Frontiers in Mineral Physics

Report of the Mineral Physics Committee of the American Geophysical Union

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Lake Arrowhead, California

September 1988

TABLE OF CONTENTS

ACKNOWLEDGMENTS

This report was produced at a workshop, "Frontiers in Mineral Physics", sponsored by the American Geophysical Union Mineral Physics Committee, which was held at Lake Arrowhead, California, September 28-30, 1988. This report is meant to update the first report of the Mineral Physics Committee, "Mineral Physics: Atomic to Global" (W.A. Bassett, Editor), produced at a previous meeting at Lake Arrowhead in October, 1985, and published by the American Geophysical Union.

We appreciate the support provided by the Division of Geological and Planetary Sciences at the California Institute of Technology, the Institute of Geophysics and Planetary Physics at the University of California in Los Angeles, and the U.S. Academy of Sciences, Geodynamics Committee. The assistance of Sue Yamada and Marilee Manley at the Workshop, and in the preparation of the manuscripts, is greatly appreciated.

The Editors

PREFACE

MINERAL PHYSICS AND EARTH AND PLANETARY SCIENCE

Mineral physics is the scientific study of the materials which make up the Earth and the planets and, thus, provides the critical data and theories to address such questions as:

1. How did the Earth and the other planets form? How did the minerals form in the primordial solar nebulae? How did the accretion from the planetesimals which formed the Earth and the other planets occur in detail? To what degree did the Earth and other planets form by homogeneous versus heterogeneous accretion?
2. How and why did the Earth become differentiated either during or after accretion? Knowledge of the properties and compositions at both low partial pressures pertinent to the accretion process and at high pressures and temperatures for the solid and liquid phases is probably required to address accretion issues. Research on differentiation problems appear to require detailed information on compositions, sources of heat, rheological properties of solid and partially molten earth materials, as well as thermal properties, such as heat capacity and conductivity, and equations of state of earth materials.
3. To what degree are the 400 and 670 km discontinuities compositional? What specific internal energies are involved in having material cross the 670 km by convection? To what degree do the equilibrium phase relationships for the materials at the 400 and 670 km discontinuities require differences in composition above and below a discontinuity?
4. What are the vertical and horizontal scale of mantle convection and how is the vertical and horizontal scale of convection constrained by the nature of the 400 and 670 km discontinuities? How can the rate of convection and viscosity in the mantle be inferred from experimental rheologies?
5. What are the causes of the Earth's apparent upper mantle and inner core's anisotropy? Knowledge of crystal symmetry of phases at high pressures and temperatures and how deviatoric stresses affect their orientations may lead to resolution of these questions. Are the lateral heterogeneities of the mantle, which were discovered by seismic tomography and inversion of the satellite geoid, the result of variations in the local temperatures on scales of 10^3 km or do they represent composition differences?
6. How far do subducted slabs descend into the mantle and what role does the subducting material play in the behavior of the mantle? The answers to these questions require a detailed knowledge of the equation of state and thermal properties of the materials both within, and adjacent to the subducting slab, as well as the effect that temperature on phase transitions in the slab both in equilibrium and disequilibrium.
7. What is the composition of the liquid outer core of the Earth and what equilibrium surface does the interface between the liquid outer core and the solid inner core represent? It is necessary to know how composition affects the equation of state and melting of iron alloys and compounds at high pressures and temperatures in order to address these issues. Why is the density of the outer core some 10% lower than that of pure Fe? If the outer core is not pure iron, what other elements are present and in what form? Equation of state and melting data for alloys of iron with other elements must be obtained to account for both the observed density and seismic velocity profiles.
8. What reactions and thermal transport take place at the core-mantle boundary? What is the nature of anomalous D" zone above the core-mantle boundary? Studies are needed on potential reactions at the mantle boundary (e.g. reactions involving metallic iron with oxides and silicates at high pressures and temperatures).
9. How does the core dynamo work and why does it reverse? Present theories tentatively link convection in the mantle with convection in the core. The thermal, rheological, and electrical properties of liquid iron and its alloys at high pressures and temperatures must be better understood to properly attack these difficult problems.
10. Where do the important boundaries within Jupiter, Saturn, and Uranus occur upon metallization of their constituent light elements such as hydrogen and nitrogen, as well as compounds such as water and hydrocarbons. A critical question for condensed matter physics concerns the pressure and temperature associated with metallization of hydrogen and other light elements and compounds. These properties must be studied at pressures and temperatures which are at least a factor of ten greater than have been achieved at present. Thus these studies present a great challenge to experimentalists and theorists.
11. How do fluids control the formation, migration, and trapping of oil and gas and a large class of minerals in the crust. Water, often in the form of groundwater, is one of the most critical needs of man. Understanding fluid flow in the crust is important because of our needs for pure water, as well as strongly affecting man's strategies for disposing of radioactive and other wastes within the Earth. Moreover, an understanding of the flow regimes of fluids in the crust, principally water and steam heated by near-surface igneous processes, is critical to the development and exploitation of geothermal resources. Fluid stability, reactions, and migration under conditions of the Earth's upper and lower crust are among the most societally significant problems addressed by mineral physicists.

12. What induces failure of rock under various fluid pressures and dry conditions and different stress states? What is the relation of various theories of rock failure to earthquake mechanics and explosive volcanic activity? These are also important issues which affect man and his cultural works.

The present report is prefaced by Executive Summaries of each section with *Overviews*, *Accomplishments*, and *Opportunities* in mineral physics. The intellectual span of the present report was intended to be extremely broad and encompasses such topics as rock physics and rheology, fluids in the crust, molten silicates and metals, metallization of hydrogen and water. Also included are summaries of mineral elasticity, thermodynamics and transport properties.

Section 2 describes the relationship between mineral physics and materials science. Sections 3, 4 and 5 deal with the interpretation of seismic data. Sections 6, 7 and 8 deal with aqueous and silicate fluids. Sections 9, 10 and 11 deal with the rheology of the crust, mantle and core. Sections 12, 13 and 14 describe thermochemical, spectroscopic and element partitioning research. Sections 15, 16 and 17 deal with the many important transport properties of earth materials. Section 18 deals with theories of mineral physics. Section 19 describes present and future sample requirements. Sections 20 and 21 describe new developments in mineral physics apparatuses. Section 22 describes metallization of light elements which occur in the major planets. Section 23 describes major problems in the understanding of the magnetism of minerals.

1. EXECUTIVE SUMMARIES

V_p AND V_s OF MINERALS

Overview

The objective of this research is to evaluate the chemical and mineralogical composition and physical state of the Earth's interior by interpreting velocity and density models based on seismic data. New challenges are being presented by expanded seismic tomographic data which reveal significant lateral velocity variations in earth structure models. The interpretation of these data in terms of material properties should provide a new level of understanding of the dynamical processes in the Earth's interior.

Accomplishments

1) Elasticity data at room pressure and temperature conditions have been obtained for solid solutions of pyroxenes and garnets and for the high-pressure polymorphs of Mg_2SiO_4 and $MgSiO_3$.
2) Ultrasonic data for the velocities of upper mantle minerals have been obtained at pressures to 3 GPa revealing important consequences for d^2V/dP^2, especially for orthopyroxene.
3) Resonance data for velocities as a function of temperature have been extended to 1800 K.

Opportunities

1) New techniques in the measurement of seismic velocities in minerals include:
   a) Brillouin and/or impulsive stimulating scattering at high pressures.
   b) Extension of measurements to higher temperature for iron-bearing minerals with control of oxygen fugacity.
   c) The measurement of $d^2V/dPdT$ at high pressures (>20 GPa) and simultaneously at high temperatures (>1000 K).
2) Future requirements for samples:
   a) Larger specimens of single crystals of high-pressure phases.
   b) Iron-bearing samples of high-pressure phases.
   c) Extension of experimental acoustic techniques to facilitate the use of smaller specimens.
3) Future developments in experimental and theoretical rock elasticity include:
   a) Measurement of the pressure derivatives of monomineralic aggregates.
   b) Development of realistic theories for elasticity of polyphase aggregates.

COMPRESSIONAL WAVE VELOCITIES IN MELTS

Overview

In order to determine the buoyancy forces controlling the rise or descent of magmatic liquids deep within the Earth, and to gain a better understanding of seismic velocity and attenuation in partially molten zones in the upper mantle, it is essential to study the elastic and anelastic properties of relevant silicate melts over a wide range of frequency, including that of interest in seismic studies. Such measurements should be conducted under *in situ* high pressure and temperature conditions, particularly with volatile (H_2O and CO_2) constituents present. Such data are needed for quantitative modelling of the terrestrial planets, and for understanding the time scales of relaxation processes in magmatic liquids at depth.

Accomplishments

Progress has been made in measuring sound velocities in both natural and synthetic melts at 1 bar and temperatures of up to 1600° C over a range of frequencies (3-22 MHz). The results from these studies have provided the only constraints on the compressibility of magmatic liquids across a wide compositional range, and have produced a systematic understanding of the relationships between density, composition, sound velocity and attenuation in melts at ambient pressures. To date, little data have been obtained on sound velocity under pressure.

Opportunities

Challenging research opportunities exist for measuring both sound velocity and attenuation in ultrasonic and lower frequency ranges utilizing presently available high pressure-high temperature technology, including gas medium, piston-cylinder and large volume pressure vessel methods. Each of these techniques has the potential of probing complementary pressure and temperature conditions. In addition, a new class of experiments is now possible, employing a combination of the heated diamond anvil cell and spectroscopic (Brillouin scattering, impulsive stimulated scattering) probes. Such studies will produce constraints on sound velocity, attenuation and compressibility in both volatile-bearing and volatile-free magmatic liquids under high pressure.

SEISMIC ATTENUATION (Q^{-1}) IN MINERALS

Overview

For 20 years seismic attenuation data have been steadily increasing in quantity and quality. Interpretation of these data has been slow because of the paucity of pertinent reliable laboratory measurements. Yet the information which must be contained in these data is staggering. Seismic attenuation data contains information on the dependence of attenuation on grain boundary structure, melt fraction, and defect structure.

Determination of these relations on carefully selected and well characterized samples will enable us to interpret seismic attenuation data. Through this we will gain new insight into the composition, temperature distribution, stress state, and rheological processes in the deep interior of the Earth.

Accomplishments

Earlier in this decade, pioneering experiments were performed at seismic frequencies and high temperatures on unconfined single crystal and natural polycrystalline samples. The attenuation was shown to depend on frequency, dislocation density and temperature.

More recently higher-frequency measurements have been achieved at high pressure and high temperature. In a natural peridotite the pressure dependence of attenuation was found to be describable in terms of the homologous temperature without explicit reference to pressure.

Opportunities

Two new classes of experiment are under development which will be capable of measuring attenuation at seismic frequencies and high temperature. New measuring techniques and meticulous attention to oxygen fugacity control and sample characterization will yield data for mantle silicates and oxides at seismic strain amplitudes of $< 10^{-6}$ under appropriate chemical conditions. High temperature capabilities are also currently being added to the high pressure apparatus used for measuring attenuation in rock samples at seismic frequencies. Other instruments are being developed for measurements on single crystals of mantle minerals.

New attenuation data are needed to evaluate various proposed absorption mechanisms. It is expected that the demand for well characterized (synthetic) single crystals will become acute. Extension of these measurements to mantle conditions (pressure > 250 GPa and temperature > 2000° C) are necessary to decipher the state and the rheology of the lower mantle. Extension to core conditions, although highly challenging, will follow.

CRUSTAL MINERAL AND FLUID PHYSICS AND CHEMISTRY

Overview

Crustal mineral physics and chemistry have a unique impact on societal problems, such as exploration for and development of mineral and petroleum resources, earthquake prediction and waste isolation. Important questions are: How can an understanding of the physical properties of rocks and minerals help to find or produce hydrocarbons? How does diagenesis in an evolving sedimentary basin depend on stress and pore pressure, and how does it affect the movement of brine, hydrocarbons, and mineralizing solutions? How is dilatancy prior to an earthquake related to man-induced hydraulic fracturing? How can one use an understanding of the properties of minerals and rocks to evaluate the effectiveness of geologic barriers to the leaking of radioactive and other waste deposits? What measurements can be made from the surface or the borehole to enhance our ability to understand these problems?

Accomplishments

We have learned how to measure shear wave velocities in the borehole environment, and how to interpret the data in terms of rock lithology and porosity. We have also recognized the ubiquitous presence of oriented cracks at all scales in crustal rocks, and adapted techniques from single-crystal acoustics to decode the seismic anisotropy on this larger scale. In addition, we have learned how to do nuclear magnetic resonance downhole, using free precession in the geomagnetic field, and how to interpret the results in terms of permeability and hydrocarbon recoverability.

Opportunities

We recognize four key areas of intellectual challenge:

1) Understanding physical properties of heterogeneous systems in the crust and lithosphere; for example, the problem of determining appropriate effective average velocity and attenuation in terms of constituent properties.
2) Understanding the problems of scale and feature resolution in a heterogeneous system; for example, the scale-dependence of permeability in the presence of cracks and joints.
3) Understanding the pervasive non-equilibrium of systems within the crust and lithosphere, in particular, the interplay between chemistry and mechanics of pore fluids acting in porous rocks in controlling such properties as seismic attenuation and mechanical strength.
4) Adapting and developing new instrumentation to obtain new and better data vital to the solution of these problems, for example, developing both downhole pulsed electrical and nuclear magnetic resonance sources, and the appropriate broad band receivers, as well as the required data processing algorithms.

WATER-MINERAL INTERACTIONS

Overview

The primary aim of research in this field is to rigorously describe the thermodynamic and kinetic behavior of mineral-water reactions from ambient conditions to elevated temperatures and pressures.

Accomplishments

Semi-empirical models have been developed which provide a basis for extrapolating thermodynamic data for aqueous systems to 1000° C and 5 kbar and for describing the non-ideal (excess) thermodynamic behavior of multicomponent salt solutions using data on possible combinations of two-salt + water systems containing the same components at the same temperature and pressure. These models accurately predict the behavior of highly concentrated natural brines and evaporites. Thermodynamic data for complex formation and ion association have been obtained in hydrothermal systems using a wide variety of laboratory measurements, including electronic absorption, Raman spectroscopic techniques, and newly developed electrochemical methods. Many high-quality measurements have been made on the kinetics of mineral-water reactions; new surface analytic techniques such as XPS, SIMS, auger spectroscopy and resonant nuclear reaction analyses are providing valuable insight into elementary reaction mechanisms. New kinetic and thermodynamic data including partial molar heat capacities, volumes, electrolyte activity coefficients and related parameters have been obtained for a wide range of temperatures, pressures and aqueous solutions.

Opportunities

There is a need to develop computer codes which simultaneously incorporate hydrodynamic, thermodynamic, and kinetic algorithms. This would permit simulation of the formation of complex natural mineral deposits, explaining the presence of metastable intermediate products and providing detailed analysis of overall reaction paths towards final equilibrium. Spectroscopic analyses (electronic, IR and Raman, NMR etc.) should provide essential insight into the structure and inorganic chemistry of high temperature aqueous solutions, and are only just beginning to be used for this purpose. Understanding the detailed atomic-scale aqueous reaction mechanisms of minerals can be improved greatly by using surface spectroscopy and related techniques to analyze reacted minerals. There is a need for *in situ* electrodes capable of measuring pH, specific ion activities and concentrations; the available technology such as optrode design is becoming feasible at the present time. Finally, there is an ever continuing need for high-quality fundamental thermodynamic data on these systems, including equilibrium constants, partial molar heat capacities and volumes, and related parameters because of the dearth of reliable data for high-temperature aqueous species.

TRANSPORT PROPERTIES, DENSITY AND COMPRESSIBILITY OF SILICATE MELTS

Overview

Characterization of magmatic processes requires an understanding of the processes of magma separation and aggregation at the source of melting, magma ascent mechanisms and rates, emplacement and/or volcanic eruption. Thus, the state and evolution of the Earth are, to a large degree, affected by the transport properties of silicate melts.

Accomplishments

Experimental transport and related property data (viscosity, density, diffusivity, conductivity and compressibility) have been obtained to pressures as high as ~8 GPa at > 1500 K, made possible by miniaturization, new high-pressure technology and computational simulation. Most transport property values decrease with increasing pressure at constant temperature. An exception to this observation is diffusivity, where network-building cations and oxygen exhibit decreasing diffusivity, whereas mobile large cations display the opposite behavior with increasing pressure. This behavior has been rationalized with results from molecular dynamics simulations.

Recent observations, using infrared and Raman spectroscopy of silicate glasses at high pressure conditions, indicate that silicon may undergo a change from 4-fold to 6-fold coordination at high pressure. Such a coordination change would result in significant differences in the transport and structural properties of melts in the lower mantle.

Opportunities

In order to ascertain the mechanisms that control the transport behavior of silicate melts, we must expand the observational data base by systematic evolution of the chemical complexity of the systems studied and couple these studies with determination of melt structure on the atomic level. The pressure and temperature ranges over which these measurements are made must be extended from the upper to middle depths of the upper mantle to those from the Earth's crust (0.1 MPa, 1000 K) to the core-mantle interface (100 GPa, 5000 K).

BRITTLE FAILURE OF ROCK

Overview

Deformation of the upper few kilometers of the Earth's crust occurs by brittle failure, resulting in faulting and the generation of earthquakes. An understanding of complex, multi-scale fault patterns, and of the instabilities which release earthquake energy requires a basic knowledge of the micromechanics of failure in compression. A complete description of the earthquake phenomenon is further complicated by the presence of fluids and the possibility of shear-melting, both of which introduce time dependence into the problem. We require laboratory studies of rock-fracture and rock-friction under crustal conditions and in the presence of fluids. We also require sufficient theoretical understanding to scale these experimental results to the time and length scales appropriate to natural faults.

Accomplishments

1) It has been known for a long time that shear failure is preceded by dilatancy associated with the growth of tensile microfractures. It has recently become possible to model the nucleation, growth, and interaction of these microcracks and thus to develop a damage mechanics model.
2) Rate- and state-dependent friction laws have been developed which describe stick-slip instabilities and can be used to model the earthquake cycle on a fault. Constitutive equations have been formulated which describe laboratory friction experiments and are capable of being extended to model earthquakes. However, the current lack of a physical interpretation of the model parameters makes the scaling uncertain.
3) The spatial heterogeneity of crustal deformation has been characterized over a large range of length scales from microns to hundreds of kilometers. The recognition of fractal geometries and other geometrical relations between faults at various scales may provide important constraints on the mechanics of brittle deformation of the crust.

Opportunities

Current important questions that must be addressed in the field of brittle failure of rocks include:

1) What is the mechanical significance of the fractal fracture geometry observed in fault zones? Does the observed independence of scale offer insight into the fracture mechanics and crustal deformation? Are there important scaling effects in rock strength between the laboratory and the field?
2) How is an earthquake best described? Is it a shear failure in a highly "damaged" fault zone or is it a frictional instability, or are the two somehow equivalent?
3) What are the micromechanics of rock friction? What is the physical significance of the parameters in rate- and state-dependent constitutive laws and how should they be scaled from the laboratory to the field? Can the stick-slip field be mapped in temperature, pressure and sliding friction space?
4) What are the effects of ground water and shear melting on earthquake instability?

RHEOLOGY OF THE MANTLE

Overview

The cooling and chemical differentiation of the Earth are controlled by thermal convection in the Earth's interior. The surface manifestation of this convection is plate tectonics, which provides a unifying theory of many important earth phenomena, such as earthquakes, tectonic movement and volcanism. All of these processes are strongly controlled by the viscosities of solid rocks and minerals. Thus, an understanding of earth dynamics requires data for the rheology of mantle rocks and minerals over a wide range of pressures and temperatures.

Accomplishments

Recent major advances in the study of the rheology of the mantle include exploratory deformation studies at lower mantle pressures using the diamond anvil cell and the multi-anvil press for several oxides and silicates. In other experiments, at temperatures to 1500° C and pressures to 3 GPa, on wet and dry minerals, deformation studies have quantified the role of point defect chemistry in governing the rheological properties of mantle minerals. There have also been direct experimental measurements of the rheology of olivine-basalt partial melts at crustal pressures.

Opportunities

High pressure experiments in the diamond cell should be extended to high temperatures in order to measure the creep properties of minerals at the conditions of the lower mantle. This is virtually an untouched area of science in which much data is needed. These experiments will require improved monitoring of the state of stress, strain rate, and chemical environment in the samples to pressures of 130 GPa and temperatures of 3000 to 4000 K.

There is a great need for obtaining and characterizing the rheology of natural and synthetic single crystals. Experiments also need to be conducted on a range of aggregates and partially molten systems. This research will provide constraints on shallow processes in the Earth bearing on the thermal convection in the mantle, preferred orientation of minerals leading to velocity anisotropy in the mantle, and processes at mid-ocean ridges.

DEEP EARTHQUAKES AND THE PHYSICS OF DEEP SUBDUCTION

Overview

The distribution of deep earthquakes is our primary observational constraint on the geometry of thermal convection in the mantle. Deep earthquakes reflect both the forces that deform the descending lithosphere and the physical mechanisms and conditions that promote deep failure. The physical process by which unstable faulting occurs at depths of 300-680 km and the corresponding pressures of 10-20 GPa has been an enigma since deep earthquakes were discovered over 60 years ago. Recent work has highlighted the importance of phase changes in the process of deep earthquake generation. Mineral physics research has the potential for inferring the stress state and failure mechanisms capable of generating such deep events. If we understand deep earthquake generation, we have a means of interpreting the cutoff of earthquakes at 680 km and making inferences as to the depth scale of mantle subduction and the dynamics of deep convection.

Accomplishments

Initial observations have been made pertaining to the mechanisms of the olivine-spinel phase transformation under non-hydrostatic stress. Mechanical instabilities (microearthquakes) have been observed in several minerals that polymorphically transform under stress. Strength contrasts have been detected across polymorphic phase changes in SiO_2 and NaCl.

Opportunities

There is a need to simulate the physical conditions of deep earthquakes (pressures of 10-25 GPa, temperatures of 400-1200° C and non-hydrostatic stresses of 0-1.0 GPa). This requires technical advances in deformation apparatus with independent and accurate control of pressure, temperature and non-hydrostatic stress. Cell volume must be increased and gradients in temperature and stress must be reduced in samples.

More detailed studies are required on phase transformations under non-hydrostatic stress as a potential source for deep focus earthquakes. In particular, there must be a search for systematics of strength changes with structural changes in minerals at low to moderate pressure, and very high pressure studies are needed of the phase transformations of deep subduction, including measurement of strength contrasts across phase boundaries, failure processes and transformation mechanisms and kinetics.

VISCOSITY OF THE CORE

Overview

The core of the Earth has a solid inner region and a fluid outer region. The inner core occupies depths greater than ~5000 km. Both the inner and outer core regions consist of more than 90 weight per cent iron. There are no direct measurements of flow in the inner core but there are several indirect observations suggesting that the viscosity of the inner core is important:

i) Seismic inversions indicate that the inner core may be non-spherical and able to support topography;

ii) Seismic data may be interpreted as evidence for anisotropy or lateral inhomogeneities related to convection of the inner core;

iii) The observed phase lag of the nutation may be related to the viscosity;

iv) The inner core is believed to have a very low Q which may be related to a viscous deformation process.

Opportunities

The outer liquid core has a high Q which may be related to liquid viscosity. There are currently no direct observational data on outer core viscosity. Nevertheless, it is important to have information on this very poorly known quantity since it could be large enough to influence core convection and the geodynamo.

Experiments to determine the viscosity of the core are difficult because of the geophysical conditions in the core: the solid iron is probably present in the hexagonal close packed ϵ phase, slowly convecting with a large grain size and possibly forming a metallic solid solution. Viscosity measurements in the diamond cell must be made on both crystalline and fluid phases of materials such as pure Fe, FeS, and metallized wustite (FeO). Viscosity measurements must also be made on the hexagonal close packed iron ϵ phase or analog hexagonal close packed metals at high temperatures.

THERMOCHEMICAL MEASUREMENTS

Overview

Whether we are interested in the nature of the core-mantle boundary, the phase transitions which control the structure of the mantle, density changes which drive mantle convection, or the diagenesis of sediments in a petroleum reservoir, we require data concerning the bulk energetics of the minerals, melts and fluids involved. Thermochemistry relates these energetics to variations in temperature and other intensive parameters, and to chemical concepts of structure and bonding (as determined by enthalpy, entropy, volume and their derivatives). Since most of the earth is at very high (>1000° C) temperatures, both entropy and energy effects are of basic importance. The complementary effects of pressure are determined by volume and its derivatives.

Accomplishments

- A key property in determining temperature effects on bulk energies is heat capacity. Very recently it has become possible to make direct and accurate C_p (heat capacity at constant pressure) measurements at high temperature, extending the feasible measurement range from the previous limit of 700° C to 1500° C, to within the range of magmatic temperatures. This opens up new possibilities for work on melts, melting, crystallization and other high temperature phase transitions.
- It is just becoming possible to calculate accurate phase diagrams for sample systems of direct relevance to the lower mantle (e.g. $(Fe,Mg)SiO_3$ perovskite). This is, in part, a direct result of improved technology in calorimetry, especially miniaturization.
- Relating thermodynamic properties and details of structure and bonding is an important development. Study of order-disorder by calorimetry and spectroscopic and diffraction methods on the same materials has enabled detailed understanding of the microscopic basis of thermochemistry.

Opportunities

- *In situ* calorimetry at high temperature and pressure is beginning to allow studies of unquenchable phases, displacive phase transitions, reaction systems with volatiles, etc. Precise measurements in high-pressure gas vessels, large-volume presses, and diamond cells should become possible within the next 5 years.
- miniaturization of instruments is part of the *in situ* effort, but also will greatly extend the range of types of samples that can be studied by low temperature and reaction calorimetry. This is particularly important for work on materials that are difficult to synthesize (e.g. high phases, deformed materials, etc.).
- thermodynamic measurements will be used increasingly to study the rates of melting and crystallization, of solid phase transitions, and of order-disorder processes.

OPTICAL SPECTROSCOPIC TECHNIQUES

Overview

Optical spectroscopic methods are used extensively to probe the molecular and electronic structures of Earth materials. These experiments are driven by the need for a microscopic understanding of the phases and processes important to fundamental geological problems. Combined with theoretical calculations, these studies provide fundamental insights into the interrelation of the structural, bonding and dynamic properties of Earth materials.

Accomplishments

Vibrational spectroscopy has provided critical constraints on the heat capacity and entropy of mantle minerals such as stishovite, silicate ilmenite and spinel. The spectroscopic data combined with theoretical calculations have been important in understanding the dynamic stability of mantle phases. For example, theory has predicted the occurrence of phonon instabilities in silicate perovskites, which could have a dramatic influence on the thermal and elastic properties of the deep mantle. Infrared and Raman spectroscopy at high pressures have been crucial in constraining the theoretical calculations, and are currently being used to observe the soft modes experimentally. Hydrogen is a primary component of the outer solar planets. Raman spectra of solid hydrogen measured to pressures above 200 GPa indicate that H_2 remains molecular under these conditions. Optical and nuclear magnetic resonance methods have played a key role in structural studies of silicate glasses and melts at high temperatures, and it has recently become possible to carry out *in situ* Raman and infrared measurements at high pressure.

Opportunities

Most of the optical spectroscopic experiments to date have been in the frequency domain, to measure the energy changes associated with electronic and vibrational transitions. We need to extend these measurements into the time domain, to explore relaxation and energy transfer processes in Earth materials. The time-resolved optical spectroscopies are already well-known in the chemical physics community, and we need only apply these techniques to mineral physics problems. We are not yet able to perform routine spectroscopic measurements over the complete range of P-T conditions within the Earth. We need to develop reliable techniques for *in situ* spectroscopy under simultaneous high temperature-high pressure conditions. The spectroscopic measurements require parallel theoretical calculations in order to interpret the results, and extrapolate these to other P-T ranges, and we need continued development of theoretical techniques in parallel with the new spectroscopic measurements.

ELEMENT PARTITIONING IN THE EARTH'S INTERIOR

Overview

Major and trace element partitioning between minerals, melts (oxide, sulfide and metal) and fluids in the Earth's interior is fundamentally important for quantitative geophysical, petrological and geochemical models of formation and evolution of the Earth. Characterization of the mineralogical constitution of the Earth's interior depends on accurate experimental determination of major element partitioning. For example, major phase boundaries in the Earth can be ascribed to subsolidus phase transformations occurring over narrow pressure intervals. Lateral chemical heterogeneities and compositional stratification of the mantle and the crust can be traced to melting processes and melt-mineral major element partitioning in the upper mantle.

Minor and trace elements are partitioned between phases the stabilities of which are defined by pressure, temperature and major element bulk composition. Thus, trace element partition experiments relevant to the Earth's interior require accurate major element partitioning data. Minor and trace element partitioning of transition elements between oxides and sulfides and metal phases control enrichments of these components in the core relative to the mantle, and experimental data at the appropriate pressures and temperatures are critical to ascertain, for example, whether the Earth's mantle is in equilibrium with its core. The thermal history and present state of the Earth depend on the concentration and distribution of radioactive trace elements in the Earth. Thus, high-pressure and high-temperature experimental measurements of the partitioning of potassium, uranium and other radioactive, geochemically incompatible elements between minerals, melts and fluids are needed.

Accomplishments

Sub- and supersolidus phase relations of bulk compositions relevant to the uppermost portion of the upper mantle have long been a focus of high-pressure, high-temperature experimentation. Extension of the pressure-temperature range to the deeper upper mantle and beyond has only recently become feasible. Major experimental efforts have focussed on the phase boundaries in the Earth. From the thermodynamically internally consistent phase diagram for the system Mg_2SiO_4-Fe_2SiO_4, the α/β and β/γ phase transformations in the system Mg_2SiO_4-Fe_2SiO_4 are sufficiently sharp in pressure-composition space to account for the changes in mantle properties associated with this boundary. Similarly, the phase transition between the transition zone and the lower mantle near 670 km can be accounted for by the transformation of the γ-spinel to the denser assemblage of perovskite pyroxene and magnesiowustite.

Chemical differentiation within the Earth to a major extent is within the upper mantle, the transition zone, the lower mantle, and the core. A fairly extensive data base exists to pressures of less than about 5 GPa, but higher-pressure data are rare. Iron-magnesium partitioning between perovskite and magnesiowustite and between γ-spinel and magnesiowustite has been reported, but the temperature, an important variable in partitioning experiments, has not been well controlled. Calcium and aluminum partitioning between mineral phases in the transition zone and the lower mantle (e.g., majorite garnet, Ca- and Mg-perovskite) have been reported, but the partitioning behavior of calcium and aluminum oxides in the deep interior of the Earth remain largely unknown.

In recent years, attention has focussed on the melting behavior of plausible mantle compositions down to the deepest portions of the Earth's upper mantle. These experimental studies reveal that,with increasing depth, the liquids in equilibrium with mantle mineral assemblages become increasingly ultramafic and, thus, more fluid and dense. Furthermore, the iron-magnesium partition coefficients between crystalline residual phases (olivine, pyroxenes and garnet) and coexisting liquid $[(Fe/Mg)_{crystal}/(Fe/Mg)_{liquid}]$ increases with pressure. The data provide important constraints on tectonic models of the Earth's upper mantle.

Partitioning of trace and minor large incompatible trace elements (LILE) and transition metals between minerals and melts have been determined experimentally under pressure conditions near those of the surface of the Earth. Significant pressure effects to pressures less than 3 GPa on melt-mineral nickel partitioning have been reported, and scattered rare earth element data in the same pressure range also exist. These data illustrate how pressure, temperature and bulk composition are important variables in governing the trace and minor element partitioning behavior in the deep interior of the Earth.

Experimental trace element partitioning data at the extreme pressures in the deep upper mantle and below are limited to a few preliminary studies involving majorite garnet, Ca- and Mg-perovskite and coexisting melts. These data indicate that such information can be employed to place powerful constraints on the role of melting processes in the early stages of the formation of the Earth, but much more information is needed before trace and minor elements can be used for quantitative modelling.

Opportunities

Advances in high-pressure and temperature technology and microanalytical techniques for major and trace element chemical analysis of μm-size phases *in situ* will be of major importance for future studies of major, minor and trace element partitioning in the Earth. With this equipment, we need to determine the phase diagrams for relevant earth composition not only at phase boundaries in the mantle, the transition zone, the lower mantle, the core and, very importantly, the core-mantle boundary, but also in the pressure and temperature ranges between the boundaries themselves. We must determine the melt-mineral partitioning behavior for major elements such as Fe, Mg, Ca, Al and Si as a function of pressure from the uppermost upper mantle into the core.

Trace and minor element partitioning behavior at almost any pressure within the Earth requires experimental determination. The behavior of trace transition metals (in particular, Ni, Co, Cr) is virtually unknown at any pressure. The data base is important for processes ranging from upper mantle melting processes to formation of the core. Large incompatible trace elements (LILE) include the radioactive isotopes responsible for important contributions to the thermal history and profile of the Earth. We need mineral-mineral and melt-mineral data for rare earth elements, alkali metals, lead, uranium and thorium.

Experimental studies such as these have not been possible previously. We are now equipped with the necessary technology to provide the necessary element partitioning data needed to establish the mineralogical, bulk compositional, minor and trace element constitution of the Earth.

THERMAL CONDUCTIVITY OF MINERALS

Overview

Geodynamic and physical processes within the Earth's core, mantle and crust involve heat flux between sources and sinks producing transient or steady-state temperature fields. Thermally induced hydrostatic instabilities that lead to redistribution by convection and plumes depend critically on thermal conductivity (k) and temperature gradients. Further, rates of polymorphic structure and phase transformations are governed by the thermal conductivities of the transforming minerals and their surrounding media.

Accomplishments

High pressure and temperature measurements of thermal conductivity have improved largely because computer control and processing have increased the rigor and accuracy of these difficult experiments. Thermal conductivity measurements across polymorphic structure and phase transformations have determined the progressive effects of changes in structure, coordination, type of bonding, and exsolution on thermal conductivity. Measuring k as a function of time through reconstructive transformations at constant P and T has provided new insight into nucleation and growth kinetics. Anisotropic thermal conductivity measurements have been used to determine the surfaces of constant heat flux and constant T-gradients in low-symmetry materials. These are of great interest for comparisons with constant slowness surfaces of elastic velocities in crystals, as well as for determining heat flux refraction and the range of divergence between heat flux and T-gradient vectors.

Opportunities

Experiments to measure optical absorption, dielectric constant, and refractive index in order to calculate radiative heat transport present challenges to those working with diamond cell and shock wave techniques. Because of the relationship between thermal conductivity and sound velocity, new information should be provided by sound velocity measurements at high pressure (e.g., by dynamic grating spectroscopy).

Laser beam and hot wire methods in both transient and steady-state techniques have come to dominate current thermal conductivity measurements. New methods of fluid encapsulation, applicable to multi-anvil presses (up to 6.5 GPa and 1,100° C in a 1,000 ton cubic press), provide ideal hydrostatic and isothermal, large-volume (~ 1.3 cm^3) environments for complicated experiments requiring many input/output leads. Sharp latent heat pulses, generated by a transforming crystal, are used as heat sources for thermal diffusivity through samples of anisotropic single crystal and polycrystalline specimens. On-line data processing and internal calibration facilitates accurate determination of the P- and T-dependence, so that T-fields can be determined from finite difference solutions of Laplace's and Poisson's equations. In cases of high temperature gradients, analyses of measurements require non-linear heat flux theory; representations in terms of heat flux potential are most suitable.

Perovskite-structure silicates and their isomorphs are interesting and crucial subjects for observation because of current interests in the D" layer at the bottom of the mantle. To the extent that D" is a thermal boundary layer, its thickness is determined by thermal conductivity.

THERMAL CONDUCTIVITY OF IRON ALLOYS

Overview

Insight into the thermal state and dynamic response of the Earth's core can be obtained through laboratory experiments and theoretical calculations on the thermal conductivity of iron alloyed with one or more light elements, such as oxygen or sulfur. As a primary thermophysical parameter, the thermal conductivity needs to be accurately known in order to support or rule out competing models of the core dynamo, whether it is driven by thermal convection or by compositional growth of the inner core. Precise knowledge is also needed for constraints on thermal gradients across the thermal boundary layer at the core-mantle boundary, and for the interpretation of shock wave and heated diamond anvil cell experiments.

Because of the difficulties involved in studying liquid iron alloys, experimentally or theoretically, under Earth core conditions, there have been no measurements of the thermal conductivity of iron under these extreme conditions. This lack of data makes this task extremely important.

Opportunities

Current techniques capable of reaching the core pressure, temperature range involve the laser-heated diamond anvil cell and the generation of strong shock waves. Although the Wiedemann-Franz-Lorenz law relates the thermal conductivity of metals to the electrical conductivity, for metals with complex electronic structure, such as iron, this relation can break down. This problem becomes greater for liquid iron alloys under pressure. Thus, direct measurements of thermal conductivity are necessary.

Theoretical calculations on the transport properties of iron alloys are very difficult for the solid state and even more so for the liquid state. However, recent progress has been made in calculational techniques for transport properties, and these should be applied to the behavior of iron under the conditions of the core of the Earth.

ELECTRICAL AND CHEMICAL TRANSPORT IN MINERALS AND RELATED FLUIDS

Overview

The processes that shape the Earth require movement of material from one location to another. Electrical and chemical transport involves the most fundamental type of material transfer, that is, the motion of individual atoms, ions, and electrons through a material. Knowledge of transport properties constrains theories of large-scale mass transport in the crust and mantle and permits interpretation of the regions of anomalous electrical conductivity that have been observed within the Earth. These properties are significant because the formation and ultimate discovery of mineral resources, hydrocarbons, and geothermal resources depend, in part, on these atomic-level transport properties. Movement and retardation of radioactive and chemical pollutants through containers, soil, and groundwater, and their detection by remote methods, all involve elements of ionic and chemical transport. Knowledge of the diffusion of water and other volatiles in magmas is necessary for understanding both magma generation processes at depth in the Earth and the nature of eruptive processes at the surface. Mass transport (diffusion) is also the rate-controlling step in the deformation of minerals and rocks at the high temperatures present in the mantle, core, and most of the crust.

Accomplishments

Specific mechanisms of electrical and diffusive transport have been identified in single crystal clinopyroxene and olivine at 1 bar pressure and high temperature. The electrical conductivity of olivine under geological oxygen pressures occurs by a combination of magnesium vacancy and electron hole migration. We now recognize the effects of chemical complexity, such as the effects of iron:magnesium ratio and trivalent iron substitution, on the electrical conductivity behavior of olivine and pyroxene. Furthermore, the relationship between electrical, diffusive, and rheological behaviors through point defect chemistry has been demonstrated, although it is imperfectly understood. The influence of surface chemical reactions on bulk properties has been demonstrated for aqueous fluid-rock aggregate systems.

Opportunities

Data on the diffusive and electrical transport properties of Earth materials under the wide range of pressure and temperature conditions characteristic of the upper crust to the lower mantle are severely lacking, yet such data can place important fundamental constraints on rates of chemical and mechanical transport at depth, and therefore also on rate-dependent metamorphic processes and creep behavior in the crust and mantle.

Research is needed on electrical conductivity and diffusion in aggregate and polycrystalline materials, in addition to examining a broader range of single crystal materials. The electrical, diffusive, and rheological behaviors of aggregates do not necessarily represent simple extrapolations and combinations of single crystal properties and must be investigated directly. The methods of surface science have barely begun to be applied in this context. Further study of mineral-solution, partially molten, and molten systems, particularly in the presence of volatile species, must also be pursued.

THEORETICAL EQUATIONS OF STATE

Overview

Much of recent theoretical research in equations of state has been motivated by the need to understand how pressure-induced changes in interatomic bonding affect crystal structure, elasticity and thermal properties.

Accomplishments

Efforts are currently being made to further develop first principles approaches, and to design more economical empirical models that incorporate the essential physics required for particular problems. Hamiltonians based on electron-gas theory now yield quantitatively reliable thermal equations of state for close-packed ionic minerals, including orthorhombic perovskites. First principles equations of state derived from band structure calculations have been shown to approach experimental measurement in reliability. Many body effects caused by the instability of the oxygen ion are now understood, and the consequences of this for elasticity and phase stability can be quantitatively calculated. Lattice dynamics calculations have proven to be powerful tools in the investigation of lattice stability. Calculated phonon spectra of $MgSiO_3$ perovskite indicate that, at pressures corresponding to the lower mantle, soft modes cause transformations from orthorhombic to tetragonal and ultimately to cubic structure. Models of covalent bonding have been developed that can accurately account for the crystal phases of silica, as well as predict thermodynamic and structural properties of liquid silica under pressure. Pressure effects cause the density of liquid silica to exceed that of several of the crystal phases at pressures exceeding 20 GPa, even if the silicon is restricted to tetrahedral coordination.

Opportunities

Extensions of current covalent models need to account for the effect of coordination changes on bonding. Since coordination changes cause rehybridization of orbitals, studies of phase transformation mechanisms must take into account the associated electronic effects. Pressure induced coordination changes in liquid silicates are also affected by this effect, so appropriate simulation techniques must be developed. Although it is now possible to compute accurate pressure and temperature derivatives of elastic constants of simple solids, these models must be extended to more complex geological materials. These efforts will require generous computer support, and graphics work stations are likely to be very important development tools. New data are needed to guide further theoretical developments, including measurements of elastic constants, infrared, Raman and optical spectra of minerals, melts and glasses as functions of pressure and temperature.

SAMPLE REQUIREMENTS FOR MINERAL PHYSICS

Overview

Samples of natural and synthetic single crystals and polymineralic aggregates are required for the experiments described in virtually all other sections of this report, and new developments in experimental techniques will increase the demand for samples. Thus, there is a clear and continuing need to provide investigators with information on the availability, degree of characterization, and measured physical properties of samples representative of minerals that constitute mantle and crustal rocks.

Accomplishments

Synthesis of Fe-Ti spinel, wustite, and $MgSiO_3$ perovskite crystals by research groups and the purchases of large batches of DeKalb diopside and Sri Lanka sillimanite crystals by museums have permitted important new sets of physical property measurements to be made.

Opportunities

To better meet present and future needs of investigators, the Mineral Physics Committee of the American Geophysical Union should take immediate action through its Mineral Acquisition and Distribution (MAD) subcommittee to establish a central facility to a) develop and maintain a database containing a registry of samples, their characterization and their measured properties, and b) procure, curate and distribute research specimens. The MAD subcommittee should also specify the basic characterization criteria required of samples for each of the various classes of measurements and, in addition, offer criteria for choosing between natural and synthetic samples for study.

NEW INSTRUMENTATION TO USE WITH THE DIAMOND ANVIL CELL, LARGE VOLUME APPARATUS, AND SHOCK WAVE FACILITIES

Overview

The pressure-temperature environment is a major factor in defining the chemical and physical properties of the materials which exist within any region of the Earth. Laboratory studies provide the most direct information concerning the consequences of these extreme conditions on earth materials. Three types of pressure-generating systems have been the focus of intensive research in the past several years: diamond-anvil cells, large-volume apparatus, and shock-wave facilities. Each system has particular advantages and limitations for addressing the diverse questions concerning the effect of pressure on earth materials. Between them, these methods provide an opportunity to study virtually all thermodynamic, mechanical, and transport properties of earth materials at the relevant pressure and temperature conditions.

Accomplishments

Over the past few years, major accomplishments of high pressure research have included the following:

1. The synthesis of 100-200 μm single crystals of $MgSiO_3$ with the perovskite crystal structure, allowing the characterization of several properties of this material, which is probably the most abundant mineral in the Earth.
2. The attainment of a record 550 GPa pressure in the diamond anvil cell, which is higher than the pressure at the center of the Earth.
3. The measurement of the density of silicate melts at high pressure and temperature under shock conditions. These observations demonstrate that liquids do in some cases become denser than the solids which form them, with significant consequences for the dynamics of crystal-melt segregation.
4. Measurements have been made on the partitioning of trace elements between solid phases and between liquid and solid phases for mantle minerals at lower mantle pressures. These data help constrain the melting history of the Earth.
5. Melting relationships have been determined in multicomponent silicate systems to pressures of the transition zone and lower mantle.
6. X-ray shadowgraphs of falling spheres have provided viscosity information on silicate melts at pressure using synchrotron radiation.
7. *In situ* phase equilibria of olivine-spinel (Fe_2SiO_4) and garnet-perovskite ($CaGeO_3$) have been determined.
8. The structure of jadeite melt at high pressure has been studied *in situ* using synchrotron radiation.
9. Measurements of electrical conductivity in liquids and solids were made to 80 GPa and 5500 K.
10. The first single-crystal x-ray diffraction studies on hydrogen have been carried out to 30 GPa.
11. Melting temperatures for iron were determined to pressures in excess of 110 GPa, with significant implications for the temperature of the Earth's interior.
12. Sound speed measurements in olivine and pyroxene were determined under shock loading.

Opportunities

Experimental studies must be performed which utilize the P-T region that is currently sampled by the high pressure equipment, including:

1. Utilize gradients of thermodynamic variables in the samples. Boundaries between two phases can be defined, rheological studies can be made, and diffusion can be investigated.
2. Measure single-crystal elastic properties via interferometric techniques at pressures and temperatures of the Earth's transition zone. This will yield very accurate data but will require synthesizing large single crystals and developing the measurement techniques.
3. Apply transducers to diamond anvil cells to measure acoustic velocities at even higher pressures.

4. Measure acoustic velocities as a function of pressure for a broader range of samples using shock waves.
5. Induce shear stress in a diamond anvil cell by rotating one anvil. This will allow the study the response of the sample to shear stress while at pressure.
6. Perform thermochemical measurements at pressure and temperature. This will provide new thermodynamic data on important materials as well as allow the study of nonquenchable phases.
7. Develop a reliable method for viscosity measurements under shock conditions.
8. Measure Raman spectra of liquid and solid silicates during shock wave experiments.
9. Develop large volume high pressure systems capable of 25 GPa that are inexpensive to build and operate.

Further experimental studies must be also performed to expand the pressure, temperature, or volume capabilities of the high pressure systems, including:
1. A large volume high pressure system capable of mantle-core pressures and temperatures.
2. A large volume high pressure system with x-ray access that can produce conditions equivalent to the upper portion of the lower mantle.
3. A diamond anvil cell with a volume for the sample assembly of 1 mm^3.

SYNCHROTRON RADIATION FACILITIES

Overview

X-ray methods provide the primary means for structurally and compositionally characterizing earth materials. This basic information is an essential part of our knowledge about the earth and its dynamic processes. A revolutionary advance in x-ray studies of materials occurred in the mid-1970's when the first synchrotron x-ray sources became available for general scientific use. These extremely intense sources of electromagnetic radiation provide highly collimated beams and cover a broad energy range which can be wavelength tuned to produce relatively monochromatic light.

In the 10 to 15 years that synchrotron radiation has been utilized for research in the physical and biological sciences, it has become a remarkably versatile and widely used analytical tool for probing the structure, composition, and bonding of materials, including those of interest in the earth sciences. The unique characteristics of this radiation make it possible to study very dilute systems, samples of very small volume, and samples of low atomic number relative to conventional electron-impact x-ray sources. These x-ray sources permit very rapid data acquisition so that the mechanisms and kinetics of transient phenomena such as phase transitions can be studied. They also produce data of high energy resolution and high signal-to-noise ratio. The high brilliance of synchrotron radiation (high flux, small spot size, and low divergence) also makes it possible to carry out most of these studies under *in situ* conditions (i.e. at high pressures and/or high temperatures or in the presence of water). It is also possible to carry out spatially-resolved structural and compositional studies of materials.

Accomplishments

Recent applications of synchrotron radiation to earth materials problems have produced unique results in several important areas. For example, synchrotron radiation has made possible the first *in situ* high pressure x-ray diffraction study of the structure and equation of state of hydrogen to 26 GPa; this work has important bearing on the nature of giant planets. In the area of x-ray absorption spectroscopy, synchrotron radiation has permitted the first direct structural studies of sorption reactions at mineral-water interfaces, *in situ*, and of cation environments in silicate melts at high temperatures. Studies of the structural environments of trace level cations at grain boundaries and defects should also be possible using these methods. Synchrotron radiation induced x-ray emission microprobe analyses (SRIXE) provided the first quantitative compositional evidence for gold associated with sulfide minerals in disseminated ore deposits of the Carlin type; these results directly affect exploration and beneficiation strategies. Another exciting application of SRIXE is the *in situ*, spatially resolved study of compositional variations in mineral fluid inclusions; this work provides one of the first looks at dilute ore-forming fluids characteristic of those in the earth's crust. These types of studies were not possible before synchrotron radiation was available.

Opportunities

Over the next five to seven years, several new synchrotron radiation sources will become available, with brilliances three or four orders of magnitude greater than existing synchrotron sources. These next-generation sources will extend current capabilities in all of the areas mentioned above.

METALLIZATION OF NON-CONDUCTORS

Overview

Metallization is the most striking example of pressure-induced electronic transitions. The process is important for five reasons: (1) It is responsible for metallic hydrogen, which is the most abundant metal in our solar system, and profoundly affects the structure and evolution of Jupiter and Saturn. (2) Metallization may determine or influence the solubility of minor constituents in the Earth's core (for example, the metallization of wustite (FeO) may favor solubility of oxygen in the core). (3) Metallization or the approach to metallization influences the behavior of the geodynamo and other planetary magnetic fields. (4) Metallization may be associated with major structural reorganization of minerals or melts. (5) Metallization is a fascinating fundamental physics issue that has attracted interest since the early days of quantum mechanics.

Accomplishments

Much recent work has focussed on hydrogen; indeed, the attempts to metallize hydrogen are a major driving force for achieving the highest possible pressure in a diamond cell. Raman experiments performed to almost 250 GPa have shown that the H_2 molecules have not yet dissociated, but the electronic state at this pressure has not yet been characterized. In earth-forming materials, FeO has been demonstrated to have metallic conductivities at high pressure and temperature. Xenon has also probably been metallized near 200 GPa.

Opportunities

The quest for still higher pressures combined with technological advances in new measurement methods and the expansion of effort to a wider range of materials are all essential. The pressure of 250 GPa so far achieved for several light elements which exist in the cores of the major planets represents only some 10% of the pressures existing at the planetary centers. Direct conductivity measurements with electrical leads sputtered onto the sample should be combined with less direct, but equally important optical infrared and Raman spectroscopic measurements. Important materials to be studied include (Mg,Fe)O, water and a series of cosmic (C-H-O-N) mixtures, and pure hydrogen. Unconventional stoichiometries should be tried, and liquid phases are at least as important as crystalline phases. In theoretical modelling, the prediction of metallization and band gaps is a challenge best met through methods that not impose artificial structural or stoichiometric limitations.

MAGNETIZATION OF VERY SMALL GRAINS IN ROCKS

Overview

Quantitative information about plate tectonic processes beyond the last 200 million years requires new techniques for the separation of multi-component magnetization of older rocks which have seen multiple thermal events. Similarly, an economically useful way of interpreting the intermediate wavelength magnetic anomalies discovered by NASA's Magsat mission requires knowledge about the changes in source rock magnetization produced by long term exposure to the geomagnetic field at elevated temperature and pressure. The objective of this research is to provide experimental data on time-, temperature- and pressure-dependence of the magnetization of critically important small (1-100μm) multi-domain grains of magnetite and titanomagnetite and to provide a theoretical description of the magnetization activation processes through a numerical micro-magnetic approach.

Accomplishments

Single crystals and polycrystals of magnetite and titanomagnetite with controlled grain sizes have been produced by hydrothermal recrystallization, glass-ceramic methods and flux growth and have been applied to test Neel's theory for thermoremanent magnetization of single domain grains of magnetite.

High resolution Scanning Electron Microscopy of dried magnetic colloid patterns, Kerr magneto-optic effect and Scanning Electron Microscopy with Polarization Analysis have been used to observe small changes in the magnetic domain structure associated with magnetization changes in grains. These observations have allowed the determination of critically needed magnetic constants of small grains in rocks *in situ*.

Local Energy Minimum magnetic states have been shown by domain studies to be responsible for unexpectedly large magnetic remanence in small multi-domain grains. Numerical micromagnetic modeling has provided a theoretical framework for the existence of such states.

Opportunities

New methods that allow simultaneous observation of domain structure changes and measurement of magnetic remanence associated with changes in magnetization in single grains *in situ* permit quantitative measurement of the primary signal in magnetized rocks. New insights into the long-term changes in magnetization at elevated temperatures and pressures, as occur upon burial in the Earth, will be obtained using high-sensitivity fluxgate, SQUID, Hall probe and piezomagnetic sensors.

It is now possible to study single grains in rocks *in situ* during laboratory-induced complex thermal histories, permitting primary magnetization to be obtained more readily for rocks upon exposure to different demagnetization treatments.

Using newly available synthetic single and polycrystalline samples, it will be possible to conduct direct observation of domain wall-stress interactions which are the basic reasons for complex magnetization histories.

Continued magnetic studies of deep crustal terranes by continental and ocean floor drilling allows the effects of remagnetization to be examined after long-term exposures to high temperatures and pressures.

New theories and computation efforts will permit incorporation of magnetostrictive and other terms in more realistic numerical micromagnetic calculations using supercomputers. Also it is likely that new analytical models for time- and temperature-dependent changes in small multi-domain grains can be developed to explain experimental observations and predict changes in rock magnetization on geologic time scales.

2. RELATION OF MINERAL PHYSICS TO MATERIALS SCIENCE

P. F. MCMILLAN[1]

Although many of the problems studied within Mineral Physics are driven by a need to provide data for and insight into major geological problems (such as the internal structure of the Earth, crustal rheology etc.), a large fraction of mineral physics studies derives from a desire to understand the basic chemistry and physics of the material itself. Many earth materials are related to important commercial structural, electronic and optical materials (such as cordierite, diamond, perovskites, silicate glasses, mullite, quartz), and many of the properties and processes studied in mineral physics (creep, fracture, fluid-solid interactions, propagation of light through materials, electron-phonon interactions, thermophysical properties of composite materials) are obvious links between the earth and materials sciences. These links should be strengthened, encouraged and exploited. Further, geoscientists have expertise in and access to a variety of unique synthesis and experimental probe techniques (such as crystal growth from gels, synthesis under controlled fluid conditions, ultra-high pressure synthesis, the use of pressure as a variable in *in situ* physical measurements) which could be valuable in new materials synthesis and characterization. Further, mineral physicists and geochemists routinely deal with materials which are compositionally and structurally complex (for example, the mineral physics involvement in the recent characterization of high T_c superconductors). These techniques and expertise can and should be publicized within the materials science community, so that mineral physics may play a more active role in the search for the next generation of materials, and the improved synthesis and characterization of existing materials.

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3. V_p AND V_s OF MINERALS

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A. Justification and Significance: Challenge From New Seismic Data

One of the most fundamental requirements in our efforts to describe and understand how the Earth works is an accurate model of the state and dynamics of the interior. Such a representation provides the basis for understanding the kinetics and evolution of the lithosphere and development of the planet as a whole. It is clear that the most definitive tool at our disposal for providing the basic observational framework from which dynamic models may be inferred is seismology. In particular, the analysis of extended sets of travel-time and normal mode data have provided radially symmetric structure models in seismic velocities (V_p,V_s) and density ρ with accuracies of better than 1/2 percent. Such efforts have been used to establish the basic constraints for the development and comparison of a variety of models that describe the chemistry, petrology, and temperature with depth through the lithosphere, mantle, and core.

Within the last decade, seismic data sets have improved in quantity and resolution to the point that lateral variations in velocities have become increasingly apparent and significant features in Earth structure models. Such anomalies are likely to provide the most definitive and key elements to unraveling the primary dynamic systems in the deep interior and how they interact with the lithosphere. Indeed, the potential scientific rewards associated with high resolution seismic tomography have spawned several major consortia (eg. COCORP, IRIS, PASSCAL) whose primary roles are to expand the facilities for acquiring and processing new refined data. As these programs develop and intensify their activities, we can anticipate a flow of three-dimensional velocity models of the lithosphere, mantle and core with increasing levels of precision and accuracy.

The desire and need to interpret seismic velocity structure models, and in particular, anomalous lateral variations from developing seismic tomography studies, poses a primary and special challenge to mineral physics. It seems clear that seismic lateral heterogeneity must result from local anomalies in composition and/or thermal structure that are most likely associated with dynamic processes. The quantitative evaluation of such features, as well as the standard model to which they are referred, requires the input of precise and accurate elastic property data for a wide range of minerals and rocks relevant to the composition of the Earth's interior. Moreover, one must be able to reliably evaluate V_p and V_s of these materials at the pressure and temperature conditions that prevail at the depth of interest. While much progress has been made over the past twenty years in the acquisition of the necessary measurements on pertinent silicates and oxides, the anticipated new resolution of the seismic information will require comparable improvements in the materials data base.

B. Data Base and Experimental Methods:

There is presently available a rich data base on sound velocities and elastic properties of solids. For many years pressure and temperature derivatives of velocities have been known for numerous halide and simple oxide compounds, as well as for several upper mantle minerals such as olivines, pyroxenes and garnets [data summarized in Sumino and Anderson, 1983]. These measurements have served as a baseline in establishing the range of magnitudes of many physical and thermodynamic properties, empirical trends between velocities and changes in P, T and composition, and as guide in attempts to theoretically model the interatomic forces within solids. Taken together with measurements on chemical analogs of silicates, these data have helped to answer many first order questions related to the state of the Earth's interior.

Recently, there have been some rather impressive accomplishments in the field of velocities and elasticity of minerals. Measurements of elastic properties, and hence V_p and V_s, are now being made using resonance techniques at temperatures up to 1825 K, which is comparable to the temperatures in the mantle [e.g., Goto and Anderson, 1988]. Elasticity measurements under ambient conditions have been performed using Brillouin spectroscopy on microcrystals ($< 100 \mu m$) of high-pressure silicate polymorphs, such as the ilmenite and perovskite phases of $MgSiO_3$, stishovite, and the spinel polymorphs of Mg_2SiO_4 [Weidner and Ito, 1985; Weidner *et al.*, 1982; 1984; 1987; Sawamoto *et al.*, 1984; Yeganeh-Haeri *et al.*, 1987]. The velocity data base now represents a much broader compositional range for minerals that form complex solid solutions, such as pyroxenes and garnets [Isaak and Anderson, 1987; Kandelin and Weidner, 1988a,b; Bass *et al.*, 1987; O'Neill *et al.*, 1988; Hong and Vaughan, 1987; Weidner *et al.*, 1987]. Ultrasonic interferometry measurements of the elastic moduli of single crystals (5-10 mm) have been extended to 3 GPa [Jackson and Niesler, 1982] and have yielded direct determinations of (d^2V/dP^2) for several mantle minerals [Webb, 1985],

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using polycrystalline specimens. These techniques have provided the first reliable pressure derivatives of high-pressure phases [Rigden *et al.*, 1988].

Nevertheless, application of these data to problems such as the compositional and thermal state of the mantle have underscored their limitations. Substantially different mineral assemblages may have only a modest contrast in elastic properties, thus making the distinction between a chemically stratified mantle and a chemically homogenous mantle critically dependent upon having accurate temperature and pressure derivatives of mineral velocities [e.g., Anderson and Bass, 1986; Weidner and Ito, 1987]. Attempts to explain lateral velocity variations in the lower mantle on the basis of thermal structure are inconsistent with our present knowledge of the higher order mixed temperature and pressure derivatives.

C. Future Targets and Specific Recommendations

For convenience, material property requirements can be divided into several general areas. Note that representation in terms of seismic wave velocities, V_p and V_s, can be achieved by direct measurments on polycrystalline (synthetic or natural) specimens, or by 'averaging' single-crystal elastic moduli (C_{ij}). The latter has the advantages of providing greater insight into structure-property relationships, allowing calculation of the isotropic properties of a diverse range of rocktypes by averaging theory, and providing a means of evaluating anisotropic rock properties (again, by appropriate methods). The following is a list of specific recommendations; their order does not reflect priority.

1) Refinements to the Present Data Set

The elastic property data for major upper mantle minerals need to be refined and augmented. In particular, discrepancies need to be resolved and relevant solid solutions fully characterized for olivine, orthopyroxene, and garnet. This applies to the full sets of elastic moduli (C_{ij}), as well as their pressure and temperature derivatives.

In addition, the elastic property data sets on almost all of the important high-pressure phases relevant to the transition region of the lower mantle are insufficient, especially with respect to Fe content. These minerals include, in particular, the beta and spinel forms of $(Mg,Fe)_2SiO_4$, ilmenite $(Mg,Fe)SiO_3$, stishovite SiO_2, magnesiowustite (Mg,Fe)O, and, especially, perovskite $(Mg,Fe)SiO_3$. Although single-crystal elastic moduli (C_{ij}) for many of these materials have been measured by Brillouin scattering and ultrasonic interferometry, applications to the composition and temperature of the mantle are severely limited because of the unknown effects of pressure, temperature, and solid-solution.

2) T = 25° C, V_p and V_s at High Pressure

Ultrasonic interferometry measurements up to 3 GPa must be applied to a wider range of single crystal materials and extended to additional polycrystalline specimens of high-pressure phases. Brillouin scattering measurements in diamond-anvil cells were pioneered by Bassett and Brody [1982] but have not yet been fully employed. The technique of impulsive stimulated scattering offers promise of providing an alternative spectroscopic approach to obtain pressure derivatives of elastic wave velocities [Brown *et al.*, 1988].

3) P = 1 bar, V_p and V_s at High Temperature

At the present state of the art, measurements of elastic moduli of single crystal minerals are now possible to 1825 K (at P = 1 bar) in minerals with no iron, using resonance techniques. Measurements on iron-bearing minerals require that the minerals be contained in an oxygen free atmosphere. This is a straightforward, but difficult, measurement that uses techniques similar to those used to control oxygen fugacity in defect sensitive experiments. Measurements can be extended up to T = 2000 K, provided the creep in the holding apparatus can be overcome. This barrier can and will be overcome by using the appropriate high temperature structural materials.

4) Higher-Order Elastic Properties

The velocity and density equation of state at very high pressure and temperature, and the small variations described by high-resolution seismic tomography (e.g., $d(\ln V_s)/d(\ln V_p)$), as well as descriptions of impending phase transitions, require the input of higher-order elastic parameters (i.e., (d^2C_{ij}/dP^2, d^2C_{ij}/dT^2, and $d^2C_{ij}/dTdP$). Possible sources of these cross-derivative data include ultrasonic experiments or velocity measurements in shock-wave experiments. One difficulty is that the temperature limit in most measurements of C_{ij} is less than the Debye temperature. And it has been shown that the temperature behavior of elastic constants is quite different above and below the Debye temperature.

5) Theories of Rock Modelling

Many, if not most, applications of elastic properties to the composition and state of the lithosphere and mantle require the evaluation of rock velocities calculated from single-crystal C_{ij} data. Averaging approaches, such as the Voight-Reuss-Hill (VRH) average and Hashin-Shtrikman bounds, have been very useful in this regard. However, VRH bounds are quite wide for low symmetry crystals, and it is not clear how pressure and temperature should be handled. It is also very important to develop realistic theories to calculate the isotropic elasticity of polycrystalline aggregates of two or more mineral phases which are intrinsically anisotropic. Moreover, tests of the various theoretical approaches against actual experimental data are very limited. General research in this important area of applied mineral physics needs to be continued.

6) Specimen Requirements

Specimen size is an important limitation in many of the above experiments. A major mission in mineral physics must be to extend our materials synthesis capability to produce larger samples, and develop the ability to accurately measure velocities under a broader range of P-T conditions with smaller samples.

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4. COMPRESSIONAL WAVE VELOCITIES IN MELTS

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Measurements of sound velocity in silicate melts have provided the only constraints on the compressibility of possible magmatic liquids at ambient pressure. These melts are the primary sources of new oceanic crust and of volcanic edifices in islands arcs, hot spots, and continental environments. Information on compressibilities of these liquids at pressure is critical in constraining the volumes of these melts at depth, and thus in determining the forces driving the buoyant rise and segregation of melts in the crust and upper mantle, as well as evaluating the pressure and compositional range in which mantle melts might sink. As pressure-induced coordination changes are likely to occur in silicate melts, major changes in the compressibilities of silicate liquids are expected to occur at mantle pressures [Rigden *et al.*, 1984; 1988; Williams and Jeanloz, 1988]. A systematic approach to determining compressibilities within silicate melts will yield greater insight both into the microscopic mechanisms by which such liquids respond to pressure, and into the changes in seismic velocity expected in partially molten regions within the Earth.

To date, sound velocity experiments on silicate liquids have been limited to 1 bar pressure but have explored a wide range of natural and synthetic compositions [Murase and McBirney, 1973; Bucaro and Dardy, 1974; Katahara *et al.*, 1981; Manghnani *et al.*, 1986; Rivers and Carmichael, 1987; Kress *et al.*, 1988]. Indeed, the only information presently available on the elastic properties of silicate liquids at high pressure is derived from shock-wave experiments [Rigden *et al.*, 1984; 1988], and from olivine flotation experiments [Agee and Walker, 1988]. The high precision of sound velocity measurements has not yet been exploited in experiments on silicate liquids at high pressure. In particular, both the pressure derivatives of the elastic constants of most silicate liquids, and the effect of volatiles on their elastic properties, are unknown.

Several techniques have been applied successfully to measure sound velocities in non-silicate liquids at high temperatures under pressure. Gas medium pressure vessels have been used to determine sound velocities in mercury to pressures of 0.2 GPa and temperatures of 1873 K [Suzuki *et al.*, 1980; Inutake *et al.*, 1979]. A piston cylinder apparatus capable of measuring sound velocities at pressures to 4 GPa and temperatures of 1073 K (high enough to access the liquidi of volatile-enriched melts) has been developed by Kimura *et al.* [1987]. Each of these techniques samples a pressure-temperature range of significant interest for crustal and upper mantle volcanism, and a pressure range sufficient for significant volatile dissolution in silicate liquids. Thus, the potential for measuring sound wave velocities in geologically-relevant silicate melts under pressure currently exists using available technology.

The large volume presses developed in Japan in the last two decades have not yet been used in any ultrasonic experiments on melts. We note, however, that Fujisawa [1987] has determined elastic wave velocities in olivine compositions to 14 GPa. Thus, the potential for using these instruments for measurements on silicate melts is great: primary problems foreseen are related to possible transformation of the transducer(s) material at high pressures and temperatures, or to reaction of the transducer with the silicate melt.

In a significantly higher pressure range, measurements of bulk sound velocity under shock-loading, using either crystalline or liquid starting materials, would be useful. Typically, it appears that mantle-type magnesium silicates, shocked at 300 K, melt under Hugoniot conditions at pressures greater than those at the base of the mantle [150 GPa: Brown *et al.*, 1987], while more siliceous compositions melt between 70 and 130 GPa [Lyzenga *et al.*, 1983; Boslough *et al.*, 1986]. Accurate determination of temperatures in conjunction with sound velocity measurements on the Hugoniot would yield valuable information on elastic properties of melts in an ultra-high pressure, high-temperature regime.

With the advent of external heating, experiments capable of attaining 1300 K and 7 GPa within the diamond anvil cell [Schiferl *et al.*, 1987], and laser-heating techniques accessing 5500 K at 110 GPa [Williams *et al.*, 1987], there exists the possibility of conducting spectroscopic measurements of sound velocities in silicate melts. Two techniques exist for such an experiment: first, Brillouin scattering, which has already proved its utility at temperatures to 1600° C at 1 bar [Bucaro and Dardy, 1974]; and second, impulsive stimulated scattering [Nelson *et al.*, 1982] which has been utilized to 6.8 GPa at ambient temperature within the diamond cell [Brown *et al.*, 1988]. Either of these techniques is, in theory, capable of measurement of phonon velocities in microscopic samples under the extreme conditions of the Earth's mantle, and either (or both) may represent the ultimate future in measurements of elastic, and possibly anelastic, properties of silicate liquids.

Although the emphasis thus far has been on the determination of sound velocities in the high frequency ultrasonic and optical regimes (1 MHz and above), we

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note that sound velocity measurements over longer timescales and varying temperatures may provide insight into structural relaxations within silicate melts and partially molten materials. Structural relaxation processes appear to be correlated with the shear viscosity of the liquid, and are therefore relevant to the high pressure flow properties of melts in the Earth. The measurement of sound velocity over a wide frequency range is not only valuable for determining these viscoelastic effects, but also in potentially resolving the actual sound velocity in liquids at the low frequencies characteristic of seismic phenomena. Although technically difficult, such low frequency measurements could possibly be conducted using resonance column methods. In short, sound velocity measurements in liquids have the potential of determining the effect of measurement frequencies on velocity determinations from the Hz to MHz range, and addressing the detailed mechanism of attenuation across this frequency band in these liquids. In terms of the effect of temperature on sound velocities of relevant mantle silicates, measurements made across a temperature range spanning solid, partially molten and entirely molten regimes is highly relevant to the properties of partially molten zones within the Earth. Finally, measurements of both compressional and shear wave velocities of candidate mantle mineral assemblages at temperatures above their solidus will yield further insight into the seismic velocities within partially molten zones within the mantle.

The present paucity of data on elastic properties of silicate melts at pressure represents a void in the understanding of physical properties of Earth materials. Detailed petrologic modelling of the mantle depends critically not only on the amount of melting early in Earth history, but also on the degree (and direction) of melt segregation. In short, quantitative modelling of the differentiation of the terrestrial planets requires a detailed knowledge of the density of liquid silicates at depth. There is currently a wide variety of complementary techniques which may be brought to bear on this problem, each of which is able to sample different sets of pressure and temperature conditions, and any of which could contribute fundamental insights into the behavior of silicate melts at pressure.

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5. SEISMIC ATTENUATION (Q^{-1}) IN MINERALS

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Over the last 20 years, seismology has yielded plentiful and unique attenuation (Q^{-1}) data for the Earth. These new data offer the promise of understanding a number of important properties at depth. However, the paucity of reliable pertinent laboratory data have prevented the interpretation of these important observations. Attenuation measurements on mantle minerals are in their infancy. Pioneering measurements by several groups (Gueguen *et al.* in France, Berckhemer *et al.* in W. Germany and Sato *et al.* in Washington, D.C.) have yielded important preliminary results.

One of the most important aspects of the experimental studies of attenuation is to investigate a correlation between attenuation and defect microstructures. The microstructures needed to be studied include the dislocation structures (dislocation density, types of dislocations, dislocation shape), the grain boundary structures (grain size, grain-boundary shape), secondary phases, and water-related defects. Unfortunately, such studies have generally not been performed for mantle minerals or rocks. The preliminary studies which have been done are summarized below.

Gueguen and his group have made measurements of attenuation at seismic frequencies and at high temperatures. A torsion pendulum apparatus was used in the frequency range of 10 to 10^{-4} Hz from room temperature to 1400° C (at atmospheric pressure) [Woirgard and Gueguen, 1978; Gueguen *et al.*, 1981; Darot *et al.*, 1987]. The samples studied include synthetic forsterite single crystals, a natural enstatite and a natural peridotite. Berckhemer and his group have made extensive studies on the high temperature and low frequency attenuation in mantle rocks [Berckhemer *et al.*, 1979; Berckhemer *et al.*, 1982a,b; Kampfmann and Berckhemer, 1985]. Their studies have been performed on polycrystalline samples (either synthetic aggregates or natural rocks) at atmospheric pressure in air. The results are subject to reservation in respect to the possible significant effects of open cracks [see e.g. Jackson, 1986] and oxidation. Sato *et al.* [1988] measured the attenuation in a natural peridotite at high temperatures (up to 1280° C), at high pressures (0.2 to 0.73 GPa), and at high frequencies (50-800 kHz), using a pulse transmission and spectral ratio technique.

The results of the above studies are compared in Figure 1. The comparison is made at a common temperature (T=1200° C). A common feature in the seismic frequency range is the predominance of the "high temperature background", namely, the general decrease of attenuation with increase in frequency. Sato *et al.*'s results at high frequencies do not resolve any frequency dependence. Also, data on single crystals of forsterite clearly show that predeformed samples have larger attenuation than undeformed samples. Measurements on polycrystalline samples at seismic and at high frequencies (>50 kHz), which extended in temperature above the solidus showed no drastic change in Q^{-1} upon partial melting. Generally, the results of experiments on single crystals of forsterite agree reasonably well with the results on hot-pressed forsterite aggregates and natural dunite. However, when the comparison is made at higher temperatures, the single crystal results show significantly smaller attenuation than that of the polycrystals, as the measured temperature dependences are significantly different between the two studies. The reason for this discrepancy is not well understood.

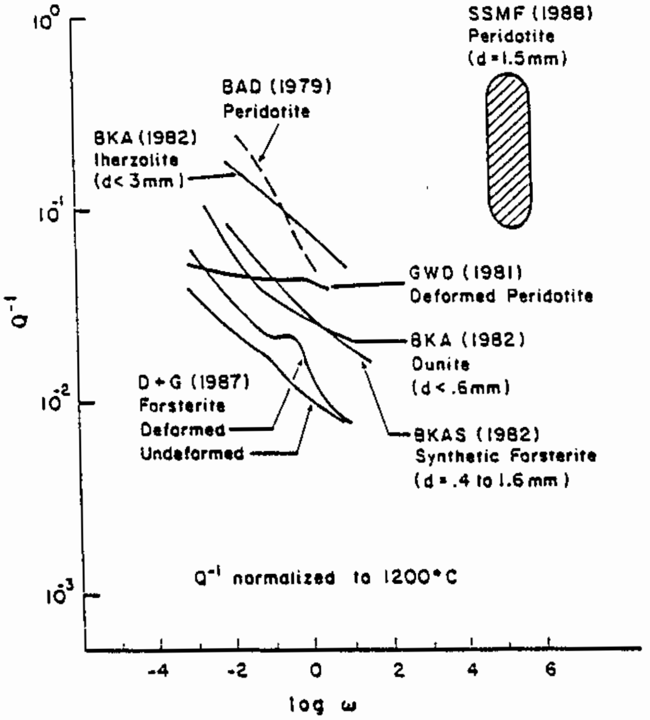

Figure 1: Comparison of the results of attenuation experiments over a range of frequencies, normalized to 1200°C.

Attenuation in the Earth occurs over a wide range of conditions (10^{-8} - 10^{+2} Hz, $T/T_m > 0.5$ in the mantle below ca. 100 km). Current experimental studies show that significant attenuation occurs at subsolidus tempera-

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tures. Also, the frequency dependence found at seismic frequencies in laboratories is such that $Q^{-1} \propto \omega^{-\alpha}$ (α = 0.1 to 0.3), where ω is the frequency, which is quite consistent with the seismological observations. However, the physical mechanisms of attenuation are not well understood and this prevents a direct application of the laboratory data to the Earth.

Karato and Spetzler [1989, in preparation] have reviewed the presently available data and the solid state models of attenuation with emphasis on those obtained at high T/T_m. They conclude that either dislocation mechanisms or grain-boundary mechanisms (or both) are likely to be the major cause of seismic wave attenuation in the Earth. It is necessary to carry out well-controlled experimental studies before reliable applications of laboratory results to Earth can be made. Such studies are now underway in Washington, D.C. [Sato *et al.*, 1988], in Canberra, Australia on polycrystalline rocks [Jackson *et al.*, 1984; Jackson and Paterson, 1987], and in Boulder, Colorado on single crystals [Getting *et al.*, 1987]. The groups in Germany and France are no longer making attenuation measurements. The first results obtained by the Carnegie group are now in press. Attenuation measurements from Canberra at simultaneously high temperature and pressure are expected in the near future. The Boulder group is building and testing their apparatus and expects to have high temperature data soon.

The new data by the Carnegie group and the forthcoming measurements by the Canberra and Boulder groups differ from those of the earlier measurements in several important ways:

1. The Carnegie and Canberra measurements will be made on polycrystalline solids under pressure, thus avoiding the vexing problems of open cracks.
2. All new measurements will be made at strain amplitudes below 10^{-6} where attenuation is independent of amplitude.
3. All new measurements will be made in chemically-buffered environments to maintain the samples within their stability fields.
4. All samples will be well characterized in terms of composition, grain size and shape, and defect structure.
5. In the single crystal measurements, shear deformation will be confined to preselected crystal planes.
6. The dislocation density and distribution will be carefully controlled in single crystal samples through annealing and the application of deviatoric stresses.

Only by carefully observing the above points will it be possible to obtain meaningful laboratory data to interpret the wealth of attenuation data which seismologists are extracting from the Earth. Extension of the present experimental efforts to conditions in the deep interior (pressures > 200 GPa and T > 2000° C) and the procurement of large single crystals of mantle minerals are top priorities for the near future. This attenuation data in the Earth will yield critical information on the defect structure and, thus, the rheology of Earth's deep interior.

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6. CRUSTAL MINERAL AND FLUID PHYSICS AND CHEMISTRY

L. THOMSEN[1], A. E. WORTHINGTON[2], AND A. NUR[3]

The principal obstacles to understanding the nature and behavior of the crust are due to the complexity of (1) solid-fluid interactions, (2) effects of significantly non-hydrostatic stress, and (3) mineralogical complexity. In this setting, the properties of aggregates of minerals (i.e., rocks) are as important as the properties of the individual minerals themselves. Hence, there is a broad area of overlap between the mineral physics community and the rock mechanics community.

Crustal studies of rocks and minerals are strongly conditioned by the possibility of economic exploitation by the mining and petroleum industries. Also, because of proximity to the surface, crustal materials are more extensively sampled, and thus easily studied in the laboratory via a wide range of techniques. Borehole probes permit the measurement of many properties *in situ*. Elastic and electromagnetic waves of short wavelength can be employed, enabling study at higher spatial resolution.

Rocks are aggregates of solid mineral grains, cements and pore fluids. In all crustal rocks, the volume fraction and microscopic geometry of the pore space, and the nature of the pore fluid, have profound effects on the physical properties of the rock. For many purposes, the pore fluid may be considered simply as another mineral constituent, whose contribution to the aggregate properties can be crucial, because its properties are so different [Han *et al.*, 1986]. For other purposes, the mobility of the pore fluid is important, causing phenomena completely unlike those found in purely solid materials [Banner *et al.*, 1988].

The state of stress in crustal rocks appears to be more complicated than in the mantle and the response of the rock is more complex. Non-hydrostatic stresses in the kilobar range are maintained over geologic time scales, whereas, below the lithosphere, the high temperatures cause mantle rocks to yield at ~10 MPa or less. Further, in the shallow crust, the rocks respond to the non-hydrostatic stress by fracturing and jointing on all spatial scales. Thus, there is a stress-related anisotropy in most crustal rocks, mediated by indigenous preferred orientations of the pore space and/or the grain shapes and contacts, which causes marked effects on seismic data [Thomsen, 1988] and on all transport phenomena.

The stress in the crust may be heterogeneous on the microscopic scale (e.g., the difference between fluid pressure in the pores and average pressure in the grains). Heterogeneity may also reach kilobar magnitudes, and will have a profound effect on rock properties. In general, the mechanical properties of rocks in a fluid-rich environment depend on "effective stresses", which are defined as linear combinations of grain and pore pressure [Zimmerman *et al.*, 1986], rather than on the grain or pore pressure separately.

Pore pressure in the sedimentary crust is generally "hydrostatic" (equal to the stress from an overlying column of pore fluid) at shallow depth, and has a transition to "lithostatic" (equal to the stress from an overlying column of rock) at 2000 to 5000 meters. This transition corresponds to some form of a pressure seal bounding regions with different pore pressures. The lithostatically pressured zones are often bounded laterally and on the bottom, as well as above (Figure 1). Often, in a sedimentary basin, there are a series of these enclosed fluid "compartments", surrounded by thin seals. Within the compartment, the local pressure gradient is hydrostatic (with an elevated head), [Powley, 1988]. The nature, and evolution, of the seals is not well understood, although they appear to be controlled more by stress and diagenesis than by lithology. The generation and time-history of the high fluid pressure within the compartments, and the migration of brines and hydrocarbons is an area of active investigation.

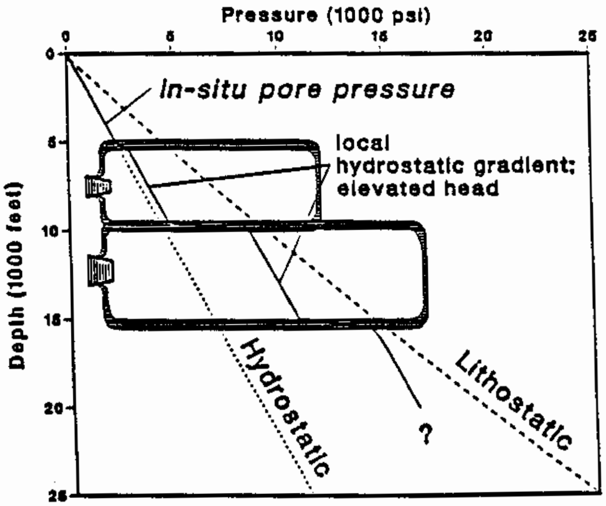

Figure 1: Schematic diagram of subsurface fluid compartments showing the lithostatic and hydrostatic pressure as a function of depth and a possible pore pressure distribution for a basin containing two compartments.

Pore fluid-rock interactions mediate many phenomena of societal and economic interest. Injection of fluid into

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the crust has been demonstrated to trigger earthquakes on shallow faults in rock that is close to incipient failure [Healy *et al.*, 1968]. The observations of fluid induced seismicity such as beneath Koyna Dam [Langston, 1976] suggest an important role for pore fluids in controlling the onset of faulting. Injection of fluids may result in rock fracture and unwanted connections between reservoir zones, a serious problem for both waste disposal and for methods of enhancing recovery of hydrocarbons. Production of oil and gas is strongly affected by fluid-mineral surface chemistry and physics in reservoir rocks. Opportunities to improve understanding and management of these phenomena exist at all levels - fundamental studies of mineral-fluid interactions, interpretation of observations made by indirect methods, rock mechanics of fluid-containing rocks, and computer modelling and interpretation of these phenomena at all scales.

The porosity, fracture intensity, permeability, and pore pressure in the crust vary in complex ways with time and position, due to numerous processes which involve both mechanical stresses, and the transfer of molecular species through the pore fluids. These processes include pressure solution, compaction, crack healing, natural hydraulic fracturing, development of high pore pressure, pulses of fluid migration, seismic pumping, dilatant deformation, etc. Although many of these processes have been identified as occurring *in situ*, little is understood in detail at present. For example, the interplay between mechanical and chemical processes in the diagenesis of sediments and the formation of hydrothermal ore deposits and veins remain poorly understood. Initial modelling of these processes with non-equilibrium chemical transport codes are starting to be conducted, although many of the rate constants and pressure effects are poorly known.

All of these phenomena strongly affect the physics of crustal rocks, whether measured directly on samples cored from boreholes, or remotely from the surface. Integration of information from these different scales is nontrivial, and mineral physics concepts frequently play an important role. Boreholes provide direct access to the complex physics and chemistry of the pore fluid rock system to depths in excess of 8 km. A variety of logging tools can be lowered into boreholes using cables containing either electrical or fiber optic data links. Alternatively, they are incorporated in the actual drilling assembly from which data may be transmitted while drilling, by creating pressure pulses in the circulating drilling fluid. With these tools, one may measure or infer porosity, permeability, density, stress, electrical conductivity, dielectric constant, sonic velocities, and mineralogic and elemental concentrations [eg. Campbell and Tittman, 1989; Jorden and Campbell, 1984; 1986; Schlumberger, 1987].

At the present time, most logging methods are based on electrical conductivity or on nuclear physics. The electrical conductivity of most sedimentary rocks is controlled by the salinity of the brine filling the pores and fractures and by details of the rock fabric. The conductivity of most minerals is negligible. However, many economic minerals exhibit much higher conductivity than their host rocks. Reduced conductivity which cannot be explained by changes in rock fabric or brine salinity are indicative of the presence of hydrocarbons. The conductivity of soft clay-rich sediments and of poorly consolidated clastics containing high salinity brine can exceed 1 S/m, while that of hydrocarbon saturated sandstones and low porosity carbonate rocks can be less than 10^{-3} S/m. Rocks of contrasting conductivity are often juxtaposed in the crust, so that electrical methods yield very detailed information which may be interpreted in terms of the geology, mineralogy, and fluid content of the section. Electrical conduction phenomena in the Earth need to be understood in sufficient detail so as to make useful interpretation of wellbore and surface observations. This entails a series as yet unsolved theoretical problems and applied mathematical problems which tax the ability of data analysts.

Passive radioactivity logging methods record the natural radioactivity in the sediments, which can be attributed to the decay of ^{40}K and other short-lived members of the uranium and thorium families of radioactive elements. Spectroscopy tools which can accurately distinguish between these three groups provide more diagnostic information than is obtained by the more usual measurement of total radioactivity. Neutron, energetic electron and other excitation sources lowered into bore holes are used to induce radiogenic activity in the surrounding rocks, and provide a quantitative basis for analyzing virtually the entire table of elements and their isotopes. Both fixed and pulsed sources are used. Neutron sources typically consist of steady state americium mixed with beryllium and produce a neutron energy distribution centered at about 5 MeV. The gamma ray energy spectrum resulting from neutron activation seen at the detector is highly degraded by passage through the rock and the borehole, but can provide atomic and, in some cases, isotopic compositions.

The scattering and attenuation of gamma rays by crustal rocks is almost a linear function of bulk density in the absence of heavy minerals. Logging tools with collimated gamma ray sources and detectors are widely used to obtain accurate estimates of bulk density. Consequently, mineral composition may be deduced. Porosity can also be obtained when the mineral and fluid densities are known.

The interpretation of all nuclear tools is confounded by effects arising from the presence of the borehole and the logging device itself. Understanding these effects with the necessary accuracy requires significant advances in quantifying the various nuclear physics effects and describing these via computer codes.

Seismic measurements in and between boreholes, in the sonic frequency band (5 to 30 kHz), are used to obtain ground truth to assist in the interpretation of surface seismic data and to obtain information on the porosity, mineralogy, fabric, permeability, and fluid content of the heterogeneous rock-mass. Both velocities and attenuation of compressional and shear waves in rocks and the measurement of the normal modes of oscillation of the borehole rock system are measured [e.g. Newmark *et al.*, 1984]. Interpretation of such borehole seismic measurements in terms of lithology, porosity and permeability is currently at the cutting edge of technology.

The concentration of ions in the borehole fluid is often significantly different from that of the formation fluids which are intersected by the borehole. This gives rise to a diffusion gradient which results in an ionic current in the bore fluid between different chemistry rocks intersected by the bore hole. These currents are detectable as potential gradients in the borehole which are recorded as the "spontaneous potential". The potential difference observed in the borehole at the boundary between two formations of differing rock type can be interpreted in terms of the difference in salinity between the fluid in the borehole and water in the pore space, and of the difference in cation transference number between the two formations. Oxidation-reduction reactions at the borehole wall may occur naturally or may he enhanced or induced by oxidizing agents in the wellbore fluid, resulting in measurable potential differences in the borehole [Veneziani *et al*, 1972]. The presence of carbon-rich materials and sulfide minerals give particularly strong responses.

The nuclear spin of protons in water and liquid hydrocarbons may be partially aligned by the application of a strong magnetic field to the rocks. If that field is removed suddenly, the vector of the resulting polarization precesses at about 2 kHz in the magnetic field of the earth and is detected by sensitive receivers. The magnitude of the polarization and the manner of its decay can be interpreted in terms of the morphology of the fluid phase, yielding information on permeability and on the maximum hydrocarbon concentration that could be contained in the rock [Freedman and Rouault, 1987]. The relaxation of the proton spin which occurs during collisions with most rock mineral surfaces is apparently attributable to surficial paramagnetic sites. The detailed nature of these sites is poorly understood and presents an opportunity for further elucidation of the pore fluid-mineral interaction over geologic time.

Sensitive gravity meters and gradiometers are used to determine minute density differences in the layers of rock between adjacent stations in the borehole. The objective is to detect lateral inhomogeneity in the surrounding rocks, to detect gas or other hydrocarbons, or abrupt changes in mineral composition laterally adjacent to but not actually penetrated by the borehole [Hinze, 1985].

Temperatures and pressures can be accurately observed in the borehole, and the pressure of the fluids in permeable rocks can be obtained from drillstem tests or by the use of a wire line "formation tester". Accurate measurement of temperatures in the undisturbed formation is complicated by the perturbation introduced by the circulation of the borehole fluid.

A hybrid science, often called petrophysics, deals with the relationships between the observations that can be made in the borehole, the direct measurements made on recovered cores, and the desired information concerning the state of the undisturbed rocks and their contained fluids [Worthington, 1985]. The coring process results in alteration of many core properties, particularly in hydrocarbon reservoirs. For instance, the relative tendency of the undisturbed reservoir to be wetted by the water phase or the hydrocarbon phase, or even by both, affects the response of many logging tools and may profoundly affect the efficient production of hydrocarbons from the reservoir. Wettability can be altered by contact with the drilling fluid and atmospheric oxygen. Porosity, permeability and electrical properties are altered by the removal of the overburden stress and release of the pore fluid pressure. Prediction of hydrocarbon recovery requires knowledge of multiphase properties, fluid flow, and mass transfer under a wide range of conditions. Petrophysics attempts to develop practical methods of determining subsurface properties and predicting fluid flow behavior by building on a combination of both fundamental science and empirical observation.

Core and borehole measurements are frequently used to calibrate surface measurements of much wider areal extent; rock and mineral physics play a role in this calibration. Over 90% of crustal investigations from the surface are seismic reflection surveys, usually in the frequency band 10 to 100 Hz. The comparison of seismic velocities with sonic velocities from borehole measurements, and with ultrasonic measurements on cored samples, involves consideration of both intrinsic and extrinsic frequency dispersion. The intrinsic dispersion is related to attenuation mechanisms, which are primarily related to fluid flow [Jones, 1986].

Electrical methods of sounding the crust from the surface depend for their interpretation on contrasts in electrical conductivity which occur in crustal rocks. Some economic minerals are highly conductive, and some become polarized by electrical currents. Polarization of such ore bodies may be induced by introducing currents at the surface and observing the decay of the polarization when the current is interrupted. Magnetotelluric methods take advantage of low-frequency currents induced in the surface of the earth by coupling with ionic currents in the upper atmosphere. The earth currents and their associated magnetic fields can be measured and mapped. Unlike acoustic methods, none of these methods is inherently capable of yielding a detailed map of the subsurface because of the long wavelengths that must be employed to gain depth penetration.

Beyond these specific issues, there are at least four general areas of major intellectual challenge for the future:

1. **The physical properties of heterogeneous systems in the crust and lithosphere.**

   We need an understanding of the physical bulk properties of heterogeneous systems in the crust and lithosphere, in terms of their composition, microstructure, and history, and the imposed stress, pore pressure, and temperature. For example, what are the appropriate average velocity and attenuation of a rock, and how does this depend upon the frequency (seismic to ultrasonic) of its measurement?

2. **Scale and resolution.**

   We need an understanding of the problems of scale and feature-resolution in rock systems with a broad distribution of heterogeneity scales. For example, where microcracks, fractures, and joints occur, the system permeability obviously depends upon the scale of measurement. How may this be quantified?

3. **Pervasive disequilibrium.**

   We must be able to model systems in the absence of full mechanical/chemical equilibrium, because of heterogeneity, stress, and fluids. Understanding how to characterize the deviations from equilibrium, and to determine when and how quasi-static models may be used is a major challenge. Theoretical and experimental research is needed into the kinetics of stressed systems, fully or partly saturated with chemically reactive fluids, and utilizing the talents of rock mechanicists, petrophysicists, and geochemists.

4. **New instrumentation.**

   We must adapt and develop new instrumentation to obtain new and better data vital for the resolution of these problems. For example:

   a. Pulsed electrical methods to obtain broadband electrical data in boreholes (and surface?)
   b. Spin echo NMR in boreholes.
   c. Broadband field seismic imaging for high resolution, mapping, and attenuation: tools and processing.
   d. System for fast determination of mineral and aggregate solubility in pore fluids as functions of stress, pressure and temperature.

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