

Our research concerns the origin, transport, and deposition of metals and sulfur in saline, high temperature geothermal systems. We are studying authigenic minerals formed in mineralized fractures in the Salton Sea geothermal system, as well as analyzing geothermal fluids produced. We developed a model for ore mineralization involving heating and upwelling of deep hypersaline brines, with mineralization occurring at the interface between these brines and overlying more dilute fluids. This model has practical applications to commercial development of the SSGS, predicting the distribution and salinity of fluids and constraining heat and mass flow models.

We recently completed a comprehensive ion microprobe study of S isotopic variations among sedimentary host-rock minerals, sulfides in igneous rocks, hydrothermal vein minerals, and aqueous S species in the geothermal system. In stratiform sulfides, $\delta^{34}\text{S}$ varies by as much as 45 permil over distances of only 0.4 mm, reflecting intimate intergrowths of early diagenetic, late diagenetic, and hydrothermal pyrite generations. In hydrothermal veins, chalcopyrite crystals are zoned in $\delta^{34}\text{S}$ by up to 10 permil over distances of 1 mm, likely recording fractionation caused by sulfide precipitation from fluids with high metal/sulfur ratios. Although vein sulfides intimately envelop sedimentary sulfides in the host rocks, their distinct $\delta^{34}\text{S}$ values indicate that, surprisingly, the metal-rich, sulfur-poor hydrothermal fluids do not recycle the sedimentary S. Although vein sulfide $\delta^{34}\text{S}$ values cluster near 0 permil, there is little or no magmatic contribution of S to ore formation in the Salton Sea geothermal system. Altered diabase sills at 3 km depth contain no primary sulfides but instead are overprinted by at least two hydrothermal sulfide-depositing events. In the deep hypersaline brines, H_2S (~0 permil) and SO_4 (~20 permil) are in dilute solution S isotopic equilibrium at 300°C, indicating that salinity effects on isotopic fractionation are negligible under these conditions. $\delta^{34}\text{S}$ for total fluid S is equal to the mean $\delta^{34}\text{S}$ value of stratiform evaporitic anhydrite in the host sediments (~10 permil). The observations indicate that H_2S is generated by partial hydrothermal reduction of evaporitic SO_4 , probably by interaction with Fe^{2+} in the upwelling diapir of reduced, metal-rich brine.

Few experimental data exist on the speciation and thermodynamics of metal chloride complexes in saline fluids at elevated temperatures; we must determine such information empirically. Our data base from the SSGS includes a series of 44 nearly isothermal (~300°C) Na-Ca-K-Cl brine analyses covering total chloride concentrations from 3-6 molal. Published thermodynamic data on alkali chloride solutions indicate that activity coefficients remain relatively constant at high salinities at elevated temperatures. Therefore, isothermal plots of log total metal molality versus log total chloride molality will yield slopes corresponding to the mean ligand number of the metal chloride complexes, assuming that a single mineral controls a given metal's solubility and that pH and mH_2S remain relatively constant over the salinity range. From such plots we determined the mean ligand numbers for several metal chloride complexes in the Salton Sea brines. Our determinations for all base metals indicate that the dominant complexes are: PbCl_3^- , ZnCl_2^0 , CdCl_2^0 , CuCl_3^{2-} , and MnCl_2^0 . Fe data are complicated by the presence of both Fe^{2+} and Fe^{3+} in the brines, yielding a mean ligand number of 4.4. This implies that Fe is carried by mixtures of FeCl_4^- and FeCl_5^- complexes. These empirical speciation data allow more accurate calculation of metal sulfide solubilities in the SSGS brines, with application to scaling problems during geothermal power production.

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 (619-452-3205)

While tremendous progress has been made in the experimental state-of-the-art for electromagnetic geophysics in recent years, our capability to model and interpret such data has lagged far behind. This is probably the largest potential obstacle to further progress in the field. This project attempts to address this problem through collaborative work between B. J. Travis of Los Alamos National Laboratory and the principal investigators, utilizing the extensive experience with the numerical solution of partial differential equations that exists at LANL and the familiarity with electromagnetic data and techniques of the Scripps researchers.

Major improvements to the modeling of two- (or three-) dimensional electrical structures can be made by utilizing some recent advances in finite element modeling and modern supercomputers. In particular, the moving finite element (MFE) method was recently proposed in an attempt to avoid some of the difficulties of conventional finite element algorithms. This method incorporates automatic and adaptively moving nodes directly into the functional minimization from which the finite element equations are derived, resulting in a major improvement in accuracy for a given size mesh. A major component of this project is the development of codes to solve two-dimensional electromagnetic problems using MFE, beginning with the magnetotelluric problem and eventually extending to controlled source types. At the same time, advantage will be made of modern supercomputer architectures, new algorithms to solve large, sparse matrices, and new approaches to the automatic generation of complex finite element meshes. The outcome will be substantially faster and more accurate numerical codes that are easy to use.

The second aspect of this project is the development of regularization methods for two-dimensional problems so that the automatic inversion of such data can be implemented. Techniques for finding the smoothest model that fits a given set of data have been developed for the one-dimensional case and will be extended to higher dimensional situations. The advantages of such a scheme are 1) the model parameterization no longer determines the form of the solution, 2) the procedure is stable and rapid, and 3) the simplest model that is consistent with the data is found automatically, reducing the natural tendency to overinterpret data. It is hoped that experience gained in the two-dimensional case will point the way to attacking three-dimensional problems.

To date, the collaboration has produced a working finite element mesh generator that can handle complex, multiple-connected models with a minimum of user input and a two-dimensional MFE forward code. Work is progressing on the numerical computation of the partial derivatives of the data with respect to the model. Substantial improvements have been made to the one-dimensional regularized inversion algorithms, including a trust region algorithm that improves the stability of the method.

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

Grant: DE-FG03-87ER13267

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)

For the past two and one-half years we have maintained an intensive sampling schedule at Long Valley caldera in the Sierra Nevadas to monitor variations in gas chemistry of fumaroles and hot springs at sites within and immediately adjacent to the caldera perimeter. Our principal objective has been to establish what relationship, if any, exists between variations in gas chemistry and the timing, magnitude, and location of seismic events in the area. To achieve this objective, the focus of our analytical effort has centered on helium isotope ratios ($^3\text{He}/^4\text{He}$), because of their unique ability to distinguish unequivocally between mantle and crustal provenance; however, 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 ($^{40}\text{Ar}/^{36}\text{Ar}$). With these additional constraints we have been able to discern a strong magmatic control on the total gas chemistry, which has proven useful to our understanding of the hydrogeology of the area.

The first point to emphasize about the helium isotope results 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, and by inference the heat source driving the hydrothermal system, is predominantly magmatic in origin. Secondly, R/R_a ratios outside the caldera perimeter and away from the Mono/Inyo craters fall dramatically to values <1 , indicating that the heat source is limited to the resurgent dome area of the caldera and northwards along the Mono/Inyo craters projection. Finally, and most importantly in the present context, significant and systematic variations in the R/R_a ratio have continued through 1987 into early 1988 even though local seismicity remains at a low level. Invariably, the highest R/R_a ratios occur in the winter/early spring period, when ground water recharge is inhibited. Then, following the initiation of snowmelt, R/R_a ratios decrease in the spring/early summer, which must result from the addition of radiogenic (low R/R_a) helium to the magmatic component. We presume that this effect is due to dilution of the deep magmatic fluid with a much shallower crustal component in the local ground water. These trends are consistent with a picture of seasonal control on the R/R_a ratio, determined largely by the recharge and mixing characteristics of the hydrothermal regime. This is an important result because it has allowed us to establish a baseline variation curve for helium isotopes that will enable us to distinguish clearly any correlations between helium and seismicity in the area.

Studies on gases other than helium have revealed a variable but not insignificant input of atmospheric gases (N_2 - O_2 -Ar). The total gas chemistry is, however, dominated by CO_2 . There is strong evidence for magmatic control of the CO_2 : the range in the He/ CO_2 ratio (2-18 ppm) overlaps with that observed on pristine, sediment-free parts of submarine spreading ridges. In addition, we observe a strong negative correlation between R/R_a and He/ CO_2 , and the narrow observed range in $\delta^{13}\text{C}(\text{CO}_2)$ (-4.21 to -7.08 per mil vs. PDB) is consistent with that found in mid-ocean ridge basalts (MORB). However, distinct differences in the $\text{CO}_2/^3\text{He}$ ratio (range 5-140 $\times 10^9$) relative to the MORB value (1 $\times 10^9$) reveal that other potentially fractionating mechanisms (e.g., boiling and/or admixture with CO_2 of different provenance) also exert an influence on the total CO_2 . Similarly, $\text{CH}_4/^3\text{He}$ ratios (up to 4 $\times 10^6$) show considerable overlap with a MORB (mantle) source (3-6 $\times 10^6$), providing further evidence of a magmatic input to the total chemistry.

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

Grant: DE-FG02-87ER13804

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

Person in Charge: H. Spetzler (303-492-8141)

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 and are in the process of adapting it to make the measurements under pressure. The interferometer has an ultimate sensitivity of $10E^{-7}$ wavelength of the laser light, i.e., approximately $10E^{-13}$ 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)

A workshop on Quantitative Dynamic Stratigraphy (QDS) was convened February 14-18, 1988, for the purposes of: (1) summarizing the state-of-the-art in deterministic approaches to stratigraphic analysis, (2) identifying major gaps in existing numerical simulation and model verification studies, and (3) defining research directions for the next decade that will significantly enhance geological predictions of stratigraphy and fluid movement in the subsurface.

The workshop was cosponsored along with DOE by the National Science Foundation and the U.S. Geological Survey. A publication is planned to include many of the workshop contributions.

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 primarily 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 segment is a seismic gap with a high probability for a great earthquake ($M > 8$) in the next two decades. Applications concern the geothermal energy potential of the Aleutian arc and seismic, volcanic, and tsunami hazards to offshore oil lease sale areas directly adjacent to the Shumagin seismic gap. Technical objectives are the sensing of wide dynamic range ground motions of moderate and large earthquakes for engineering applications. The digital data are also used for particle motion and spectral studies of harmonic tremor at Pavlof volcano.

Recent results include a 3-D kinematic model of slab flow and the in-plane deformation required to obtain the observed subduction geometry. This model explains a diverse set of geophysical observations in the Aleutian subduction zone. The subducting slab is modeled as a thin sheet with a Newtonian rheology sliding through a lower-viscosity mantle. The calculation provides an estimate of the minimum in-plane strain rate associated with the variations in the slab area and shear required of the slab to obtain its observed geometry. A thermal model is computed from the kinematic flow model. The kinematic flow models predict that the obliquely subducted slab in the central Aleutians is transported laterally westward producing cold slab material extending to depths of at least 900 km along the entire arc after only 30 m.y. of subduction. This lateral transport may dehydrate subducted oceanic crust in the western Aleutians and be the cause of the lack of island arc volcanics there. The decrease in the seismicity cutoff depth from east to west is coincident with the calculated 600°C potential temperature isotherm, suggesting a transition from brittle to ductile deformation. Below 125 km, the spatial distributions of both source mechanisms and seismic energy release vary along the arc and are qualitatively explained by the strain-rates predicted from the kinematic model.

As a first step towards predictive modeling of the strong ground motions expected in the Shumagin Island region, aftershocks of the 1986 $M = 8$ Andreanof Islands earthquake as recorded digitally in the Shumagin Islands (1000 km ENE of the rupture) were used as empirical Green's functions to simulate the mainshock record. Summations were done both randomly and semi-randomly according to the kinematic rupture propagation. We find that in the high frequency range where contributions from the Green's functions superimpose incoherently, a good overall fit of simulated and observed records can be obtained using ~ 1000 $M = 6$ events. Similar superpositions of local $M = 6$ events may allow us to estimate strong ground motions in regions of potential offshore oil platforms.

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. Silicate liquids show mixing behavior that requires models at least as complex as an asymmetric regular solution. Parameters quantitatively extracted so far include ordinary diffusion coefficients, heats of transport, and energies of mixing for SiO_2 in silicate liquid.

Additional recent application of thermal diffusion studies to magmatic systems involving coexistence of crystals with silicate melts has shown that there is a substantial potential for inducing chemical migration. Laboratory observations of cumulate maturation under the influence of thermal diffusion are in progress.

Grantee: GEO-CHEM RESEARCH ASSOCIATES
400 East Third Street
Bloomington, Indiana 47401

Grant: DE-FG02-87ER13802

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

Person in Charge: P. J. Ortoleva (812-332-3277)

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.

We will concentrate on the formation of secondary minerals during basin diagenesis and localization of metals at reaction interfaces resulting in ore-body formation. Both of these occur because transport and reaction processes interact to spatially and temporally localize mineral deposition and dissolution. This localization can lead to permeability enhancement or occlusion thereby affecting hydrocarbon reservoir quality. If the accumulating minerals are metals, as in uranium roll fronts, their localization may result in the formation of an ore body. Understanding the natural processes related to these phenomena and the resulting geochemical signatures may lead to better methods of exploration for and exploitation of these resources. Engineered reaction fronts, such as those generated by secondary/tertiary hydrocarbon recovery methods or underground high-level nuclear waste disposal, can also be studied using the methods we have developed and propose here to develop.

All the above phenomena involve the coupling of aqueous phase chemical reactions, grain growth/dissolution kinetics, and transport. Therefore, a theory capable of capturing their salient features must involve the coupling of finite rate reaction processes with transport. To our knowledge our modeling approach is the only one that correctly incorporates all these features and furthermore has led to the only computer reaction-transport code that can describe these phenomena in reasonable computational times. We shall both apply and extend our mathematical techniques developed earlier for the study of reaction fronts and optimize and generalize our existing code, REACTRAN, in a number of ways.

Grantee: HARVARD UNIVERSITY
Department of Earth and Planetary Sciences
Hoffman Laboratory
Cambridge, Massachusetts 02138

Grant: DE-FG02-87ER13799

Title: Energetics and Thermochemical Properties of
Rocks and Minerals

Person in Charge: J. B. Thompson (617-495-2351)

Our instruments for quantitative differential scanning calorimetry (177-1000K) and differential thermal analysis (270-1750K) and the related thermogravimetric apparatus are now fully operative and calibrated. We have begun investigation of the heat capacities of several rock-forming minerals and also of the lambda transformations in quartz and alkali feldspar. The latter are lambda transformations of the unquenchable (or displacive) type and hence are readily observable with our instrument.

A major emphasis is being placed on the thermodynamic properties of the mineral cordierite as dependent on degree of Al-Si order, degree of hydration, and degree of carbonation. Cordierite is a common product of the thermal metamorphism of clay-rich sedimentary rocks and perhaps unique among silicates in having a continuously variable (rather than stepwise) level of hydration (or carbonation).

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

Grant: DE-FG03-85ER13418

Title: Physical Characterization of Magma Samples

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

The goals of the proposed research are threefold: 1) to understand how the high-temperature elastic and viscoelastic behavior and thermodynamic properties of basalts and relevant silicate melts pertaining to geothermal exploration and thermal modeling in a volcanically active area 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. This research program provides an impetus to basic energy research 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 types of basalts; 2) investigation of electrical conductivity and V_p , V_s , and Q^{-1} of melts of these and related samples as a function of temperature and pressure, and 3) Brillouin 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.

Our efforts have focused on the elastic, anelastic, and electrical properties of melts of basalts using ultrasonic interferometry and the four-electrode conductivity method. Ultrasonic measurements carried out on the melts of various compositions to $\sim 1550^\circ\text{C}$ and in the frequency range 3-22 MHz have enabled us to establish the velocity-density (Birch's linear law) and attenuation-temperature-frequency systematics and to interpret the viscoelastic properties (viscosity, relaxation time, etc.) in terms of composition and structure of melt. We are now turning to synthetic binary silicate systems (e.g., albite, anorthite, anorthite-diopside) and also employing the recently set-up Brillouin scattering system and diamond anvil to study the compressibility of silicate melts at high pressures. As preliminary progress in this direction, the experiments have been successfully carried out to 7 GPa (at ambient temperature) and to 1000°C (at ambient pressure) on $\text{TiO}_2\text{-SiO}_2$ glass system. 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. The electrical conductivity measurements on the nepheline-sodium disilicate ($\text{NaAlSiO}_4\text{-Na}_2\text{SiO}_3$) system to $\sim 900^\circ\text{C}$ to determine the effect of partial melting (solidus = 768°C) on the electrical properties. These measurements will be extended to high (crustal) pressures.

Grantee: UNIVERSITY OF HOUSTON
Department of Geosciences
Houston, Texas 77004

Grant: DE-FG05-87ER13771

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

Person in Charge: H. S. Chafetz (713-749-1803)

Recent investigations have indicated that bacteria are important in influencing the precipitation of CaCO₃ in many environments. Due to the nature of geological investigations, carbonate petrologists have overlooked the significant contributions of bacteria due to their size and the rapidity with which they commonly undergo decay. Calcium carbonates that precipitated due to the influence of bacteria undoubtedly had different physical and chemical constraints on the conditions under which they formed than either purely abiotically precipitated CaCO₃ or CaCO₃ whose precipitation was due to some other taxa. It is, therefore, important to determine the origin of cements and other related constituents, i.e., to be able to recognize bacterially influenced precipitation.

We will evaluate the role of bacteria in the lithification of cyanobacterial (blue-green algal) mats and provide criteria so that bacterially induced lithified stromatolites can be recognized in the rock record. This will involve a study of the initial lithification of modern cyanobacterial mats, laboratory experiments to try and produce 'lithified' cyanobacterial mats as a result of bacterial activity, and an examination of stromatolites from the rock record to see if we can determine if they are the product, at least in part, of bacterially induced carbonate precipitation.

Grantee: INDIANA UNIVERSITY
Department of Geology
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)

To provide the information required for eventual evaluation of the hydrocarbon potential of the Midcontinent Rift System (MRS) and other late Proterozoic sediments, studies in organic geochemistry, isotopic biogeochemistry, sedimentology, and micropaleontology will be directed toward improving knowledge of: 1) the quantity and quality of organic material in sedimentary rocks from the widest possible variety of locations within the MRS, 2) the level of maturity of that material as a function of location, 3) the biota that produced the organic material, 4) the paleoenvironments in which the organic material was synthesized and preserved, 5) global patterns of middle and late Proterozoic biogeochemistry, and 6) possible correlations between midcontinental rift basins and basins elsewhere that are related temporally or developmentally.

The contributions will be significant because: 1) analyses of MRS rocks have been focused nearly exclusively on readily available materials from the region of the White Pine ore deposit, which may not be representative of the bulk of rift sedimentary rocks; 2) essentially no information is available regarding the maturity of organic material (not even color, let alone elemental composition of organic material); 3) there have been no modern investigations of the micropaleontology of MRS sedimentary rocks; 4) the conflicting views of the depositional environment have not been tested against organic- and isotopic-geochemical evidence; 5) little is known of the global biogeochemistry in the interval 1400-800 million years ago; and 6) MRS sedimentary rocks have not been explicitly compared to coeval rocks from other localities or to other rift sediments (e.g, Triassic rocks of the eastern margin of North America).

Within our group we will integrate lines of inquiry that are usually pursued separately, namely: structural and quantitative analyses of extractable organic material; quantitative and elemental analyses of kerogen; carbon-isotopic analyses, ranging from pure organic compounds to carbonate minerals; micropaleontology and organic petrography; and sedimentology and related field geological work on fine-grained facies.

Grantee: INTERNATIONAL BASEMENT TECTONICS
ASSOCIATION, INC.
675 South 4th East
Salt Lake City, Utah 84111

Grant: DE-FG02-88ER13962

Title: 8th International Conference on Basement Tectonics:
Characterization and Comparison of Precambrian through
Mesozoic Continental Margins.

Person in Charge: M. J. Bartholomew (406-496-4177)

The objective of this meeting was to bring together a group of researchers interested in diverse aspects of ancient continental margins. The associated proceedings volume will provide overviews of the processes and techniques used in identifying and analyzing ancient margins and terrane boundaries. Both the proceedings and the field guide volumes also characterize different aspects of specific margins.

The sequential technical sessions began with an overview of convergent-plate tectonics and presentations on plutonic, volcanic, metamorphic, structural, and sedimentological aspects of the Mesozoic margin of western North America. An overview of Precambrian margins was followed by comparison of Archean high-grade terranes and greenstone belts with Proterozoic orogenic belts. A session on geophysical characteristics demonstrated the uses of reflection profiles, paleomagnetism, and aeromagnetic and gravity data in interpreting suspected terrane boundaries. The session on structural characteristics compared collisional, extensional, and oblique-slip boundaries as well as reviewed the use of kinematic indicators, definition of the seismogenic crust, and the zone of weakness concept. The geochemistry session reviewed the uses of geochronology, radiogenic and isotope systematics, and trace elements for evaluation of different terranes and fault zones. The relationship of tectonic environments with various lithologic/metallogenic associations was explored in one session and provided the background for the symposium on the tectonic setting of hydrothermal gold deposits. Additional sessions dealt with Precambrian and Phanerozoic tectonism and ancient margins: in Asia and Europe, in the Canadian shield and western North America, and in eastern North America.

The field trips examined Precambrian and Mesozoic margins in Montana, Idaho, and Wyoming. In addition to the eleven field guides, the volume also contains eight papers on the Precambrian rocks of Montana and Wyoming and three on the Mesozoic boundary in Idaho and Oregon.

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

Grant: DE-FG05-87ER13748

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

Person in Charge: R. E. Ferrell, Jr. (504-388-3353) and L. B. Williams

The objective of this research is to define the conditions (physical and chemical) under which ammonium (NH_4^+) is incorporated or fixed in clay minerals at diagenetic temperatures. Further investigation of the degree of maturation necessary for the release of NH_3 from organic matter will lead to a better understanding of anomalously high NH_4^+ concentrations in clays associated with organic-rich sediments and hydrocarbons.

Experimental work in progress is attempting to define the role of layer-charge, solution composition, temperature, and time in the fixation of ammonium by clay minerals. Several field investigations are attempting to document the variation in fixed- NH_4 with increased depth of burial and levels of organic maturity. Clays are being examined from hydrocarbon reservoirs and source rocks ranging in age from Pennsylvanian to Pleistocene and Holocene. Additional samples have been collected from shales intruded by dikes to evaluate the effects of more severe thermal conditions on NH_4 -fixation. Preliminary results from three Gulf Coast hydrocarbon reservoirs show higher fixed- NH_4 concentrations are associated with more mature hydrocarbons and a two-fold increase, over background, occurs in the shales directly above one reservoir. A comparison of fixed- NH_4 and total organic matter (TOM) shows no significant correlation. This suggests that the amount fixed is not simply a consequence of inheritance.

The successful completion of this project should better define the time, temperature, and concentrations of NH_3 in pore fluids necessary to form NH_4^+ -clays. If NH_4^+ substitution in silicates is anomalous near hydrocarbon reservoirs, our results may improve exploration and evaluation procedures for hydrocarbons. The research may lead to the formulation of an alternative or improved technique for evaluating organic maturity levels in certain types of rocks.

Grantee: UNIVERSITY OF MARYLAND
Department of Chemistry and Biochemistry
College Park, Maryland 20742

Grant: DE-FG05-85ER13410

Title: Study of the Salton Sea Geothermal System Using
 ^{10}Be Isotope and Trace Element Chemistry

Person in Charge: N. J. Valette-Silver (301-454-1531)

The aim of the work was to characterize the dominant geochemical processes acting in the Salton Sea geothermal reservoir using ^9Be and its natural radioactive isotope ^{10}Be .

To make an adequate use of these indicators, we studied the general behavior of Be as a function of temperature, pH, salinity, Fe, and organic matter contents. We observed that Be solubility is greater at pH <5.5 and high salinity and organic matter contents, which are the prevailing conditions in the Salton Sea geothermal system.

We analyzed ^{10}Be and ^9Be on waters collected from California State 2-14 well (SSSDP well) and Fee #5 (Republic Geothermal Inc.) as well as core and cutting samples from the SSSDP well. Based on ^{10}Be inventory in the core, it appears that the whole host rocks, from surface to 3250-m depth, are young sediments, less than few million years old, metamorphosed by the hydrothermal process.

Even keeping in mind the possible contamination due to the persistence in the system of some of the coring material in the SSSDP well, the first aquifer (~1850 m) sampled has a different chemical signature than the second one (~3250 m). The ^{10}Be and ^9Be distribution coefficients and $^{10}\text{Be}/^9\text{Be}$ ratios in the rocks decrease with depth whereas the $^{10}\text{Be}/^9\text{Be}$ ratios in the fluids increase. At pH <5.5 and high salinity (~25%), ^{10}Be and ^9Be are leached out of the surrounding rocks; ^{10}Be is more actively removed showing that in the solid material the chemical sites occupied by ^{10}Be are more accessible than those occupied by ^9Be . This explains why ^{10}Be is an excellent tracer of sediment involvement in geological processes. However, this behavior jeopardizes its possible use as a dating tool in open systems with pH <5.5.

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

Grant: DE-FG02-86ER13636

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

Person in Charge: M. N. Toksoz and C. H. A. Cheng (617-253-3381)

The purpose of this work is to study methods of determining *in situ* permeability or hydraulic conductivity of a fracture using full waveform acoustic logging (FWAL) and vertical seismic profiling (VSP) techniques. In the past year, we have worked towards this goal by developing the theory of wave propagation across a fracture and by doing ultrasonic laboratory scaled experiments of logging across a fracture and comparing the experimental results with theoretical predictions.

During the past year, we have developed a model for wave propagation in a borehole across a horizontal fracture and along a vertical fracture. The significant result is that when the width of the fracture is much greater than the viscous skin depth (high frequency case), the motion in the fracture is propagative. When the viscous skin depth is comparable to the fracture width (low frequency case), the motion becomes diffusive. The result of this is that comparing the "equivalent" single fracture thickness of an *in situ* fracture measured from a pump or packer test and from acoustic logging is rather meaningless because the *in situ* fracture is not likely to behave like a single parallel wall fracture over the wide range of frequencies involved. We have compared our model with results obtained from our laboratory ultrasonic scaled experiments involving both horizontal and vertical fractures and find that the theory and experiment results agree very well. We plan to incorporate this model into our fracture generated VSP tube wave model.

In cooperation with Dr. Michael Fehler of Los Alamos National Laboratory we have been working on a travel time tomography algorithm to image the low velocity zone around induced fractures in the Hot Dry Rock Experiment using microearthquake arrival times. Preliminary results show that resolution may be limited by the geometry involved. We plan to continue working on this problem in the coming year.

Grantee: MICHIGAN STATE UNIVERSITY
Department of Geological Sciences
East Lansing, Michigan 48824-1115

Grant: DE-FG02-87ER13721

Title: Constraints on Magma Ascent, Emplacement, and
Eruption: Geochemical and Mineralogical Data
from Drill Core at Inyo Craters, Inyo Chain,
California

Person in Charge: T. A. Vogel (517-355-4626)

The drilling under Inyo craters (Inyo-4) is a continuation of our investigations of the compositional and mineralogical variations in the Inyo dike system. This system is much better constrained than are ash-flow sheets in terms of their eruptive histories; that is, they are not complicated by eruption, transportation, or deposition dynamics. The chemistry and mineralogy of these samples are influenced only by the original conditions within the magma chamber, the conditions during emplacement, and the evacuation dynamics of the magma reservoir.

During the past year we participated in the drilling, sampling, and analyzing of the material beneath south Inyo crater. The purpose of this drilling was to obtain samples of the Inyo magma that was intruded into an environment (caldera fill) that was substantially different from that at Obsidian dome (crystalline basement). In this drilling we intersected a breccia zone with juvenile vesiculated magma underneath the crater. This juvenile magmatic material is chemically distinct from the other magma types in the Inyo volcanic system, and these data support the idea that the magma reservoir for the Inyo system contained different magma types.

We are in the processes of chemically and mineralogically analyzing the individual juvenile clasts as well as the wallrock of the breccia zone. Hopefully these data will allow us to interpret the magmatic conditions at the time of magma fragmentation. We will compare these data with our data from Obsidian dome (Inyo-1 - Inyo-3 plus surface samples).

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 (202-334-2744)

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

The Geophysics Study Committee of the National Research Council (NRC) 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 [202-334-2744]*)

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 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 the actions that have resulted from its recommendations; 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 panel on seismic hazard analysis has finished its report on *Probability of Seismic Hazard Analysis*, which is in press. Two new panels have been set up: one to advise on the feasibility of real-time earthquake warning and one to examine the problems of regional seismic networks.

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 24, 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. Future work of the USGC includes: providing input to the International Geosphere-Biosphere Program and the International Decade for Natural Disaster Reduction.

D. Board on Earth Sciences (*R. S. Long [202-334-2744]*)

The fundamental mission of the Board on Earth Sciences of the Commission on Physical Sciences, Mathematics, and Resources is to provide oversight of the solid-earth science activities within the NRC, to provide a review of research and public activities in the solid-earth sciences, to assess the health of the disciplines, and to identify research opportunities. This group is to take a leading role in helping to establish scientific policy bearing on larger earth science programs in and on behalf of the United States. A major charge of the Board and its committees is to assess and recommend basic research and its applications to meet national and societal needs. The Board has concentrated on publications and outreach and has reduced a backlog of reports as well as the number of committees. Nine reports were produced in the past year, and one is in press. The Board has underway: plans for a report on Status and Research Opportunities in the Solid-Earth Sciences--A Critical Assessment; a symposium to be held on geographic information systems in Denver in September 1988; a workshop on the evolution of continental margins in cooperation with the Ocean Studies Board. 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. Committee on Hydrocarbon Research Drilling (*R. S. Long [202-334-2744]*)

In 1987, the DOE asked the NRC to appoint a committee to review scientific drilling options to contribute to a better understanding of the scientific foundations that underlie hydrocarbon technologies. In response to this request, the NRC established the Committee on Hydrocarbon Research Drilling in September 1987 under the Board on Mineral and Energy Resources. In considering its charge, the committee focused on research involving, first, scientific drilling to benefit national hydrocarbon energy priorities; second, areas of hydrocarbon research not being undertaken by industry; and third, how scientific drilling could contribute to such research. The committee also considered criteria for selecting drilling sites and projects and has suggested sites, or classes of sites, as appropriate. The committee's recommendations include research ranging from exploration to extraction, from reservoir characterization to deep drilling in unknown terrains, and a full spectrum of applied and basic research. An interim report of the committee was transmitted to DOE on March 31, 1988 and a final report on May 31, 1988.

F. Support of the Numerical Data Advisory Board (*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."

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.

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

Contract No.: DE-AI05-ER13976

Title: Workshop on Long-Term Scientific Objectives for
Continental Scientific Drilling

Person-in-charge: M. A. Mayhew (202-357-7971)

The U.S. Continental Scientific Drilling Program is currently functioning as a cooperative effort of three federal agencies: Department of Energy (Office of Basic Energy Sciences), National Science Foundation (Earth Sciences Division), and Department of Interior (U.S. Geological Survey). Coordination is accomplished through the Interagency Coordinating Group (ICG) as provided by an Interagency Accord. Recent legislation (HB 2737, SB 52) calls for a plan for a comprehensive, integrated, long-range national scientific drilling program to be formulated and submitted to Congress in six months. To acquire the scientific portion of the plan and to document the body of critical scientific problems in the earth sciences where drilling can play a crucial role, the ICG is seeking input from the broad geoscience community as represented in the nation's universities, national laboratories, industries, and relevant federal agencies. Accordingly, the ICG is sponsoring a working group to prepare the science report.

NSF is taking the role as the contracting agency for the working group but with costs split equally among the three agencies.

This project has special scientific merit because it helps us document the body of scientific opportunities in the earth sciences where the drill is an essential tool. The Continental Scientific Drilling Program has completed ten holes and two new ones are starting this summer. Of this set of twelve holes, DOE has been responsible or lead agency for eleven. Thus, this workshop and report are particularly relevant to the Geosciences Program. The proposed approach, i.e., through a workshop and a report prepared by the interested scientific community, is appropriate.

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

Contract No.: 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: UNIVERSITY OF NEVADA-RENO
Seismological Laboratory
Reno, Nevada 89557-0047

Grant: DE-FG08-86ER13628

Title: Shallow-Crustal Magma Zones in and South of
Long Valley Caldera

Person in Charge: W. A. Peppin (702-784-4975)

In a recent paper we summarize seven lines of evidence for the existence of a shallow-crustal anomaly near the south end of Hilton Creek fault in California. We estimate that the anomaly is an ellipsoid centered at 37.46°N, 118.73°W at a depth of 6 ± 1 km with approximate dimensions 4 km EW, 3 km NS, and a few km vertically. This paper makes an argument that this feature, delineated by S-wave shadowing and by a P to P reflection observed at a temporary digital event recording site, is likely to be associated with magma that may have traveled south from the caldera along the Hilton Creek fault acting as a feeder dyke. This latter is an inferential result that cannot be taken as clearly established, but which deserves further attention. This paper suggests that analysis of routine network data taken near structures like Long Valley caldera can be useful in pinpointing the location of such shallow anomalous zones.

In other work a small array of vertical and three-component matched instruments were placed near station SLK, NW of Long Valley caldera. Work by Peppin and Delaplain had shown that pre-S observations observed here were consistent with an S to P conversion across a plane striking NE and dipping about 45° SE to the NW of the caldera, approximately under the Inyo craters. Work by Zucca, Kasamayer, and Mills had interpreted a similar pre-S observation as a deep reflection from a large magma body under Long Valley caldera. However, our present work has quite definitively ruled out this interpretation. The mini-array produced pre-S observations from three earthquakes. With considerable effort, timing precision of 0.001 second was obtained from the mini-array, allowing the conclusions that: 1) the pre-S phase at SLK has longitudinal particle motion and an apparent velocity comparable to P, meaning it is almost certainly the same phase observed by Zucca and others, 2) the direction of approach is from 10 to 20° west of the direct P arrival, and 3) the apparent velocity is comparable or faster than P. All these observations are consistent with the S to P conversion model proposed by Peppin and Delaplain and with the work of Zucca and others. At present our best guess is that the best explanation for the pre-S observation will be a conversion in a fairly narrow dyke in the vicinity of the Inyo craters, as all of the more obvious and prosaic explanations for the phase can now be ruled out.

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)

The purpose of this research program is to study the diagenesis of carbonate rocks with emphasis on the evolution of rock textures, mineralogy, 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 and one Mesozoic carbonate reservoir units have been studied and compared: the Early Ordovician Ellenburger dolomite, Delaware basin; the Late Ordovician Red River formation, Williston basin; the Late Ordovician to Early Devonian Hunton group, Anadarko basin; and the Late Jurassic Smackover formation, Gulf Coast basin. 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. The four basins studied have adequate control on thermal and burial history. Comparative analysis of results from the four basins suggests strong relationships between reservoir performance and other rock characteristics such as lithology, porosity, pore-throat size, capillary-pressure curve form, and geophysical log response. Dolostones are consistently more porous and permeable than limestones.

This investigation grew out of earlier work involving experimental compaction tests of natural carbonate sediments to study the evolution of porosity and study texture, mineralogy, and geochemistry of deeply buried carbonate rocks from boreholes. Rock textures characteristic of deeply buried carbonate rocks were discovered in strata currently exposed at the surface, and this became a third line of investigation in the early phases of this project. It appears that some strata now exposed at the surface were once heated to temperatures implying former burial to depths of 6 km or more and subsequent uplift and erosion.

Most-recent results suggest that dolostones exhibit common petrophysical characteristics independent of basin and burial depth. Porosity and recovery efficiency are inversely correlated, and recovery efficiency can be accurately predicted from a combination of lithology and capillary-pressure curve form. Optimum carbonate reservoir rocks are dolostones characterized by intermediate pore-throat sizes (entry pressures) and capillary-pressure curves with near-horizontal segments accounting for nearly all fluid intrusion. A relatively small number of large pores may enhance pore volume without inhibiting fluid recovery if pore-throats are relatively large and mean throat/pore size ratio high.

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 proposed to study 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. Moreover the organic components are to be identified as to which biotal member produces them, and through what steps they pass on their way to becoming hydrocarbons. The formation and maturation of the organic material will be tied to the depositional and diagenetic history of the sediments so that both the sediment and its organic companions can become better understood.

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)

Quantitative estimates for heating duration and provenance age for sandstones from the Salton Sea geothermal field, southern California have been obtained from $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum analyses of detrital K-feldspars and muscovite. Samples were taken from 1553 to 4283 feet from the State 2-14 well, which are currently at temperatures of between 148 to 286°C. The four deepest K-feldspars yield age spectra that reveal present day argon loss, whereas 1553 appears not to have been thermally disturbed. Similar Arrhenius parameters are observed for all but one sample and are characterized by an activation energy (E) of 37 kcal/mol and a frequency factor (D_0/a^2) of 4000/s. The apparent lack of recent argon loss from 1553 is consistent with the current temperature and heating times less than 100 ka, and its age spectrum is taken to be representative of the argon distribution prior to heating of all samples. Radiogenic argon losses vary between 40 and >99%. Assuming instantaneous warming to present temperatures, the fractional loss and kinetic data indicate heating durations of ~1000-12,000 years, consistent with results obtained from heat flow calculations. Muscovites yield plateau ages of ~1100 to 1300 Ma indicating a component of Proterozoic detritus and aid in distinguishing between excess ^{40}Ar in the K-feldspars versus very old source material.

K-feldspars from accretionary prism sediments along the convergent margins in southwest Alaska and southwest Japan have been analyzed to assess whether or not thermal information related to ridge subduction has been recorded. The sediments from which the K-feldspars have been separated have inferred paleotemperatures of ~200°C, based mainly on vitrinite reflectance data. These anomalously high temperatures for an accretionary complex environment are believed to be related to heating by subduction of active spreading centers. The age of the igneous rocks thought to be generated from ridge subduction are Early to Middle Miocene (12-18 Ma) in southwest Japan and ~59 Ma in southwest Alaska, and the heating of the accretionary sediments is inferred to be coeval. The sample from the Kenai Peninsula, Alaska is from a Late Cretaceous formation (75-80 Ma). The K-feldspar from this unit yields a release spectrum that exhibits an age gradient from ~63-90 Ma. The fact that the age spectrum reveals ages younger than the stratigraphic age indicates heating of this unit above ~100°C. The youngest apparent age of 63.0 ± 3.5 Ma is in good agreement with the proposed 59 Ma age for ridge subduction. A second sample comes from a Late Oligocene-Early Miocene formation to the Hioki complex, southwest Japan. This K-feldspar spectrum has an age gradient from ~70-120 Ma. There is no clear evidence for a Miocene thermal disturbance causing temperatures greater than ~100°C in this area. The argon data do not support the vitrinite reflectance data, at least in the sense that the paleotemperatures were reached in the Miocene. These preliminary results allow specific constraints on the timing and intensity of ridge subduction heating as well as a hydrocarbon maturation estimate to be made.

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 (518-564-2028)

Reefs of the Eifelian Edgecliff member of the Onondaga formation crop out along the Siluro-Devonian strike belt in New York State from south of Albany westwards to Buffalo and then into Ontario. Subsurface pinnacle reefs follow a northeast-southwest trend from southcentral New York into Pennsylvania. These reefs have been interpreted as near identical structures, consisting of bafflestone mounds built by small branching tabulates and phaceloid colonial rugose corals, surrounded by gently dipping crinoidal packstone to grainstone flank beds with massive favositids.

The current model depicts reef growth during a transgressive pulse on a gently subsiding shelf; but, the basal contact of the Edgecliff presents difficulties with this model. A major unconformity to the west of Syracuse, to the east this contact is marked by an apparent upwards shallowing transition from clastics to limestone. This suggests a tectonically active basin, with shallowing in the east, transgression in the west, and major subsidence in central New York State (based on Onondaga stratigraphy).

The two models of basin development are being tested through detailed mapping of reef exposures and examination of a pinnacle reef core, which has led to the recognition of wide diversity in reef development patterns. A shallowing upward succession of coral genera has been established based upon both petrographic and biological criteria. In bafflestone mound facies, the branching tabulate *Cladopora* is characteristic of deepest or quietest water conditions, with increasing water energy marked by a succession of phaceloid colonial rugosans: *Acinophyllum*, *Cylindrophyllum*, and *Cyathocylindrium*. Highest energy conditions are indicated by crinoidal sands.

Analysis of reef growth patterns in light of this coral succession supports the model of a tectonically active basin. Eastern reefs exhibit shallowing upward patterns indicative of falling sea level, while large reefs in central New York display cyclic "catch up/fall back" patterns (reef growth affected by periods of rapid subsidence). A major western reef exposure consists of a *Cladopora* core (quiet water), capped by crinoidal grainstone (high energy), with the core/flank contact exhibiting evidence of significant, possibly subaerial, erosion prior to the deposition of the flank beds. Examination of the core/flank contact was spurred by the apparent contradiction of the coral succession model, illustrating its predictive ability. The active basin model is strongly supported by evidence of sea-level fluctuation in the west.

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

Grant: DE-FG02-87ER13416

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 Relationships 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.

We recently completed a set of over 100 experiments on the one-atmosphere phase equilibria of basalt-rhyolite mixtures. This work has led to the construction of a phase diagram that can be used to predict the phase-equilibrium consequences of mixing mafic and silicic magmas. Significant results of this work are that: 1) olivine can crystallize directly, as the liquidus phase, from liquids with as much as 63 wt% SiO₂--because olivine is dense and easily fractionated, this result has important implications for the evolution of andesites; 2) the large stability field of olivine is apparently related to the high concentrations of K₂O in the mixtures--this reinforces the view that K₂O significantly depolymerizes silicate liquids; 3) the density of a liquid is much more strongly reduced by mixing than by crystal fractionation, implying that contamination and mixing may be important to magma ascent; 4) the ratio of the Ca/Na ratio in plagioclase to the Ca/Na ratio in the liquid is a strong function of liquid composition and cannot be used to model magma evolution; 5) the bulk heat capacity of a given magma varies strongly with crystallization and generally increases as crystallization proceeds; and 6) phase boundaries are not significantly curved in enthalpy-composition coordinates. Work in progress includes: 1) a series of lengthy, low-temperature experiments designed to fill in the low-temperature portion of the phase diagram; 2) doping studies to examine the effects of K₂O and other components on olivine stability; and 3) development of a simple model to describe plagioclase-liquid equilibria in anhydrous magmas.

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

Grant: DE-FG02-87ER13749

Title: Investigation 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.

Theoretical analysis of ultrasonic wave interaction with fluid/fluid-saturated porous solid interfaces has been developed recently by using the concepts of mode conversion at the interface. Acoustic Poynting energy flux vector and energy intensities of different bulk waves in a fluid-saturated porous medium have been derived to achieve energy transmission and reflection coefficients for which numerical calculations were conducted associated with two general cases: 1) an initial wave is incident from the liquid to the interface and generates three transmitted bulk waves in the fluid-saturated porous solid; and 2) an initial wave is incident from the fluid-saturated porous solid to the interface and generates three reflected bulk waves in the same medium. Our analysis is also focused on the effect of pore surface boundary conditions (determined by the value of surface flow impedance). Theoretical predictions found that with sealed pore boundary (surface flow impedance equals infinite), the energy transmission of slow compressional wave is much weaker than the case where pores are open at the boundary (surface flow impedance equals zero). This result is in good agreement with our experimental data.

The investigation of generalized leaky Lamb wave interaction with a fluid-saturated porous plate has been initiated and carried out recently. Our preliminary theoretical and experimental results were reported and will be published in the Proceedings of the Review of Progress in QNDE. Theoretical treatment of generalized Lamb waves in a fluid-saturated porous plate includes calculations of velocity dispersion curves for different Lamb modes and evaluation of zeros and poles of reflection coefficients from a porous plate immersed in a liquid, which provides a new technique using generalized Lamb modes to detect slow compressional waves as well as to evaluate natural porous rocks. The advantage of the new technique over previous methods is that it can be applied to very thin porous plates, which are more easily saturated with liquid.

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 on 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 such that parameters can be derived that will be of use in correlation of altered and unaltered oils with their suspected source rocks. Techniques are also being developed to examine hydrocarbons and organosulphur compounds produced from source rocks and asphaltenes by microscale pyrolysis.

In the early part of our work we showed that the majority of oils in the Pauls Valley area of the Anadarko basin were sourced from the Woodford shale. Hydrocarbons and porphyrins from tar sands of the Oil Creek sandstone have also been examined in some detail. The porphyrins were not affected by biodegradation and could be used to demonstrate that the oils responsible for the tar sands had a similar origin to the majority of other oils in the basin. Porphyrins from various source rocks in the basin have been examined to study variations in their distributions resulting from source and maturity differences. Characterization of asphaltenes and kerogens is being undertaken by microscale pyrolysis techniques to the study of organosulphur compounds and their use as source and maturity parameters. Preliminary investigations of nitrogen containing compounds are also being undertaken.

The overall aim of this work is to develop, define, and evaluate new and existing geochemical parameters that can be used in the continued 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: 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)

Transposed-temperature-drop calorimetry was used to study directly the melting at 1773 K of mixtures of crystalline albite, anorthite, and diopside and of anorthite and forsterite. The enthalpy of albite at 1000-1773 K, starting with both crystalline and glassy samples, was also measured. The results confirm previously measured enthalpies of fusion of albite, diopside, and anorthite. The new results use thermochemical cycles that completely avoid the glassy state by transforming crystals directly to melts. The enthalpy of fusion of forsterite is estimated to be 89 ± 12 kJ/mol at 1773 K and 114 ± 20 kJ/mol at its melting point of 2163 K. The data allow semiquantitative evaluation of heats of mixing in the molten silicates. Along the Ab-An join, enthalpies of mixing in the liquid at 1773 K are the same or somewhat more negative than those in the glass at 986 K, whereas along Ab-Di and An-Di, enthalpies of mixing in the liquid are distinctly more positive than in the glass. These differences correlate with excess heat capacities in the liquids suggested by other workers.

Solution calorimetric methods are being developed and applied to hydrous phases, including amphiboles and micas. A systematic study, involving synthesis, x-ray work, IR and Raman spectra, Si and Al NMR, and calorimetry, is underway of aluminum substitution in MgAl biotites.

Calorimetry of glasses along the joins $\text{SiO}_2\text{-NaGaO}_2$ has been completed. The enthalpy of stabilization correlates with differences in bonding between Si-O and $\text{M}^{3+}\text{-O}$ for the series of substitutions $\text{Si}^{++} = \text{Na}^+ + \text{M}^{3+}$ ($\text{M} = \text{Al, B, Ga, Fe}$). Work on glasses containing rare earths, Cr, Ti, and Nd is beginning.

The data and models developed in this work 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: SOUTH DAKOTA SCHOOL OF MINES AND TECHNOLOGY
Rapid City, South Dakota 57701-3995

Grant: DE-FG01-87ER13259

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 1987-88 we continued to attack these problems through studies in two different geologic settings: the Salton Sea geothermal field and granite-pegmatite systems of the Black Hills, South Dakota.

In the Salton Sea geothermal field, scientific drilling into a zone of active metamorphism is providing a unique opportunity to monitor the effects of mineral-fluid equilibria and burial in a well-characterized thermal regime. The fine-grained nature of these samples, however, prevents application of many important petrologic techniques that rely on the modal abundance of different mineral phases. We have circumvented this problem through combined application of whole-rock and mineral chemistry along with the XRD-reference intensity method to determine modal variations. Our results demonstrate that downhole variations in bulk composition, structural ordering in minerals, and mineral chemistry can be directly correlated with changes in mineral assemblage and progress of key mineral-fluid reactions.

In the granite-pegmatite systems of the Black Hills, the production of highly fractionated, volatile-enriched granites occurred at ~2500 Ma and again at ~1700 Ma. The high volatile content of these silicic melts resulted in fluid exsolution during crystallization and characteristic modification of crystal-melt equilibria in addition to widespread chemical interaction between the granitic bodies and their wall rocks. Most notable among these effects are: 1) generation of K, Ba, and Sr-rich pegmatitic segregations, 2) development of anomalous, "kinked" rare-earth element patterns in granite samples, 3) overlapping fractionation trends in successive zones of pegmatites as a result of element communication via a continuous fluid phase, 4) dramatic inter- and intracrystal variations in REE in apatites attributed to the effects of exsolving fluids on element partitioning and/or melt structure, and 5) promotion of textural and chemical segregation within cogenetic bodies of granite and pegmatite.

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

Grant: DE-FG03-87ER13807

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

Person in Charge: K. Aki (213-743-2717)

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 made considerable progress in 1) studying magma chamber under the Valles caldera using teleseismic wave forms, 2) investigating uniqueness problem in seismological delineation of a magma chamber by a combined use of the Gaussian beam method and the Boundary Integral method, 3) developing ray methods for anisotropic, three-dimensionally heterogeneous media for application to VSP data, and 4) interpretation of long-period events observed at the Fenton Hill hot dry rock site, Mt. St. Helens, and Kilauea volcanoes using the fluid-filled crack model.

The above four areas will be our building blocks with which we shall construct the interpretation method for seismology in the continental thermal regime. One of our goals is to develop a computer program for calculating synthetic seismograms for three-dimensionally heterogeneous anisotropic 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-FG03-87ER13601

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

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

We are studying rock physics problems related to crustal processes and the exploration for and production from hydrocarbon reservoirs. Our focus is on laboratory studies of the relationships among pore pressure, stress, mineralogy, deformation, and the acoustic properties in rocks saturated with brine, CO₂, and hydrocarbon.

Anisotropy and borehole breakouts. Using laboratory data on stress induced elastic anisotropy, stress concentrations at the surface of a borehole have been computed. The results imply that the borehole breakout directions can deviate significantly from the minimum tectonic principle stress. These results are used to better determine *in situ* stress conditions.

Attenuation anisotropy. We have numerically investigated wave propagation in linear anelastic media with an anisotropic Q factor. The results reveal how Q anisotropy causes wave energy focusing even in homogeneous media. The results provide means to interpret seismic waves traveling through complex reservoirs.

Velocities in sand/clay mixtures. A model for the effect of clay minerals in unconsolidated sand-clay mixtures on porosity and velocities predicts that the mixture porosity decreases with increasing clay content, to a minimum at clay volume fraction of about 40%, and increases when clay content becomes greater. In contrast, velocity increases with increasing clay content to clay fraction of 40% and decreases when clay volume fraction is greater. The result provides a major improvement for interpreting sonic logs.

CO₂ flooding. P and S wave velocities were measured in the laboratory in sandstones and unconsolidated sand saturated with n-hexadecane both before and after carbon dioxide flooding: CO₂ decreases the compressional wave velocities significantly, while the shear wave velocities are unaffected. The results imply that seismic methods may be used to monitor a CO₂ enhanced oil recovery *in situ*.

Crustal pore pressure. We feel that the depth of free water in the Earth's crust is controlled by the time dependence of crustal porosity, permeability, and pore pressure. The controlling factor is the ratio between porosity reduction rate and permeability, $R = \dot{\phi}/k$. For $R \ll 1$ the crust will gradually drain while pore pressure P_p remains around hydrostatic. If $R \gg 1$ episodic pressure build up and release by natural hydraulic fracturing will take place. Tens to hundreds of P_p cycles are possible, each with duration of 10^3 - 10^5 years; the duration of the entire process would be 10^6 - 10^7 years. Episodic water expulsion may explain the episodic formation of hydrothermal ore deposits, the recurrence of large earthquakes, and the nature of crustal detachment zones.

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, 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 in five weeks of field work this summer. Topographic profiles were surveyed to assist in identifying structures and the magnitude of associated displacement. This work identified four regions and types of deformation: 1) translational block slides on Broken Mountain, 2) arcuate grabens between Broken Mountain and Trident, 3) opening fractures on the flanks of Trident and near Novarupta, and 4) grabens on the crest of the Turtle, a large mound of tephra adjacent to Novarupta dome. 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. Studies of snow slab movement may provide analogues to the apparently shallow block slides on Broken Mountain.

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,
SW Montana and East-Central Idaho and Determination
of Rare Earth Element Abundances in Diagenetic Carbonates

Person in Charge: S. L. Dorobek (409-845-2451)

This is a study of the sedimentologic and diagenetic history of the Mississippian Mission Canyon formation and its stratigraphic equivalents in southwestern Montana and east-central Idaho. Sedimentologic studies will concentrate on documentation of the platform-to-basin transition through the use of detailed logs of measured stratigraphic sections. Definition of facies geometry and thickness distribution may prove useful for future exploration for hydrocarbon reservoirs in these rocks. Additionally, this study will examine the relative effects of sea level fluctuation, regional subsidence, and sedimentation rates and how these parameters influenced overall platform evolution.

Laboratory analyses of intergranular cements, fracture-filling cements, and diagenetic replacement minerals will allow documentation of the diagenetic history of the Mission Canyon formation and its stratigraphic equivalents. Special emphasis will be placed on defining the sources and migration pathways of pore waters involved in diagenesis. Analyses of diagenetic phases will involve standard petrography, cathodoluminescence and epifluorescence petrography, electron microprobe analyses, stable isotope analyses, x-ray diffraction studies, and instrumental neutron activation analyses.

A relatively new approach to this study will be the determination of rare earth element (REE) abundances in various diagenetic phases. Preliminary REE data from the Mission Canyon formation suggest that the REE may be extremely useful indicators of the types of pore fluids involved in diagenesis.

This study will provide important information on a widespread carbonate sequence in the Northern Rockies, which is a proven hydrocarbon reservoir and potable groundwater aquifer in many other parts of the Northern Rockies.

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 exploration and development of sources of geothermal energy associated with buried magma chambers and regions of high heat flow require drilling to depths of up to 10 km at temperatures ranging from ambient surface temperatures to those of partial melting. Successful drilling to these depths within steepened geothermal gradients depends upon rock strengths sufficient to support the stress fields generated around the borehole at depth. Previous experimental studies, directed towards determining the strengths and ductilities of rocks under conditions appropriate to the borehole environment, have provided useful constraints on the conditions for which borehole failure may be anticipated for massive, relatively isotropic rocks. However, predictions of borehole stability in such strongly foliated rocks as slates, schists, and gneisses cannot be made using isotropic failure envelopes.

We have initiated a study of the mechanical behavior of foliated rocks using anisotropic yield criteria with the view of predicting their behavior in the stress field surrounding a borehole at temperatures and pressures representative of the borehole environment. Our approach is to perform a suite of experiments designed to determine the full anisotropy of yielding for granite (presumed to be nearly isotropic), a layered gneiss, and a strongly foliated quartz-mica schist, followed by modeling their behavior in the vicinity of a borehole. Within the first year of the project, progress has been made in three areas: the experimental determination of an anisotropic yield envelope for the layered gneiss, theoretical treatment of the results, and characterization of foliations in and surrounding buried magma bodies. Specific tasks completed to date are as follows:

1. All of the starting materials for the three-year project have been collected. Included in our collection are relatively fine-grained, fresh, oriented blocks of schist from the Partridge formation, Four-Mile gneiss, and Westerly granite. The schist and gneiss exhibit well-developed foliations as well as lineations. The Westerly granite blocks have been oriented with respect to the principal quarrying orientations, the rift, grain, and hardway.
2. A suite of samples has been collected from an exposed granite stock and surrounding country rocks in order to evaluate the strengths and distribution of fabrics that may be encountered while drilling. These fabrics appear to be directly related to the forceful emplacement of the pluton.
3. The literature on the mechanics of intrusion has been reviewed with regard to strain gradients and foliation development associated with diapiric flow. This information will be used to evaluate the effect of varying fabrics on yield criteria within and surrounding magma chambers.
4. Forty-five successful experiments have been performed on samples of gneiss cored along six different orientations at temperatures ranging from 25 to 700°C. These experiments include extension tests, unconfined compression tests, and compression tests at $P_c = 100$ to 400 MPa.
5. Theoretical yield conditions for anisotropic materials have been reviewed and are currently being used to fit the experimental results for Four-Mile gneiss. The anisotropic constitutive parameters may be determined by solving ten simultaneous, nonlinear equations. Methods for solving these equations are currently being developed.

Grantee: TEXAS A&M UNIVERSITY
Department of Geophysics and Center for Tectonophysics
College Station, Texas 77843

Grant: DE-FG05-88ER13165

Title: Stress-Induced Seismic Anisotropy

Person in Charge: R. L. Carlson (409-845-1371)

Particle motions detected on arrays of 3-component digital seismographs and on borehole instruments used in vertical seismic profiling and oblique seismic experiments indicate *in situ* elastic anisotropy. The observed anisotropy is thought to arise from alignments of cracks that, in turn, are caused by tectonic stresses. Such interpretations are supported by theoretical and numerical models and by a few experiments conducted at low stress levels, but the phenomenon of stress-induced elastic anisotropy in rocks has not been thoroughly investigated.

We are undertaking a series of laboratory experiments with the aim of ascertaining the effects of deviatoric stress on rocks containing natural microcracks. More specifically, our objectives are: 1) to relate the dynamic elastic stiffness tensor to the stress tensor for different stress fields, 2) to determine how the elastic stiffness coefficients are affected by the level of stress, and 3) to replicate field observations in the laboratory under known stress conditions.

The materials used in these experiments will be Westerly granite and Maryland diabase. Specimens will be machined to form cubes 15 cm on a side, and suitably oriented P- and S-wave ceramic transducers will be mounted on the faces, edges, and corners of the cubes. Dynamic elastic constants will be calculated from measured P- and S-wave velocities. Stresses up to 40 MPa will be applied using flat jacks. The free faces of the cubes will be instrumented with strain gauges to monitor the uniformity of the applied stresses. Replication of field experiments will be done using transducers mounted on the free faces of the specimens.

We are in the process of refining the experimental design and assembling the apparatus, some of which must be fabricated. Samples of Westerly granite will be used in the experiments and characterized immediately thereafter.

Grantee: UNIVERSITY OF TEXAS AT ARLINGTON
Department of Geology
Arlington, Texas 76019

Grant: DE-FG05-87ER13795

Title: Isotopic and Trace Element Characteristics of Rhyolites
from the Valles Caldera, New Mexico: Post-Eruptive
Alteration, Petrogenesis, and Applications to Hydrothermal
Alteration and Emplacement Mechanisms

Person in Charge: J. A. Wolff (817-273-2989) and S. Self (817-273-2978)

The two Bandelier tuffs, erupted at 1.46 and 1.12 Ma, represent the climatic phase of rhyolitic magmatism during development of the Jemez Mountains volcanic field. This project is a detailed geochemical and petrologic study of the Bandelier tuffs and associated minor rhyolite eruptives, with the dual aim of understanding rhyolite magma genesis beneath large continental silicic caldera systems and to provide a detailed geochemical data base on fresh rhyolitic Bandelier glassy ash and pumice for comparison with equivalent hydrothermally altered material sampled in CSDP coreholes VC-2A and VC-2B.

The Bandelier tuffs and associated rhyolites consist largely of two crustal components mixed in varying proportions. Although the local crustal candidate compositions have not yet been identified, these two components have the general characteristics of upper crust and lower crust, respectively. A pool of melt dominated by the upper crustal component began to form beneath the central Jemez Mountains at 2-3 Ma. Eruptions from this magma body produced the two small-volume San Diego Canyon ignimbrites exposed in the southwest Jemez Mountains. At some time prior to the eruption of the large-volume (400 km³) Lower Bandelier tuff (LBT), a proportion of the lower crustal component was mixed into the system. Lower crustal involvement increased steadily through the LBT, intra-Bandelier Cerro Toledo tuffs, and reached a maximum in the Upper Bandelier tuff (UBT) magma. Following the UBT eruption at 1.12 Ma, a new magmatic cycle began, again dominated by upper crustal melts. The Valles caldera is believed to currently be in a condition where transient, small-volume rhyolite magma bodies are generated by the periodic injection of mafic magma into the hot column of rock extending beneath the Jemez Mountains probably to the base of the crust.

Previous models of silicic magma chambers have not considered how the geochemical evolution of a system may in part be controlled by the drawdown mechanics of repeated eruptions. Variability in the proportions of the two components within individual Bandelier pumice fragments indicates that eruptive drawdown may have been the principal mechanism by which upper-crustal and lower-crustal melts became mixed during the lifetime of the Bandelier magma chamber.

Grantee: UNIVERSITY OF TULSA
Tulsa, Oklahoma 74104

Grant: DE-FG05-87ER13417

Title: Stability of Natural Gas in the Deep Subsurface

Person in Charge: C. Barker and N. Takach (918-592-6000, ext. 2517)

Investigations of the stability of methane and the composition of deep gas have continued using a combined experimental and theoretical approach. Many important geological processes with significance for energy systems (such as ultra deep gas, hydrothermal) occur in regions that are not currently accessible by drilling. Samples of the gases may be trapped in primary fluid inclusions in minerals and brought to the surface by uplift and erosion. Past experience in analyzing gases in individual fluid inclusions has been used to build a "second generation" system that has a pair of mass spectrometers operating in parallel under microcomputer control. Data are now transferred to 9-track tape for post-acquisition processing on a Sun 3/280. This provides essentially unlimited time for data reduction--unlike the previous system where much of the processing was done within the time constraints of a bursting inclusion. Even at the very fast scan rates being used, peak shape is good and is currently defined by 7 or 8 data points per mass unit. Calibration shows that reproducibility with the new system is excellent. Unlike the previous analytical system there is no fixed number of inclusions that can be analyzed and the number will depend on the selection criteria used. Since all of the data are now stored on tape they can be re-processed at any time with amended selection criteria.

Thermodynamic calculations of deep gas compositions have continued and the program has been rewritten in C language and restructured to run on a microcomputer (PC) with math co-processor, hard disc, and 640 K memory. This should improve the utility of the program by making it more easily transported to other users.

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 (703-648-6785)

This workshop is being funded jointly by NSF, NASA, and DOE, and supported operationally by the USGS, and will be held February 12-15, 1989 at the Asilomar Conference Center. The conveners are John Rundle, Sandia National Laboratories; Donald Turcotte, Cornell University; and Kevin Burke, Lunar and Planetary Institute. The workshop is to bring together earth scientists, physicists, and mathematicians to discuss new approaches to problem-related earthquakes and crustal dynamics.

During the preceding decade, the general subject area of chaotic behavior in complicated dynamical systems has received a great deal of attention in a variety of fundamental and applied scientific disciplines. Closely related subjects are fractals, the phase transition analogy, and the renormalization group approach. The recognition of the existence of deterministic chaos raises important questions about the role of causality, chance, and the prospects for deterministic prediction in physical processes. Only a small number of earth scientists are actively working in these areas, due to a general ignorance of how to proceed. Therefore, the conveners and the program committee feel that a small workshop-format conference would be invaluable in stimulating interest and developing expertise in this area.

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)

The Sulphur Springs area, with vigorously active surface thermal phenomena and widespread, intense, surficial alteration, is the most obvious target for geothermal and scientific drilling in the Valles caldera of north-central New Mexico. Late in 1986, the first scientific core hole in this area, VC-2A, penetrated 528 m into the Sulphur Springs hydrothermal system, encountering first a high-level, vapor-dominated cap, then at greater depths a liquid-dominated, neutral-chloride geothermal reservoir. VC-2A penetrated the most pervasively and intensely altered rocks yet discovered in the caldera. Within 25 m of the present ground surface, the core hole began intersecting a unique occurrence of poorly crystalline molybdenite. Clay mineral geothermometry and fluid-inclusion evidence show that even though presently within the high-level, low-temperature vapor cap at Sulphur Springs, the molybdenite and associated alteration and vein-filling phases were deposited from water at temperatures near 200°C; the vapor cap has clearly evolved from a liquid-dominated precursor.

VC-2B, a companion to VC-2A, will penetrate more deeply into the Sulphur Springs system and should provide evidence to clarify how the system has evolved since inception. The core hole could drill through the high-temperature liquid-dominated portion of the system into a hypothetical, subjacent, impermeable zone of conductive heat transfer. VC-2B should provide the opportunity to obtain measurements of temperatures, pressures, and fluid compositions through a large vertical extent in an active system in an instant of geologic time--values impossible to obtain from study of fossil systems alone. These measurements should improve our ability to model both active geothermal systems and ancient systems that formed a variety of epithermal ores.

In collaboration with Los Alamos National Laboratory and the Geoscience Research Drilling Office of Sandia National Laboratories, UURI will complete baseline scientific studies in support of detailed research to follow and help manage the project to maximize its scientific yield.

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 (703-961-5580)

The proposed research consists of three interrelated studies. First, we gather zircons with varying U-Th abundances of different ages to insure variable degrees of radiation damage in the samples. We also synthesize zircons with various elements substituting for Zr^{4+} in the structure. These two sets of samples (natural and synthetic) will be fully characterized (physically, chemically, and isotopically) prior to hydrothermal studies. Such a controlled sample selection technique has not been utilized in considering the retention of radionuclides and radiogenic daughter products under hydrothermal conditions.

After complete characterization of the starting materials, we will investigate the mobility of U-Pb (Th, Hf, Dy, P, Y) under low temperature-pressure hydrothermal conditions as a function of α -damage (synthetic materials must be regarded as equivalent to natural zircons being formed at the present time), P-T conditions of the experiments, and fluid composition. The retention of radiogenic lead has previously been cited as a possible criterion by which the retentiveness of various solid waste forms could be evaluated. Pb or U loss trends in natural zircons with known radiation damage, as well as from synthetic crystals, will add to our understanding of the complex interplay between α -dosage, crystal chemistry, and the loss of radioisotopes in hydrothermal environments. Earlier studies by Ewing et al. (1982) and Tole (1984) at low temperatures ($<100^{\circ}C$) showed that zircon solubility was enhanced in samples with higher α -dosages. Unlike previous studies, we examine zircon stability in a wide range of fluid compositions, including fluids chemically buffered by granitic phase assemblages. Therefore, our data will represent a reasonable approximation of zircon stability in fluids expected to be in equilibrium with granitic waste repository sites.

The third aspect of our research will be to document and model the initiation and propagation of microfractures associated with metamictization. These fractures allow the penetration of fluids into the crystal, whereby solution reactions become more effective than the diffusion-controlled transfer of cations. Because of the inhomogeneity of uranium-rich domains in zircons, the metamict microdomains that undergo anisotropic volume expansion will generate tensile fractures in the crystalline material. Our research program will use transmission electron microscopy (TEM) and scanning electron microscopy (SEM) in conjunction with x-ray emission maps to characterize the orientation and density of dislocations and fractures and their relationship to the α -dosage and chemical heterogeneities.

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)

Our objective is to interpret magnetotelluric (MT) data when the electrical properties of the Earth vary laterally as well as vertically. Since most real MT data are significantly affected by lateral structure, understanding the multi-dimensional inverse problem is critical to reliable use of MT in exploring for thermal and hydrocarbon energy resources. Our approach uses the fact that the Frechet derivative of MT data with respect to vertical conductivity structure is closely related in the one and higher dimensional cases. They are the same except that the electric field that must be used in calculating the Frechet derivative is the true electric field existing in the laterally varying structure. This suggests an efficient iterative inversion scheme. At each step, the data at each site are inverted as though they were one-dimensional, except that the Frechet derivatives use the electric field from a forward calculation using a laterally varying model based on all the one-dimensional inversions at the previous step. This process should converge to a laterally varying model that fits the data. Understanding this convergence and subsequent appraisal of the model are our major tasks.

We have developed a very stable one-dimensional inversion that produces models that have the least possible structure. The minimization of structure is important as it eliminates spurious structures whose significance may be difficult to assess. We have adapted the one-dimensional inversion code to allow minimization of a norm of the laplacian of two- and three-dimensional models. We have embedded the adapted code within a main program for inverting two-dimensional data. Initial tests inverting two-dimensional data show success in finding models that fit the data and resemble the structures that produced the data.

We have written a two-dimensional (finite difference) forward modeling program that is used at each iteration of the two-dimensional inversion program to find the electric and magnetic fields that would be induced in the conductivity model of that iteration. We plan to modify this to take advantage of new highly efficient iterative methods (incomplete factorization) of solving the resultant equation for the forward problem.

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)

The potential of subcooled boiling (i.e., boiling in which vapor rapidly condenses upon buoyant rise or forceful injection into subcooled liquid) in volcanic hydrothermal systems for generating harmonic tremor will be studied. The objectives of the research are: 1) to determine whether or not subcooled hydrothermal boiling could generate harmonic tremor, and 2) to gain insight into the fundamental characteristics of fluid vibrations and seismicity produced by collapsing steam bubbles during subcooled hydrothermal boiling.

A preliminary analysis suggests that subcooled boiling occurring at condensation heat transfer rates of 10^{-3} MW - 10^2 MW in ground water flow channels with lengths of the order of 10 m - 1000 m could generate sufficient seismic power at typical dominant harmonic tremor frequencies to account for typically observed tremor amplitudes. A number of assumptions were made in this analysis, some of which can be tested directly by experimentation. We will conduct experimental simulations of subcooled hydrothermal boiling in a ground water flow channel, both in the laboratory and in the field. The simulations will be done by injecting steam into subcooled water contained in a small vertical pipe (lab experiment) and in a deep water well (field experiment). Measurement and analysis of the experimental fluid- and ground-vibration data will allow us to assess the validity of four specific assumptions made in our preliminary analysis. The results should lead us to a definitive answer as to whether or not subcooled hydrothermal boiling could generate harmonic tremor, a question that has not previously received attention beyond mere speculation. In addition, the experimental work will provide us with heretofore unavailable information on the fundamental characteristics of a possible source of seismicity in two-phase geothermal systems.

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

Grant: DE-FG06-87ER13796

Title: Three-Dimensional Computer Analysis and Modeling of
Structural Geologic Problems

Person in Charge: R. Thiessen (509-335-3009), J. Eliason, and K. Johnson

The future of structural geologic analysis and three-dimensional structural modeling is now developing rapidly as a result of the availability of advanced digital systems. This research has taken a major step forward since 1982 when Washington State University (WSU) and Battelle Pacific Northwest Laboratory (PNL) initiated joint research directed toward development of quantitative geologic spatial analysis (GSA) techniques. The GSA techniques are being designed to provide three-dimensional models of fault, fracture, and lithologic contact orientations and locations in space. These geometries are based on analysis of digital data bases developed from topography, earthquake foci, lineaments from satellite imagery and radar data bases, faults and joints observed in the field and on seismic profiles, and gravity, magnetics, and borehole data. The GSA programs use digital analysis techniques that determine if structures in three-dimensional space are controlled by the same planar structure and are, therefore, coplanar. The unique power of GSA is this three-dimensionality; older techniques looked at orientations of structures or their surface traces, but rarely both. In addition, most of the GSA techniques will be computer-automated eliminating the need for analysis of structures by human operators.

The GSA methods will provide data for quantitative analyses of structural and tectonic domains, stress fields, and physical characteristics of rock units. The DOE needs these geologic data now to assess many of the current mission requirements for waste management, facility siting, national security, and energy resource exploration and assessment. WSU and PNL are currently working with staff at DOE's Morgantown Energy Technology Center who have shown that fracture systems strongly affect hydrocarbon production by enhancing permeabilities in reservoir rocks. The techniques are also being evaluated for detection and estimation of yields of underground nuclear tests. Other DOE programs including waste management, facility siting, and energy resource exploration and assessment have expressed interest in utilizing the technology in its present infant state.

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

Grant: DE-FG02-87ER13184

Title: Thermal Stress Microfracturing of Crystalline and
Sedimentary Rock

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

High temperatures in crustal rocks are associated with energy technologies such as nuclear waste disposal, thermal recovery of hydrocarbons, and geothermal energy production. High temperatures are also associated with natural geologic processes such as magma injection and hydrothermal circulation. The high temperatures are accompanied by large thermal stresses and physical property changes within the rock mass.

The goal of the research program is to understand mechanisms of thermal cracking in granitic rocks. The research plan includes development of a theoretical understanding of cracking due to thermal stresses, laboratory work to characterize crack strain in rocks thermally stressed under different conditions (including natural thermal histories), and microscopic work to count and catalog crack occurrences.

Results have been integrated from several experimental techniques to characterize the behavior of granite during heating. We count acoustic emissions and measure compressional wave velocities while a sample is heated. After a heating cycle, we measure crack porosity and crack compressibility. We count the cracks under an SEM, sorting them by grain boundary and intragranular types and by mineral pair occurrence. Most newly created thermal cracks close at pressures between 20 and 40 MPa. The acoustic emission counts in Westerly granite during heating show one or more peaks of activity as a function of temperature, with more peaks at lower pressures. The curves of total acoustic emission counts can be fit by summing one to three Gaussian density functions.

Fracture mechanical modeling, based on two-dimensional, four-grain array embedded in an infinite, elastic medium, has been undertaken recently to help quantify the cracking mechanism in thermally cycled granite. Thermal stresses arise along grain boundaries due to the differences in thermal expansion properties of each grain relative to the surrounding medium. The numerical model has the potential to predict cracking events as a function of temperature and confining pressure.

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

Grant: DE-FG02-86ER13593

Title: Deformation and Stress Modeling of Recent Magmatic
Tectonics at Long Valley, California

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

Ground deformation and seismicity strongly suggest the existence of magma beneath the central part of the Long Valley caldera. Deformations from 1975 to the present have been modeled by 0.15 to 0.20 cubic kilometers of magma injected into a chamber 5 to 10 km beneath the resurgent dome. Due to its highly non-unique nature, inversion of surface deformation at Long Valley has a very limited power to resolve the magma source geometry.

The Magma Energy Technology Program plans to drill a 6-km deep hole over the top of the resurgent dome of the caldera. Our objective is to study the stress field to analyze borehole stability and to guide and interpret stress measurements with depth near the center of the resurgent dome, which may permit discrimination between various models of the magma chamber. We calculated the stress field due to magma inflation for a spherical shape and for a prolate ellipsoid, such that both shapes fit the 1975 - 1982 uplift data reasonably well. In the region directly above the source, the horizontal stress for the prolate ellipsoid is about one order of magnitude higher than for the spherical source that gives the same uplift.

The normal compressive stress for a 5-km radius source is much higher than the lithostatic stress near the top of the magma chamber. Such large normal stress will mean large shear stresses around the boundary of the deep hole when it approaches the top of the magma chamber. The high shear stresses may result in borehole breakouts and borehole stability problems. The stress gradient is not very sensitive to the aspect ratio of the magma chamber nor to the amount of injected magma.

In addition, the strike-slip South Moat fault may have a quite strong effect on *in situ* stress measurements in the deep hole since the length of the fault is no less than its distance to the well. The South Moat fault is calculated to affect hydrofracturing breakdown pressures by as much as 10 MPa at a depth of two kilometers and an assumed ratio of two for the principal horizontal stresses.

Grantee: WOODS HOLE OCEANOGRAPHIC INSTITUTION
Department of Chemistry
Woods Hole, Massachusetts 02543

Grant: DE-FG02-88ER13466

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.

Detailed C_{15+} profiles for the Alaskan North Slope Ikpikpuk and Seabee wells have been completed. Both wells become overmature with respect to oil and gas generation in the deepest sections. Thus, the sterane and hopane biomarker signals--widely used in the petroleum industry to determine degree of oil maturation as well as for source-reservoir correlations in less mature sediments--are not detectable by normal (low resolution) GCMS mass scans due to very large interference by other molecules. Therefore, chemical ionization mass spectrometry (CIMS) was used to determine sterane compositions in these intervals because it is very specific for the compounds of interest. In spite of the fairly noisy signal because of the low concentrations, the maturation profiles obtained for the mono-/tri-aromatic steranes are consistent with those obtained from the methylphenanthrenes, which correlate fairly well with vitrinite reflectance within fine-grained (source) sections. To our knowledge, CIMS results have not previously been described for this analysis. MS-MS or high resolution MS, both requiring much more expensive instrumentation than that utilized here, are the techniques applied in other laboratories to eliminate interference from co-eluting compounds during the analysis.

Geochemical work was also completed on the Tiglukpuk well to the south in the Brooks Mountain Range (in collaborative work with Dr. Ken Peters of Chevron). Vitrinite reflectance profiles indicate that up to 18,000 ft of erosion may have occurred at this site in an area where almost no geochemical work has been reported for these highly overmature sediments.

The remaining pyrolyzable kerogen yields of C_1 , C_2 , and C_3 in most of the North Slope sediments indicate that dry gas (C_1) and C_2 (but not C_3) generating potential remains up to very high maturities ($R_o = 4.3 - 4.8\%$). Possibly some of this is derived from anthracite coals reported in some of the deepest section in the Inigok well. In addition, initial data from a new pyrolysis technique, thermogravimetric fourier transform infrared spectroscopy, suggest that following methane evolution curves provides a new method for determining maturities of both whole rocks (from the Alaskan Seabee well) and from a series of isolated kerogens up to an R_o of 3.8% (somewhat above the limit of 3.2% generally thought to represent the end of the methane generation zone). Thus, both of these methods appear to provide means for examining bitumen maturities in the gas generation zone in much the same way that the oil generation zone is currently routinely defined using pyrolysis techniques.

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

Grant: DE-FG02-87ER13805

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)

The solution of two problems is paramount in delineating liquid hydrocarbon targets. First, the maturation history of potential oil source rocks must be discerned. Factors that affect the maturation history include the temporal variation of terrestrial heat flow, sediment thermal properties, the burial history of the sediments, and the chemical kinetic properties of the hydrocarbon source rock. Second, the potential for reservoirs to accept the expelled hydrocarbons must be estimated. Factors that affect the ability of a reservoir to become charged with hydrocarbons include the depositional character of the reservoir rocks, early and late diagenesis of the reservoir rock, and the timing of intense diagenesis in relation to hydrocarbon expulsion from oil source rocks.

We are evaluating many of these critical factors that affect the delineation of liquid hydrocarbon targets. In general, we will consider three foreland basins of Wyoming (Bighorn, Powder River, and Wind River) in order to supply geologic constraints for our models. We will then develop and integrate thermal, maturation, and diagenetic models. Using our developed models constrained by field and laboratory data, we will construct a general scenario for the temporal maturation of liquid hydrocarbons in relation to enhanced reservoir porosity for Wyoming foreland basins.

Grantee: YALE UNIVERSITY
Department of Geology & Geophysics
New Haven, Connecticut 06511

Grant: DE-FG02-84ER10455

Title: Opening Mode Crack Growth in Rock

Person in Charge: R. B. Gordon (203-432-3125)

The microstructural determinants of the tensile fracture characteristics of rock are being investigated by laboratory methods to help with the interpretation of fractures in rock in the field, particularly where the passage of fluids is of interest. Measurements of fracture energies have been made on samples of rocks having a wide range of fracture characteristics. The geometrical characteristics of crack growth have been observed by following an advancing crack with an optical microscope while a test specimen is loaded in a testing machine. We are now studying how the fracture energy and the distance that a crack must advance before attaining steady state propagation are determined by the microstructure of the rock and the mechanical properties of its constituent minerals. The focus of this part of the research is now on the mechanisms of energy dissipation that are active in the vicinity of the crack tip.

Experiments are being conducted to investigate the relation between the rebound hardness of rock and microstructure. The amount of mechanical energy dissipated in the impact of an indenter with rock surfaces is measured. The structural changes in the rock produced by the indentation process are also observed optically. From these observations the amount of impact energy used in the formation of cracks and in plastic deformation is estimated. The results show that sliding friction on existing interfaces within the rock is the principal mechanism of energy dissipation and that this process is sensitive to the formation of weathering products within the rock structure. The results are used to interpret the large changes in hardness that occur in the weathering of the crystalline 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>
ANL	\$ 140	\$ 240	\$ 310	\$ 330	\$ 330	\$ 360	\$ 360	\$ 355	\$ 340	\$ 335
BNL	—	—	—	—	—	—	—	—	—	50
LANL	1,084	1,420	1,500	1,375	1,684	2,343	2,289	2,263	2,603	2,868
LBL	735	995	1,075	1,180	1,405	1,485	1,596	1,632	2,162	2,100
LLNL	630	910	1,060	1,110	1,280	1,815	1,898	1,521	1,837	1,732
ORNL	240	280	380	430	430	470	480	492	690	785
PNL	450	565	580	520	520	578	595	605	725	850
SNL/A	800	1,165	1,310	1,546	1,682	2,087	1,861	2,256	2,462	2,711
<u>ON-SITE TOTALS</u>	<u>\$4,079</u>	<u>\$5,575</u>	<u>\$ 6,215</u>	<u>\$ 6,491</u>	<u>\$ 7,331</u>	<u>\$ 9,138</u>	<u>\$ 9,079</u>	<u>\$ 9,350</u>	<u>\$10,819</u>	<u>\$11,431</u>
<u>TOTAL OFF-SITE</u>	<u>\$1,895</u>	<u>\$2,509</u>	<u>\$ 3,030</u>	<u>\$ 3,141</u>	<u>\$ 4,523</u>	<u>\$ 3,309</u>	<u>\$ 4,253</u>	<u>\$ 3,507</u>	<u>\$ 4,449</u>	<u>\$ 4,868</u>
<u>TOTAL OPERATING</u>	<u>\$5,974</u>	<u>\$8,084</u>	<u>\$ 9,245</u>	<u>\$ 9,632</u>	<u>\$11,854</u>	<u>\$12,447</u>	<u>\$13,339</u>	<u>\$12,857</u>	<u>\$15,268</u>	<u>\$16,299</u>
<u>TOTAL EQUIPMENT</u>	<u>\$ 355</u>	<u>\$ 560</u>	<u>\$ 923</u>	<u>\$ 900</u>	<u>\$ 890</u>	<u>\$ 960</u>	<u>\$ 1,100</u>	<u>\$ 1,094</u>	<u>\$ 1,150</u>	<u>\$ 1,150</u>
<u>TOTAL GEOSCIENCES</u>	<u>\$6,329</u>	<u>\$8,644</u>	<u>\$10,168</u>	<u>\$10,532</u>	<u>\$12,744</u>	<u>\$13,407</u>	<u>\$14,439</u>	<u>\$13,951</u>	<u>\$16,418</u>	<u>\$17,449</u>

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(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/ALASKA (LEE)	\$ 85	\$ 84	\$108	\$113	\$117	\$120	\$126	\$126	\$128	\$140
U/ALASKA (PULPAU)	113	87	70	—	—	—	—	—	—	—
U/ARIZONA (HILL)	—	91	96	99	101	90	121	—	101	103
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 (HERMANCIE)	95	140	164	165	333	—	166	—	150	150
*CAL TECH (AHRENS)	—	—	—	—	72	81	160	—	150	100
CAL TECH (STOLPER)	—	—	—	—	—	—	50	98	—	78
CAL TECH (WASSERBURG)	—	—	—	—	—	—	—	—	—	200
U/CALIFORNIA-B (HELGESON)	—	—	—	—	204	—	120	120	135	116
U/CALIFORNIA-B (REYNOLDS)	127	168	144	150	165	196	233	200	200	210
U/CALIFORNIA-D (Mac GREGOR)	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 (WARREN)	103	107	121	NFX	—	—	—	—	—	—
*U/CALIFORNIA-R (Mc KIBBEN)	—	—	—	—	—	—	50	—	40	—
U/CALIFORNIA-SD (CHAVE)	—	—	—	—	—	—	—	—	120	—
U/CALIFORNIA-SD (CRAIG)	—	—	—	—	—	35	41	41	42	35
U/CHICAGO (ANDERSON)	—	54	NFX	38	98	NFX	46	—	—	—
U/COLORADO-B (SPETZLER)	—	—	—	—	—	—	—	—	95	87
COLO SCH MINES (CROSS)	—	—	—	—	—	—	—	—	—	10
COLUMBIA U (ENGELDER)	100	140	150	156	289	—	150	75	—	—
COLUMBIA U (TABER)	274	312	318	318	337	359	360	360	360	360
COLUMBIA U (WALKER)	—	—	—	—	—	73	79	106	—	85
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	—
HEADQUARTERS SERVICES	—	—	—	6	1	3	15	5	3	3
INDIANA (HAYES)	—	—	—	—	—	—	—	—	—	186

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<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>
LOUISIANA STATE (FERRELL)	—	—	—	—	—	—	—	—	\$ 60	\$ 59
U/MARYLAND (VALETTE-SILVER)	—	—	—	—	—	—	43	—	NFX	—
U/MINNESOTA (JOHNSON)	—	—	68	57	NFX	—	—	—	—	—
MIT (AKI)	142	152	160	151	158	147	—	—	—	—
MIT (SIMMONS)	100	90	100	106	106	110	80	80	—	—
MIT (TOKSOZ)	—	—	—	—	—	—	—	142	—	113
*MICHIGAN STATE (VOGEL)	—	—	—	—	—	—	31	NFX	34	—
*MICHIGAN TECH (McDOWELL)	—	—	—	—	—	—	50	—	—	—
MONTANA TECH., BU. MINES & TECH. (BARTHOLOMEW)	—	—	—	—	—	—	—	—	—	8
NAS/NRC (HART)	44	116	168	282	—	200	187	124	202	132
NATL CTR ATM RES (HERRING)	—	—	—	—	—	—	—	—	10	—
28TH INT'L GEOL CONGRESS (NSF) (WRIGHT)	—	—	—	—	—	—	—	—	200	—
NAS/NRC (CORELL)	—	—	—	—	—	—	—	—	—	5
*U/NEVEDA (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
SUNY-A (DEWEY)	—	—	86	—	—	—	—	—	—	—
SUNY-A (HARRISON)	—	—	—	39	136	—	58	60	54	52
SUNY-P (WOLOSZ)	—	—	—	—	—	—	—	—	72	—
SUNY-SB (HANSON)	—	—	—	—	112	118	120	120	128	128
SUNY-SB (PAPIKE)	51	59	65	—	—	—	—	—	—	—
U/N. CAROLINA (GLAZNER)	—	—	—	—	—	—	38	39	—	35
OHIO STATE UNIV (ADLER)	—	—	—	—	—	—	—	—	50	52
*U/OKLAHOMA (PHILP)	—	—	—	—	—	—	—	28	—	—
U/OKLAHOMA (PHILP)	—	—	—	—	—	—	84	88	106	110
U/OREGON (WEIL)	—	—	—	—	103	94	—	—	—	—
OREGON STATE (FEHLER)	—	—	—	38	—	—	—	—	—	—
PENN STATE (MARTIN)	—	62	83	NFX	—	—	—	—	—	—
PENN STATE (GIVEN)	—	—	—	—	—	100	—	NFX	—	—
PURDUE UNIV (HINZE)	—	—	—	—	—	—	—	—	8	—
PRINCETON U (NAVROTSKY)	—	—	—	—	—	—	100	—	85	120
RPI (FRIEDMAN)	—	—	91	99	150	—	—	—	—	—
RICE (AVE LALLEMENT)	—	—	—	—	120	121	—	—	—	—

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

<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>
S. DAKOTA SCH. M&T (PAPIKE)	—	—	—	67	100	130	150	99	100	\$ 105
*U/S. CALIFORNIA (AKI)	—	—	—	—	—	—	150	150	155	159
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
STANFORD U PARKS)	—	—	—	57	56	56	—	—	—	—
*STANFORD U (POLLARD)	—	—	—	—	—	—	39	42	44	70
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 (DOROBEK)	—	—	—	—	—	—	—	—	52	55
TEXAS A&M (FRIEDMAN)	63	208	202	200	201	93	100	194	—	—
TEXAS A&M (GILBERT)	—	—	—	—	—	—	—	98	88	101
TEXAS A&M (KRONENBERG)	—	—	—	—	—	—	—	—	117	156
U/TULSA (BARKER)	60	NFX	75	71	75	80	80	81	133	—
USGS (HAAS)	54	—	—	—	—	—	—	—	—	—
USGS (MORGAN)	—	—	—	—	—	—	—	—	35	—
USGS (WESSON)	—	—	—	—	—	—	—	—	—	6
*UURI (NEILSON)	—	—	—	—	—	—	—	114	—	—
*UURI (HULEN)	—	—	—	—	—	—	—	—	—	125
VPI & SU (SINHA)	—	—	—	—	—	—	—	—	—	82
U/WASHINGTON (BOOKER)	—	—	—	—	—	—	—	27	30	—
U/WASHINGTON (MALONE)	—	—	—	—	—	—	—	—	—	32
U/WISCONSIN (WANG)	—	57	38	—	—	48	52	97	84	87
U/WYOMING (SURDAM)	—	—	—	—	—	—	—	—	65	65
WASHINGTON STATE UNIV (THIESSEN)	—	—	—	—	—	—	—	—	103	—
WOODS HOLE (WHELAN/FARRINGTON)	—	—	—	—	—	—	223	223	226	238
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
OFF—SITE TOTALS:	\$1,895	\$2,509	\$3,030	\$3,141	\$4,523	\$3,309	\$4,260	\$3,507	\$4,453	\$4,868

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