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Report of a Workshop on
Physics and Chemistry of Earth Materials

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The report concludes that an enhanced effort of earth materials research is necessary to advance our understanding of the processes that shape our planet. In support of such an effort, there are new classes of experiments, new levels of analytical sensitivity and precision, and new levels of theory that are now appicable in understanding the physical and chemical properties of geological materials. The application of these capabilities involve the need to upgrade and make greater use of existing facilities as well as the development of new techniques. A concomitant need is for a sample program involving their collection, synthesis, distribution, and analysis.

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EARTH MATERIALS RESEARCH

Report of a Workshop on
Physics and Chemistry of Earth Materials

Committee on Physics and Chemistry of Earth Materials
Board on Earth Sciences
Commission on Physical Sciences, Mathematics, and Resources
National Research Council

National Academy Press
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NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Preface

The initiative for this project began at the May 1984 meeting of the American Geophysical Union (AGU) in Cincinnati when several people met to express their concern about the lack of coordination among geoscientists interested in the area of geological materials science. The idea of a workshop was proposed and open discussions were held at the November 1984 meeting of the Geological Society of America in Reno and the December 1984 meeting of the AGU in San Francisco to discuss the state of geological materials science and the possibility of organizing a workshop under the auspices of the National Research Council. Those attending the open sessions were invited to provide written input on important problems and objectives in earth materials research to the Board on Earth Sciences; 32 responses were received, all of which proved to be valuable in the planning and execution of the workshop.

The Board on Earth Sciences appointed an ad hoc group to refine further the objectives and desirability of such a workshop. This group met informally at the spring 1985 AGU meeting, in Baltimore, and its discussions led to the initiation of the project by the Board on Earth Sciences. Once the project was approved by the Governing Board of the National Research Council, the steering committee was appointed. The steering committee then developed the plans and goals of the workshop and its report.

The initial purpose of the workshop was to bring together geoscientists working in different aspects of geological materials science for discussion of how our national effort should be organized to include the following:

1. exploit advances made in the study of materials by physicists, chemists, and materials scientists,
2. make better use of the facilities we now have,
3. develop major goals and initiatives for research,
4. foster collaborative research,
5. discuss the creation and utilization of data bases on materials properties,
6. evaluate the quality and quantity of human resources for staffing programs in earth materials research, and
7. suggest a plan for implementing the recommendations of the workshop.

Of these items, manpower (number 6) was considered to be an important concern but beyond the scope of the main objectives of the workshop; in addition, facts about such human resources were not available.

The workshop was held on April 24-26, 1986, in Airlie, Virginia. In addition to plenary workshop sessions there were several sessions that were discipline related. Four subgroups were formed, one each for the broadly defined disciplines of geochemistry, petrology, mineral physics, and rock physics. Interactions between these various subgroups were encouraged at the working level in addition to the interaction that took place at the plenary sessions. The products of these subgroups are included as appendixes to this report. The main body of the report was written by the steering committee based on these subgroup products along with discussions that occurred at the workshop.

Contents

Executive Summary

A national effort of earth materials research at a fundamental physical/chemical level is realistic and timely. This is driven by the need to develop a better understanding of the Earth and its dynamics, including the major processes that control the distribution and transport of materials in the Earth's crust and on its surface. The physical and chemical properties of the materials that make up our planet control these processes. Therefore, the study of earth materials is crucial in advancing our understanding of how the Earth works. New classes of experiments, new levels of analytical sensitivity and precision, and new levels of theory are now applicable to earth materials because of rapid progress in instrumentation and computational ability. Therefore, considerable progress is to be expected over the next decade.

Although this report stresses earth material properties as they apply to understanding the Earth's internal processes, an overall effort should include those material properties important to surficial processes, hydrocarbon migration and recovery, ore beneficiation, waste disposal, and groundwater transport, among many industrial and technological applications.

The study of earth materials will play a key role in the interpretation of the results from several other major scientific efforts.

Earth materials research not only serves as an anchor to geological and geophysical theory and field measurements, but also is needed in practical applications involving the evaluation of earth resources and prediction of natural hazards.

Three major scientific topics provide examples where significant advances through accelerated research on earth materials are possible: (1) mantle convection, (2) fluid flow, and (3) continental evolution.

1. Mantle convection represents the driving force for plate motion, for much of volcanic and earthquake activity, and for the redistribution of crustal and mantle material throughout geologic time. Systematic characterization of the isotopic compositions of erupted magma is one of the means available for studying the time dependence of mantle convection. With appropriate sampling and analysis, it is now possible to use isotopic, chemical, and physical property data to characterize the convective flow regime, and improve our understanding of the thermochemical evolution of the Earth.

2. Migration of fluids redistributes the constituents of the Earth's crust and mantle through melting and intrusion, metasomatism, metamorphism, and ore genesis. Fluids also affect a variety of rock properties including seismic-wave velocity, electrical resistivity, strength, and permeability.

3. Characterization of continental evolution is a global-scale task. At present there are a number of areas that have been moderately well characterized in terms of age, origin, and structure, but these may not be representative of the entire crust. Vast areas are untouched using modern techniques. There can be no real understanding of the origin of continents in the absence of a uniform, modern data set that represents all of the continental mass. This may require a coordinated sampling program of basement rocks, younger igneous and metamorphic rocks, and sedimentary rocks; such a program would need to be international in scope.

RECOMMENDATIONS

In order to maintain our momentum and accelerate our progress in fundamental research on physics and chemistry of earth materials, the committee has two major recommendations:

1. **Increased support is recommended for (a) upgrading and**

greater use of existing experimental and analytical facilities, (b) development and application of new experimental and analytical techniques, and (c) interpretation of experimental and analytical results.

Development and/or greater use need to be made of the following four specific technologies: (i) synchrotron radiation facilities; (ii) high-pressure, high-temperature, large-volume experimentation; (iii) microscale, in situ analytical instrumentation, and (iv) accelerator mass spectrometry.

Several new capabilities exist or are under development for analytical and material properties investigations under the extreme conditions found within the Earth. Laboratory control of high-pressure, high-temperature, and chemical variables allow measurement of several of the fundamental parameters needed in Earth models. Analytical techniques are evolving to measure physical and chemical properties of synthetic and natural materials over an extraordinarily broad range of conditions. These capabilities along with recent theoretical developments offer a wealth of opportunities to advance our understanding of the Earth as a whole and to define essential properties of the Earth's interior.

2. **A concerted program is recommended for the collection, synthesis, distribution, and analysis of samples required for earth materials research.** This includes (a) coordination of efforts to obtain appropriate solid, liquid, and gaseous samples; (b) development and use of laboratory facilities for synthesizing important minerals, rocks, and their analogs; and (c) a system for curating samples and disseminating information about their availability.

A primary barrier to better understanding of the Earth's evolution is the lack of appropriate mineral and rock samples. The emphasis here is on quantifying the variability of rocks and their source regions in order to reveal the nature and history of the Earth's internal processes. There are several specific problems or processes that will require extensive sampling on a local scale, for example, the study of the nature of fluid flow and the reaction of the fluid with the host rocks. There is also a need for high-quality, well characterized samples, including synthetic single crystals and polycrystalline aggregates. These are essential for the laboratory determination of physical and chemical properties of materials such as $MgSiO_3$-perovskite, which is not stable at the Earth's surface but probably constitutes much of the interior.

1
Introduction

The application of the experimental and theoretical techniques of physics and chemistry to the study of earth materials has become a realistic and important goal of contemporary earth science. This emphasis is motivated by the need to decipher the nature of the Earth's interior and its dynamics, and to better understand the major processes that control the distribution and transport of materials in the Earth's crust and on its surface. New classes of experiments, new levels of analytical sensitivity and precision, and new advances in theory are now applicable to earth materials because of rapid progress in instrumentation and computation. Therefore, considerable progress is to be expected over the next decade in gaining a fundamental level of understanding of the materials that make up the Earth.

In addition to improving our understanding of earth processes, earth materials research has important implications for a broad range of societal problems and for technological advances. The understanding of the mechanisms of earthquakes and volcanic eruptions; the location and extraction of ores, fossil fuels, and geothermal energy; the safe disposal of hazardous wastes; and the development and production of new high-technology materials are all linked directly to advances in earth materials science that are now on the horizon. For example, a detailed understanding of how water and other fluids seep through rock enhances our knowledge of how ores are formed and how petroleum accumulates. Such knowledge is important for finding new reserves of natural resources and for increasing the efficiency with which these reserves are extracted.

Earth materials research is an extraordinarily broad subject. Because of this breadth, the workshop narrowed its focus to a subset concerning the major overlaps of earth materials research with the "hard-rock" disciplines of petrology, geochemistry, mineral physics, and rock physics/rock mechanics. There are several important areas that were not emphasized at the workshop that also have significant overlap with earth materials research; these include, for example, weathering and surficial processes, hydrocarbon migration and recovery, ore beneficiation, waste disposal and groundwater transport, and the use of zeolites as chemical catalysts. The focus of the workshop included earth materials research and, as examples of how this research is important in major earth science problems, its contribution to studies of mantle convection, fluid flow, and continental evolution.

Recent conferences and publications show that earth materials research is becoming an exciting field in the earth sciences. Growing numbers of scientists from different disciplines who have never worked together before are combining resources in coordinated systematic studies of the fundamental behavior and properties of earth materials. This is not an isolated phenomenon because technologically advanced countries, especially Japan and the Soviet Union, also are generating and maintaining productive initiatives in this area. The reason for this is that the field, theoretical, and applied branches of the earth sciences are rapidly developing critical needs for earth materials data to advance their studies.

The study of materials and their properties is a vital component of physics, chemistry, biology, and various fields of engineering. Materials science departments have been founded and have flourished in many universities. The study of geological materials on the other hand has rarely been emphasized and usually has remained imbedded within the descriptive context of earth science courses in mineralogy, petrology, and sometimes crystallography. Many geoscience students do not obtain an in-depth exposure to the physical and chemical properties of minerals and rocks, e.g., magnetism, thermal and electrical conductivity, spectral properties, diffusivity, and rheology. This deficiency in earth materials education creates a self-sustaining cycle. As a consequence, the important relations between rocks or minerals and large-scale geological phenomena often are not recognized. On the other hand, many important contributions to materials science have been made by geoscientists. Notable among these are research on mineral structures that have important industrial and materials applications such as garnet, spinel, perovskite, quartz, and zeolite. In addition, this research has resulted in the development of the electron microprobe, invention and development of the diamond-anvil cell, advancement of a wide range of material synthesis technologies including control of oxygen fugacity, structural determination of liquids and glasses, and advancement of mineral spectroscopy. With greater emphasis on the study of earth materials and their properties, even more significant progress should result.

A number of fundamental problems and broad opportunities have emerged from today's dynamic environment in the earth sciences. The plate tectonics revolution, planetary exploration, new instrumental capabilities, and major new programs such as continental and ocean drilling, seismic profiling, global seismic networks, and continental geophysical arrays allow investigation of the Earth's crust, mantle, and core as never before. The study of earth materials will play a key role in the interpretation of the results from these major scientific efforts. Specifically, earth materials research provides unique data to interpret solid-earth properties in terms of crystal structure, composition, thermal state, and dynamic processes. This discipline not only serves as an anchor to geological and geophysical theory and field measurements, but it is also needed in practical applications involving the evaluation of earth resources and prediction of natural hazards. Therefore, much more emphasis should be given to the study of earth materials in academic, industrial, and government laboratories.

2

Research in Physics and Chemistry of Earth Materials

From the earliest development of ceramics for pottery to the most recent use of zeolites as catalysts, the study of earth materials and their synthetic counterparts has been central to the progress of society. All of the raw materials on which mankind depends are derived ultimately from the Earth's crust and interior. In addition, characterizing the physical and chemical properties of the materials that make up our planet is a prerequisite for understanding geological processes.

The Earth is an active planet. On a geological time scale, continents move, mountain chains are formed or destroyed, and ore bodies are deposited. On a human time scale we see the effects of these processes in the occurrences of earthquakes, tsunamis, volcanoes, landslides, and hot springs.

In the laboratory both experimental and theoretical techniques allow the determination of how earth materials behave in response to changes in physical and chemical conditions. For example, the stress required to induce plastic flow in rocks, or the temperatures and chemical environment required for a specific reaction, has been documented systematically for a wide variety of minerals, rocks, and synthetic analogs. When similar effects are identified in nature it is possible to understand the underlying processes—the stresses involved, the amounts and sources of energy required, and the timing of these processes can be revealed in detail.

Minerals, which make up our planet as well as the hard parts of living organisms, are among the most complex inorganic substances known. The interest in studying earth materials is matched by the difficulty in understanding their properties. Nevertheless, we can now interpret many of the physical and chemical properties measured in the laboratory in terms of bonding forces and geometries on an atomic scale. Such an atomistic understanding makes it possible to create synthetic analogs or totally new substances, that can have broad technological applications—examples include synthetic diamonds and garnets for solid-state lasers. In this sense, the study of earth materials is closely related to materials science, condensed-matter physics, and chemistry. The prospects for developing novel materials, including new ceramics and alloys with unforeseen technological applications, are great. A good example is provided by the recently discovered high-temperature superconductors, whose structures are related to the perovskite-type minerals that make up much of our planet.

Unlike materials science, condensed-matter physics, or chemistry, however, the study of earth materials involves scales of space and time far beyond human experience (Figure 1). When considering geological processes, the time scales are four to ten orders of magnitude larger than those achieved experimentally, and the spatial scales are up to seven orders of magnitude larger than in the laboratory. This range of scale is more akin to astrophysics; an enormous extrapolation of our laboratory experimental and theoretical knowledge of earth materials is involved in understanding geological processes.

Geological investigations reveal that earth materials can behave very differently over extremely long times or over extremely large distances than they do on laboratory scales. For example, the strength of small rock samples can be measured accurately, but rocks behave as much weaker materials on the length scale of continents. Similarly, our everyday experience is that rocks are solid. Yet on a geological time scale, the solid mantle behaves like a fluid and convects. Convection is the basic process by which heat is most effectively lost from the deep interiors of planets. Although heat is conducted through solid rock, tectonic flow of the

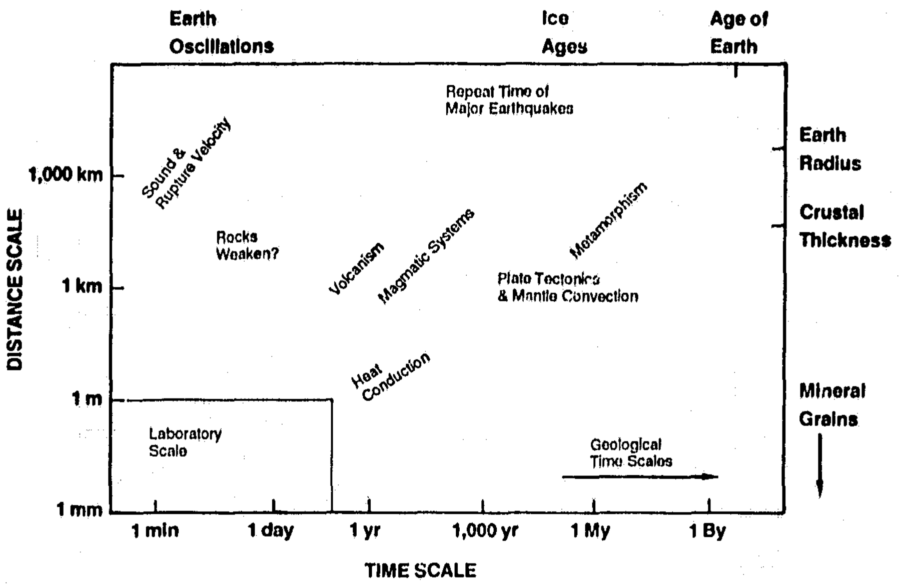

FIGURE 1 Time and distance scales of earth materials research.

"solid" interior provides a much more efficient means of transporting heat on a global scale. Mantle convection is intimately related to the occurrence of major belts of volcanic and earthquake activity around the world and to the formation and movements of the continents, and it determines the long-term evolution of planetary bodies, whether the Earth, the Moon, or Mars.

GEOPHYSICS OF THE EARTH'S INTERIOR

One of the important goals of studying earth materials has been to determine the nature of the Earth's deep interior. The only direct information about the deep interior comes from seismology. But the interpretation of seismic observations in terms of temperature, pressure, and composition requires a thorough knowledge of the properties of minerals and rocks under the appropriate conditions existing throughout the Earth. Major new efforts now under way to observe the structure of the Earth's crust, mantle, and core through seismic tomography therefore require a new level of understanding of the physical and chemical properties of earth materials.

Considerable progress has been achieved, especially in evaluating the average values of density, temperature, and composition throughout the Earth's interior. With the recognition that the Earth is a dynamic planet, however, comes a new interest in the variations of properties, reflecting spatial variations in composition or temperature at each depth, not just their average values. The promise of higher resolution seismological data that will reveal quantitatively the lateral variations of physical properties inside the Earth places increased demands on the accuracy, precision, and scope of corresponding laboratory measurements. Although relatively subtle compared to the radial variations, it is precisely these lateral differences in properties that drive convective flow in the mantle and the resulting plate-tectonic cycle. Specifically, heterogeneities in density at any given depth produce the motions that ultimately result in plate tectonics. Dense rocks sink relative to less dense rocks, whether the density variations are caused by contrasts in temperature, composition, or other properties. Thus, to understand fundamentally what makes the interior flow, the lithosphere to deform and fracture, or the planetary heat to escape, we must characterize the heterogeneity of the crust and mantle.

GEOCHEMISTRY OF THE EARTH'S INTERIOR

An important feature of earth materials, and of the study of the Earth in general, is that many of the naturally occurring elements, such as U, Th, Rb, K, Sm, and Lu, are radioactive. The systematic nature of radioactive decay means that earth materials carry internal clocks that permit precise measurement of the duration of geologic processes on many different time scales. The measurement of these elemental and isotopic compositions in rocks and minerals has advanced to the stage where, for some cases, only 10^6 to 10^8 atoms are needed for an analysis. Thus, the information provided by these radionuclides and their decay products is obtainable from a wide variety of earth materials. In fact, the precise determination of the concentrations and isotopic compositions of trace metals in nonmetallic substances is more and more the domain of earth sciences rather than of chemistry or physics.

Whereas the geophysical studies described above reveal the heterogeneities that have been produced by geological processes, the relevant time scales are determined almost exclusively from the study of isotopic compositions of rocks. One of the major successes of the lunar science program was the determination of a lunar evolutionary time scale and the discovery that it differs tremendously from that of the Earth. The fact that isotopic properties of earth materials give information about the age as well as the composition of chemical units in the Earth makes them particularly valuable as tracers in processes that have occurred throughout geologic time. Their value is greatly enhanced if the processes of trace-element fractionation are well understood.

One valuable application of geochemistry has been to determine the chemical structure of the mantle by studies of oceanic basalts. The demonstration of pervasive, long-lived chemical heterogeneity in the mantle is one of the major achievements of earth sciences. It adds an entirely new dimension to our view of the interior based on geophysical measurements, namely the temporal evolution of the planet. In terms of mantle structure and dynamics alone, we now recognize plumes, isolated mantle reservoirs, and mantle flows capable of dispersing heterogeneities and recycled crust.

While the existence of chemical and isotopic heterogeneities is well established, the details regarding origin, age, and spatial structure are problematic and disputed. Uncertainty arises, in part, from the complexity of inferring the nature of the mantle source from rocks that are found at the surface; much of this complexity arises from a suite of petrologic processes that occur during transit from the mantle to eruption. The diversity of magmas produced in the mantle and the irregular distribution of sites that can be sampled also contribute to this uncertainty. Yet it is crucial that we unravel the origins of internal heterogeneities, for it is in these heterogeneities that the history of our planet's interior is recorded.

STRUCTURAL PROPERTIES

Earth materials researchers have long recognized that bulk-rock properties must be understood from the scale of atomic interactions to aggregates consisting of different minerals. Until recently, however, most minerals and rocks have proven too complex to connect fully their microscopic and macroscopic properties. Nevertheless, new techniques ranging from ultrahigh-pressure experiments to ab initio quantum mechanical calculations offer the prospect of major new insights into the properties of earth materials.

Possibly the most fundamental data required are the properties of single crystals of the various minerals found on and in the Earth. These include a wide variety of physical properties that are summarized, along with some of their applications, in Table 1. In addition to these measurements, theoretical calculations of bonding energies, lattice vibrations, and defect states are central to understanding the properties of minerals at a fundamental level. Such an understanding is the basis on which properties can be estimated for conditions of pressure, temperature, or time that are not accessible in the laboratory.

MINERALOGICAL PROPERTIES

The development of the diamond-anvil cell and microfurnaces that can be used with the single-crystal x-ray diffractometer has allowed the systematic investigation of how crystal structures accommodate changing conditions of pressure or temperature. In the past 15 years, crystallographers have shown that silicate crystal structures expand and compress systematically with temperature and pressure, depending on the composition of individual structural polyhedra (describing the atomic linkages) and on the ways in which the polyhedra are joined together. These experiments have led to great advances in understanding how phase transformations occur and how thermal expansion and elasticity are related to crystal structure.

Over the past two decades several precise techniques have been developed to measure the elastic moduli of minerals as well as their pressure and temperature derivatives. These experiments include ultrasonic interferometry, Brillouin scattering, and resonance techniques. These methods have allowed determinations of

TABLE 1 Understanding Physical Properties of Minerals

Measurement	Application
Pressure-Volume-Temperature Relations	Equation of State; basis for evaluating models of the Earth's interior
Elastic and Inelastic Properties	Interpretation of seismological measurements Verification of theoretical models of mineral properties
Crystal Structure	Basis for understanding physical and chemical properties of minerals, and the nature of phase transformations
Spectroscopy Infrared, Raman, Neutron	Determining vibrational states for evaluating thermodynamic properties and checking theoretical models
UV-Visible	Determining bonding states in minerals
NMR, EPR, EXAF	Observing local structure, including coordination and defects
Thermal Conductivity	Calculation of heat flow from observed temperature gradients
Electrical Conductivity	Evaluation of electronic states and remote determinations of temperature (e.g., planetary interiors)
Chemical Diffusivity	Quantifying kinetics of elemental or isotopic partitioning and of phase equilibria; time and length scales of equilibration and deformation
Strength, Plastic Deformation, and Rheology	Evaluating the mechanical state and structure of the Earth's interior

densities and wave velocities of minerals at very high pressures and temperatures. Such a capability is necessary in order to infer planetary compositions and thermal states from the seismically determined profiles of density and wave velocities with depth.

The electronic structure of a mineral defines the energies and wave functions of its electronic and vibrational states. Transitions between such states give rise to the absorption bands observed in the infrared, visible, and near-ultraviolet spectra of minerals. Such spectra, in turn, are used in spectroscopic remote sensing techniques for the identification of minerals on the surface of the Earth and other planetary objects.

PROPERTIES OF AGGREGATES

The rock masses that make up the Earth are multiphase aggregates of crystals and voids that may be randomly oriented or that may have a crystallographic preferred orientation. Calculation of the bulk properties of these rock masses involves complex summation of the single crystal properties—taking account of different proportions and orientations of the various phases and their different thermal expansions and compressibilities. The problem is akin to those of self-consistent field theories in quantum and statistical physics in that high-order correlations are poorly known, either from theory or experiments. Still, understanding the properties of aggregates from those of the constituents is a topic of great practical importance that is currently receiving much attention.

PHASE TRANSFORMATIONS

SOLID-SOLID

Phase transformations in minerals are responsible for a variety of major earth and planetary features and processes. For example, the major discontinuities observed seismically at 400- and 670-km depths in the Earth are at least in part a result of these transformations, and have motivated a great many laboratory investigations of phase equilibria among silicates and oxides. Experimental data on phase equilibria at pressures and temperatures characteristic of the Earth's crust and upper mantle, when compared with observations of coexisting minerals in rocks, provide the main empirical constraints on the pressure and temperature

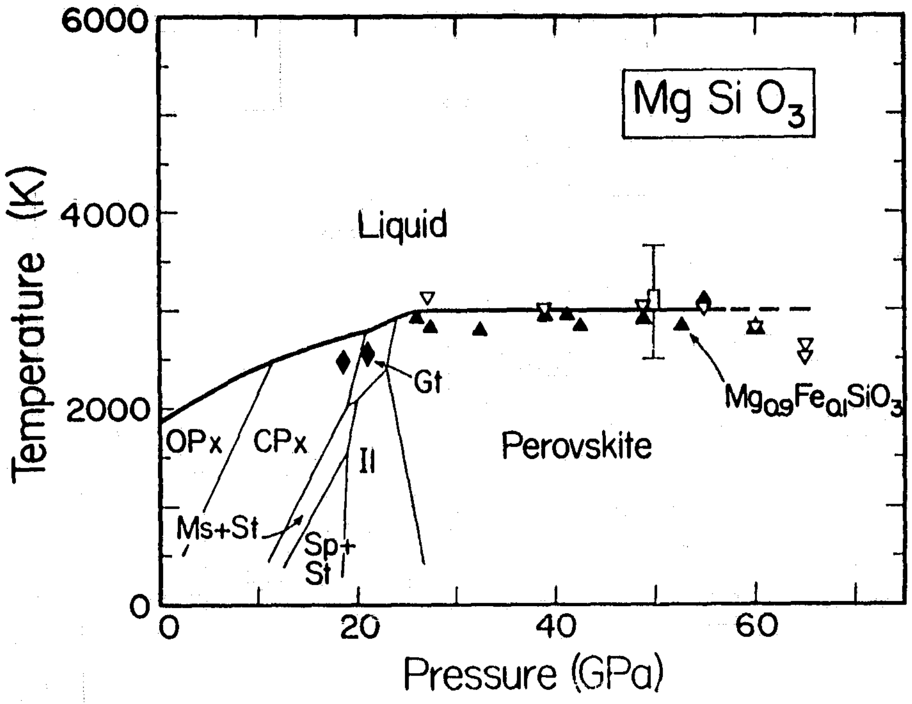

FIGURE 2 The experimental melting curve of $Mg_{0.9}Fe_{0.1}SiO_3$ plotted on a phase diagram of $MgSiO_3$. OPx - orthopyroxene, CPx - clinopyroxene, Gt - garnet, Sp - spinel, St - stishovite, Il - ilmenite, and Ms - modified spinel (beta). From Heinz and Jeanloz (1987, in preparation).

history of rocks. Much interest and attention has been focussed on phase transformations in silicates at high pressure and temperature (e.g., Figure 2) to unravel the structure of the Earth's interior and to determine how that structure has influenced the geological evolution of our planet. It now appears that under lower mantle conditions all the likely mantle minerals transform into a single phase with a perovskite structure. The implications of a monominerallic lower mantle to earth processes are not yet clear.

In addition to studies of the conditions required for phase transitions, there has been increased attention on the kinetics and mechanisms of these transformations. Kinetic data are extremely important, as many transitions of interest are sluggish even over geologic times, at least under crustal conditions. If kinetic data were available, observations of disequilibrium assemblages in rocks could allow one to deduce a great deal of information on the thermomechanical history of the rocks.

Determinations of transformation mechanisms are equally important as these may be intimately connected to tectonic deformations. For example, there is particular interest in determining whether some mantle transitions may proceed unstably and give rise to deep-focus earthquakes. In addition, phase transitions may produce transformational superplasticity that affects the ease of solid-state convective flow. Knowledge of the kinetics and mechanisms of phase transformations at high temperatures and pressures is therefore crucial to constraining models of the thermal evolution of the Earth, of mantle convection, and of deep-focus earthquakes.

SOLID-LIQUID

Melting and crystallization are important mechanisms of geological change. Data on melting temperatures and pressures, as well as density and viscosity of the melt, have been the basis for models of the origin and migration of magmas in the crust and mantle. Because melting and crystallization have been the major mechanisms for crust-mantle-core differentiation, the characterization of crystal-melt equilibria is important in understanding the evolution of the Earth and other terrestrial planets.

Information about the formation and movement of melts within the Earth's interior provides the basis for understanding the temperature distribution and dynamics of the Earth. In general, melting and migration of melts are considered to be two of the dominant mechanisms by which the compositions, structures, and temperatures of planetary interiors evolve with time. Of more immediate interest to the public, however, is that volcanic eruptions and their associated hazards of ashflows, landslides, lahars, and earthquakes result from molten rock reaching the Earth's surface. Therefore, studies of earth materials at very high pressures and temperatures are providing some of the most important information on the interior of our planet and on the processes that create volcanoes.

Numerous experimental studies have been made to characterize the thermodynamic properties of melts and the nature of the melting transition. In addition, theoretical computations of the structure and properties of melts (e.g., using molecular dynamics) advance our understanding of the behavior of melts throughout the Earth.

Melts existing as thin films along grain boundaries in nearly solid rock are likely to play as significant role in dynamic earth processes as are regions of completely molten rocks. The distribution and geometry of liquid at grain boundaries can have profound effects on the strength of rock and on the potential for earthquakes being generated. Electrical conductivity and the propagation of seismic waves are also affected through regions of partial melting. This fact makes it possible to document where in the Earth melts may be present along grain boundaries. The chemical and mechanical effects of melts on mineral surfaces need to be more fully understood through further studies, however.

Unsolved problems of melt-solid interactions include the mechanisms of melting at the molecular level, the nature of the forces controlling the geometry and distribution of partial melts, the role of water and other volatiles in controlling melt properties such as viscosity and element diffusion at high pressures and temperatures, and the magnitude of compressibilities and densities of melts of different compositions under different pressure-temperature conditions. X-ray absorption techniques using synchrotron radiation and nuclear magnetic resonance (NMR) can now provide a great deal of information about the structures of melts and glasses that could not be ascertained before. Improvements in the determination of cation-coordination numbers, the nature of compression at an atomic level, and the character of solid-melt interfaces are now possible using such techniques.

MAGNETIC PROPERTIES

Studies of rock magnetism have provided some of the most important constraints on continental evolution and the tectonic history of the Earth, as well as fundamental information on the magnetic field itself: its magnitude and orientation throughout geological time; the possible mechanisms by which the field has repeatedly reversed itself; and the presence of convection in the core by which the field is generated. For these reasons, there is considerable interest in understanding magnetic transitions in minerals. How is remanent magnetism acquired in a particular rock? How stable is it, and, therefore, how representative is it of the field in the geologic past? A better understanding of mineral magnetic properties is crucial to further applications of paleomagnetism in stratigraphy and tectonics. Already the discoveries based on rock-magnetic studies, such as plate tectonics, the presence of accreted terranes at continental margins, and the existence of large, unusually magnetic regions of the lower crust, have been among the most significant in the geological sciences.

Complicating the study of mineral magnetism are the complex crystal structures (hence spin-alignment processes) involved and the small domain sizes that are commonly found. Yet the magnetic domains are usually not so small as to be ideal single domains, so a more thorough understanding of complex pseudosingle-domain magnetic behavior has emerged from the study of minerals. Such studies are helping to elucidate how, in detail, the oceanic crust acquires, modifies, and retains its magnetism. Although the "magnetic stripes" recognized in ocean basins were a major foundation of the revolution in the earth sciences, the exact mechanisms by which they are produced are still poorly understood.

Separation of multiple components of magnetization from samples, such as Precambrian rocks or rocks that record transitional directions during a reversal, may require the measurement of the magnetic vector of single mineral grains. For a single grain, the study of how remanence is acquired and lost requires observation of the shape and movement of magnetic domain walls at elevated temperatures. A superconducting SQUID microgradiometer appears to be able to make such measurements. Simultaneous measurements of grain magnetization and domain geometry would allow one to pick out grains likely to carry stable remanent magnetization, the direction and intensity of which could be followed on heating and cooling or alternating-field demagnetization. A second major component of such an instrument would be a low energy electron diffraction source, lens and collimator, modified so as to impose no more than 100 nT leakage field at the magnetic sample. Enhanced detection of electrons scattered by the fringing field of magnetic domain walls would produce a new type of domain imager capable of operating at temperatures up to 700°C. The application of newly-developed instrumentation, such as the microgradiometer and domain imager mentioned here, would represent a major plate-tectonics breakthrough for investigations of the Earth's magnetic field, its evolution through time, and paleomagnetic signatures of continental growth.

SURFACES, INTERFACES, AND AGGREGATES

The physical properties of rocks result in large measure from complex interactions between the properties of the individual minerals. Also important to the bulk properties of rock masses, however, are the mineral interfaces and surfaces, which represent regions of disrupted bonding and thus higher energy. The energy of grain boundaries generally increases with angular orientation between like phases, although special low-energy coincidence orientations may occur. The energy of boundaries between unlike phases is even higher, although again there may be certain topotactic or coincidence orientations of good fit and lower energy. In general the disrupted structure of grain boundaries lowers the energy required for nucleation of new phases or of fractures. The holes and channels along grain boundaries favor segregation of impurities. Although there is still much debate about the effective width of grain boundaries in silicate minerals, it seems clear that these regions have different compositions and thus different properties from the crystal cores. In addition, the more open structure of grain boundaries can render, even at low temperatures, much faster transport than through the crystal lattice itself, thus constituting the rate-controlling step for processes including deformation and growth of new phases. It is because the grain boundaries have different properties that the grain size of an aggregate is important to its behavior.

Free surfaces are also an important component of polycrystalline aggregates. Especially at shallow depths, rocks contain open cracks and pores that are occupied by gasses or fluids. Such surfaces strongly influence the mechanical properties of the aggregates.

FLUID-SOLID SYSTEMS

The grain boundaries and other internal surfaces within aggregates are important reservoirs and passageways for both melts and aqueous solutions. These fluids, in turn, profoundly affect almost all of the properties of the aggregate. In addition, the geometrical distribution of melt in aggregates of different composition has a major effect on the collection of melt into larger magma bodies. For both felsic and basaltic systems the surface energies are such that the melt appears to occupy interconnected grain triple-junction

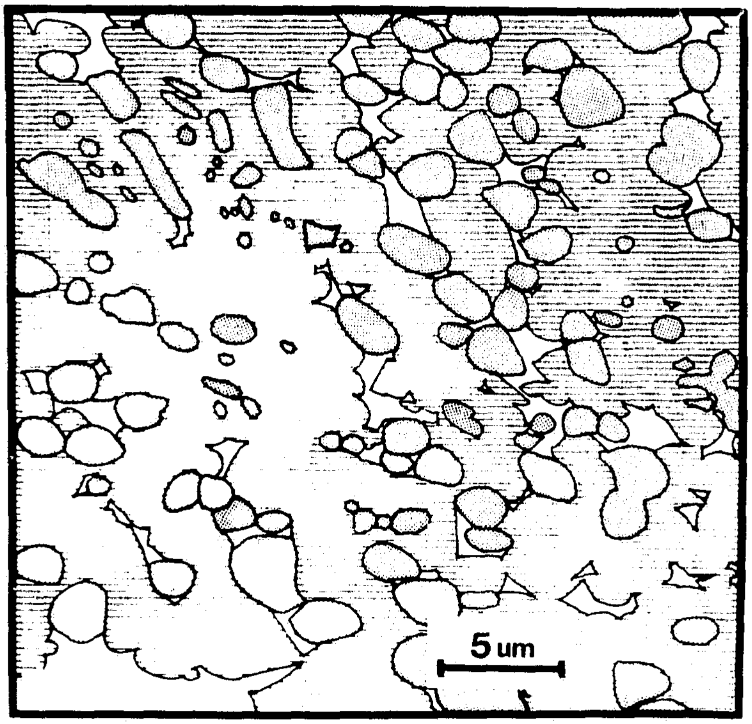

FIGURE 3 Partially-molten quartz-feldspar aggregate (1000°C, 10 kbar) showing concentration of melt at grain intersections and a highly interconnected nature of feldspar. Stippled areas are quartz, lined areas are feldspar, and white areas are melt. Figure courtesy of B. Watson (Rensselaer Polytechnic Institute).

channels (Figure 3). Regardless of the quantity of melt generated, the equilibrium texture dictates that only about 1 percent melt can be accommodated in this geometry. Whether the excess slowly oozes out and upward, forms local pools, or generates a high fluid pressure causing fractures remains to be determined. It is also uncertain how electrical conductivity and propagation of seismic waves are affected by composition, quantity, and distribution of melt along grain boundaries. This information is critical for assessing quantitatively the extent of partial melt in the lithosphere and asthenosphere from the geophysically observed electrical conductivity and seismic wave velocities and attenuation.

Aqueous fluids are common along grain boundaries, cracks, and pores. Experimental quantification of their effect on rock properties for different fluid compositions, quantities, and geometries is an important component for assessing the extent of circulating fluid systems in the crust. These fluids also contribute to dissolution of minerals, transport of the dissolved species, and reprecipitation. They thus influence the kinetics of phase transitions and accommodate transport of material, leading in some cases to ore deposits. The presence of fluids affects all known deformation mechanisms, always serving to weaken a rock. An increase in fluid pressure may promote a switch from plastic deformation to brittle fracture, and thus may be a factor in earthquake generation. Fluids also accelerate the rate of stable crack propagation due to stress corrosion, and cause pressure solution and hydrolytic weakening.

3
Earth and Materials Properties

CONVECTION

Perhaps the single most important breakthrough in earth sciences since the plate-tectonic revolution is the realization that the Earth's mantle behaves as a viscous fluid that convects. This convection transfers the Earth's internal heat to the surface where it is lost to space (Figure 4). It is this process, which drives plate movements and magmatism, that has produced the Earth's oceanic and continental crust, the atmosphere, and the hydrosphere.

Understanding convective mechanisms requires extensive knowledge of earth materials and their properties. One major mechanism of energy transport in the lower mantle, for example, may be radiation; at locations where mantle materials become radiatively opaque, energy may be concentrated locally, leading to thermal anomalies and lateral seismic heterogeneities. Knowledge of the electronic properties of mantle materials and of phase transitions from electrical and thermal conductor to insulator states is fundamental to the correct interpretation of the mantle's electrical and thermal conditions, and therefore of mechanisms of mantle convection.

Solid and multiphase mantle flow has been important in the redistribution of material throughout the Earth's history and in the

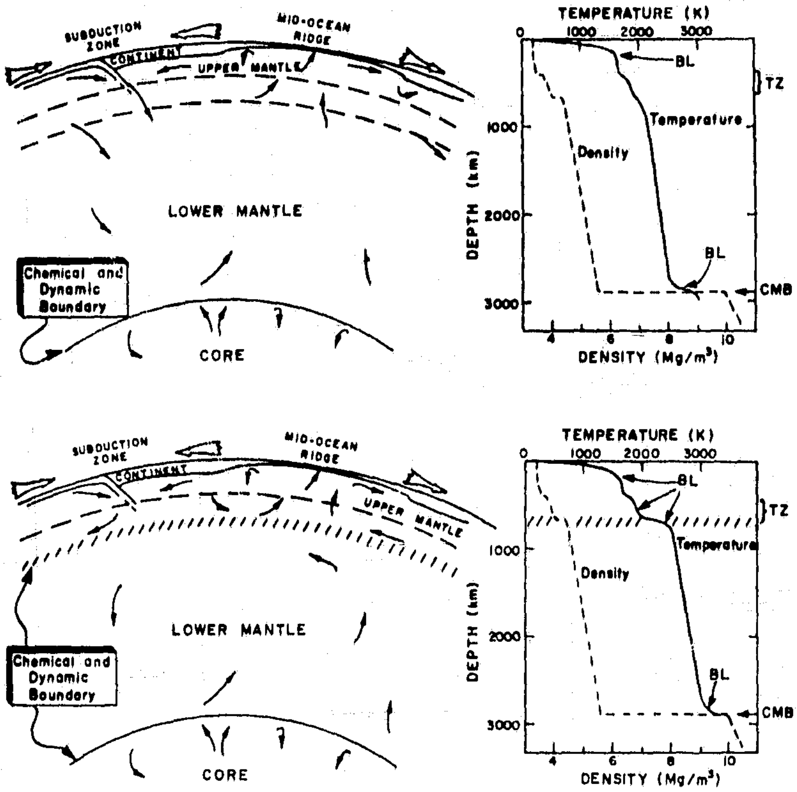

FIGURE 4 Two alternative models for large-scale flow in the mantle with the resulting profiles of average temperature as a function of depth given on the right. In the upper model, convection stirs the mantle homogeneously, and thermal boundary layers (BL) occur only at the top and bottom of the mantle. In the lower model, the presence of a barrier to convection at the top of the lower mantle results in an additional set of thermal boundary layers and in higher temperatures in the lower mantle. From R. Jeanloz, in *Mantle Convection*, Gordon & Breach, New York, 1986.

rates of material transfer. Physical/chemical stratification of the planet and the degree of chemical heterogeneity in the crust must also depend on dominant flow processes. Reciprocally, such properties and processes are dependent not only on the normally considered physical parameters (pressure, temperature, stress, strain rate) but also on grain boundary properties and the bulk chemical environment.

Variations in the flow field with time are fundamental to characterizing convective flow in the Earth. Isotopic measurements offer the possibility for studying the time dependence of mantle convection. This can be done by systematic characterization of the isotopic compositions of magma that is erupted from the mantle. With appropriate sampling, it is possible to use the isotopic data in conjunction with other chemical data to characterize the convective flow regime, and thereby improve our understanding of the thermochemical evolution of the Earth.

MANTLE HETEROGENEITIES

Lateral inhomogeneities and anisotropies have been found to be extensive in the mantle but these are still poorly understood. Models of the mantle's constitution use data from a wide range of remote geophysical observations, including seismology, gravity, heat flow, electrical methods, and magnetics. The composition of the rock and the laws of deformation (rheology) must be deduced under appropriate conditions of temperature and pressure. The stabilities of mantle minerals need to be more fully established, and their rheological properties that likely may lead to the development of anisotropy and deformation must be determined.

Seismic discontinuities can be interpreted as either phase or chemical boundaries; they can be used to tell us about the temperature distribution in the mantle. Seismic tomography and lithospheric seismic arrays are starting to provide models of seismic-wave velocities with unprecedented resolution. Seismic waves measure physical properties, but cannot uniquely discern what causes variations in these properties because they, in turn, depend on several parameters. In the past, seismology was mainly used as a mapping tool to determine the gross structure of the Earth. Somewhat later it was used to provide first-order constraints on chemical composition. More recently, the study of anisotropy has allowed inferences about crystal orientation and mantle flow.

Other advances in theory make it possible to estimate temperature and stress from the damping of seismic waves. The same theory provides a connection between seismic anelasticity and viscosity. These new uses of seismic data, however, must be tested and calibrated in the laboratory if they are to be employed to their fullest potential of characterizing how the Earth's deep interior is evolving at present.

MATERIAL TRANSPORT

The processes and rates of transport of geomaterials are fundamental for understanding earth history. Material transport can occur (a) by melting and its subsequent movement dictated by the Earth's rheological states, (b) by fluid circulation, (c) by diffusion, and (d) by solid-state convection, as well as by combinations of these processes. It is essential to understand earth materials properties to constrain models of transport. Important material properties to be measured include composition, phase equilibria, equations of state, and thermochemistry. Equally important are the behavior of grain boundaries and mineral surfaces in controlling melt and fluid transport. Geochemical and isotopic signatures are valuable in deciphering the varied pathways by which transport has occurred in the Earth's mantle and crust. The evolution of the Earth's crust can be chronicled by geochemical and isotopic analyses, which provide the primary data base and define the relative importance of different processes in specific environments.

MAGMATISM

Partial melting is one important, yet poorly understood, mechanism for material transport and development of the patterns observed in seismic data. The role of melt and fluid phases in the rheology of mantle material, in healing of crystal defects and development of rock fabric, must be studied with the aid of measurements of high-pressure and high-temperature phase equilibria. Additional thermochemical data will provide the necessary base to extrapolate phase-equilibria data to complex natural systems.

Over 1000 potentially active volcanoes dot the continents; more occur on the ocean's floor. Erupting magma that originally formed some 50 to 200 km below at temperatures near 1200°C, these volcanoes are probes of the Earth's interior. Their magmas can reveal constraints on the composition and physical state of the source regions, the chemical nature of the magmatic plumbing system itself, the dynamic conditions that give rise to volcanoes, and the history of the magmatic source materials in the mantle through chemical and isotopic compositions. The solidified rock is all we generally see, and the key to unraveling the various magmatic processes rests in understanding the details of the physics and chemistry of the origin and evolution of magma. How is melt separated from partially molten rock? Are the time scales of the processes such that chemical equilibration is maintained or are the chemical fractionations kinetically controlled? How does magma rise? Do the crystals that grow during ascent settle out, changing the composition of the resultant magma, or are they carried along by turbulent flow? Is there a reservoir of magma a short distance below each volcano? Are these reservoirs in turbulent convection or are they stagnant? Why does magma erupt at all?

Understanding the processes particular to a single volcano does not immediately allow the result to be generalized to all volcanoes. But studying a large number would give us an increasingly systematic view of the chemical processes occurring on a global scale within the Earth. A worldwide survey would give a measure of the Earth's deeper temperatures, chemical composition and homogeneity, and dynamic state. Including the submarine volcanoes, only a small fraction of the Earth's volcanoes have so far been examined, and yet they hold a large part of the key to understanding planetary magmatism, the motion of the inner Earth, and its general thermochemical evolution. A particular problem is that the interior of the Earth's largest volcanoes—those of oceanic islands—are hidden from view so that these evolutionary histories remain a mystery. These represent important targets for sampling using advanced drilling techniques.

FLUID FLOW

The role of fluids in the evolution of the Earth is both fundamental and pervasive. Interactions between hydrous fluids and rocks control most terrestrial petrologic processes and many of these are important to our domestic well-being and national security. Fluid-rock interactions control the transport and deposition of many strategic commodities, including metals, hydrocarbons, and geothermal energy. A detailed understanding of heat and mass transfer in water-rock systems is important to our hazardous and nuclear waste disposal programs. Indeed, fluids are so fundamentally important in transporting solutes, promoting melting, and redistributing the constituents of the crust that our understanding of the gross geochemical evolution of the planet will require an intensive effort to characterize a variety of fluid-rock systems.

Continents are built through time as rafts of lighter materials; their rocks are extremely diverse. Some, having once been laid down in shallow seas, become buried, metamorphosed, and stripped of their fluids. Such aqueous solutions, traveling along cracks and pore spaces, pervade the crust, locally dissolving precious elements from some rocks and concentrating them in others.

The heat from crystallizing magma drives continually circulating fluids again and again through narrow regions, lacing the rocks with ores, charging geyser systems, and stewing the country rock. How are these solutions generated and transported? How do they move and dissolve or deposit minerals at the same time? Are the passageways cracks, veins, or grain boundaries? What type of solutions can carry the most metals; can travel the farthest; can dissolve rock?

The rocks themselves hold the answers. The mineral compositions record genetically the ancestry of their fluid parentage, fluids that have long since vanished. The crust provides a vast store of informational riches—telling this history of fluid and rock in the crust. The tools exist, an adequate suite of crustal samples does not.

ORIGIN AND EVOLUTION OF CONTINENTAL CRATONS

An understanding of the origin and evolution of continental cratons would help determine the role of plate tectonics in the formation of Archean and Proterozoic crust and the relationships between early crust and mantle. This understanding would result in quantitative models for the formation and maturation of the Earth's continental crust, which would provide a basis for evaluating crustal formation and evolution on the other terrestrial planets. The necessary research on craton formation would complement existing continental lithosphere projects such as continental drilling and seismic profiling.

An interdisciplinary research effort in physics and chemistry of earth materials will be necessary to provide answers to major questions concerning cratons, such as the pressure-temperature-time path of rocks within once active tectonic belts, the parentage of cratonic rocks (i.e., mantle versus sedimentary materials derived from crustal processes), the degree of melting and/or fluid transport within cratons, their deformational history, and the sequence of events.

In addition to an increased understanding of cratons, the evolution of internal processes is potentially retrievable from the continental crust from its >3.8-billion-year-long record. Mantle-derived rocks, which can be used to determine properties of the mantle at earlier times in Earth history, are present in the crust. These rocks are generally no longer in their original tectonic context and detailed geologic study is required to understand how their properties relate to those of the ancient mantle. In particular, crust production is associated with subduction of the oceanic lithosphere, so the production rate is likely to be a function of global heat flux. Thus, the history of the fundamental physical and chemical processes and properties of the mantle and core of the Earth can be determined by studies of the mass-age function of the continents.

4

Approaches to Earth Materials Research

Research in the disciplines encompassing physics and chemistry of earth materials has several commonalities. Most of the research takes place in small groups. This, however, is necessary and complimentary to the advances that could be made in intra- or inter-institutional cooperative efforts. The sharing of all or portions of the same sample to determine a suite of physical or chemical properties can form the basis for a collaborative effort. In other areas of earth materials research, the technological challenges are too complex for the individual investigator approach; such problems need to be attacked from a consortium or institute approach. For an increasing segment of earth materials research, complex and expensive equipment is required—examples include synchrotron x-ray sources, accelerator mass spectrometers, and large-volume high-pressure equipment. Such costly equipment necessitates the careful examination of the potential use of "national" or "regional" facilities or dedicated research centers. A major policy challenge will be in determining the "proper mix" of the varying approaches to earth materials research; there is a significant role for all such approaches to greatly accelerate our understanding of geomaterials and the controls they provide to the other areas of earth science.

SMALL-GROUP RESEARCH

Traditionally, earth materials research has been the product of individual scientists or small research groups in one or a few institutions. The direction that research takes is controlled largely by interactions among these people through personal contacts, scientific meetings, and the scientific literature. It is further modified by the funding system where a certain kind of proposed research is supported or rejected in the peer review and panel selection process. The scientific priorities are dominantly established by the number of researchers who pursue each particular subject area. This is referred to as "proposal pressure" and often comprises the basis on which funding priorities are set.

Small-group research is generally pursued by a few investigators, possibly only a single scientist with a few students, most often using equipment in their own laboratories. Major advances often occur by a multitude of discoveries that fit together to reveal a fundamental principle, in contrast to research that is organized around a single conceptual theme. Research carried out in such small groups plays a major role in the education of earth scientists. The report *Physics through the 1990s* (National Research Council, 1986) stated that the most important aspect of small-group research may well be the opportunities for initiative and innovation provided for research students. These opportunities are necessary if earth materials research is to continue rapid intellectual advancement.

Small groups of earth materials researchers face a number of problems. Foremost is a critical need for laboratory equipment or instrumentation. Several reports, e.g., *Academic Research in the Physical and Computer Sciences and Engineering* (National Science Foundation, 1984), show that equipment in university research laboratories is obsolete or simply nonexistent. The needed instrumentation ranges from moderately expensive (>$500,000) analytical tools, such as electron microprobes, to much less expensive spectrophotometers. The lack of up-to-date equipment can stifle the ability of universities to undertake modern, let alone forefront, research. One consequence is that students are not being trained in state-of-the-art techniques. Some relief has been provided by NSF's instrumentation program (<$5 million per year in FY 1987 in NSF's Division of Earth Sciences), but the demand for instrumentation and equipment exceeds available funds.

A second problem becoming common to small-group earth materials research in universities is the loss of the infrastructure of support services that are essential for cutting-edge research. Machine shops, electronic shops, and special services such as materials preparation have deteriorated or disappeared from universities across the nation. This problem also presents a major obstacle in innovative development of the next generation of analytical instrumentation.

The costs of research and operation of a university research laboratory usually far exceeds the average grant size in earth materials research. For NSF's Division of Earth Sciences, the average annual grant size was slightly more than $60,000 in 1985. With the support of graduate students and related expenses including overhead, there often is little left for actual research and publications expenses. Probably the most serious impact of underfunding, however, is on the development of young talent, including the support of postdoctoral researchers. The number of new grants has not kept up with the requests: in NSF Division of Earth Sciences the percentage of proposals funded has declined from about 66 percent in 1967 to 36 percent in 1986. A prospective faculty member may have to wait several years to launch a research project. Beyond this difficulty lies the prospect of pursuing a research career in a situation of perpetual shortage, which may deter many promising young scientists. The outward appearance of this situation is strong discouragement among young scientists; coping with establishing a career and a research program on little or no funds drive many from frontier research.

LARGE GROUP (CONSORTIA) RESEARCH

There are several types of investigations that only are amenable to cooperative efforts, which combine a range of scientific expertise and experimental and analytical facilities; they do not exclude the role or contribution of the above small-group research. Often these cooperative enterprises are organized to take advantage of a major platform or sampling capability. Several major new programs such as continental (DOSECC) and ocean drilling (JOI/ODP), seismic profiling (COCORP and others), global seismic networks and continental arrays (IRIS) have been initiated in recent years to attack large-scale problems in the earth sciences. No comparable programs featuring earth materials science exist at present and none are being planned. In contrast, comprehensive large-group programs have been part of the materials science scene for many years. The NSF Materials Research Laboratory Program is an important part of materials research at many universities and a new program based on materials research groups has been active in the last two or three years.

Opportunities do exist for the formation of informal consortia to address problems of common interest. These problems, however, are generally very specialized and reflect the common interests of individuals in different institutions. Funding usually comes from grants or other sources available to individual participants; although investigators are often encouraged to submit consortium-type proposals, it is the perception of some of the Workshop participants that it is difficult to obtain block funding for larger groups of investigators. In a time when competition for research funds is intense, block or group proposals may be vulnerable because budgets will be larger than those in proposals from individuals. Furthermore, most investigators hesitate to depend on a group proposal as the only source of funding. If such proposals are submitted in addition to an investigators's individual grants or proposals, it could appear to reviewers and panels as though these individuals are asking for too much money.

In spite of the above situation, it is felt that considerable opportunity exists for the formation of larger-scale research groups in earth materials science and that this kind of activity should be considered seriously by funding agencies. These groups might consist of investigators from different institutions, whose individual research objectives would focus on relatively narrow topics, but whose aggregate output would be of much broader interest and applicability. Ideally, the investigators would encompass a variety of skills and capabilities, thus allowing for a comprehensive study of the selected problem.

What are the inducements or barriers involved in organizing cooperative research programs? Common interests of the participants and financial or logistical support are the main inducements; lack of communication or information, inertia, alternative priorities, and limited financial support are the barriers. Attention needs to be given to ensure that imagination, creativity, and productivity are emphasized in the large-group programs rather than the designing of bureaucratic structures that use a lot of personnel time but produce few scientific results.

5

Future Directions

Although interest in earth materials research is growing, several things must occur before it reaches its full potential. These involve organization, facilities, samples, and personnel. With regard to organization, means must be found to collect and disseminate information about earth materials research. Current journals and societies perform this function in part, but there is little specific leadership in the field. A recent example of organizational leadership is that provided by the AGU Mineral Physics Committee. This committee meets at least twice a year and has been instrumental in making mineral physics an important component of AGU meetings. It has also sponsored a workshop and has initiated a project to seek funding for synthesis of crystals to be used in mineral physics research.

A continuing focus on physics and chemistry of earth materials by the Board on Earth Sciences of the National Research Council would be helpful in defining the specific manpower, funding, and equipment needs to meet the objectives outlined in this report.

Current facilities, including laboratories and instrumentation, are inadequate to provide the quantitative data that are needed to address the most pressing questions in the earth sciences. A concerted effort in improving these facilities is a high priority, not only to obtain new equipment, but also to make the best use of equipment already available through training of personnel and making it possible to maintain and upgrade equipment through adequate funding.

To a great degree, earth materials research involves the measurement and interpretation of mineral and rock properties under varying conditions of temperature, pressure, and chemical environment. Such measurements are significant only with suitable samples, including natural solid, liquid, and gas samples as well as those synthesized in the laboratory. We must further define our sample needs along with the concomitant collection, synthesis, and distribution of these samples. New approaches are emerging through field observations in which an entire site is treated like a sample in the laboratory. In addition, some investigators should continue to develop new and improved measurement techniques. Further, the results of measurements must be interpreted and disseminated so that others can make use of this information and continue the process.

The education and training of future scientists for earth materials research must be addressed. Although assessment of manpower requirements was beyond the scope of the Workshop, many participants were concerned about the quality and quantity of students in American geoscience graduate programs. Some believe that, if present trends continue, American universities and research laboratories will be largely staffed with foreigners because not enough American students with strong backgrounds in the physical sciences are entering earth science graduate schools. Although this is a national problem common to all sciences, it is recommended that an assessment of our human resources becomes a major concern of the Board on Earth Sciences.

RECOMMENDATIONS

In order to maintain our momentum and accelerate our progress in fundamental research on physics and chemistry of earth materials, which can be applied to understanding a variety of earth science problems such as convection, fluid flow, and continental evolution, the committee has two major recommendations:

1. **There should be increased support for (a) greater use of existing experimental and analytical facilities**, including those that reside outside of the earth sciences community; (b) **development**

and improvement of experimental and analytical techniques, especially for analysis of trace concentrations of atoms/isotopes, of small samples, or of physical properties (e.g., elastic constants) under high-pressure and high-temperature conditions; and (c) **interpretation and modeling of experimental and analytical results**.

Development and/or greater use needs to be made of the following four specific technologies: *(i) synchrotron radiation facilities; (ii) high-pressure, high-temperature, large-volume experimentation; (iii) microscale, in-situ analytical instrumentation, and (iv) accelerator mass spectrometry*. Discussion of these is given in the Instrumentation section below.

2. **A concerted program is recommended for the collection, synthesis, and distribution of samples required for earth materials research.** This program should include (a) coordination of efforts to obtain appropriate solid, liquid, and gaseous samples; (b) development and use of laboratory facilities for synthesizing important minerals, rocks, and their analogs; and (c) a system for curating samples and disseminating information about their availability. Details are given below.

INSTRUMENTATION

Several new research capabilities now exist or are under development for analytical and material properties investigations under the extreme conditions that are fundamental to Earth models. High-pressure, high-temperature, and chemical variables can be controlled and calibrated in laboratory experiments to synthesize earth materials that exist at the surface and at depths. Indeed, geophysicists and geochemists have pioneered the techniques for achieving the most extreme (sustained) pressure-temperature conditions that can now be generated in the laboratory (Figure 5). Analytical techniques are evolving to determine and measure in situ physical and chemical properties of synthetic and natural materials over an extraordinarily broad range of conditions. These capabilities offer a wealth of opportunities to advance our understanding of the Earth as a whole and to define essential properties of the Earth's interior.

Analytical capabilities for sample investigations include those where the sample is under extreme conditions of pressure and temperature or where the sample is measured in situ on the microscale. These approaches may be used to obtain precise data on,

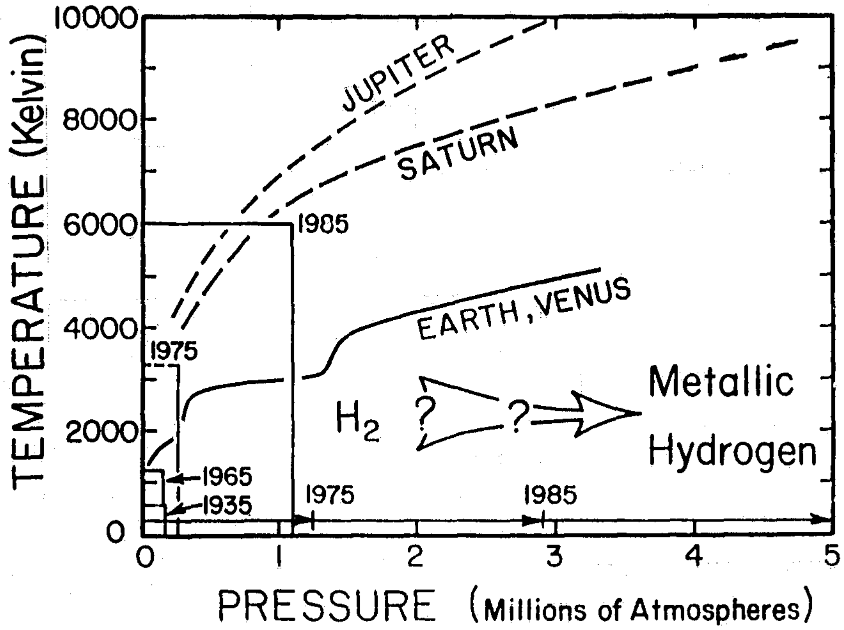

FIGURE 5 Pressure and temperature capabilities for laboratory experiments as a function of time.

for example, composition, structure, density, thermal expansion, and elastic and transport properties. These capabilities include use of synchrotron beams, tandem accelerator mass spectrometry, and laser spectroscopy. Techniques include, in part, x-ray diffraction and absorption, trace-element and isotope analysis, Fourier-transform infrared spectroscopy, Brillouin and Raman scattering and Mössbauer spectroscopy, high-resolution electron microscopy, and computational capabilities for theoretical modeling.

An important aspect of instrument-oriented research that has been neglected is the actual operation and maintenance of equipment. A typical situation is that a university earth science department will purchase an expensive piece of equipment without addressing the obligation incurred to keep the equipment running over a long period. Often a faculty member writes a proposal that, if successful, generates enough money to buy an instrument, but does not provide for sustained operation and maintenance. Many instruments, such as electron microprobes, electron microscopes, or Fourier-transform spectrometers, cost several hundred thousand dollars and require a full-time personnel effort for efficient operation. For a $400,000 electron microprobe, the cost of a technician and maintenance contract plus overhead could be $80,000 per year. Few, if any, earth science research grants can accommodate this kind of expenditure and the only solution is to pool resources of several investigators and the university or to skimp on maintenance and end up with a relatively inefficient operation. Although not as difficult to manage, these problems apply also to less-expensive equipment, especially when a department contains a variety of research projects. As much attention must be paid to operation and maintenance as to the original purchase of the equipment.

SYNCHROTRON RADIATION

The development of extremely intense, highly collimated synchrotron x-ray sources has provided earth scientists with some extraordinary new techniques that have great potential for solving problems in the earth sciences. Synchrotron radiation can be used to investigate the mechanisms and kinetics of phase transformations as they are taking place in high-pressure and high-temperature apparatus. It provides new methods for studying structures of minerals as well as melts and solutions. It can be used to study the nature of grain boundaries, mineral surfaces and interfaces, and partitioning of trace elements between minerals and melts. There are certain to be many more applications as the potential of synchrotron radiation is further realized. Plans are in progress on second-generation synchrotron beam lines that will have 10,000 times the existing intensities. This very high intensity will enable earth scientists to make diffraction studies on samples that are very small (~10 μm) and therefore can be taken to very high pressures and temperatures. It will make it possible to penetrate even thicker walls in high-pressure devices. It is important for the earth sciences community to take advantage of the opportunity to play a role in the development of these new intense synchrotron sources so that they will be designed to meet the needs of the earth sciences.

It is also important that earth scientists become more involved in the use of currently available synchrotron sources, not only to use them for solving research problems, but also to become part of the synchrotron users community. Although, there is intense competition for beam time at existing synchrotron facilities, several opportunities exist for earth scientists to participate in the planning and construction of new beam lines at the National Synchrotron Light Source (NSLS), Cornell High Energy Synchrotron Source (CHESS), and the Stanford Synchrotron Research Laboratory (SSRL). In the next few years efforts will be made to design, construct, and operate beam lines largely dedicated to high-pressure and related research. Research groups that can provide funds for equipment or manpower for operations undoubtedly will be welcome at these facilities. Therefore, with a certain amount of organization and effort, earth scientists could become significant contributors to synchrotron research activities.

HIGH-PRESSURE, HIGH-TEMPERATURE, LARGE-VOLUME TECHNOLOGY

An achievable goal in the next 5 to 10 years is the development of new technology to enable in situ measurements on sample volumes of ~1 mm^3 to pressures of 1 Mbar or more at temperatures of 5000 K, conditions corresponding to the core-mantle boundary. Such equipment does not now exist anywhere in the world, but is needed for the study of phase equilibria (including melting), chemical partitioning and transport properties, and the synthesis of new phases at extreme conditions. The requirement of large sample volumes (compared to the currently achievable 0.0001 mm^3 at the conditions quoted) is especially critical for investigating polyphase equilibria, geochemical partitioning, deformation mechanisms, and interfacial or grain-boundary phenomena. The development of this equipment will require new superhard materials, such as sintered compacts of diamond, and thus will rely on close collaboration with the rest of the materials community.

In addition to the "super high-pressure" hydrostatic equipment, there is a need for a new generation of triaxial apparatus capable of deformation experiments to pressures of 50 kbar and temperatures of 1500°C. The volume inside the pressure vessel should be large enough for internal force and pressure cells as well as control of the chemical environment. This would enable direct study of deformation mechanisms and the rheology of mantle phases.

Currently, most activity in large-volume high-pressure research is centered in Japan, although a new high-pressure laboratory has been established in the United States at State University of New York at Stony Brook, and several more are in operation or being planned in other countries such as Australia, West Germany, Canada, and the Soviet Union. There is a need for more laboratories of this type in the United States, and it is recommended that the earth science community develop a program for constructing and operating new high-pressure facilities that will include "off-the-shelf" apparatus as well as for pushing the technology for achieving higher pressures and temperatures with larger sample volumes.

MICROSCALE, IN SITU ANALYTICAL INSTRUMENTATION

Development of microchemical/isotopic probes, using double focusing optics or ion cyclotron resonance designs and with capabilities far exceeding present commercial instruments, is essential for research on continental evolution, oxygen-isotope thermometry, and study of kinetics of various processes. Synchrotron radiation also offers the possibility of in situ quantitative trace-element analyses at the sub-ppm level on a microscale, which would enable important questions relating to trace-element distributions in petrogenic processes to be addressed.

To complement these microchemical techniques, microanalytical tools for physical properties should be further developed. In particular, microgradiometers and domain imagers of a resolution and sensitivity well beyond what has so far been used can be developed for mineral and rock magnetic studies combining a small leakage field (100 nT) at the sample and the ability to cycle routinely both to low and high temperatures (>1000 K). Such microimaging tools will play a crucial role in the next generation of paleomagnetic studies.

ACCELERATOR MASS SPECTROMETRY

Tandem accelerator mass spectrometry (AMS) was greeted with a great deal of enthusiasm and hope in the earth sciences community and already has had an important and exciting impact on the earth sciences. It has enhanced the utility of a great variety of cosmogenic radioisotopes in geological studies, and opened up entire fields to quantitative study—the ages of groundwater, the rates of physical and chemical erosion in surface and near-surface crustal environments, and the percentage contribution of sediments to island-arc volcanics. An understanding of the compositional evolution of island arcs and of the role of marine sediments in that evolution is being developed through the measurement of ^{10}Be in island-arc volcanic rocks. The extension of the ^{14}C dating technique to small samples allows the ratio of carbon transfer between the great variety of carbon reservoirs to be defined.

The applications to earth science research have stretched the capacities of the functioning AMS facilities to their limits. The major facilities are the University of Arizona, the University of Pennsylvania, and the University of Rochester. Of these facilities, only that at the University of Arizona is dedicated to AMS; in addition, the University of Rochester's facility is currently being upgraded for physics research, hence its future as an AMS facility is unclear. The present situation is critical; it will soon become acute. Additional AMS facilities should be identified and supported.

The future needs of the earth sciences for AMS can best be satisfied by the following:

1. An additional ^{14}C facility, dedicated primarily to oceanographic work.
2. An upgraded University of Pennsylvania facility, dedicated primarily to ^{10}Be, ^{14}C, and ^{26}Al.
3. A third facility with a complete range of abilities from ^{10}Be to ^{129}I and the osmium isotopes. A natural site for this facility is at one of the national laboratories or at a university that has an operating accelerator of sufficiently high terminal voltage.

SAMPLES

Research programs on geological materials must have access to a broad range of synthetic samples of controlled purity, grain size, and structure, as well as natural samples representative of the different Earth regimes. Another need is for curation and allocation of samples so that they will be preserved and available for use by the scientific community. Activities centered around sampling, synthesis, and curating are often viewed as scientifically mundane and not worthy of high-level attention and support. However, adequate samples are of central importance to many investigations, and research on the wrong material can lead to erroneous results. Work on inadequate samples can be not only a waste of investigators' time, but also an unnecessary waste of resources.

Attention and support must be given to sampling and material synthesis programs over a period of years to establish the necessary collections. In addition, efforts must be made to provide for adequate curation of the samples and correlative data, allocation, and distribution of information about sample availability. The sampling and curatorial efforts organized by the Ocean Drilling Project for ocean floor materials and the Continental Scientific Drilling Program for continental materials are excellent examples of the attention that sampling deserves. Existing museums should be willing to help in this enterprise as might other institutions, particularly for samples of specific geographic or geologic regions. Continued long-term support for curatorial facilities is required; not everything needs to be in one place as long as catalogs of curated materials are widely available.

GLOBAL SAMPLING

A primary barrier to a better understanding of the Earth's evolution is the lack of problem-oriented, global-scale, systematic sample libraries. The emphasis here is on quantifying the variability of rocks and their source regions in order to reveal the nature and history of the Earth's internal processes.

The convective flow regime in the mantle can be characterized through a systematic program of sampling the mid-ocean ridge system (dredging and drilling at about a 50-km spacing), seamounts, and oceanic volcanoes on a global scale. Integration of the resulting geochemical and petrological data bases with the emerging global geophysical structure (e.g., seismic tomography) will help us to understand the present picture of mantle convection. Such a sample library exists for most of the Mid-Atlantic Ridge; very little exists for the Indian and Pacific oceans, with the exception of fairly good coverage on the Juan de Fuca Ridge. A sampling program and resulting sample library and data base is a long-term goal over the next few decades and can only be undertaken on an international cooperative basis.

Long-term variations of mantle convection might be determined through dated samples of the ocean crust, but as there is no ocean floor older than about 150 million years, one also needs to analyze the magmatic products preserved in the continental crust. Only through a carefully designed global isotopic study of the continents will we begin to understand the long-term variations of mantle behavior.

Studies of long-term atmosphere-hydrosphere-crustal interactions, such as weathering, use the sedimentary record, but this record cannot be read without modern baseline data derived from soils and sediments now being deposited. As with deep earth processes, the need is for sampling at the appropriate scale and creating a global data base.

DETAILED SAMPLING

There are several specific problems or processes—for example, the study of the nature of fluid flow and the reaction of the fluid with the host rocks—that will require extensive sampling on a local scale. Previous efforts to characterize fluid-rock systems have suffered from two principal flaws related to scale: (1) most characterization studies have been based on samples taken from small parts of large systems; and (2) large-scale studies have had a rather narrow focus. Large-scale efforts to understand mass/heat transfer will be most productive if a large number (1000 to 10,000) of samples are examined by a variety of geochemical/mineralogical/isotopic and other methods. Such characterization programs will, by nature, be most successful as collaborative efforts involving a large number of analyses and investigators. However, the symbiotic feedback inherent in such collaborative efforts will lead to profound advances in our understanding of many important earth processes.

It is becoming increasingly clear that some material properties can most realistically be measured only in the field, utilizing large-scale sample sizes. Permeability to fluid flow, for example, may only be meaningful if measured over regions on the scale of tens to hundreds of meters. The viscosity of crystal-bubble suspensions in silicate melts and their ability to convectively transfer heat can be studied in far greater detail using naturally occurring lava lakes than in the laboratory. The bulk properties (e.g., acoustic, rheologic, particulate behavior) of volcanic plumes can only be measured at the time of emission. Thus there is a strong need for "field observatories" through which such measurements can be made by instrumenting the appropriate terrain to study not only the instantaneous properties but also their temporal variation. Such a detailed characterization by many disciplines should also involve a field lab concept, where a careful three-dimensional field characterization is done along with a variety of in situ tests, e.g., the present flow field or stress regime.

HIGH-QUALITY SAMPLES

There is a need for high-quality, well characterized samples, including synthetic single crystals and polycrystalline aggregates. These are required for the laboratory determination of the physical and chemical properties.

For the next generation of experiments on physical and chemical properties, synthetic single crystal and polycrystalline starting materials are required. All rocks that are accessible at the surface of the Earth contain weathering or alteration phases that melt or decompose under high temperatures and pressures or otherwise affect the measurement of physical properties. To avoid such problems, synthetic, polycrystalline aggregates with controlled microstructure and composition must be fabricated. Some research groups occasionally hot-press small experimental samples; this approach is sufficient for exploratory experiments but clearly is unsuited for a concerted experimental program where sample-to-sample variations must be minimized. Likewise, other experiments require single-crystal samples, for example, to isolate matrix contributions to deformation from grain boundary effects, and to enable careful control and variations of structure and composition, e.g., in the determination of diffusion coefficients or transport properties.

Synthetic samples are required to study phases that are only stable under extremes of pressure and temperature. Synthetic crystals of $MgSiO_3$-perovskite, for example, are necessary because natural specimens are not stable at the Earth's surface (but probably constitute much of the lower mantle). Likewise, the synthesis of high-pressure polycrystalline aggregates would allow investigation of a wide variety of deformational and physical properties.

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Conclusions

Powerful new experimental and computational capabilities make a national effort in earth materials research logical and timely. Great opportunities exist for cooperative research activities among government, industry, and academic entities, as well as among the several geologic disciplines—geochemistry, geophysics, mineralogy, mineral physics, petrology, and rock mechanics. All of these groups are concerned with the physical and chemical behavior of earth materials. With such knowledge, great advances will result in understanding the processes that continually shape our planet. These advances should also lead to several practical applications, e.g., hazard analysis, resource exploration, and new materials.

Identification of common objectives, especially with respect to the procurement and use of new instrumentation and computational facilities, will lead to a more integrated and cost-effective national program of earth materials research. Not only is there a need for new instrumentation, but sustained support of existing instrumentation and techniques will allow continued progress in earth materials research. Development and/or greater use needs to be made of the following four specific technologies: (1) synchrotron radiation facilities, (2) high-pressure, high-temperature, large-volume experimental capabilities, (3) microscale, in situ analytical instrumentation, and (4) accelerator mass spectrometry.

To be successful, programs in earth materials research must have access to a broad range of representative samples to study. This includes the materials in which the physical and chemical properties are determined (both natural and synthetic samples) as well as those applied to investigations of a wide variety of geologic processes.

Finally, success with these and other related initiatives will require continued review, assessment, and implementation by those interested in physics and chemistry of earth materials—the Board on Earth Sciences, geoscience societies, funding agencies, and the investigators themselves.

Appendix A: Geochemistry

SUMMARY STATEMENT

The study of the isotopic and chemical composition of earth materials is unique in that the techniques available yield information about the history or provenance of a rock sample in addition to information about the processes involved in its formation. Almost all other observational methods can only characterize rocks as they are at present (e.g., seismology) or as they were at the specific time they formed (e.g., petrology and structure). Observational evidence relating to the rates or time scales of earth processes comes almost exclusively from isotopic measurements of geological samples. Measurements of the chemical composition of rock samples, especially trace element concentrations, provide complementary information about petrogenetic processes. By providing the ability to directly investigate processes and temporal evolution, these geochemical tools offer a means of studying earth evolution that extends far beyond what is usually thought of as the physical characterization of earth materials.

This appendix was largely developed by the following workshop group: Donald J. DePaolo (*Group Leader*), Thure E. Cerling, T. Mark Harrison, Ian D. Hutcheon, Mark Kurz, Marc C. Monaghan, Frank M. Richter, and Brian M. Smith. For affiliations, see Appendix E.

Unlike some other methods, precise measurements of isotopic composition are not generally possible by remote-sensing techniques. Consequently, the application of many powerful geochemical techniques to global problems is limited by the methods and programs available for sampling earth materials. In fact, at no other time has the field been so well equipped analytically and poised on the brink of major breakthroughs that can be achieved simply by optimal application of the available methods.

Present methods of geochemical analysis are powerful and diverse, but even better tools could be developed with modest advancement of existing technology. However, there is at present no mechanism for earth scientists to focus attention and resources on the development of new instruments. The lack of effort in this direction may severely compromise the future development of this area of research, both because of the lack of instrumentation development itself and because of the failure to provide a sufficient number of suitably trained young people to design the instruments of the future.

The focus of this section is on proposed means of advancing knowledge of the Earth's evolution by the initiation of major and parallel efforts in global sampling and geochemical analysis of the Earth's crust and in geochemical instrument development. We emphasize that the primary immediate barrier to major advances in this field is the lack of a mechanism to assemble problem-oriented, global-scale, systematic sample libraries for study with modern geochemical techniques. In addition, the capabilities within the earth sciences community for developing the analytical techniques of the future are eroding. A viable, efficient vehicle for geochemical instrument development must be found soon.

DEEP EARTH PROCESSES

MANTLE DYNAMICS

Problem

Perhaps the single most important breakthrough in earth sciences since the plate tectonic revolution is the realization that the Earth's mantle behaves as a viscous fluid that convects in order to move the Earth's internal heat to the surface where it is lost to space. It is this process that drives plate movements and magmatism that has produced the Earth's oceanic and continental crust, the atmosphere, and the hydrosphere. Now that this view of the mantle has been accepted, the next step is to better understand how the convection in the Earth's mantle behaves, what the behavior depends on, and how it is related to the processes we can observe at the surface—processes whose effects are available to be studied in the geologic record.

One important aspect of the characterization of mantle convection is its nature at the present. A major program of the Incorporated Research Institutions for Seismology (IRIS) has been established in order to construct a global, three-dimensional view of the present state of the Earth's mantle. Seismic waves measure physical properties of the mantle, but cannot uniquely discern the causes of variations in these properties because they in turn depend on several parameters. Heat-flow measurements are another important means of characterizing the state of the modern mantle, and efforts at defining global heat flow have been mounted already, although it may be necessary to reevaluate this problem as the other data bases mature.

A snapshot view of a convecting fluid is important, but just as fundamental to characterizing the flow is the question of how the flow field changes with time. Isotopic measurements represent the only means available for studying the time dependence of mantle convection. This can be done by systematic characterization of the isotopic compositions of magma that is spewed from the mantle. With global sampling, it is now possible to use isotopic measurements to characterize the convective flow regime, and thereby understand the thermochemical evolution of the Earth in a way that can never be accomplished by other means.

The demonstration of pervasive, long-lived chemical heterogeneity in the mantle is one of the major achievements of geochemistry as can be seen from the large number of new concepts it has produced for other areas of the earth sciences that only a few years ago were considered separate and remote from geochemistry. In terms of mantle structure and dynamics alone we now have plumes, isolated mantle reservoirs (layered mantle?), and an apparent need for mantle flows capable of dispersing heterogeneities and recycled crust. While the existence of chemical heterogeneity is now well established, the details regarding origin, age, and spatial structure of mantle heterogeneities are disputed and often vague. This level of uncertainty arises in part from the complexity of inferring the mantle source from the properties of the magmas observed at the surface, but also from the unsystematic distribution of sites sampled. Future efforts to better characterize and understand chemical heterogeneity in the mantle need to consider the potential distortions and biases that might arise from the type and distribution of materials analyzed.

Most would argue that the best (certainly most extensive) chemical probe of the mantle is volcanism in the oceans since the likelihood of crustal contamination is minimized. The types of volcanism available for study are mid-ocean ridge basalts (MORB), ocean island basalts, and a vast number of seamounts. If sampled in detail, each of these should provide a firm data base with which to test key concepts regarding the nature of chemical heterogeneities themselves and the structure, flow, and evolution of the mantle.

Mid-ocean ridge basalts provide the best opportunity to define the long-wavelength (>100 km) spatial spectrum of isotopic variation in the mantle. The spectral properties are a special measure of residence time in the mantle of heterogeneous material and of the ability of mantle convection to disperse it. In contrast to heat transfer, which is mainly sensitive to the amplitude of convection, the dispersal of chemical tracers is sensitive to the time dependence of the flow and thus provides an opportunity to examine the historical record of mantle convection. The data set needed to characterize the spectrum consists of a uniform sampling at 50- to 100-km spacing along the entire mid-ocean ridge system (~40,000 km). Demonstrating that such samples are representative will require occasional local sampling on an even more detailed scale.

Smaller scale (<100 km) variations can be studied using data from seamounts. Seamounts near the East Pacific Rise, for example, show a much larger range of isotopic variation than the nearby basalts from the ridge. This behavior is most easily understood in terms of small-scale heterogeneity that would be averaged by the large partial melt zone associated with MORB but evident in the small scale melting volumes of seamounts.

Intraplate seamounts (seamounts younger than the age of seafloor they sit on) are of great interest in terms of the concept of a chemical plume such as generally invoked for the Hawaiian Island chain. If intraplate seamounts prove to be very similar to Hawaii in their trace element and isotopic properties, the present thinking regarding plumes will have to be revised. One would have to argue for plumes everywhere or abandon the concept, at least in its chemical connotations. If the seamounts are different from Hawaii, then the special nature of plumes would be reinforced. The data from intraplate seamounts has the further potential of mapping the return flow and dispersal of subducted material, if it is isotopically distinct from normal sub-lithospheric mantle that presumably has the properties of MORB. The ability to characterize the properties of materials recycled back into the mantle is a fundamental question for both mantle and continental evolution through geologic time.

Despite their importance in shaping our ideas regarding mantle plumes, ocean island basalts have been sampled in a very haphazard and limited way. A deep drilling program to obtain the time evolution of the geochemical properties of Hawaiian volcanoes would provide further tests of the plume concept itself, the amount of mixing between plume source and MORB, and a key constraint on the physical processes by which magmas segregate from their mantle plume source. Secular chemical trends during the main tholeiitic stage of volcanism contain information on both the mixing of distinct mantle sources and the relative rate of melting versus segregation.

Recommendation

In order to advance fundamental knowledge of the Earth's evolution in an unprecedented way, a program of systematic sampling of the igneous rocks of the oceanic crust is proposed. This must include dredging and drilling along the entire length of the mid-ocean ridge system because the ridges sample the mantle in a relatively unbiased manner that allows the spectrum of geochemical variations to be evaluated quantitatively. In addition, drilling into seamounts using ship-based ocean drilling methods, and deep on-land drilling into intraplate oceanic volcanoes is necessary on a global scale to understand the origin of hotspots and other phenomena that represent yet poorly understood aspects of mantle convection. These samples must then be analyzed for chemical composition and particularly for the isotopic compositions of the elements Nd, Pb, Sr, Hf, O, H, Xe, Ar, N, C, and S, and possibly also Ca and Ce. In some cases analytical advances with regard to the precision of measurement are necessary to fully utilize the available methods. This program would produce a global geochemical data base that could be integrated with the global geophysical data base to produce a complete view of the mechanisms of evolution of the Earth's interior.

CRUST/MANTLE EVOLUTION

Problem

Characterization of the Earth's mantle through the study of oceanic basaltic rocks provides important information on processes in relatively recent Earth history. However, an equally important problem is how Earth's internal processes have evolved on time scales greater than a billion years. In this regard it is necessary to know whether mantle convection is quasi-steady-state, i.e., slowly changing with time, or whether there are singularities in the flow that could cause catastrophic changes in the convective regime. The long-time-scale effects can only be studied by observing their products as they are recorded in the continental crust, which preserves a 3.8-billion-year-long record. In particular, crust production is associated with subduction of the oceanic lithosphere, so the production rate must be a function of global heat flux. Thus the history of the fundamental physical and chemical processes and properties of the mantle and core of the Earth can be constrained by studies of the continental mass, i.e., the "mass-age" function of the continents.

Although this is a well-recognized problem in Earth evolution, the reason that it now appears important to undertake a concerted effort to determine the fundamental properties of the continents is the advent of powerful new isotopic tools that provide accessibility to the answers. The new tools are the isotopic systems that are sensitive to the times at which continental crust was spawned from the mantle (Sm-Nd and Lu-Hf), and the ion probe and other microanalytical approaches to the dating of zircons and other phases that preserve evidence of the times of the signal events in the evolution of continental rocks.

This problem can be studied by two parallel and reinforcing approaches. One is to characterize the isotopic variations in the ancient mantle by analyzing basaltic rocks; in other words, perform an experiment analogous to that of characterizing the modern oceanic crust. A more powerful approach is to measure the mass-age spectrum of the continental crust. The production of new continental crust is coupled to mantle convection through subduction zone magmatism. Consequently, the mass-age spectrum of the continents is the fundamental data by which solid Earth evolution can be characterized over the whole history of the Earth. The isotopic tools necessary to determine the mass-age curve have been developed over the past 10 years, and the analytical capabilities are currently being built up through the NSF instrumentation program. There is no chance of ever understanding long-time-scale variations in the behavior of the mantle except by a global isotopic study of the continents designed to address this problem.

The characterization of the evolution of the continents is a global-scale task. At present there are a number of areas that have been moderately well characterized in terms of age, origin, and structure, but vast areas are untouched by modern techniques. There can be no answer to the most fundamental questions in the absence of a uniform, modern data set that represents all of the continental mass.

Recommendation

A coordinated sampling and analysis program of continental basement rocks, younger granitic rocks, and sedimentary rocks must be undertaken. The analysis must include petrological and chemical characterization of the rocks, and particularly trace element concentrations and the isotopic compositions of the elements Nd, Pb, Sr, Hf, O, H, Xe, Ar, N. C, Ca, Ce, Ba, and S. This program must be international in scope, and involve geologists, petrologists, geophysicists, tectonophysicists, and geochemists in order to maximize the value of the sampling effort. What is needed is a global sampling effort and a commitment to fund isotopic measurements and collateral geologic and petrologic studies over a period of 10 to 15 years. The requirement is for the logistical support to ensure adequate sampling and for a commitment to a long-term program. This program must eventually be international; cooperation and contributions by many other nations are highly likely given the level of interest in this problem that is already evident outside the United States.

INTERACTION OF THE LITHOSPHERE-HYDROSPHERE-ATMOSPHERE

PROBLEM

The atmosphere, hydrosphere, and the upper lithosphere represent a very small fraction of the Earth's mass, but they are of extreme importance because they are the parts of the Earth with which human beings interact. The interest in these systems comes both from the need to manage the environment and from a desire to understand the evolution of surface processes through earth history, especially with regard to changes in climate and the relationship of these changes to processes in the crust and mantle, and to the evolution of life. The lithosphere, hydrosphere, and atmosphere interact on varying time scales, ranging up to the age of the Earth.

The important issue to be addressed in the study of the lithosphere, hydrosphere, and atmosphere is the rates of transfer of chemical elements between these and within these reservoirs, and how these rates may have changed through the course of earth history. For example, the Earth's atmosphere may have formed by the expulsion of gases from the Earth's interior associated with magmatism. Some of these gaseous materials condense and are contributed to the oceans. Some are fixed in rocks as the rocks undergo weathering on the continental surfaces or on the ocean floor. The weathered continental rocks can be eroded and deposited on the ocean floor, and then eventually subducted and returned to the mantle to restart the cycle. At present some theories hold that most of the gases now being spewed from the mantle were previously already at the surface and were returned to the mantle by the recycling processes. Others hold that most of the gas coming from the mantle is primordial. The issue of whether the Earth's atmosphere has been gradually changing throughout earth history, or has been in a steady state for a long time, is, for example, crucial to our views of how earth surface conditions have affected the evolution of life.

The most important geochemical interface between the mantle, the crust, and the surface systems is in subduction zones and their associated arc magmatism. These are the primary regions in which surface and crustal materials are returned to the mantle and mantle materials are transferred to the crust. These regions, which can be referred to simply as the arc-trench environment are the single most important link in the global cycles. It is in the arc-trench systems that continental crust production is linked to mantle convection, and that injection rates of surface materials into the mantle can be determined. The lack of quantitative data on the geochemical fluxes in the arc-trench environment is a major barrier in understanding earth evolution.

Even without considering the deep mantle, there is much to be learned about the cycling of chemical elements among near-surface reservoirs. The rates of transfer of elements between the land surface and the oceans, and between the oceans and the sediment layer of the ocean floor, are still poorly constrained. Likewise, the chemistry and evolution of groundwaters is still poorly known, especially when the effects of groundwater processes are considered on a global scale. The need to improve the understanding of the geochemistry of surface processes is partly in order to be able to better manage the environment. However, the history of these processes on the Earth is also of major interest. A rich record is held in ancient sedimentary rocks, but at present there are severe limitations to how well this record can be interpreted. These limitations have persisted because of a lack of systematic studies aimed at characterizing the modern global surficial geochemical system, and until recently, a lack of appropriate analytical tools to define the time scales of processes.

An example of the type of study needed is the dating of groundwaters in many different environments. This has immediate application to pollutant transport, radioactive waste disposal, aquifer management, and geothermal systems. It also applies to the general problem of understanding fluid flow in porous media. Another high priority target is the estimation of global weathering rates and soil development and their dependence on global climate. Weathering of continental materials is one of the most important processes for chemical exchange between the atmosphere, oceans, and crust. These studies have applications in areas such as acid precipitation, paleoclimatology, and the supergene enrichment of ore deposits.

Recent and impending improvements in analytical capabilities for measuring the abundances and isotopic compositions of short-lived cosmogenic nuclides are now making feasible a wide variety of investigations that hitherto had been impossible. The new tools, especially when combined with existing methods of light stable isotope geochemistry, can provide answers to fundamental questions that had not previously even been asked because of the lack of realistic investigative approaches. In the past, the rates of the relatively short-time scale surficial processes have been measured principally using radioisotopes, and by observing radioisotope decay in conventional detector systems. There is now a great opportunity to improve the measurement capabilities enormously by increasing the sensitivity by several orders of magnitude. This is accomplished principally by directly counting the mass ratio of radionuclides using accelerator mass spectroscopy (AMS) or by nonconventional counting techniques (single-atom detection). These analytical techniques allow much smaller sample sizes to be used (e.g., for ^{14}C, ^{10}Be) or allow the use of isotopes previously beyond the limit of measurement using conventional counting techniques for geological samples (e.g., ^{36}Cl, ^{81}Kr, ^{41}Ca). In addition new dating techniques can be applied to surface processes using some analytical tools previously used in petrologic studies but little used in chronologic studies (e.g., ^{3}He, ^{4}He). This arsenal of tools is now poised and ready for application to a myriad of fundamental geochemical problems.

RECOMMENDATION

The most important questions in the context of earth evolution have to do with global geochemical fluxes and global climate. These questions cannot be answered in the absence of global studies. As with deep earth processes, the need here is for systematic problem-oriented studies and the creation of a global data base. Because the analytical tools necessary for these studies are in place or imminent, the primary barrier to understanding the surficial geochemical systems in a global perspective is the lack of a program for sampling of solids and waters on a global scale, and for integrated studies of these samples.

A systematic global sampling strategy needs to be developed so that we may define the weathering structures of the Earth and quantify the rates of weathering of the continental crust on a global basis. In addition we will then develop an understanding of evolution of soils and sedimentary systems in a variety of climatic situations. This is absolutely necessary to extract and utilize the great deal of information buried in the stratigraphic record. Isotopic and mineralogical characterization of soil materials and profiles in a variety of environments that have a high probability of becoming part of the stratigraphic record are needed.

Another key element of a consolidated program to understand global geochemical cycles would be integrated studies of the types of hydrothermal systems that are the major mechanisms for the transfer of elements between and within reservoirs. Advancement in this field will require studies of hydrologic systems on the scale of sedimentary basins, continental hydrothermal systems, and ocean crust hydrothermal systems, using the full range of available chemical and isotopic techniques, and employing improved models of the properties of hydrothermal solutions at elevated temperatures and pressures and the properties of flow in porous media.

To address the problem of chemical exchange rates between the Earth's surface and the deep Earth, a series of geochemical arc-trench transects should be aimed at establishing the net geochemical fluxes in the arc-trench environment. The major components of this program would be systematic sampling and analysis, and would require drilling-to-basement on the oceanic side of trenches, dredging and drilling in the trenches and in the submarine forearc and back arc regions, and surface sampling and drilling on land. The full range of present and future analytical techniques could then be applied to the samples.

INSTRUMENT DEVELOPMENT

Implicit in our targeting of these compelling areas of research is the availability of analytical instrumentation with unprecedented capabilities. In particular, high-sensitivity, microscale, in situ isotope measurements on a wide variety of elements of geochemical interest are required in the entire spectrum of studies outlined above.

The development of sophisticated new instrumentation appears to be inextricably linked to the need for specialized research facilities. The financial and technical resources required to develop the next generation of analytical equipment is simply beyond those available to individual research groups in the earth sciences. There is a critical need to advance technology, which is impossible to meet with the present structure of research funding and management. Indeed, a concern of most laboratories is simply to keep present equipment running. There is a greater emphasis on training students to follow instructions and be operators rather than innovators—a greater reliance on purchasing equipment rather than designing it. Because of the limited commercial interest in specialized instrumentation for earth science needs, leadership in the development of new technologies must come from independently funded research centers. The support for these facilities should not be tied to the existing funding structure for individual research groups. We cannot "nickel and dime" the way to future excellence in the earth sciences and it must be clear from the outset that additional funds will be provided to ensure a renewed national effort in development of geochemical instrumentation. This would reverse the decade-long drift toward reliance on foreign manufactured instruments. The facilities should not be set up in competition with existing research groups but should be directed toward unique contributions in the areas of isotope ratio precision, spatial resolution, and dynamic range.

A high priority of these research centers must be to ensure the continuity of technical skills and education required to maintain strength in these areas.

The development of this next generation of geochemical instrumentation will require, in part, technologies anticipated but not yet realized. In the immediate future, we can identify specific instruments that can satisfy certain of the above mentioned scientific goals.

ACCELERATOR MASS SPECTROMETRY

The ability to directly measure the abundances of rare short-lived radioactive nuclides has allowed the determination of the ages of groundwater, of the rates of physical and chemical erosion in surface and near-surface crustal environments, and of the percentage contribution of sediments to island-arc volcanics. The future is rich with other applications.

MICROSCALE IN SITU ISOTOPIC ANALYSES

Development of micro-geochronological-isotopic probes, utilizing double focusing optics or ion cyclotron resonance designs, with capabilities exceeding present commercial instruments is essential for research in the following areas: U/Pb studies of continental evolution, oxygen isotope thermometry, and kinetic processes in natural and synthetic systems.

SYNCHROTRON RADIATION

Quantitative trace element abundances at the sub-ppm level on a microscale can be measured using techniques associated with synchrotron radiation. Such an ability allows important questions relating to trace element distributions in petrogenic processes to be addressed.

SPECIALIZED MASS SPECTROMETERS

Mass spectrometers designed optimally for specific applications, such as to allow: (1) precision isotope ratio measurements (e.g., Sr, Nd) at the ppm level; (2) improved efficiency for Lu-Hf analysis; (3) realization of Re-Os dating; (4) direct measurement of uranium decay products (e.g., ^{230}Th) for disequilibrium studies; and (5) optimization or realization of other radioactive isotope systems of great potential value, such as the K-Ca, La-Ba, and La-Ce systems.

Appendix B:
Petrology

SUCCESSES

Petrology began as a systematic attempt to organize and classify information about the diverse rocks that crop out at the Earth's surface. In its initial stages, the science was descriptive; dominant questions were: What is it? Where is it from? How old is it? There has been a steady evolution beyond this phase in thought and understanding, driven primarily by process-oriented hypotheses that are soundly based on the principles of chemistry and physics.

The chief success of petrology has been the identity of processes operating within the Earth's crust and mantle. Characterization of the processes responsible for volcanic eruptions, for example, are by no means complete but may be enumerated as initiation of melting at depth, segregation of melt from a solid-liquid mush, ascent of magma, its crystallization and differentiation, and eruption. Many ore deposits are expressions of this process of heat

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This appendix was largely developed by the following workshop group: Bruce D. Marsh (*Group Leader*), Philip H. Bethke, George H. Brimhall, W. Gary Ernst, John M. Ferry, Alexandra Navrotsky, Richard J. O'Connell, Michael F. Sheridan, and Bruce Watson. For affiliations, see Appendix E.

and mass transfer via aqueous solutions that operate at all levels throughout the crust.

Basic research on earth materials has, in the past, contributed to the discovery and utilization of mineral resources, and it is likely to continue to do so. Physicochemical research, for example, has made progress towards understanding the origin of ore deposits. Mineral exploration companies have used genetic theories of ore deposition to locate favorable districts in which to concentrate their exploration efforts; four examples follow.

1. A joint U.S.-Japan study of the copper-bearing Kuroko (black ore) district led to recognition of the environment most favorable for their formation, e.g., shallow ocean basins characterized by active volcanism. The results of Kuroko studies have guided exploration in Japan, Haiti, Vancouver Island, and elsewhere, and have resulted in the discovery of millions of dollars worth of copper reserves.
2. Studies of fluid inclusions in shallow, gold- and silver-bearing quartz veins led to recognition that mineralization was concentrated near the top of hydrothermal systems where boiling occurred. These observations have guided additional discoveries in veins in Creede, Colorado, and Winston, New Mexico, previously believed to have been mined out.
3. The discovery of "blind" ore deposits (those that are not exposed at the Earth's surface) has been made possible by research on the environment of ore deposition and on the fracture patterns that localize fluid flow and mineral precipitation. The giant Olympic Dam deposit (Australia) was discovered by drilling through 100 m of barren volcanics after a detailed analysis of factors favorable to the formation of such deposits.
4. The development of the theory of reaction path models led to a renewed interest and emphasis on mass balance relationships in ore deposits. From a basic science point-of-view this led to quantitative mapping of the source regions, transport, and deposition of supergene enrichment blankets. The theory has proved to be useful to mining companies for obtaining more accurate estimates of unmined mineral reserves.

A key contribution to identifying and understanding the operation of those processes has been made by field studies that determined the sequence and spatial relations of rocks involved in these processes. In the case of magmatic rocks, for example, the sequence of crystallization and differentiation followed by mixing of residual magma will lead to very different rocks than the sequence of initial magma mixing, followed by wall-rock assimilation.

Petrology is now following a natural evolutionary path that embodies the scientific method. Advancing beyond the stages of initial description and classification, and still further beyond the identification of processes, current work is now directed toward building objectively testable hypotheses using quantitative, predictive models. Significant advances are being made by combining classical geologic observation with the fundamentals of physics and chemistry. A significant area of investigation is the use of chemical microanalysis, thermobarometry, and radiometric dating to deduce the pressure-temperature-time history of specific portions of the crust. The physical and chemical properties recorded by crustal rocks are now being used to test dynamic physical models of subsidence, thickening, and uplift of the crust in relation to motions of the great crustal plates. Future prospects for continued success are bright, but it is also clear that, as quantitative models become more realistic, the basic data base is being rapidly outstripped.

CURRENT CHALLENGES

THE ROLE OF MICROORGANISMS IN SEDIMENTARY ORE DEPOSITS

Sedimentary basins are host to virtually all of our petroleum and natural gas resources. The basins are of equally great importance as sources of metals such as iron, copper, zinc, and manganese. Among the more fascinating recent discoveries is the recognition of genetic links between some metal deposits and hydrocarbons through bacteria processes. It may appear at first glance to be an implausible marriage: hydrocarbons, metals, and bacteria. It would indeed be implausible were it not for the existence of a favorable environment in which such a union could flourish. The special environment is found in the cap-rock of salt domes. Salt domes are structures unique to sedimentary basins that form when low-density salt is driven upwards by buoyancy through overlying, denser sedimentary rocks. The salt of the domes is relatively impermeable in relation to the more permeable sandstones it disrupts. The preserve of a relatively impermeable body crosscutting more permeable rocks acts to focus and trap fluids migrating through the sandstones. As is well known, salt domes are effective traps for hydrocarbons; but, for the same reasons, they also focus and trap basin brines flowing along aquifers. Research on salt-dome-hosted ore deposits offers the opportunity to evaluate the little understood role of bacteria in crustal processes. Bacteria are now known to live in the most inhospitable environments—hot springs, ocean depths, sedimentary basins; they also conduct the most unexpected activities, such as helping to produce ore deposits. Future discoveries may reveal even more surprises.

CHEMICAL AND PHYSICAL EVOLUTION OF SEDIMENTARY BASINS

Variations in porosity and permeability with depth in sedimentary basins are of fundamental concern in sediment accumulation, diagenesis, burial, hydrocarbon migration, generation of geopressure zones, and formation of brines. Porosity decrease with depth by pore volume collapse during sediment deposition is a central issue in understanding the evolution of sedimentary basins.

Understanding the broad range of chemical and physical transport dynamics in evolving sedimentary basins is severely limited by the present knowledge of rates of mineral dissolution, precipitation, and replacement as well as two-phase fluid flow and immiscible displacement. This inadequacy limits the full analytical treatment of heat and mass transport. Changes in physical properties during chemical interaction of fluids and rocks produce time-dependent circulation patterns and fluid plumes, and govern the temperature field in sedimentary basins.

Several research disciplines need to cooperate and interact in order to address the large-scale problems existing in sedimentary basins. These include organic geochemistry, particularly in treating the chemical thermodynamics of organic species as an active part of dynamic mass and heat transport systems. These organic constituents record more than just the thermal history of sedimentary basins. Through recent advances in chemical modeling, a more deterministic view of such systems is becoming possible, although much remains to be done on thermodynamic properties, reaction kinetics, and catalysis. Combinations of heat flow with computational models including chemical reactions are now starting to produce insights into the behavior of sedimentary basins such as the origin of geopressured zones and the effects of uplift and faulting.

Intensive industrial research efforts in applied areas have greatly aided in the discovery of oil and gas and in secondary and tertiary recovery systems, but many problems of a fundamental nature remain.

1. The generation of saline brines in sedimentary basins has long been used to explain the occurrence and distribution of Pb-Zn deposits in limestones at the margins of basins. The origin of the brines, however, their migration, and the precipitation mechanisms of Pb and Zn sulfides are matters of active debate.

2. Some hydrothermal ore deposits have no apparent association with a localized heat source such as a magma. However when ore forming fluids come in contact with specific lithologic units in sedimentary basins, their interaction often precipitates ores. Large scale aspects of these problems remain unresolved; heat flow, localized advective heat transport, and crustal tectonics need to be unified into a comprehensive model of sedimentary basins.

3. The source of energy driving hydrothermal systems within basins is not clear. Various models include tectonically induced gravity-driven flow, episodic flow resulting from overpressuring in the deeper parts of the basin, and introduction of a heat source in the deeper part of the basin. Each has substantial implications for the duration of transport, mass transport, and deposition. Perhaps all are operative mechanisms in different environments. How do we identify which one was operative in any specific environment?

SURFICIAL TRANSPORT PROCESSES

Studies of surficial processes present a wide array of potentially useful applications. These include important processes in economic geology, slope stability, metallogenesis, petroleum geology, and long-term toxic-waste isolation. Some applications have been known and widely exploited in industry; for example, chemical weathering processes can result in upgrading of metallic elements from proto-ore—these processes have been applied to mineral beneficiation technology. These surficial processes include secondary enrichment of Cu, Ag, and Au by oxidative weathering of primary sulfate ores and the formation of Ni-Co oxides through residual chemical weathering. Toxic-waste isolation and clean-up of existing contaminants utilizes principles developed in scientific studies of aqueous fluid flow and chemical interaction in surficial processes.

Chronosequences relating the spectrum of products of weathering are viewed as differing only in the age of the profiles developed from the same probabilities under identical conditions of climate, topography, and biota. Furthermore surficial environments present rich problems in petrology and geochemistry, as it is here that the lithosphere is interfaced with the atmosphere, hydrosphere, and biosphere. Chemical communication between these systems is enhanced by relatively high permeabilities, fracture densities, flow velocities, and reactivity of complex surficial aqueous fluids, which transport a wide variety of solutes derived through interactions with the subsystems.

While opportunities exist for research and in making continuing technological advances from studying surficial environments, our understanding is ironically incomplete and many potential applications await solution of outstanding problems. In large measure this is because the past focus has been on the chemical descriptions, and physical aspects, when considered, have been viewed as being essentially independent of chemical factors. A number of complications have delayed progress in both these aspects of fluid flow. First, chemical reactions in many cases are known to be strongly affected by kinetic factors and catalysts, which in some cases involves bacterial agents. We lack systematic evaluation of these effects. Second, porous media flow near the groundwater table involves complex two-phase flow processes and ground-air displacement involving gas diffusion, which may dominate oxidation-reduction processes above or near the capillary fringe zone that separates the unsaturated zone from the underlying saturated zone.

Those complex transport problems occurring at physical and chemical interfaces present outstanding opportunities for integrating fluid flow, solute transport, gas diffusion, and chemical reaction. It is clear that rigorous and useful solutions to these problems require more than simple model calculation using available groundwater flow programs that incorporate a reaction term in which all factors involved in chemical reactions are added to advection, diffusion, and dispersional terms. On the contrary, there is a vital need for understanding the physical and chemical processes involved in porous media flow and the rates of chemical reactions to advection and dispersive velocities. While groundwater flow models have been formulated and used effectively, much remains to be solved in understanding the complex interrelationships between aqueous fluid flow, geochemical transport, hillslope processes, ore deposition, chemical and mechanical weathering, pedogenesis (soil formation), and biological activity. Few problems are as yet sufficiently well-posed in terms of testable hypotheses.

MAGMA-DRIVEN HYDROTHERMAL SYSTEMS

Hydrothermal systems driven by heat-transfer from magmas emplaced into relatively shallow levels of the Earth's crust are of great economic as well as scientific interest. Active systems are exploited for geothermal power as in the Salton Sea and Geysers geothermal areas in California. Fossil systems, operating throughout the Earth's history, have concentrated important metals such as gold, silver, copper, molybdenum, tungsten, tin, lead, zinc, mercury, and others into mineable deposits.

These systems generally operate in the upper five kilometers of the Earth's crust and over the temperature range of 100 to 400°C. They affect volumes of rock in the range of tens to hundreds of cubic kilometers. Individual systems appear to average over durations of tens to hundreds of thousands of years, but are often superimposed on one another in space over a period of several million years. The fluids involved in the circulation are of both meteoric and magmatic origin. The chemistry of these systems is determined, in part, by the composition of the source fluids, but is greatly influenced by interaction of the fluids with the rocks through which they flow. Fluid compositions range from nearly fresh water to brines containing >35 wt.% salts—primarily alkali chlorides. Dissolved gases, particularly CO_2, may be important constituents.

Critical Problems

The intensive study of both active geothermal systems and ore deposits over the past decade has resulted in the development of comprehensive, comparative, quantitative models of magma-driven hydrothermal systems. The critical remaining problems lie in the qualification (and modification) of these models to make them truly predictive. First-order problems are the determination of the heat and mass budgets of such systems. To establish the boundary conditions for the quantitative formulation of such budgets, we must first resolve such fundamental issues as (1) the source of heat that drives the system; (2) the nature of the transition from conductive to convective heat transfer; (3) the sources, pathways, and depositional sinks of metallic and nonmetallic constituents; and (4) the spatial relationships between the thermal anomalies and zones of ore deposition. Some of these problems must be addressed, in part, by the development of new sampling programs (e.g., deep drilling). All, however, require the development of accurate predictive models that allow the testing of the results of changing the boundary conditions against the observational base.

Numerical models are useful in integrating mass and energy transfer with chemical and isotope evolution in time and space, and mineral solution and precipitation. The principal limitation to their utility is the inadequacy of our knowledge of the equation of state for complex brines, the thermodynamic properties of many minerals and solutes, and the kinetics of heterogeneous reactions in the 100 to 400°C and 1- to 2000-bar ranges. To be sure, improvements in treatment of fracture-controlled fluid flow and refinements of fundamental boundary conditions will remain important. The fact is, however, that our knowledge of many of the fundamental physical and chemical properties of most of the important phases is so poor, over the P-T range of interest, that it is a major bottleneck in our understanding of magma-driven hydrothermal systems.

The Observational Base

Because of the economic significance of ore deposits, their productive parts have been studied intensively, but represent only small parts of the overall system. In those parts of the systems available for study, the principal sources of information are the mineral assemblage and fluid samples. Studies of phase assemblages and chemical and isotopic compositions of minerals allow the estimation of the chemical and isotopic compositions of fluids presumed to have been in equilibrium with the assemblages.

Such estimates are made by reference to laboratory determined phase equilibria and measured thermodynamic properties of the minerals. Fluid samples from active systems are obtained at the well head during flow tests, and their compositions and thermodynamic properties (enthalpy) must be corrected for phase separation (flashing) and possible mixing from more than one productive zone. In fossil systems, fluid samples are obtained as inclusions of fluids trapped during mineral growth. Such fluid inclusions are generally on the order of tens of micrometers in largest dimension and are used in estimating temperature of entrapment, bulk salinity, and hydrogen and oxygen isotopic composition of the fluids. Such studies reveal that very large changes in temperature and salinity (and sometimes in isotopic composition) of the fluids occurred during the period of time over which the containing crystal grew, indicating (among other things) that fluid inclusions must be sampled individually. Similarly, electron microprobe analysis of the chemical composition of many vein-filling minerals has indicated that the record of variations in the composition of fluids in the time is written on a micrometer scale. Recent analysis by high resolution ion microprobe has indicated that variations in isotopic composition are preserved on a similarly fine scale.

Our observational base on magma-driven hydrothermal systems is limited to a small fraction of the system, and the variation in many of the most critical parameters must be determined by the analysis of very small (microgram range) samples. One of the most substantial impediments to progress in the understanding of magma-driven hydrothermal systems is the difficulty in obtaining such analyses.

FLUIDS AND MASS TRANSPORT IN THE CRUST/MANTLE

Regional Metamorphism

Introduction

Both stable isotopic and petrologic data indicate that the flux of fluids through at least some rock types during metamorphism may be enormous (10^5 rock volumes). Although the existence and chemistry of metamorphic fluids are well-established, the consequences of a large fluid flux through the lower crust during metamorphism is profound and must be investigated. The compositions of metamorphic fluids are controlled by mineral-fluid equilibria. These equilibria, calibrated by laboratory experiment, indicate that the C-O-H-S fraction of the fluid typically is dominated by H_2O, CO_2, and CH_4.

Investigations of active crustal processes testify to the important role of fluids as agents of the transfer of heat and matter in the Earth's crust. The Salton Sea Scientific Drilling Project recently drilled 3.2 km into an active geothermal system. The discovery of calc-silicate mineral assemblages forming at temperatures of 300°C, far cooler than the temperatures at which they are stable with their reaction products, demonstrates that infiltration-driven metamorphism is currently active in geothermal/contact metamorphic environments. These observations provide a basis for interpreting evidence of infiltration-driven metamorphism in ancient rocks once buried to depths of 10 km or more.

Scientists on board the submersible Alvin have found warm water springs and an oceanic ridge crest-like biota along the walls of deep trenches in the Pacific Ocean. This discovery, together with other studies of fluid-rock interaction in accretionary wedges, suggests that subducting slabs do not release their water into the overlying upper plate; instead, at least some of the water driven off by compaction, heating, and the breakdown of hydrous minerals follows aquifers and fractures back up the inclined slab to return to the ocean. The focusing of fluid flow within the subducting slab leads to high fluid-rock ratios and is undoubtedly responsible for the pervasive stable isotope equilibration between different rock types seen in exhumed subducted slabs such as the Franciscan.

Recognition of modern metamorphic waters being driven from great depths toward the Earth's surface supports current efforts to infer the nature and magnitude of fluid flow in ancient crust.

Issues and Problems

The amount of chemically reactive fluid that flowed through a rock during metamorphism (expressed as a fluid-rock ratio) may be estimated, under favorable circumstances, from either isotopic or petrologic data. Fluid-rock ratios should be determined for a wide variety of rock types from the spectrum of metamorphic regimes on scales ranging from individual mineral grains to entire metamorphic belts. Results should show which rock types are infiltrated by large amounts of fluids in which parts of the crust. More importantly, it needs to be established whether the flow of large volumes of fluid through rocks during metamorphism is a general phenomenon affecting thousands of cubic kilometers of the crust or an exotic phenomenon affecting only special rock types under special conditions.

Fluid-rock ratios should be mapped in metamorphic rocks on scales ranging from orogenic belts to outcrops to individual hand specimens. Results for hand specimens and outcrops will identify how fluid flows through rocks deep in the crust, e.g., is flow pervasive on a grain-size scale or is it channelized? If fluid flow is localized, the channelways will be identified by the mapped patterns of fluid-rock ratio (e.g., lithologic layers, fractures, and foliation), and controls on the location of the channels may be determined. On a regional scale, major "freeways" for fluid flow may exist.

Although isochemical metamorphism is an implicit assumption in many studies of metamorphic rocks, it has been demonstrated in surprisingly few instances. Correlation of chemical data with calculated fluid-rock ratios of certain rock types, however, demonstrate that metamorphic fluids may remove or exchange 70 to 90 percent of the rocks' alkalis. The mobilization, transport, and redeposition of elements and isotopic species by metamorphic fluids need to be carefully examined. Studies of the major-, minor-, and trace-element and stable-isotope composition of a wide variety of metamorphic rocks and the unmetamorphosed equivalents should be determined in the diversity of metamorphic regimes. Fluid-rock ratios should be estimated for all samples from petrologic or isotopic data. Results will lead to a new level of understanding of the role of fluids in the chemical and mineralogical evolution of metamorphic terranes, the development of the large-scale geochemical structure of the crust, and the origin of several important kinds of ore deposit.

Metamorphism is almost universally considered a thermally-driven process. Recent studies, however, have shown that metamorphic mineral-fluid reactions may also be driven by infiltration; active infiltration-driven metamorphism has been observed recently in the Salton Sea drill hole. The role and extent of infiltration-driven metamorphism should be investigated, which may bear on the origin of granulites, which apparently constitute much of the lower crust.

Prograde regional metamorphism is an endothermic process. The most popular numerical models consider that the required heat is transported exclusively by conduction. While these models are generally successful, they have a number of peculiar features: (1) they require a long time for metamorphism—typically 50 to 100 million years; (2) they require tectonic burial of tens of thousands of square kilometers of rock by 30 to 50 km of overburden; (3) they are incapable of simulating andalusite-sillimanite type rocks; and (4) they are incapable of simulating the sharp ground-surface thermal gradients observed in many metamorphic terranes. All these problems could be alleviated if there were significant heat transport during metamorphism by fluids. Further research is called for on two fronts. (1) Thermal models of regional metamorphism should be generalized to include heat transfer by convection as well as by conduction to determine whether the combination eliminates some or all of the above problems. (2) Field-based petrologic studies should seek correlations on scales ranging from individual outcrops to entire orogenic belts between (a) regions of high heat budget, short duration of metamorphism, and/or high thermal gradients and (b) regions of high fluid flow.

Mantle Metasomatism

Introduction

Until a decade ago the mantle was assumed to be relatively homogeneous with its long-term chemical evolution principally controlled by extraction of partial melts and return of the lithosphere via subduction. Recently, mafic volcanic rocks have been discovered, however, with Sm-Nd isotopic compositions that indicate they were derived from ancient "depleted" mantle but were anomalously enriched in light rare-earth elements (LREEs), large-ion lithophile elements (LILs), Ti, and other elements beyond the level expected for magmas derived from depleted mantle. The source rock evidently was enriched in these elements after the depletion event but prior to magma generation. This and related observations suggest a family of processes other than magmatism and subduction that mobilize, transport, and deposit elements in the mantle—metasomatism. Other evidence in volcanic rocks for mantle metasomatism include peridotite xenoliths in which olivine and pyroxene deviate greatly from oxygen isotope exchange equilibrium. The characterization and implications for mantle metasomatism are not well developed.

Issues and Problems

Although mantle metasomatism commonly involves LREEs and LILs, there is an incomplete understanding of which elements may be involved or whether there are distinctive patterns of element mobility as a function of position in the mantle. The reactions by which elements are mobilized and precipitated are unknown as is the nature of the transport agent (i.e., silicate melt versus C-O-H fluid). The detailed comparison between "pristine" and metasomatized mantle xenoliths should provide clues to some of these questions. Although the relative timing of mantle metasomatism is postdepletion and premelting, the time scale of the process is unknown. Most importantly, the role that mantle metasomatism plays in triggering melting and in controlling the chemical evolution and chemical heterogeneity of the mantle is not clear.

MAGMA PRODUCTION, ASCENSION, AND ERUPTION

Volcanoes are tacit reminders of the dynamic nature of the Earth's interior. Magma is produced generally within 100 km of the surface. How it segregates into movable bodies, how these bodies themselves move, how they chemically and physically evolve during ascent, and how and why they erupt onto the surface are central issues of interest.

Magma is the prime carrier of heat and mass into the upper levels of the Earth, which furnishes the energy to rework the crust, sustain geothermal fields, and generate ore deposits.

The study of magmatic rocks has long been a chemical investigation, but physical studies over the past 15 years have proven so important that it now holds an equally important role. We thus currently enjoy a revolution in magmatology whereby possible processes are investigated from a unified view of both physics and chemistry. What is outlined here are the essentials of the magmatic life cycle from inception to eruption.

Melt Production and Segregation

Understanding the physico-chemical process of magma production and evolution is central to understanding volcanism and to further development of both geochemical and geophysical models of crust and mantle structure and evolution. A basic knowledge of relevant phase equilibria is needed before melt generation can be discussed in terms of specific pressure-temperature (P-T) regimes in the Earth. Here, however, the focus is on the *process*, not specific conditions.

Melting

Melt production begins when the solidus of a particular region in the crust or mantle is exceeded. The first-formed melt is localized at the grain edges of the preexisting rock, forming a network that is interconnected in three dimensions (at least in peridotite source regions). The extent to which these localized channels of melt penetrate the planar grain boundaries is determined by the balance between the interfacial energy of the solid-solid boundary and that of a solid-liquid interface. For systems studied to date, this penetration is not very great, so grain boundaries remain generally unwetted, resulting in continuous solid-to-solid contact in the early stages of melting.

Experimental confirmation of the above-described partial melting texture, in which both solid and liquid are continuous in three dimensions, was a milestone not only in our understanding of the initial stages of magma production, but also in our ability to predict the physical properties of partially molten regions of the Earth. For example, the elastic properties, electrical conductivity, and bulk viscosity are markedly affected by the degree of interconnectedness of the solid and liquid phases. Results for the peridotite/basalt system suggest a high degree of liquid-phase connectivity for the entire partial melting range from <<1 percent to as much as 30 percent. This conclusion cannot at this time be generalized to other systems.

Melt Extraction

Once the initial melting texture is understood, the question then arises as to when and how the melt begins to leave the partially-molten system. Our present state of thinking is that two factors begin to operate. On the one hand, we recognize that a "column" of partially-molten rock in a gravity field tends to collapse as the continuous bridgework of residual crystals deforms by viscous flow under its own weight, thus expelling the melt upward. Models incorporating realistic physical parameters for basaltic melt and residual olivine suggest that quite rapid and efficient upward expulsion of melt will occur.

On the other hand, however, it must also be recognized that a system will tend to minimize its total surface energy; this state is achieved when a certain, highly-specific melt fraction is present along grain edges. Larger amounts of melt tend to be expelled, but the system resists expulsion of melt fractions below the critical amount. Experiments suggest that this value is 1 to 2 percent partial melt for the mantle.

Both physical and chemical considerations enter into the melt generation/segregation problem. At present, we do not know how these factors play off against each other to determine the overall behavior of even the relatively well-studied peridotite/basalt system. Melt production in other systems (e.g., the continental crust) is even more open to question, in part because the wetting characteristics are less well known and also because no gravitational compaction/expulsion models have been attempted.

The problem of melt production and segregation in any region of the Earth is further complicated by the probable competition between the tendency for the melt to leave its source region and the tendency for bulk, diapiric rise of the melt/residue system. Our ability to assess the overall behavior of a partially-molten region is hampered by lack of fundamental physical property data, perhaps most importantly the rheological properties of crystal and liquid aggregates.

Melting Dynamics and Trace-Element Geochemistry

The residence time of a partial melt in its source region, or more specifically the interplay between the rates of production and extraction, can have major effects on the trace element character of magmas that eventually reach the Earth's surface. For lack of better boundary conditions, trace element geochemists have assumed simple "end-number" melting processes such as complete (batch) equilibrium or Rayleigh fractionation. The frequent failure of these simplified models to explain observed trace element abundances underscores the importance of gaining a better understanding of melting dynamics.

Cooling and Crystallization of Magma During Ascent

Crystal Fractionation

Magma appearing at the Earth's surface can be vastly different chemically from that originally produced in the source region. This potentially extensive modification occurs by gravitational separation of crystals from the moving body; i.e., crystal fractionation. The exact amount and composition of these crystals rests critically on an accurate and detailed knowledge of phase equilibria over a wide range of pressures and temperatures. The P-T trajectory taken by the ascending magma depends on the mode and rate of ascent, rate of heat loss, and the thermal properties of the crystals themselves. The magma is continually evolving chemically throughout its ascent and, although the heat transfer attending ascent is somewhat known, the chemical evolution itself can only be understood via detailed and accurate P-T phase diagrams. The great tragedy of the present situation is that there is a general perception that such information is already well known. In fact, nearly all phase equilibria known to 30 to 40 kbar are based on studies in the 1960s where the run times were too short to approach equilibrium, the capsules strongly absorbed iron, and the fugacity of oxygen was uncontrolled. These deficiencies largely invalidate these results for quantitative applications. This lack of information severely cripples all attempts to model accurately the chemical evolution of magmas during ascent.

Crystals can only separate efficiently from magma if their settling velocities are considerably greater than the convective velocity of the magma itself. Convection is driven by the rate of heat transfer to the wall rock, and convective velocity can be fairly well predicted from parameterized models of fluid and flows. The rate of settling of crystals depends largely on their size and density. Crystal density can be measured at low pressures, but knowledge of crystal size depends intimately on the kinetics of crystallization. Rates of nucleation and growth depend on the degree of undercooling, melt composition, kinetic order of the reactions, and the style of nuclei formation. In convecting magmatic systems, undercooling is apt to be small everywhere in the system, and thus crystal sizes, both in terms of size variation per volume and spatially, can be predicted with adequate information of the rates of crystal growth in silicate melts; at present, this information is lacking.

Magma-Wall Rock Interaction

The initial penetration of magma through the lithosphere and crust allows for extensive chemical exchange between the magma body and its wall rock. This exchange can overwhelm certain trace element and isotopic tracers to the degree that the original chemical signature of the source is greatly obscured. Repeated use of the same magmatic passageway, probably a common event, lessens the chemical exchange due to formation of an insulating halo of magmatic contaminants within the wall rock itself. Succeeding magmas thus increasingly reflect the detailed major, trace, and isotopic element signature of the source, while the earlier magmas carry a significant signal from the wall rock encountered during ascent. This picture is only now beginning to evolve; to understand fully such exchanges, the diffusional flux between magma and wall rock of major, trace, and isotopic elements must be studied. This entails measuring the coefficients of diffusion under conditions of high pressure and temperature. At the same time, field studies of recent volcanic centers must be made to delineate the critical conditions of magmatic flux and longevity that lead to producing a "clean" magmatic plumbing system. Some small systems may never reach a mature state, while others may be so active that the wall rock itself, either by melting or erosion as in stoping, is continually refreshed and never allowed to become chemically insulating. A detailed knowledge of the thermal evolution of magmatic plumbing systems is thus also necessary to understand the process of secondary magma generation in both the mantle and crust due to ascending magma. Large silicic systems characteristic of continents are thought to arise from heat from basaltic precursors, but the means by which this is possible is not clear—nor is proof available.

Such studies should select representative samples from well mapped volcanic centers where the context of the sample is known within the eruptive sequence and the sample itself is thoroughly characterized in terms of major and trace elements, abundances model mineralogy, mineral composition, and phase equilibria. Programs that aim merely at field sampling with less than a full chemical characterization should be discouraged.

Dynamics of Magma Chambers

Magmas approaching the Earth's surface can lose their buoyancy and pond in the subsurface environment, forming magma chambers. These are the magmatic staging areas for volcanic eruptions. The diversity of igneous rocks, often observed within a single volcanic sequence, is thought to have its origin in such magma chambers.

The principal goal here is to understand the intimate interplay between the dynamical motions of the magma, leading to crystal sorting and fractionation, in response to cooling and crystallization. The style of convection itself, whether it is turbulent, laminar, large scale, of multiple scales, tiered, or localized and intermittent, is very much at question. Such convective processes largely determine the chemical evolution of the magma, the pattern of mineral deposition along the margins of the body, and possibly the eruptive behavior of the body itself.

Magmatic Wall Rock: Fracturing, Hydrothermal Flow, and Heat Transfer

Upon intrusion of magma, adjacent wall rock is heated, expands and seals against fluid flow. Outward, beyond some critical distance, the rock is under tension, is fractured, and supports a hydrothermal system driven by heat flow from the magma chamber. Just after emplacement, the fracture envelope retreats from the magma in response to heating of the wall rock, reaches an equilibrium distance, and then advances inward with continued cooling of the magmatic body until it invades the body itself.

At the same time, extended cooling and crystal fractionation promotes formation of an aqueous-rich vapor phase that may produce enough vapor pressure to fracture intermittently the sealed envelope and communicate with the more expansive external hydrothermal systems. This interaction between internal and external aqueous-dominated systems is the critical process in transport of soluble magmatic chemical components from the magma to the hydrothermal system, which carries and cools the fluid, enabling alteration and ore deposition within the wall rock.

This general multifaceted process is of considerable interest and yet is poorly understood. What is needed is an interdisciplinary, collaborative effort to develop an accurate numerical model describing magma cooling, wall rock fracturing, and hydrothermal flows with chemical reaction. This model must incorporate physical properties and scales actually observed and common to such systems.

Magma Withdrawal and Eruption

Pyroclastic flows, surges, and blasts of large-volume volcanic eruptions offer the greatest source of risk to human life and property of any natural phenomenon. The physical understanding of these dramatic processes and their general role in magmatism is of paramount importance to mankind. The central issue in this study is the desire to understand what the depositional sequence of volcanic materials on the Earth's surface can tell of the magmatic processes that lead to their eruption and deposition.

Magma Withdrawal

Beginning with the concept of magma held in a near-surface container where temperature and viscosity are strong functions of space, it is of great interest to consider what the pattern of withdrawal to the surface might be if this system was suddenly tapped. The geometry of the tapping system is clearly important as is the detailed viscosity-density field within the body. Fundamental questions include the following: Can the spatial distribution and relative volumes of erupted materials be used to infer the structure of the magma chamber? Do most lavas come from the least viscous parts of the system? What is the probability of any parcel of magma being erupted during a cycle of chamber evacuation? How does the volume of erupted material relate to the volume of the chamber itself and to the dynamics of the eruptive process?

A second fundamental issue involves why volcanoes erupt at all. What makes magma want to leave the confines of the Earth? It is clearly a bulk density differential that leads to a pressure gradient that produces an eruption. But is this density differential a result of a tall, standing column of magma whose lower levels really foster eruption? Or is it due to the much more local effect of exsolution of volatiles from magma as it ascends and gets the "bends"? In what instances do tectonic factors stimulate eruption? The key to gaining insight into such processes is the construction of quantitative models of withdrawal using forced flows but with realistically strong spatial variations in magmatic viscosity. Through such models, the observed deposits of volcanic materials can be reassembled and reconstituted as they once must have existed in a magma chamber or column within the Earth—a central goal of this research. It is clear that field studies form an integral part of such investigations. Insight into this general process might be readily at hand through studies of the transition from magma to lava, which is occasionally found in volcanic terranes; hand-in-hand with such studies is an explanation of the transition from volcanic to plutonic igneous textures.

Eruption of Magma

Although the mechanical passage of magma from chamber to surface is critical in understanding the end volcanic products, it is the dramatic eruption itself that is perhaps most readily at hand to study. It is just these eruption processes about which so relatively little is known. Why and how does a magma fragment into particles ranging in size from dust to boulders? Is it the mechanics of volatile exsolution and bubble growth that largely determines the style of fragmentation? What controls the depth where such fragmentation takes place and how does this influence the spectrum of particle sizes produced? The questions seem limitless, but most revolve around the general subject of liquid fragmentation during turbulent, explosive eruptions and the processes by which such flows sort and deposit these fragments.

Within the eruptive column itself, there are many questions concerning the geometry of the vent and its relation to the nature of the eruption itself. Are magmatic shock fronts produced in the conventional sense of bursting of a membrane across which a pressure jump occurs? Are such shock fronts common and do they travel both outward and downward, stimulating further bubble nucleation and vaporization within the chamber?

Eruptive plumes can be directed upward, laterally, or anywhere in between. They can be weak or very strong—some entering the stratosphere—and their behavior is largely dependent on their particle load. Simple models have been developed with good success to study the relation of eruptive column rise height, rise rate, water content, and eruptive conduit size. These studies also give useful insight into the pattern of deposition of particles as a function of column energetics and its interaction with the atmosphere. Three-dimensional models can be developed where the dynamics of the column can be studied in relation to particle sorting, dispersal, and fractionation, especially in relation to stability of the column as a whole. The initiation of pyroclastic flows and surges in general may be related simply to the behavior of a dusty gas with a concentrated basal layer moving by grain flow. In this respect, the cause of separation into high-concentration pyroclastic flows (ash flows) and low-concentration pyroclastic flows (surges) is still to be determined.

In no other aspect of magmatism is the spatial distribution and sequential arrangement, in terms of particle size and bulk composition, so abundantly available for interpretation and deciphering. Such information is critical in constraining and refining quantitative eruptive models. At the same time, real-time measurements of column load, velocity, mass flux, bulk composition, particle-size distribution, and temperature can possibly be made at the nozzle or orifice itself. The fruit of such quantitative measurements and modeling will be the ability to interpret older volcaniclastic deposits in terms of style and evolution of explosive eruptions.

Mitigation of Volcanic Hazards

Volcanic calamitics are usually more localized than the effects of earthquakes and tidal waves, but the destruction and loss of life can be far greater. Because humans, especially in the Americas, have only now lived long enough near volcanoes to experience their life cycle, the dangers seem strongly on the increase. The situation will clearly worsen.

Mitigation of hazards is best accomplished by pre-crisis study and dissemination to the populace of critical information on the spectrum of real dangers. It is essential to know the basic real-time style of behavior of volcanoes. The first-order risks in terms of topographic effects of channeling flows and what to do about them or in case of eruption must be carefully evaluated and of general knowledge to the populace.

Systematic and straightforward monitoring of volcanoes in closest proximity to significant populations can become a routine matter if modern and classical techniques are combined.

CRUST-MANTLE EVOLUTION

Reservoir Recycling

What Happens to the Descending Slab?

The descending slab starts out as a sandwich of sediments and water, invariably altered oceanic crust, and depleted mantle material. New additions to the continents eventually come from this material in a poorly understood process in which the chemical and physical evolution, time scale, and fraction of material recycled are poorly constrained. There is a fractionation of elements between material ultimately returning to the crust and that sequestered in the mantle. The fundamental problem is to gain a quantitative appreciation of the fundamental physical and chemical processes governing this process. We have relatively clear field evidence from Mesozoic to recent times; we have suggestive evidence that this process has evolved in time.

We need elemental and isotopic tracers to fingerprint the fate of various components of the downgoing slab. These data must be integrated with better phase equilibrium data to constrain P-T composition history. Currently, phase equilibrium data are fragmentary, especially concerning melt compositions. Therefore the partitioning of tracers among melt, solid, and fluid phases, especially at high P and T, are poorly constrained. The compositions of coexisting crystalline phases, especially high-pressure solid solutions, are poorly known. Actualistic thermal structures of convergent plate settings await more realistic assessment of advective heat terms including aqueous fluid flow. The actual styles of heat flow and mass transfer will be determined by the mechanical and thermal properties of minerals and their aggregates, by the kind and amounts of fluids present, and by the thermodynamics of mineral reactions, especially phase transitions.

What is the Fate of Tectonically Thickened Crustal Sections?

The average continental crust appears to be more silicic and alkalic than can be accounted for by production in island arcs. If this is not sampling bias, it requires another process to be operative in the formation of the continents. This requires some differentiation at deep crustal levels, a rise of silicic material and sinking of the refractory residuum into the mantle. These processes can be better constrained by the same approaches and data mentioned above. An understanding of the physics and chemistry is even more central to describing such processes because we have very few, if any, samples from the field that clearly document the process.

PreCambrian Crustal Evolution

When and how did the crust form and how did it evolve? The early stages of crustal evolution, as seen in fragmentary records, show a preponderance of very primitive mafic and ultramafic lavas, widespread gray gneiss terrains, and sediments that are dominantly volcanogenic and unsorted. Detritus also suggests a far less oxidizing atmosphere. This argues for very different conditions in the crust and at the surface and for higher temperatures and higher heat flow in the mantle. The detail of this evolution requires knowledge of the rates of accumulation and compositions. To constrain this, we need better phase equilibrium data, especially on ultramafic systems and trace element and isotopic data for rocks and minerals. Thermal modeling of the early Earth must be combined with petrologic evidence. Model studies of convection in early analogs of plate tectonics are needed.

Mantle Petrology

What is the physical and chemical basis of heterogeneity in the mantle? Seismology has documented radial heterogeneity in terms of upper mantle transition zone, and lower mantle. More dynamically significant heterogeneity (both radially and laterally) is being inferred from free oscillations, surface waves, and body-wave tomography. There is isotopic evidence for distinct reservoirs in the mantle, but their locations are poorly constrained. Direct petrologic evidence is all but lacking; those samples that arrive at the surface (kimberlite diatremes) may be atypical. Indirect knowledge based on the composition of mantle-derived melts is complicated by an unknown degree of modification during ascent. Therefore, much of the petrology must be obtained from experimental studies. These are still fragmentary and insufficient in detail. We need liquidus-solidus curves for mantle relevant systems, subsolidus equilibria, and partitioning of trace and major elements between solid and melt. We need elastic properties and densities, electrical and thermal properties. Studies of complex petrologic compositions will complement those on simple end-member components. Changes in proportions and morphology of phases in multiphase aggregates will affect elastic properties and densities. Pronounced changes can occur at reaction boundaries.

Is there a crossover in density ratio of crystals to melt with increasing pressure? If melt in equilibrium with crystals has a higher density, it will not rise and refractory constituents will no longer be concentrated toward the deep interior. To identify and locate such a crossover, detailed phase equilibria and density measurements of crystals and melts at simultaneous high pressures and temperatures are necessary; these are at or exceed the current limitations of high-pressure equipment.

TECTONICS AND PETROLOGY

Why Does the Earth Have Plate Tectonics?

Plate tectonics is an expression of the mechanical properties of earth materials. Phenomena associated with plate tectonics include extensive partial melting under ridges, production of oceanic crust, convergent plate settings typified by trenches and reincorporation and subsequent partial fusion of previously differentiated material. The continents and ocean basins are the most spectacular manifestation of plate tectonics. Venus shows no clear evidence of plate tectonics. It appears to have little water and considerably higher surface temperatures. What features of the petrologic evolution of the two planets led to these differences? Without considering the detailed physics and chemistry of the materials and the energy balance of the planets, models of planetary evolution are ad hoc. Phase equilibrium studies in the presence of volatile constituents (H_2O and CO_2) are crucial in this context.

Petrology of the Mantle—Relation to Seismic Data

Our knowledge of the structure and properties of the Earth's interior comes primarily from remote sensing with seismic techniques. Recent seismological initiatives have revealed detailed lateral heterogeneities that must be related to current dynamical processes such as convection and flow; for the first time it may be possible to actually observe and understand the large-scale dynamic processes that govern the evolution of the planet. We cannot, however, do so unless we know what causes the observed variations of seismic properties.

What is needed is knowledge of the elastic properties and densities of mineral assemblages that may exist at high pressure in the mantle. The elastic properties of an aggregate represents an appropriate average of the single crystal elastic constants of the individual minerals, modified by the effects of grain boundaries and other consequences of aggregation (such as cracks or voids or fluid phases). The proportion and compositions of the individual minerals are determined by the constraints of phase equilibria for the given composition at the temperature and pressure in the mantle. Thus the seismic properties will reflect the pressure as well as the variations in relative proportions of various minerals and contrasting properties of individual minerals.

Anisotropy of aggregates caused by the preferred orientation of anisotropic minerals, or by a strong directional fabric of grain shapes provides a direct method of inferring the stress field and plastic flow in the mantle. Seismic determinations of anisotropy may thus allow three-dimensional imaging of convective flow in the Earth better than it can be done in the laboratory! The seismic results will not be scientifically interpretable, however, unless we know the anisotropy of mantle minerals, and the relation of preferred orientation and fabric of grains in a rock to the stress field and deformational history.

NEEDS

Needs are similar to the overall needs of the geoscience community, but are also unique in several areas.

SAMPLING

Extensive global and regional sampling is needed to understand the dynamics of global cycles and how the smaller scale reservoirs and processes participate in the grand scheme.

It is of paramount importance to petrology, however, that sampling be done in as meaningful a way as possible, with samples being from geologically well characterized terrains and the sampling sites themselves well documented. The samples must, whenever possible, be fully characterized in terms of petrographic, mineralogic, bulk chemical, and isotopic composition. In some regions or instances sampling may be necessary over time to capture a process.

MATERIAL PROPERTIES

The mechanical properties of rocks, including fracture strength and rheology, should be known beginning at temperatures of about 300°C and continuing through the melting interval to the liquidus; the effects of bubbles on suspension rheology should be gauged. Kinetics of crystal nucleation and growth in meaningful petrologic systems, both at the hydrothermal and magmatic stages, should be studied. The thermodynamic properties of minerals and solutions, especially hydrothermal solutions at high temperatures and pressures (i.e., 300-600°C and 2-15 kb), should be investigated by state-of-the-art calorimetry and solubility experiments. Large-scale properties such as hydrothermal permeability, magma rheology, and acoustical properties of volcanic plumes need to be studied in the field with real-time monitoring—using the concept of field observatories (see below).

INSTRUMENTATION AND TECHNOLOGY

Methods are needed to improve the characterization of mineral surfaces, the control of oxidation state at high pressures, the measurement of liquid and solid densities at elevated pressures and temperatures, the determination of elastic properties of very small samples, the employment of catalysts to encourage equilibrium in experiments at low temperature, and the use of large-volume experiments at ultrahigh pressures.

FIELD OBSERVATORIES

The dynamics of convection, cooling, and crystallization of lakes of lava, the flow and reaction of hydrothermal fluids, the dynamics of eruptive plumes, and the chemical role of plants and the atmosphere in forming ore deposits can best be studied with an ongoing, real-time effort centered around a field observatory. This new concept would allow unprecedented research advances on subjects of paramount importance to petrology.

MANPOWER

A collective pool of postdoctoral internships should be formed. Open competition would determine the awards, with awardees free to study at any laboratory where the director would receive them. The present number of fellowships is much too small to be effective in advancing research in any significant fashion. The current procedures and limitations appear to be overly restrictive.

Appendix C:
Mineral Physics

INTRODUCTION

HIGHLIGHTS

Research on physics and chemistry of earth materials has provided major constraints on deciphering the composition and evolution of planetary interiors. At the same time, the discovery of Pyrex glass, the development of zeolite sieves, and the synthesis of ruby, garnets, and related laser crystals are some of the important technological contributions of this research area. Following are some examples of geological discoveries and advances that would not have been possible without key contributions from the study of earth materials.

1. *The internal compositions of the Earth and Moon are now broadly known.* Measurements of elastic moduli, phase equilibria, and electrical properties under high pressure and temperature, coupled with seismological determinations of velocity and density

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This appendix was largely developed by the following workshop group: Raymond Jeanloz (*Group Leader*), Orson L. Anderson, Subir K. Banerjee, William A. Bassett, Gordon E. Brown, Michael Brown, Robert M. Hazen, Russell J. Hemley, Robert C. Liebermann, and George A. Parks. For affiliations, see Appendix E.

profiles and electromagnetic determinations of conductivity profiles, have largely defined the composition and temperatures deep within the Earth and Moon.

2. *Techniques have been developed to simulate the pressure and temperature conditions throughout the Earth.* Mineral physicists pioneered the development of the diamond anvil cell to generate pressures and temperatures in excess of those existing at the center of the Earth. Current techniques enable in situ measurement of a wide variety of physical properties to pressures exceeding 5 million atmospheres (5 Mbar).

3. *Magmas deep in the Earth may sink rather than rise toward the surface.* High-pressure experiments demonstrate that silicate melts can be denser than the coexisting crystals. As melts can readily transport heat by movement through the mantle, this result has far-reaching implications for the long-term cooling of the planetary interior. Moreover, the separation of melts and crystals determines the nature of planetary differentiation, the process by which a planet evolves and becomes internally layered in composition.

4. *The Earth's solid mantle flows.* Laboratory studies of solid-state creep in minerals demonstrate that the Earth's interior is weak; thus heat can be transported mainly by convection. In general, global tectonics and thermal evolution of terrestrial planets are dictated by the deformation properties of minerals.

5. *The transformation of minerals to dense structural forms at high pressures is an important cause of the observed radial distribution of physical properties throughout the Earth's mantle.* One of the most important discoveries has been that iron-magnesium silicate assumes a dense perovskite form at high pressure (see Figure C.1). This phase is now believed to be the most abundant mineral in the Earth. Early work on phase transformations included the synthesis of diamond, which has broad industrial applications. The experimental discovery of coesite and stishovite forms of SiO_2 (quartz) and the spinel form of Mg_2SiO_4 (olivine) was followed by their identification in nature. The natural occurrences are associated with high transient pressures caused by meteorite impacts on planetary surfaces. Major new insights into the structure and bonding of crystals have emerged from experimental and theoretical studies of high-pressure transformations in minerals and their analogs.

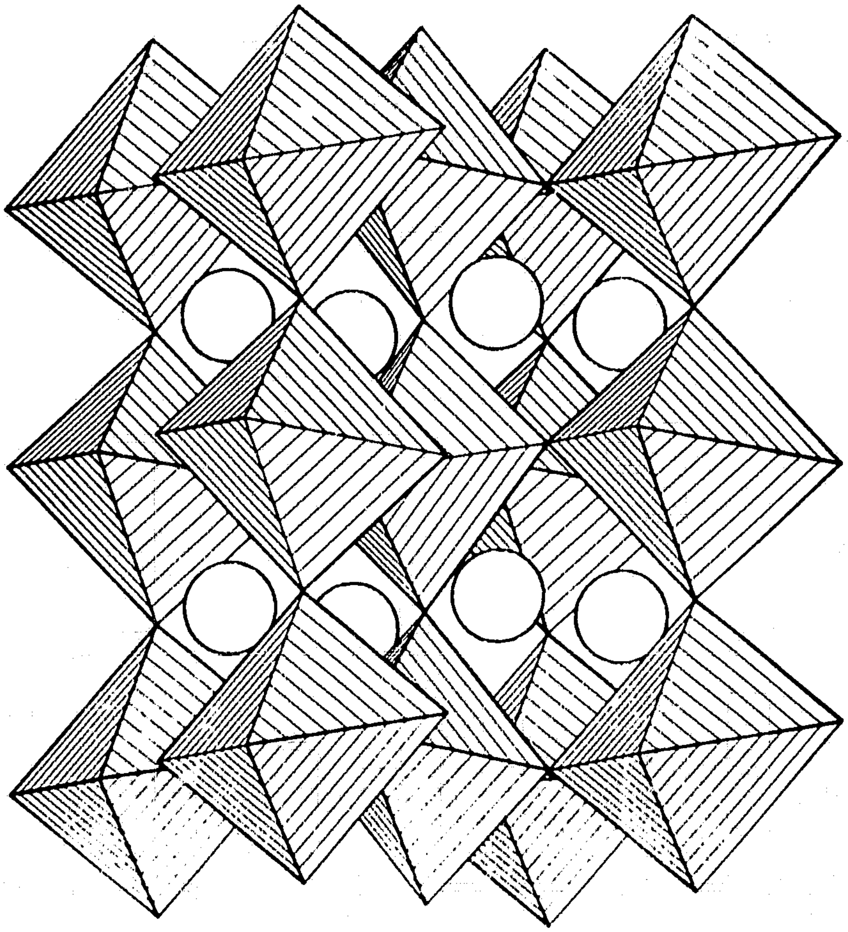

FIGURE C.1 The bulk of the material making up the lower mantle is believed to have the perovskite structure. This is a model of $CaTiO_3$, which has the same structure as high-pressure $MgSiO_3$ when it is quenched to room pressure.

6. *The Earth's core is predominantly iron, with a central temperature near 6000 K.* The density and elastic properties of the outer core match those of a molten iron alloy under high pressure-temperature conditions, not those of silicates. The temperature is constrained by experimental observations of the melting curve of iron at core pressures.

7. *The chemistry of planetary surfaces has been constrained.* The surface compositions and possible mineral phases of planets, moons, and asteroids have been revealed by the combinations of mineral spectroscopy and remote sensing studies. A surprising variability has been documented ranging from frozen ices and sulfur lavas on Jovian moons to titaniferous mare basalts *on the Moon* and iron oxides in Martian regoliths.

CHALLENGES AND OPPORTUNITIES

A number of broad fundamental problems and related opportunities have emerged from today's dynamic environment in the earth sciences. The plate tectonics revolution, new instrumental capabilities, and major new programs such as continental and ocean drilling (DOSECC, ODP), seismic profiling (COCORP), global seismic networks (IRIS/GSN), and continental arrays (IRIS/PASSCAL) allow exploration of the Earth's crust, mantle, and core as never before. The study of earth materials will play a key role in the interpretation of the results from these major scientific efforts. Specifically, mineral physics provides unique data to interpret solid-earth properties in terms of crystal structure, composition, thermal state, and dynamic processes. This discipline not only serves as an anchor to geological theory and field measurements, but also has application in areas such as the evaluation of earth resources and hazards.

Pressure, temperature, and chemical variables can be controlled and calibrated in laboratory experiments to synthesize materials that exist throughout the interior of the Earth. In many cases the new materials that are formed at high pressures can be quenched and retrieved to ambient conditions. Analytical techniques are evolving to determine physical and chemical properties of synthetic and natural materials over an extraordinary broad range of conditions. The new technological capabilities offer a wealth of opportunities to understand the essential properties of planetary interiors.

The fundamental nature of mineral physics requires several types of interdisciplinary communication: (1) with other geoscientists whose research is impacted broadly by the results of mineral physics investigations; (2) with physics, chemistry, and material science communities with whom mineral physics shares concepts and techniques; and (3) between university, government, and industrial laboratories that share common interests in the synthesis and characterization of materials, as well as advanced training for the next generation of professional scientists in this field. Increased interaction with the facilities and personnel of the national and industrial laboratories is desirable to tap these specific resources.

The field and theoretical branches of the earth sciences are rapidly developing critical needs for experimental data to guide and to constrain their studies. This report describes some major problems in earth sciences that cannot be resolved without significant advances in our understanding of the physical and chemical properties of geological materials.

CURRENT DIRECTIONS

A number of fundamental questions about the nature and dynamics of the interior of the Earth and terrestrial planets remain unanswered. These range from the global to the atomic scale. What are the driving forces responsible for plate tectonics? What is the nature of the boundary between the core and the mantle? How are crystalline (or noncrystalline) structures, physical properties, and kinetic responses of earth materials interrelated? How do these vary with pressure and temperature?

Using a new array of sophisticated experimental techniques, new theoretical models, and modern computational facilities, earth scientists are in a position to provide answers to some of these questions. Some of the main topics being addressed are described below. These are but a few examples of problems in which the study of earth materials is likely to produce major advances in the near future.

PHASE TRANSFORMATIONS

Earth scientists are interested in phase transformations because these are responsible for a variety of major features and processes in planetary interiors. For example, the major discontinuities observed seismically at 400- and 670-km depths in the Earth are due in part to these transformations, and have motivated a great many laboratory investigations of phase equilibria in silicates.

Recently, the understanding of mechanisms and kinetics of phase transformations has become an important objective of laboratory studies. With the advent of plate tectonic theories, we have recognized that large amounts of material move through pressure-temperature (P-T) conditions under which phase transformations take place. Therefore, kinetics of phase transformations (especially in cold downgoing slabs extending beneath oceanic trenches) can play an important role in modifying global tectonic processes, and hence the associated volcanism and seismicity. In particular, the kinetics of phase transformations may be the determining factor in causing intermediate- and deep-focus earthquakes beneath ocean trenches, such as those rimming the Pacific Ocean.

New techniques, especially those using the very intense x-ray sources now available at synchrotrons, are making it possible to obtain detailed structural information on samples as they undergo phase transformations. For the first time, information about the mechanisms and kinetics of phase transformations occurring within the Earth is becoming available.

Thermochemistry can also yield valuable information about phase equilibria. Enthalpies of phase transformations can be obtained by combining calorimetric data and the known transformation pressures. For calorimetric studies, improved instrumentation and techniques have decreased the amount of sample required to the range of ~10 mg, enabling study of phases synthesized at pressures as high as 10 to 25 GPa. Enthalpies of transformation can also be obtained by lattice vibrational modeling based on infrared and Raman spectra and on inelastic neutron scattering measurements. Phase diagrams can thus be calculated independent of the high P-T experiments. This provides a check on P-T calibrations and on the attainment of equlibrium in high-pressure synthesis experiments.

ELASTICITY, CRYSTALLOGRAPHY, AND ROCK PROPERTIES

Earth materials researchers have long recognized that bulk rock properties must be understood and related from the scale of atomic interactions to polymineralic aggregates. Until recently, however, most minerals and rocks have proven far too complex to connect their microscopic and macroscopic descriptions.

The development of the diamond anvil cell and microfurnaces that can be used with the single-crystal x-ray diffractometer has opened up new possibilities for investigating how crystal structures adapt to changing conditions of pressure and temperature. In the past 15 years, crystallographers have been able to show that silicate crystal structures expand and compress systematically with temperature and pressure, depending on the composition of individual structural polyhedra (describing the atomic linkages) and on the ways in which the polyhedra are linked together. This has led to great advances in understanding how phase transformations occur, and how thermal expansion and elasticity are related to crystal structure. Current research is centered around extending the limits of achievable pressure and temperature, and in designing pressure cells that will allow measurement of diffraction intensities from single crystals while both pressure and temperature are applied. Although crystallographers have attained pressures of 15 GPa and temperatures greater than 1500°C separately, it has thus far been possible to sustain simultaneous pressures and temperatures up to only 5 GPa and 500°C in externally-heated diamond cells for single-crystal studies.

Over the past two decades several precise techniques have been developed to measure the elastic moduli of minerals, and their pressure and temperature derivatives. These directly complement the diamond cell experiments, and include acoustic interferometry, Brillouin scattering, and ultrasonic resonance techniques. These methods have allowed prediction of densities and wave velocities of minerals at very high pressures and temperatures. Such a capability is necessary in order to infer planetary compositions and thermal states from the seismically determined profiles of density and wave velocities with depth.

Considerable progress has been achieved, especially in evaluating the average values of density, temperature, and composition throughout the Earth's interior. The promise of higher resolution seismological data that will quantitatively reveal the lateral (horizontal) variations of elastic properties inside the Earth places increased demands on the accuracy, precision, and scope of corresponding laboratory measurements. Although relatively subtle compared to the radial variations, it is precisely these lateral variations in properties that drive flow in the mantle and the resulting plate-tectonic cycle. To understand the seismologically observable variations, and hence the causes of global tectonics, experimental techniques have to be improved so as to produce measurements of the pressure and temperature dependence of elastic properties, especially for high-pressure phases that are not yet available in sufficient quantity.

Additional work is needed on the properties of aggregates. Ironically, in many problems we have more information from laboratory studies than can be used in geophysical interpretation. An example is the complete set of elastic moduli of low-symmetry crystals such as feldspar, one of the commonest rock-forming minerals in the crust. Yet the way these properties combine to produce the bulk elastic behavior of an aggregate is not well understood. Theories relating single-crystal data to those of mineral aggregates continue to be needed to reduce full sets of elastic moduli to those appropriate for mineral aggregates and especially the multiphase aggregates that exist in the crust and mantle. An improved understanding of the elastic and anelastic properties of multiphase aggregates is critically important in applied and exploration geophysics, as well as in studies of the Earth's interior. In particular, these properties must be characterized as a function of frequency, grain size, and the extent and nature of grain boundaries and fluid phases that fill them.

THEORETICAL MODELS

The theoretical foundation for all properties of earth materials and global processes is a function of the interactions existing between the component atoms and ions. The forces between the particles are determined by quantum mechanics, and the relationship between microscopic bonding forces and macroscopic properties can be understood with classical statistical mechanics. In the past, semiempirical models have provided a unifying description of the relationship between crystal structures and physical properties of minerals. In the past few years significant advances have been made in fundamental theory, computational methods, and computer hardware. These allow us to model a variety of earth materials from first principles. Properties that can now be calculated a priori include crystal structures, phase transitions, electronic excitations, vibrational motions, and elastic properties as functions of pressure and temperature. For example, theoretically determined phase diagrams for alkali metals, alkali halides, alkaline earth oxides, and some silicates now closely match observations.

New theoretical methods include sophisticated total-energy, band structure calculations for accurate calculations of electronic properties. More approximate, yet still first-principle-type, models have been developed and refined for application to complex and distorted materials, such as minerals with defects. In addition, the recent development of constant-pressure molecular dynamics and Monte Carlo simulation methods provide a means to understand high P-T behavior such as the nature of melting at high pressure, an important geophysical phenomenon. A related important area is the dynamical modeling of surfaces and interfaces, including crystal growth and transport properties. These new theoretical methods can be applied to understand mechanisms of solid-solid phase transitions and chemical reactions.

Many problems in earth science concern properties of materials at extreme pressures and temperatures, conditions in some cases that are just now becoming accessible experimentally. It is therefore essential that theoretical calculations be performed to support the experimental work. Theory can be used as a powerful guide to making new measurements. Also, theory helps to provide quantitative interpretations of observations, and to provide useful predictions for material properties beyond the current range of measurements at high pressures and temperatures. Finally, experimental work at high pressure supplies an important feedback to theory as a test of approximations and methods, and as a guide to further refining our theoretical simulations of material properties.

INELASTIC DEFORMATION AND TRANSPORT PROCESSES

The inelastic properties of rocks and minerals play an important role in a wide range of geophysical phenomena. On a large scale, brittle fracturing is associated with crustal earthquakes while plastic flow is essential to convective processes in the mantle. Numerous important topics need to be addressed by systematic laboratory experiments. For instance, little is known about the relationship between the transport of fluids in the crust and how this is related to fracturing of rocks. Such fluid-rock interactions play a central role in the transport of heat through the crust, the generation of ore deposits, and the concentration of petroleum reservoirs. Similarly, the transport of melt through the mantle must be coupled with plastic flow of the host rock. Little is known about the rheology of partially melted rocks or how melt can be transported through a largely crystalline matrix to result in volcanic eruptions observed at the surface. The high-temperature flow of crystalline rocks appears to be strongly affected by small amounts of water and other volatiles, but almost nothing is known about the mechanism by which the weakening occurs. For example, what sorts of mechanisms allow deformation to become localized in shear zones? Answers to such questions are crucial to an understanding of plate tectonics and mantle dynamics.

Transport properties govern the movement of matter or energy in response to an applied field, and include thermal and electrical conductivities, diffusivity, and creep.

Thermal conductivity describes the transport of heat down a thermal gradient by lattice vibrations (phonons), electron motions, and electromagnetic radiation (photons). Although thermal conductivities of crustal materials have long been used to calculate the flow of heat out of the Earth on the basis of observed temperature gradients, little is known of thermal conductivities of mantle materials under mantle conditions. Information on thermal conductivity is vital to understanding thermal boundary layers in the mantle, particularly the D" layer where core heat enters the mantle and where thermal instabilities may lead to the formation of mantle plumes. New experiments, such as those based on shock-wave techniques, have become available to provide the much-needed measurements of thermal conductivity at deep-Earth conditions.

Electrical conductivity of minerals is highly temperature dependent and thus is commonly used to infer temperature from profiles of conductivity with depth in the Earth. Only in olivine and orthopyroxene do reproducible measurements exist; there are almost no determinations of electrical properties for constituents of supposed high-pressure mantle assemblages. Most mantle minerals are insulators or poor semiconductors at ambient pressures and temperatures; hence, additional measurements such as drift mobility or thermoelectric effect are needed to elucidate conductivity mechanisms in order to extrapolate laboratory measurements to mantle conditions. These data could help explain observed conductivity increases in the upper mantle at about 40 to 120 km and again at 400 km.

Diffusivity, like electrical conductivity, is strongly controlled by point-defect structures; ionic species migrate in response to a chemical potential gradient. As an example of an application, the kinetics of chemical migration governs the equilibration of minerals in natural assemblages. Chemical equilibria among minerals provide the basis for petrological estimates of temperatures, pressures, and rates of processes inside the Earth (geothermometers, geobarometers, and geospeedometers). Diffusion coefficients have been measured only in a limited number of minerals, however, and most data have been obtained only for olivine.

Creep deformation also involves point-defect migration. Rheologies of planetary materials (including ice) have been measured for only a limited number of compositions and structures, again mainly olivines, pyroxenes, and quartz; deeper mantle materials have yet to be examined. In recent years, the effect of volatiles, e.g., water, has been shown to be important in determining the mechanical strength of minerals and rocks. A persistent problem is that the lowest laboratory strain rates are several orders of magnitude greater than convective deformation in the Earth. In this regard, advanced theoretical modeling can help to relate the geological deformations of the crust and mantle to laboratory investigations of rock deformation.

Defects exist in all crystals at temperatures above absolute zero. Common defect types are line and point defects, the former typically arising from external stresses and the latter from thermodynamic or substitutional disorder. Very small concentrations of defects have been shown to control or to participate in physical and chemical properties. The need to solve problems posed by recent advances in the geosciences (the development of plate tectonics, the determination of thermal gradients) necessitates the extension of present concepts to the more complex silicate systems. In order to do this, experimental measurements of the above properties must be made on well characterized silicate crystals under controlled conditions (pressure, temperature, oxygen fugacity) thought to represent deep crustal and mantle conditions.

MINERAL SURFACES, INTERFACES, AND GRAIN BOUNDARIES

The surfaces of minerals and melts, and the interfaces between them, have compositions, structures, and energy contents different from the bulk phases they bound. These distinctive properties have independent manifestations in many areas of geophysics and geochemistry.

Surface energy reduces the melting points of solids in thin films and capillary pores. Minimization of surface energy is the principal driving force for sintering of solids and coalescence of droplets of immiscible fluids. This minimization competes with differential crystallization rates to determine equilibrium shapes of crystals and fluid inclusions. Surface energy controls the nucleation, formation energy, and equilibrium size of gas bubbles in fluids. High surface energy enhances the solubilities of solids in liquids, but inhibits both homogeneous and heterogeneous nucleation of solids and gases in aqueous solutions and melts. Surface energy is the principal determinant of fracture strength; environmental effects (e.g., the presence of water) on surface energy are among the key factors controlling the slow growth of cracks. Liquids adjacent to surfaces may be bound to the surface resulting in altered viscosity, acoustic and electromagnetic absorption properties, thermodynamic activity, and diffusion properties.

Clearly, the surface and interfacial energies play a role in many processes of importance in the Earth, including melting and melt segregation, grain and crystal growth, element partitioning, and transport along grain boundaries and mineral-liquid interfaces. Conceptual models exist for all of these phenomena, but validation and application are precluded because we have virtually no unambiguous data on surface and grain-boundary energies. Existing measurement methods may be capable of providing this information if used with care, but no unambiguous method exists for measuring the energies of pristine crystal-vacuum surfaces. Theoretical computation of surface and interfacial energies is handicapped by too little knowledge of the structures of surfaces. Surface energies change in response to changes in surface composition, so all of these phenomena are sensitive to composition. Again, however, both experimental data and theoretical studies are needed if surface composition and physical properties are to be linked quantitatively. Such work will shed light on how fractures are initiated, a problem of considerable importance for understanding the deformation of the Earth's crust and the generation of earthquakes.

A number of surface-active solutes tend to absorb or accommodate near surfaces, perhaps binding in surface complexes. Some solutes are rejected from the interface; adsorption is found to be an important mode of partitioning. In aqueous systems for which sophisticated adsorption models are already available, testing and use of adsorption models are hindered by a lack of knowledge of the structures and compositions of the solid surfaces, and the adsorption complexes involved. Both data and models are lacking for solid-melt and solid-solid grain boundary systems, so the significance of adsorptive partitioning cannot be assessed. Furthermore, experimental data are needed to assess the importance of adsorption as a sink for minor and trace constituents of melts. These advances are of critical importance for interpreting the next generation of geochemical (trace element, isotopic) measurements.

Direct measurement of the structures and compositions of surfaces, interfaces, and grain boundaries is clearly needed, particularly in systematic research directed toward defining adsorption mechanisms. In systems in which samples can be examined in vacuum without perturbing the surface, this will require measuring composition as a function of distance from the interface at a spatial resolution taxing the limits of existing instruments. In aqueous and molten systems, adsorption complexes are likely to be altered or destroyed if removed from the equilibrium liquid measurement of surface composition and structure must therefore be done in situ to minimize ambiguity. This will require spectroscopic methods like EXAFS, which permit the determination of bond distances, atomic coordinations, and bonding properties at P and T, with the fluid or melt present.

THE NATURE AND MOVEMENT OF MELTS IN THE EARTH'S INTERIOR

Information about the formation and movement of melts within the Earth's interior is vital to our understanding of the temperature distribution and dynamics of the Earth, including earth processes of great societal importance such as volcanism and earthquake generation. Furthermore, melting is considered to be one of the dominant mechanisms by which the compositions, structures, and temperatures of planetary interiors evolve with time. Studies of earth materials at very high pressures and temperatures are providing some of that important information. For instance, measurements of the melting temperature of iron to ultrahigh pressures have provided information about the temperature of the Earth's core; melting studies of silicates by shock and static methods indicate that some melts may sink rather than rise in the mantle; melting of samples in the diamond anvil cell by electrical resistance and by laser heating provides valuable information on the nature of melts in the mantle as well as about the core; structure-property studies of melts and quenched melts, including those containing important volatile constituents like H_2O, are providing needed data on how melt structure, composition, volatile solubility, and transport properties are related.

The thermodynamics of melts and the melting transition must be better characterized so that models for the behavior of melts over a range of compositions and conditions can be used to quantitatively understand processes of melting and the migration of melts within the Earth. Calorimetry at high temperature and atmospheric pressure and differential thermal analysis at high pressure and high temperature can do this to some degree. In addition, structural models for melts and theoretical computations using, for example, molecular dynamics of the structure and properties of melts at high pressure and temperature will advance our understanding of the behavior of melts throughout the Earth. There are many unanswered questions concerning cation coordination and long-range ordering, and their changes with pressure and temperature, which have significance for melt properties.

It is likely that melts at grain boundaries play a significant role in dynamical processes occurring within the Earth, such as earthquake generation. The distribution and geometry of liquid at grain boundaries have profound effects on the propagation of seismic waves through regions of partial melt; electrical conductivity and mechanical properties are strongly affected, as well.

Unanswered problems include the mechanisms of melting at the atomic level, the nature of the forces controlling the geometry and distribution of partial melts, the role of volatiles in controlling melt properties such as viscosity and element diffusion at high pressures and temperatures, and the magnitude of compressibilities and densities of melts of different compositions under different pressure-temperature conditions. X-ray absorption techniques using synchrotron radiation can now provide a great deal of information about the structures of melts and glasses that could not be ascertained before these techniques existed. With these new techniques it is becoming feasible to determine coordination numbers, cation site compressibilities, and the nature of solid-melt interfaces, as well as other valuable information about melts.

Two-wavelength x-ray radiography on partial melts held in large-volume high-pressure cells using synchrotron radiation can yield observations on the geometry and distribution of the melts. Such imaging could make use of x-ray absorption of elements selectively partitioned into the melt, much like the recently developed x-ray angiographic imaging of iodine in blood vessels around the heart.

MINERAL MAGNETISM

Magnetic properties of planetary materials arise from the cooperative behavior of the spin magnetic moments carried by individual transition metal ions. Those materials that are ferromagnetic (e.g., magnetite) or canted antiferromagnetics (e.g., hematite) have been studied by earth scientists who have identified a new magnetic domain state in ultrafine grains called pseudo-single domain grains. These grains have been found to be responsible for carrying the stable components of natural magnetization in rocks.

The history of continental drift and plate tectonics during the last 3 to 4 billion years of earth history can be determined quantitatively from the record of geomagnetic field directions imprinted in rocks of known age. Indeed, paleomagnetic studies have played an important role in documenting the accretion of old terranes onto continental margins, this being perhaps the dominant mechanism by which continents grow. Also, the evolution of the Earth's magnetic field itself is documented by the natural remanent magnetization of rocks that provides evidence for changes in field intensity, in the orientation of the magnetic poles and in the actual polarity of the field (north- and south-magnetic poles reversing).

Separation of the stable or characteristic component of natural remanent magnetization (NRM) of a rock sample must be accomplished before an ancient direction of magnetization and, hence, of the past geomagnetic field can be assigned to a rock sample. The present techniques of demagnetizing rocks by subjecting them to a supposedly optimum value of alternating field or temperature (determined by prior testing of a few samples) have proven to be inadequate for rocks or sediments with multiple magnetization histories. In particular, challenging problems such as deciphering the nature of the magnetic field during a reversal or determining paleolatitudes of early Paleozoic or Precambrian rocks require individualized demagnetization treatments of each sample (of, say, 100 from a single site alone) so as to separate the stable component of magnetization associated with the most tightly pinned domain walls in the sample. A combined approach involving (1) micromagnetic theories of statistical mechanics, (2) observations of domain wall-defect interactions at elevated temperatures, and (3) the development of micromagnetometers employing superconducting gradiometers for measuring single-grain magnetizations—these three techniques can together be used to extract magnetization components in a way that will allow separation of each major component of NRM. For older rocks, ^{40}Ar/^{39}Ar dating and thermal demagnetization can be done in discrete steps, thus leading to an assignment of age for each magnetic component that is separated.

PLANETARY GASES AT HIGH PRESSURES AND TEMPERATURES

Hydrogen is the most abundant element in the universe, and its properties are of fundamental concern to modern quantum physics, as well as the planetary sciences. The mantles of the Jovian planets contain mixtures of helium and hydrogen, with hydrogen believed to be mostly in a metallic form under extreme P-T conditions. With the development of high-pressure diamond-cell techniques, the experimental range of measurements for planetary gases such as hydrogen and helium have been extended from 30 kbar to over 2000 kbar in the last decade. The frequency of the intermolecular stretching vibration of hydrogen has been found to decrease significantly at high pressures, thus suggesting a weakening of the molecular bond as a precursor of metallization. This behavior has also been found in deuterium and nitrogen at megabar pressures. Such discoveries have required revision of fundamental theories of bonding in these materials, providing an important feedback to basic physics.

The theoretically predicted metallization pressure of ~3 Mbar for hydrogen is now in reach with current static high-pressure techniques. Therefore, an important near-term goal of experimentalists is the testing of this theoretical prediction. Future directions also include the synthesis and characterization of metallic hydrogen, measurement of the equation of state of hydrogen-helium mixtures, and the study of the phase equilibria and unmixing properties of hydrogen and helium under megabar pressures directly applicable to planetary interiors. In addition, the properties of other abundant planetary materials, including H_2O, CH_4, and NH_3 at megabar pressures, need to be characterized.

NEW INITIATIVES

SYNCHROTRON RADIATION THRUST

The recent development of extremely intense synchrotron x-ray sources has led to major advances in our ability to study earth materials at the atomic level and under high pressure and temperature conditions that simulate those in the Earth's interior (see Figure C.2). Plans to build second generation synchrotron beam lines to generate even higher x-ray intensities (roughly 10,000 times that of existing capabilities) are well under way. Because of the great demands to develop these new sources, it is critical that the earth sciences community act quickly to take advantage of this opportunity while it is available. The proposed new x-ray facilities will make it possible to tackle some of the major research problems in geophysics and geochemistry such as the in situ study of mechanisms and kinetics of phase transformations, the nature of grain boundaries, mineral surfaces and interfaces, the partitioning of trace elements between minerals and melts, and the structure of melts. Experiments of this kind are needed for assessing major processes of the Earth's interior such as the possibility that phase transformations play a role in earthquake

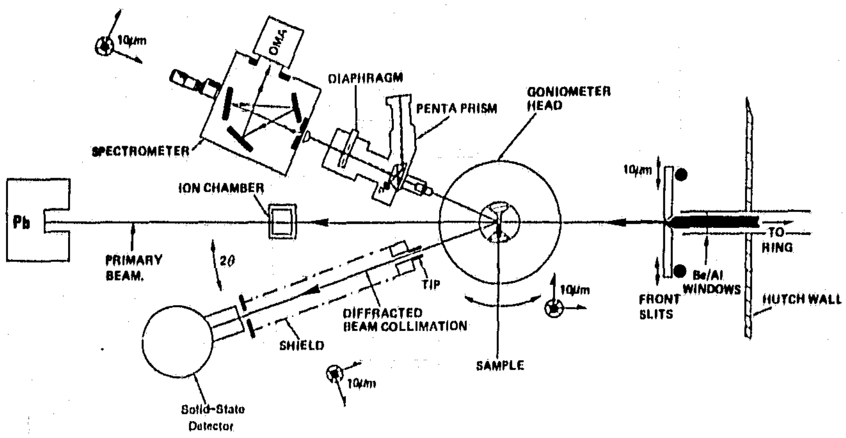

FIGURE C.2 Schematic diagram of the experimental apparatus used to investigate solid hydrogen at high pressures using diamond-anvil cell with synchrotron radiation.

generation. The key need in all of these investigations is to make x-ray scattering, x-ray absorption, or x-ray emission measurements in situ over a range of temperatures and pressures up to those at the Earth's center. The extreme intensity or brilliance that the new sources can provide will permit such measurements to be made through the relatively thick walls of diamond-anvil and solid-medium, large-volume, high-pressure devices.

Estimated costs for participation include the following:

- $4 million for beam line design and construction
- $3 million for beam line instrumentation and development of new detectors
- $4 million for completion of an advanced x-ray microprobe.

NEW GENERATION OF LARGE-VOLUME, HIGH-PRESSURE, HIGH-TEMPERATURE FACILITY

A critical achievable goal in the next 5 to 10 years is the development of new technology to enable in situ measurements on sample volumes of 1 mm^3 to pressures of 1.5 Mbar at temperatures of 5000 K, conditions corresponding to the core-mantle boundary. Such equipment does not now exist anywhere in the world, but is essential to the study of phase equilibria (including melting), chemical partitioning and transport properties, and the synthesis of new phases at extreme conditions. The requirement of large sample volumes (compare to the currently achievable 0.0001 mm^3 at the conditions quoted) is especially critical for investigating deformation mechanisms, polyphase equilibria, geochemical partitioning, and interfacial or grain-boundary phenomena. Also, the production of commercially useful quantities of novel materials produced at extreme conditions requires sample volumes considerably larger than now available. The development of this equipment will require new superhard materials such as sintered compacts of diamond, and thus will rely on close collaboration with the materials community.

MICROMAGNETOMETER/DOMAIN IMAGER

Separation of multiple components of magnetization from especially important samples, such as Precambrian rocks recording the earliest history of the Earth's field or igneous rocks that have recorded the transitional directions during a reversal, requires special treatment. It may be necessary to measure the magnetic vector of a single magnetic grain. Similarly, the study of how remanence is acquired and how it is lost by demagnetization is of critical importance for further advances in mineral magnetism. For a single grain, this requires "ground truth" observation in the shape and movement of magnetic domain walls at elevated temperatures, up to 700°C.

An instrument that can meet this challenge would be a superconducting SQUID microgradiometer whose sensitivity well exceeds that of the magnetization of a single grain (10 μm) of magnetite. A second major component of such an instrument would be a Low Energy Electron Diffraction Source, lens and collimator, modified so as to impose no more than 100 nT leakage field at the magnetic sample. Enhanced detection of electrons scattered by the fringing field of magnetic domain walls would produce a new type of domain imager capable of operating at temperatures up to 700°C. Simultaneous measurement of grain magnetization and domain geometry would allow one to pick out grains likely to carry stable remanent magnetization, the direction and intensity of which could be followed upon exposure to heating and cooling or alternating-field demagnetization.

Appendix D:
Rock Physics

HIGHLIGHTS

1. Theoretical modeling and laboratory measurements of friction have been successfully employed in studies of earthquake instabilities, source mechanisms, and distributions, as well as the orientations and distributions of faults. These efforts have revolutionized seismology and the structural geology of the upper 30 km of the lithosphere.

2. The effect of fluid pressure in promoting brittle fracture and frictional sliding on faults has been quantified by controlled fluid pressure deformation experiments on porous rocks as well as by in situ hydrofracture experiments. This has allowed the recognition of natural hydrofractures, which are of great importance in ore localization; it has provided a basis for understanding the troubling occurrences of reservoir-induced seismicity; and it has indicated a possible approach for future attempts to control earthquakes.

3. Experiments have successfully induced solid-state ductile flow in crustal and upper mantle lithologies; the deformation

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This appendix was largely developed by the following workshop group: Julia Ann Tullis (*Group Leader*), James Dietrich, Brian J. Evans, Stephen H. Kirby, David L. Kohlstedt, John M. Logan, William F. Murphy, and Leon Thomsen. For affiliations, see Appendix E.

mechanisms producing this flow have been identified, and the microstructures and flow laws associated with them have been determined. These experimentally-determined rheologies have made possible for the first time quantitative models of such diverse phenomena as upper mantle convection, flexure and extension of the lithosphere, subduction mechanics, folding of layered rocks, and the stability of excavations in salt bodies considered as repositories for high-level nuclear waste.

4. Laboratory and theoretical work have documented the relations between crystallographic preferred orientations in ductily deformed rocks and the stresses and finite strains that produce them, as well as the resulting anisotropy of physical properties. These results allow the interpretation of the directional variations of P-wave velocity that have been recognized in the mantle and more recently the core in terms of the stress and deformation in these remote regions. For example, the P-wave velocity maximum parallel to the direction of relative plate motion is now understood to originate from resistive basal shear based on the known elastic anisotropy and slip systems of olivine.

5. Laboratory correlations of non-hydrostatic stress with textural features such as dislocation density and recrystallized grain size have provided paleopiezometers, which have allowed us to conclude that naturally deformed rocks from mid to lower crust and uppermost mantle have undergone large-scale, solid-state flow at low tectonic stress. These inferences are fully consistent with current models of the thermal structure of the lithosphere, the experimentally-determined rheologies of rocks, and the shutoff of most earthquakes below 35 km (subduction zones excepted).

6. Laboratory deformation experiments have shown that the strength of the continental crust is significantly reduced by interactions with hydrothermal and other chemically aggressive fluids such as silicate melts. These weakening effects, which include slow crack growth in the presence of moisture, solution transfer mechanisms directed by nonhydrostatic stress, and hydrolytic weakening, may have considerable practical applications.

7. Laboratory measurements of the elasticity of polycrystalline and porous aggregates have provided powerful tools for interpreting structures revealed by reflections of seismic waves in the continental lithosphere. This has considerable practical applications in petroleum exploration.

8. Experimental determination of microstructures resulting

from impact deformation have been crucial in deciphering the history of other planets and satellites as well as contributing to the identification of impacts in the Earth's geologic record.

INTRODUCTION AND STATE OF THE FIELD

Determination of the physical/mechanical properties of rocks is a necessary step in understanding dynamic processes and subsurface structure at all scales in the Earth. Interpretations of the structure and compositions of rocks not accessible to direct observations rely on correlation of remote measurements with physical properties. Understanding of dynamic processes as diverse as mantle flow, earthquake mechanisms, transport of water and magma through the crust, and sedimentary basin development involves interplay between rock properties, modeling, and observation.

Factors that determine the behavior of rocks include not only the properties of the constituent minerals, but also their volume proportions, geometrical arrangement, grain size and shape, and crystallographic orientation, as well as the geometry of atomic defects, cracks and pores, and the composition and pressure of any fluid phase. At present the means to predict or specify the properties of rocks from the characteristics of their constituents are poorly developed. Similarly, the integration of controlling processes having vastly different and often unknown scaling lengths is not well understood. Progress in understanding dynamic processes and earth structure will depend upon progress in these areas of rock physics.

The challenges facing rock physics are conceptual in character, requiring development of new experimental and observational techniques, as well as new ideas and theories, to proceed from mineral properties and processes to rock properties. A number of research opportunities currently exist that are expected to yield significant advances. In view of the emerging understanding of the complex interplay of factors controlling the physical properties of rocks, new multidisciplinary approaches are necessary, requiring instrument development to test and drive theoretical advances.

FRONTIERS

There are a number of exciting and significant research questions in rock physics that are capable of solution in the next 5 to 10 years; examples are grouped below into three major areas.

FLUID-ROCK INTERACTION

The rocks of the Earth's surface are permeated by aqueous fluids on various scales ranging from fluid inclusions and grain boundary films, to grain-scale pores and cracks, to fractures and regional joints, and the rocks of the crust and mantle are also locally subjected to partial melting. These associations involve a number of fluid-rock interactions of great importance: physical properties such as seismic wave velocity, electrical conductivity, strength, and permeability are strongly affected by the presence of fluids, and fluid compositions and transport rates are strongly affected by the rocks they traverse. Considerable research has already been devoted to this important topic, but many important questions remain unanswered. Studies of fluid-rock interactions would contribute greatly to our understanding of such scientific problems as diagenesis in sedimentary basins, hydrothermal circulation associated with cooling plutons, partial melt extraction and upward migration, the strength of the lower crust, and seismic attenuation in the upper mantle. In addition, such studies would have a number of important practical applications including the containment of nuclear and hazardous wastes in underground repositories, the prediction of natural hazards such as earthquakes and volcanic eruptions, and the location and extraction of natural resources such as petroleum and steam. Given the scientific and practical importance of this topic it is surprising to discover how little is known about the fundamental processes of the chemical and physical interaction of rocks under even modest temperatures and pressures. A multidisciplinary approach, integrating research from geochemistry, surface chemistry, mineral physics, fluid transport and rock deformation is necessary for future progress.

Specific examples of the possible mechanisms and effects of fluid-rock interactions include the following:

1. Trace amounts of water are known to have a profound effect on the frictional properties of rocks; the short times required for introduced humidity to produce a noticeable effect suggest that

adsorption on surfaces is involved, but the mechanism by which the frictional behavior is altered remains unknown, in large part because the physical processes involved in frictional sliding are not well understood. There is a critical need to identify the mechanisms responsible for the velocity and fluid dependence of friction, in order to more accurately extrapolate laboratory constitutive laws to the larger length and times scales of natural fault systems.

2. Trace amounts of water and other fluids are known to have a profound effect on the rates of subcritical crack growth in minerals; the mechanisms remain poorly known, and there are very few accurate measurements of rates. An understanding of this process is critical for an evaluation of fatigue and other processes in fault zones, and the transition with increasing depth from brittle faulting to ductile cataclastic flow.

3. It is well known that fluid pressure acts to reduce the normal stress, so that fluid pressures close to total pressure can induce brittle faulting even at high temperatures and pressures where rocks are capable of steady state ductile flow. However, details of the process remain unclear; for example, in some situations magma bodies cause hydrofractures whereas in other situations they rise slowly as diapirs through a ductily deforming skin. The development of high fluid pressures depends on the rate of fluid evolution (by partial melting, dehydration reactions, etc.), the interconnectedness of the fluid (which depends on the wetting angles), and the rates of grain boundary diffusion and fluid flow; and the effects of a high fluid pressure depend on the viscosity of the fluid and the strain rate, but there are not sufficient data on most of these properties and processes to make accurate models and predictions.

4. Pressure solution involving aqueous fluids is an important mechanism of compaction and diagenesis in sedimentary basins, an important deformation mechanism in accretionary prisms and other rocks of low metamorphic grade, and possibly (when it involves melt rather than aqueous fluids) an important deformation mechanism in the lower crust and upper mantle. However, fundamental data are needed on the kinetics of the process at different conditions and fluid compositions, the scale of transport of the dissolved material, and the flow law.

5. Trace amounts of water have long been known to cause a profound hydrolytic weakening in rocks deforming by dislocation creep, but the details of the mechanism by which this occurs still

provoke intense debate. This effect has a profound importance on our understanding of the ductile strength of the mid to lower crust and upper mantle, but at present we do not know whether flow laws have been experimentally determined for "water" contents appropriate to the tectonic region of interest, so that extrapolation is valid. Fundamental data required include the solubility and speciation of "water" in the crystal structure of various minerals, at temperature and pressure if possible; the mechanisms and kinetics of the equilibration process; and the amounts and speciation of "water" in naturally deformed rocks of various compositions from different metamorphic grades.

6. The mechanisms and rates of fluid transport in the crust and upper mantle remain poorly known. There are almost no data on grain boundary diffusivities in rocks, and few data on grain boundary and fracture permeabilities, especially accompanying deformation; thus we cannot accurately model the transfer of heat and material in various tectonic situations of interest.

7. Chemical reactions at surfaces and interfaces can cause profound changes in aggregate properties, but the mechanisms of these reactions are poorly understood.

8. There are preliminary data on the effects of partial melt on the rheology of ductily deforming granitic and olivine aggregates, but there are no data on the effects of partial melt at higher pressures where there may be a profound change in melt properties, including a possible density inversion. In addition, there are very few data detailing the effects of ductile deformation on the processes and rates of melt extraction and magma collection.

Progress on these topics will require considerations of the rock, the fluid phases, their interfaces, chemical reactions on surfaces and interfaces, the distribution of fluids, and the transport of solutes on all scales.

INTERACTION OF DEFORMATION AND PHASE CHANGES

Pressure and temperature gradients within the Earth cause polymorphic phase changes in both mineralogy and crystal structure with increasing depth. Some of these transformations have been studied by petrologists and mineral physicists. However, most of these studies have not taken account of the fact that the rocks undergoing the phase transformations are subject to nonhydrostatic stress and plastic strains. Similarly, structural geologists and rock physicists traditionally have not considered the effects of coincident phase transformations on the operative deformation mechanisms and rheology of the rocks in question. There is a critical need to investigate these phenomena in an integrated systems approach. Such studies would have applications in the following three important areas:

- Shallow crustal sedimentary basins experiencing diagenesis and compaction.
- Deeper crustal levels where rocks undergoing metamorphic reactions are subject to rifting, strike-slip faulting, and compression.
- The Earth's mantle, which undergoes solid state convective flow, also has a number of phase transitions defined by seismic discontinuities.

Specific examples of the possible mechanisms and effects of interaction between deformation and phase transformations include the following:

Effects of Nonhydrostatic Stress on Phase Transformations

1. Local regions of high mean stress will be generated along grain boundaries (or other discontinuities) between differently oriented, anisotropic crystals. These local mean stresses may cross a phase boundary and be sufficient to nucleate a new, higher pressure phase. Such effects would tend to enlarge the depth interval over which phase transitions occurred.

2. Some isochemical phase changes involve a shape change rather than a volume change and so are directly facilitated by shear stress (martensitic transformations); these could be important for deep-focus earthquakes.

Effects of Plastic Strain on Phase Transformations

1. Deformed phases with a high internal strain energy may allow strain-free nuclei of other phases to grow outside of their stability field; this would affect the inferences of P-T paths made from preserved phase equilibria.

2. Plastic strain energy resulting from deformation may be important in speeding the kinetics of phase transformations. The production of high dislocation densities and smaller recrystallized

grains will increase volume-diffusion rates, bulk-diffusion rates, and dissolution rates.

Influence of Phase Transformations on Rheology

1. Nucleation of new phases decreases the grain size and may cause a switch in dominant deformation mechanism from dislocation creep to diffusion creep. This would produce an increase of strain rate at the same stress or a decrease in stress at the same strain rate, leading to strain localization in ductile shear zones.
2. A transformation will produce strain hardening or strain softening according to whether the new phases are harder or softer than the original phases. In general "prograde" reactions will result in harder as well as denser phases; these may cause precipitation hardening even when they are still small and dispersed, and would cause additional hardening when they grow to the point of impingement, forming a stress-supporting framework.
3. Most phase transformations involve a volume change; the accommodation required may cause the transforming phase to undergo additional plastic deformation or even transformational superplasticity.
4. Phase transformations may be exothermic or endothermic; we know very little about the effect of the heat released or consumed upon the rock rheology, but in some cases it could be important.
5. Martensitic and possibly other phase transformations may occur unstably; this may produce a sudden earthquake at conditions where there has been steady-state ductile flow.

These various mutual interactions may be pertinent to a number of major geodynamic problems including the following:

The Mechanism of Deep-Focus Earthquakes. Shallow crustal earthquakes are successfully explained by the Mohr-Coulomb shear fracture criterion, but earthquakes occurring at depths of ~100 to 650 km require a completely different explanation that still eludes investigators. It is possible that polymorphic phase changes are involved, since a large number of them are known to occur in this same depth interval, under conditions where negative bouyancy forces lead to nonhydrostatic stresses. High-pressure laboratory deformation experiments are needed to investigate whether any of these upper mantle phase transformations occur unstably.

The Scale of Convection in the Mantle. One of the principal debates involving geophysicists, geochemists, and petrologists concerns whether phase transformations, in particular the 650-km discontinuity, can coexist with full mantle convection or force two or more separate convection systems in the upper and lower mantle. A combination of high-pressure deformation experiments and theoretical modeling is critical for the resolution of this debate.

Shear Zones in the Continental Lithosphere. Shear zones are now thought to account for a large fraction of intraplate deformation in the continental lithosphere; such features are observed at the surface in orogenic zones and inferred at depth from deep seismic reflection profiles. There are several possible mechanisms that might contribute to this localization, including a switch to grain-size dependent deformation resulting from neomineralization, recrystallization or cataclasis, and a change in metamorphic assemblage, perhaps due to hydration from fluid infiltration. Long-term experiments in apparatus with high-stress sensitivity are required to evaluate the different possibilities.

EFFECTIVE PROPERTIES OF HETEROGENEOUS ROCK MASSES

Real rocks are three-dimensional aggregates of mineral grains containing a complex assemblage of defects such as dislocations, grain boundaries, and fractures, which often contain impurities or fluids. Rocks also possess structures on a variety of scales, including bedding, foliation, crystallographic preferred orientations, folds, and faults. A fundamental problem of rock physics is to understand how the properties, proportions, and arrangements of the component phases interact to determine the overall or effective properties (e.g., electromagnetic, acoustic, fluid transport, and rheologic) of rock bodies.

A combination of theory and experiments on small homogeneous rock samples has served to lay the foundation for interpreting remote measurements on large rock masses in the Earth. However, rock masses are generally not homogeneous. Many fundamental and applied problems in earth science, such as deep seismic exploration, movement and cycling of water through the crust, secondary/tertiary recovery of oil, percolation of magma through the crust, explosive volcanism, and earthquake mechanisms, all involve length scales over which rock masses are highly heterogeneous. Future progress in rock physics depends on understanding the scale dependence of structures and properties in these heterogeneous rock masses. This problem is fundamental for several key geological areas, including the following:

Seismic Interpretation. A combination of theory and experiments on large, heterogeneous samples is critical for improving the types and details of information that can be obtained from remote seismic observations. Development of such techniques would allow identification of lateral and vertical compositional differences in the mantle, thus providing strong constraints on models of global tectonics; determination of sedimentary lithology including the nature of fluids present (brine and hydrocarbons), thus providing better guides to exploration; identification of mylonites, which might be associated with major faults and shear zones in the crust; and location of open or filled fracture systems, thus allowing mapping of the conduits for aqueous fluids and magma in the upper crust.

Fluid Transport. The transport of water, hydrocarbons, and melt in the upper crust is often dominated by complex fracture systems, with variable connectedness; an ability to model and predict transport rates is of critical importance in a number of applications such as hazardous waste disposal, but our knowledge of patterns and rates of large scale transport in the Earth's crust is still rudimentary. A combination of theoretical modeling, laboratory experiments on large heterogeneous rock samples, and large-scale field tests are required.

Rheology of Polyphase Aggregates. Most crustal rocks are complex multiphase aggregates, whose constituent minerals have anisotropic elastic properties as well as very different rheologies. Considerable attention has been given to developing expressions for the bulk elastic properties of randomly oriented aggregates, but there has been relatively little progress in modeling aggregate rheologies in terms of the volume fractions, flow laws, and geometrical arrangements of the constituent phases. Theoretical modeling tested by synthetic aggregates of controlled composition and volume fractions is required.

A related problem concerns the fact that aggregates deforming by dislocation creep develop crystallographic preferred orientations whose symmetry is related to the stresses and whose strength is related to the finite strain. Experimental deformations can supply information on the slip systems operative at different conditions, but the limitation to an axial compression geometry means that one cannot directly determine the patterns produced by different strain geometries and histories. Theoretical models are needed for this, more complex and sophisticated than those borrowed from metallurgists. Accurate models would not only allow more detailed interpretations of the strain history of naturally deformed rocks from the crust, mantle, and core, but would also allow predictions as to the magnitude of strain weakening or hardening to be expected from preferred orientation development in different situations.

A second type of problem is exhibited by modeling the brittle failure of rocks, since it depends critically on the density, distribution, and geometry of flaws. Larger rock volumes tend to be weaker, because they contain larger flaws. There are practical limits to experimental tests, and new theoretical approaches are needed to more accurately model the strength of the upper, brittle portions of the crust.

Large-Scale Structures. The development of large-scale structures such as folds, nappes, thrust fault ramps and flats, detachment faults, and ductile shear zones commonly is controlled by preexisting heterogeneities such as sedimentary beds, which are inherently weak or have a high fluid pressure, facies changes within sedimentary beds, contrasts between crystalline basement and sedimentary cover, foliations and crystallographic preferred orientations in deformed crystalline rocks, and fractures containing fluids or weaker retrograde phase assemblages. Our abilities to accurately model such structures are still relatively crude because of our lack of knowledge of the effective properties of the rock masses.

RESEARCH NEEDS

SAMPLES

For the next generation of experiments on physical and chemical properties, synthetic single crystal and polycrystalline starting materials are required, which do not exist as natural rocks at the Earth's surface. For example, essentially all rocks that are accessible at the surface of the Earth contain weathering/alteration phases that melt or decompose under high temperature and pressure conditions; thus, fundamental measurements of the rheology of melt-free rocks are impossible. Consequently, synthetic, polycrystalline aggregates with controlled microstructures and compositions must be fabricated. Some research groups hot-press small experimental samples on an irregular basis; this approach is sufficient for exploration experiments but clearly is unsuited for a concerted experimental program where sample-to-sample variations must be vanishingly small. Likewise, other experiments require single crystal samples, for example, to isolate matrix contributions to deformation from grain boundary effects, and to enable tests of carefully controlled variations of structure and composition. Facilities for fabricating high-density polycrystalline aggregates and for growing silicate single crystals are essential. Large starting blocks or boules are needed (10 cm) so that numerous experiments in several laboratories can be carried out on identical samples. Large-volume isostatic hot-pressure and arc-image crystal growth furnaces are available commercially and would represent a capital equipment investment of $1-2 million.

Related to the requirement for synthetic samples is the need for curation of natural samples used in laboratory experiments and for a central repository for data on these samples. Such curation would facilitate the use of rocks from one locality as samples for several types of experiments (e.g., conductivity, attenuation, and deformation) in several different laboratories. In addition, as new techniques for experiments and analysis became available, it would guarantee that cross-checks and new detailed analyses could be made. In many cases, experiments as well as microstructural and chemical characterization on a given suite of samples are performed by different groups throughout the country. A central repository of these data would be extremely valuable. Such a data base might include properties such as flow strength, electrical conductivity, and elastic module as well as grain size, phase distribution, and grain-boundary characterization.

EQUIPMENT

Major needs exist in the area of experimental equipment for measurement of physical and chemical properties. Three new generation-type deformation apparatus are required, for different applications.

Large Sample Apparatus. Many of the defects that control brittle deformation in rocks are on the order of 1 cm in size, but the largest sample size currently utilized in a triaxial apparatus capable of modest temperature and confining pressure is ~5 × 10 cm. In order to develop accurate scaling relations for application to large rock masses in the Earth, significant progress can be made using theory and scale models, but an apparatus capable of deforming large-volume (~1 m) samples is also required. Such apparatus should be capable of pressures to 2 MPa, temperatures to 300°C, and controlled fluid pressure. The costs of such an apparatus would be high, and probably one, designated as a national facility, would be sufficient.

Gas Apparatus. Determinations of the mechanisms, microstructures, and rheologies of ductile deformation are currently made using either gas or solid medium apparatus; these have been remarkably successful in providing fundamental data which have provided important constraints on Earth processes, but a new generation of each is required. Gas apparatus have the stress sensitivity required for accurate flow law determination, and recent advances have enabled experiments at very high temperatures (~1300°C) under controlled chemical environments. However, they are limited to relatively short times (low strains or fast strain rates) and low pressures (<1.0 GPa) where even some crustal silicates cannot be rendered ductile. A new generation of apparatus with higher pressure capability (1.0-1.5 GPa) is needed to supply accurate flow laws for crustal and upper mantle rocks, although there is some question of whether gas at such pressures can ever be (safely) contained within moving seals. It is anticipated that such apparatus, if successfully developed, will be needed at approximately 2 to 4 regional centers.

Solid-Medium Apparatus. Solid-medium apparatus are routinely operated at pressures up to 1.5 GPa, temperatures up to 1400°C, and long times (high strains and/or slow strain rates); these conditions are sufficient to render all crustal and upper mantle silicates ductile. However, the stress sensitivity of these apparatus is relatively poor (+0.5 to 1.0 MPa) because the load is measured externally. This problem is critical because differential stresses in the earth are mostly <1.0 to 2.0 MPa; experiments performed at higher stresses may activate deformation mechanisms and rheologies different from those characteristic of natural deformations. There is a critical need to develop an improved version of these apparatus having a larger pressurized volume (~50 mm diameter and 300 mm long); this would allow room for an internal load cell and pressure transducer, as well as additional improvements such as controlled chemical environments. It would be highly desirable for all existing laboratories (~8 to 10) will solid-medium apparatus to convert their apparatus to incorporate these improvements.

In addition there is a need to build a new generation of solid-medium deformation apparatus capable of operation at considerably increased pressures (~100 MPa); this should be possible by end-loading pressure vessel cores, improvements in vessel design, and utilization of new high strength materials. This high pressure capability would allow direct measurements of various aspects of mantle flow, including the activation volume for steady state flow of mantle materials; the effects of stress and deformation on the rates of polymorphic phase changes and the relative stabilities of mineral polymorphs, as well as the role of phase transformations in shear instabilities; and the properties of partial melts at high pressures where their structures change. Assuming it will be feasible to seal such high pressures against moving pistons, and to incorporate internal stress and pressure transducers, it is anticipated that having such apparatus in 2 to 3 regional facilities will suffice.

OTHER

In addition to the major items outlined above, there are other needs for observational and measurement techniques including the following:

Electron Microscopy. Needs include access to high voltage TEM instruments for mapping dislocations over large areas, to HRVEM and other techniques for characterizing grain boundary width and structure, and to EDAX for measuring compositional differences on extremely fine scales.

Computers. Needs include computerization of apparatus as well as access to the most powerful computers for theoretical modeling of deformation of heterogeneous, polyphase aggregates.

Infrared Techniques. Needs include the investigation of the amounts and speciation of "water" in natural and experimentally deformed samples. It is critical to develop the ability to accurately analyze individual mineral grains (~100 μm) within a polycrystalline aggregate, to distinguish the water within the crystal structure from that along the grain boundaries.

Simple Shear Apparatus. Almost all high temperature and pressure experimental deformations involve an axial geometry, but most natural deformations have a lower symmetry, often involving a significant component of simple shear, and it is impossible to extrapolate data from the former to the latter because the microstructural development is different. It would be highly desirable to design and build a simple shear apparatus capable of temperatures and pressures sufficiently high to deform crustal silicates ductily, or at least to develop sample assemblies for standard axial compression apparatus which produce close to simple shear geometry.

Collaboration. There is an increased need for communication between laboratory experimentalists and observationalists; between experimentalists, theoreticians, and field observers; between geoscientists and materials scientists; between university, government, and company research groups. In addition to regional and national facilities, there is a need for coordinated but individual proposals on important geologic problems (for instance, using standardized samples).

Appendix E:
Workshop Participants

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