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Physical Properties and Mantle Dynamics

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Because planetary interiors are remote, laboratory methods and associated theory are an essential step for interpreting geophysical measurements in terms of quantities that are needed for understanding Earth—temperature, composition, stress state, history, and hazards. One *objective* is the study of minerals and rocks as materials using experimental methods; another is to develop new methods, as in high pressure research, codes for computation in rock/soil physics, or nuclear-

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based analysis. *Accomplishments* include developing a single-crystal x-ray diffraction apparatus with application to materials at extremely high pressure and temperature; P-V-T equations of state and seismic velocity measurements for understanding the composition of Earth's outer 1000 km; creating computational tools to explain complex stress-strain histories of rocks; and measuring tungsten/thorium ratios W/Th that agree with the hypothesis that Earth accreted heterogeneously. Work performed in this project applies to geosciences, geothermal energy, mineral and rock properties, seismic detection, and isotope dating.

Background and Research Objectives

The methods of mineral physics use laboratory methods and associated theory to reveal properties and processes in the Earth and events in its history. One approach is study of minerals and rocks as materials by using methods from materials sciences; another is development of new methods as in high-pressure research, nuclear-based analysis, or computations of rock and soil properties. Because planetary interiors are remote in distance, pressure, and temperature, work in this field is an essential step for interpreting field measurements from seismology, geodesy, gravity, electromagnetism, heat flow, remote sensing, and geological structure in terms of quantities that we need for understanding our planet and other bodies in the solar system—temperature, compositional variations, phase changes, viscosity, stress state, convective flow, planetary history, and planetary magnetic fields. Similarly, isotopic studies shed new light on evolutionary development on the Earth's surface and suggest patterns of crust-mantle links in the convective processes that produce plate tectonics. Additionally, the focus includes the capability for experiment and modeling effects such as fluid movement, isotope migration, and geochemical reactions that concern waste isolation and hydrocarbon reservoirs.

Work under this focus falls into three major groups. In the first we undertake laboratory studies of physical properties. The studies include such related topics as equations of state, mineral textures of deformed rocks, electrical conductivity, and Mössbauer effect. When used in connection with corresponding physical properties determined from geophysical and geological observations, we can illuminate the dynamical picture of convective motions that geophysical patterns represent. Each kind of measurement sheds light on aspects of the heterogeneities that drive plate tectonics and disturbances of the Earth's surface. For instance, densities and seismic velocities reveal compositions while electrical conductivity reflects temperature and fluid content of rocks. The second group involves nuclear- and isotope-based studies that address Earth's

geological history. There is particular emphasis on isotope production rates; they can be applied to determining rates of near-surface processes such as erosion, source regions of lavas from the mantle together with possible mineral structures for retaining heat-producing isotopes, and isotopic investigations of past extinction periods in relation to the meteorite impact hypothesis. In recent years collaborations have developed with the Los Alamos Neutron Science Center (LANSCE). Work with the Los Alamos Center for Materials Sciences (CMS) has evolved from a common interest in textures of polycrystalline technological and geological materials. A third, new group is theory, modeling, and experiment on near-surface materials involved in fluid or waste transport and storage reservoirs.

Importance to LANL's Science and Technology Base and National R&D Needs

Laboratory studies of the physical properties of minerals under the (often extreme) conditions of the Earth's interior form the bridge between what we know and what we wish to know about the Earth. For example, seismologists can produce profiles of elastic wave velocities in the Earth, but if we wish to interpret them in terms of composition or temperature, we must have laboratory data on velocities as functions of pressure, temperature, and composition. Similarly, to infer stress history during geological time from textures of deformed rocks, we must study such textures in deformed laboratory specimens. Dating of geological events near proposed waste repositories frequently requires calibration of isotope production rates induced by neutron sources in the laboratory. Thus, in a great variety of ways, studies of earth materials provide the measure of physical processes responsible for crustal movements, seismic and volcanic hazards, and fluid migration; they impact the basic discoveries about our planet. Just as important, this field is at the center of significant defense problems, for instance, maintaining the capability to characterize materials at high pressures and temperatures and to understand isotopic signatures of clandestine activities. For instance, research on creep and deformation of rocks, on equations of state, and on possible compositional layering in the mantle are necessary background for convective modeling of planetary interiors and for understanding the medium through which pass seismic waves used for treaty verification. Isotopic studies reveal aspects of geological and atmospheric evolution, a background to environmental research; they are necessary for understanding global climate change in the Earth's past and processes relating to retention of wastes in soils and rocks.

Our work contributes to the Laboratory's core technical competency in Nuclear and Advanced Materials because geophysicists investigate properties associated with the perovskite crystal structure. The complexities of this mineral are now being investigated in relation to high-temperature superconductors. In addition, as the phase into which all silicate minerals transform at high pressure, perovskite is the most abundant mineral in the Earth. Our work also contributes to the Laboratory's core technical competency in Theory, Modeling and High Performance Computing in that data on creep in minerals, equations of state, isotope production, and other physical properties are required as input to global convection and climate codes.

Scientific Approach and Accomplishments

This research has treated the problems of properties and processes in the Earth using a variety of isotopic studies and physical measurements of rocks and minerals as given below. Important issues for nuclear nonproliferation, such as discriminating between natural and artificial seismic sources and locating those sources more accurately, requires understanding the nature of deep mantle paths for seismic wave propagation. Seismic velocities and densities provide the best means for probing the deep Earth, and knowing mantle composition is essential to resolve such questions as whether there is layered or whole mantle convection (through the seismic velocity and density discontinuity at 670 km depth whose nature has constituted a major geophysical issue for about two decades). A phase change at this depth represents a relatively small inhibition to convection through the discontinuity. On the other hand, if there is a density discontinuity arising from a compositional discontinuity, then thermally driven convection would require a large thermal boundary layer before there could be exchange of material between upper and lower mantle. Reliable data on candidate mantle minerals of known composition at both high temperatures and high pressures are necessary to successfully address questions of (a) the degree of radial stratification within the mantle, (b) alternative interpretations of lateral seismic heterogeneity in terms of thermal or compositional differences, and (c) dynamical behavior linked to thermophysical properties of minerals.

To resolve these issues, it is necessary to accurately measure the sound speeds and densities of candidate mantle minerals of known composition at both high temperatures and high pressures. We have constructed the first apparatus for high-temperature/high-pressure (up to 1000 K at 20 GPa) *single-crystal* x-ray diffraction in a unique diamond-

anvil cell (DAC) to yield both lattice constants and atom positions. The lattice constants provide accurate isothermal bulk moduli and thermal expansion coefficients along with their pressure and temperature derivatives for reliable extrapolation to temperatures and pressures beyond our present experimental capability. In addition, the bond distances determined should prove useful in developing models for the nonlinear pressure dependence of elastic constants.

A byproduct is a new peak searching and centering algorithm (RSCU-SOS) developed to minimize data collection time. The algorithm is crucial for our high-pressure/high-temperature studies because high pressures and temperatures cannot be maintained indefinitely. The algorithm was designed from the outset to be compatible with modern x-ray area detectors; possible applications are under discussion with Siemens, USA. Previous records for single-crystal diffraction at high T-P have been broken in a study of thermoelastic parameters (bulk modulus, thermal expansion, etc.) of orthoenstatite MgSiO_3 up to 1000 K at 1.5 GPa, with pressures up to 4.5 GPa at lower temperatures. In fact, these measurements have defined a new state-of-the-art for high-T/high-P single-crystal diffraction.

Jadeite $\text{NaAlSi}_2\text{O}_6$ is a major sodium- and aluminum-bearing mineral in the clinopyroxene structure. Its thermodynamic properties are important for understanding phase relations of upper mantle compositions and modeling of seismic profiles and the discontinuity at the top of the transition zone that is related to the pyroxene-to-garnet transition. High P-T *in-situ* x-ray diffraction experiments in the energy dispersive mode together with Rietveld refinement provide simultaneous peak positions and lattice parameters and were used to obtain unit cell parameters for jadeite at pressures to 8.2 GPa and temperatures to 1280 K. These observations greatly extend our knowledge of pyroxene structure by mapping a corresponding volume in P-V-T space (Figure 1). From this information a complete set of internally consistent thermoelastic parameters can be derived. Thermoelastic parameters of jadeite differ strongly from those of orthoenstatite MgSiO_3 .

Elastic wave velocities complement information from equations of state. They can be measured under extreme conditions using the impulsively stimulated Brillouin scattering (ISBS) on fluids and solids under simultaneous high temperature and high pressure. We have established our experimental capability to obtain ISBS data on a variety of high pressure fluids, H_2O ice, and minerals. Results from this project demonstrate how the scattering of acoustic waves in high pressure solids can be used to yield useful information on the equation of state and dynamic relaxation mechanisms inherent to the material.

Acoustic velocities are obtained under variable high pressure conditions in a DAC by the generation and time evolution of laser-induced acoustic gratings. The acoustic velocity as a function of applied pressure is obtained by measuring the frequency of the oscillations in an acoustic grating formed in a diamond anvil cell, and the attenuation time of the transient grating measurement probes the decay of the thermal grating due to diffusion. ISBS provides a means of measuring the sound velocity u that is suited for a fluid and solid samples in a high-temperature diamond-anvil cell. The light-scattering geometry matches the apertures in such cells, the diamond-anvil index of refraction plays no role, and the signal is strong enough to observe relatively easily. In these experiments, a mode-locked, Q-switched laser produces a train of short (<100 ps) laser pulses, each with an energy of about 50 μ J. Two of these pulses enter the sample simultaneously at a well-determined angle θ (measured outside the sample chamber) and are each focused to a spot in the DAC. These spots overlap spatially and temporally to form an interference pattern in the sample from which elastic wave velocities can be derived.

Pressure dependent ISBS transient grating results have been obtained for H₂O over the pressure range 0-12 kbar. Figure 2 summarizes the pressure-dependent sound speed results for H₂O water as well as a comparison with ice at 25°C.

Room-temperature elasticity studies over the entire range of upper mantle pressure for San Carlos olivine, Kilbourne Hole orthopyroxene, and a pyrope-rich garnet were completed, and a study of the elastic constants of a Kilbourne Hole clinopyroxene has been initiated. In supporting research a method was developed to measure nonhydrostatic stresses on samples in the diamond anvil cell and was applied to determinations of the yield strength of olivine at pressures in excess of 10 GPa.

Properties of San Carlos olivine were calculated along isotherms and a geotherm. Compressional velocities (Figure 3) and shear velocities for olivine along a geotherm show qualitatively similar behavior. Olivine is a good match to the seismic velocities at the base of the upper mantle. Compressional velocities lie above both seismic models in the uppermost mantle. The olivine compressional velocity is faster than two relatively warm mantle regions, California to Juan de Fuca (CJF) and Gulf of California (GCA). Both compressional and shear wave profiles show minima that are suggestive of the low velocity zone (LVZ) shown in the seismic profiles. Based on estimated temperature derivatives, olivine can be made to match most of the seismic profiles with temperature differences of less than 500 K at any depth.

New data for orthopyroxene (Mg,Fe)SiO₃ from Kilbourne Hole, NM lead to several significant modifications of "conventional wisdom". (1) Prior studies have assumed an incorrect pressure derivative for the bulk modulus and (2) a small aluminum

content can have a significant impact on the elasticity of pyroxenes. Despite some contrary evidence, efforts to construct mineral physics interpretations of the upper mantle have accepted the premise that the pressure derivative of the bulk modulus for pyroxenes are "normal" (in the range from 4 to 5). The measured derivative is closer to 8 at one bar and only approaches 4 at pressures above 10 Gpa. The significance of this lies in the idea that the properties of the upper mantle are "olivine like." Because the mantle must have some pyroxene and garnet, the simplistic assumption is that a garnet component (with high seismic velocity) is balanced by a pyroxene component with low velocities.

A parallel effort to study thermal conductivity of silicates with ISBS was completed—a significant instrumentation development. A substantial degree of anisotropy in upper mantle silicates has been documented. Thermal diffusivity tensors were determined at ambient pressure and temperature for three silicate mineral phases abundant in the upper mantle: San Carlos olivine $[(\text{Mg}_{.89}\text{Fe}_{.11})_2\text{SiO}_4]$; Kilbourne Hole pyroxene; and a garnet of intermediate composition. Data for olivine were also obtained at high pressure. Diffusivity in the two orthorhombic materials is highly anisotropic: components of the tensor along the a , b , c crystallographic axes in units of mm^2/sec are [2.16, 1.25, 1.87] for olivine and [1.26, 1.05, 1.66] for pyroxene. Isotropic thermal diffusivity in garnet is $1.06 \text{ mm}^2/\text{sec}$. Geophysical implications of this anisotropy are important. Olivine and pyroxene crystals comprising the upper mantle align under progressive simple shear strain to form a preferred texture. Because both these crystals have anisotropic viscosities and thermal diffusivities, shear strain changes vertical heat flow in the upper mantle and viscous impedance to plate motion. The largest changes in thermal diffusivity and effective viscosity in the mantle-lithosphere profile occur in and above the asthenosphere, where total strains are greatest. Vertical diffusivity decreases with shear strain as the olivine b axes become vertically oriented. This causes higher temperatures than predicted by an isotropic half-space cooling model to prevail at shallow mantle depths, compounding the viscosity reduction in the lithosphere.

A defining characteristic of Earth materials is their deformation state. Deformation of rocks reflects their previous history and indicates possible future geological hazards. Because rocks deform by mechanisms similar to those in man-made materials where processes are better understood, the goal of this research is to borrow methodology from materials science to quantitatively characterize deformation features and texture (preferred crystallographic orientation) at all scales (using electron microscopy, neutron and x-ray diffraction, and advanced methods of data processing) and to interpret results with the help of polycrystal plasticity theory. Thus, the influence of recrystallization on the texture and microstructure of different materials (copper, calcite,

quartz) has been investigated using naturally and experimentally recrystallized samples. One application is to explain seismic anisotropy patterns at mid-ocean ridges and to distinguish models for buoyant and for passive flow. A second is to explain the observed oblique anisotropy pattern in the mantle beneath the San Andreas fault as a result of shearing. A third application is to examine ice textures with relevance to icy satellites of the giant planetets.

Deformation of peridotite caused by mantle flow beneath an oceanic spreading center can result in the development of seismic anisotropy. Travel-time anomalies and shear-wave splitting will develop as seismic energy propagates through an anisotropic region, thus providing a signature of the deformation field at depth. This collaborative study with seismologists from Scripps Institute of Oceanography investigated the nature of deformation associated with mantle upwelling for two models of flow in the upper 100 km of the mantle. The finite-strain fields of the passive upwelling model driven by spreading of the lithospheric plates versus the buoyancy-enhanced model driven by thermal heating are quite different. Numerical estimates of the corresponding mineral textures were made with polycrystal plasticity theory for olivine (Figure 4). Given the mineral orientation distributions and elastic parameters for single crystals, the propagation of waves through this anisotropic medium can be calculated. Relative P-wave seismic travel time delays of up to one second are predicted for the buoyant model and less for the passive model. The former is in good correspondence with observed seismic data.

A proposed model for the vicinity of the San Andreas fault based on seismic transverse (S) wave-splitting data has an upper layer in which the fast velocity direction is more or less parallel to the San Andreas fault (SE-NW), and a lower layer with a fast direction is inclined about 60° to the San Andreas fault (E-W). These results for the lower layer can be interpreted based on polycrystal plasticity modeling of olivine. In simple shear simulations, 500 initially randomly oriented grains were deformed in 100 increments of simple shear to a total equivalent strain of 200%. During this deformation the principal axis of the strain ellipse gradually rotated into the shear plane. Thus, knowing elastic properties of single crystals and the orientation distribution, one can calculate P-velocity surfaces for the shear zone. The velocity maximum is inclined about 30° to the shear plane, which is close to what is observed. If the movements of the Pacific and the North American plates are driven by similar shear displacements in the upper mantle, then the observed type of anisotropy should also develop. From the pattern of seismic anisotropy and the assumption that olivine is the major constituent of the shear zone, one can also interpret the correct right lateral sense of shear.

The various icy satellites belonging to the outer planets display mappable terrains, tectonic activity, and plastic deformation as found on Earth. However, the satellites consist mainly of water-ice or ice-rock mixtures. For this reason, understanding macroscopic deformations on these icy bodies or their geophysical evolutions requires knowledge of the strain evolution of crystalline water ice at high pressure and low temperature. At conditions of the outer solar system water ice behaves very much like silicates during plastic deformation. Mechanical data for ice I and the high-pressure ice polymorphs are extensive. However, quantitative analyses of their textures during deformation or phase changes do not exist, mainly because there has been no convenient way to measure texture at such low temperatures (<245 K). Because some of the experimental ice polymorphs require texture measurement at extremely low temperatures to retain their phase and structures, a new low-temperature neutron diffraction technique was developed to measure texture of polycrystalline materials at 77 K. High pressure, low temperature deformation and phase change experiments were performed on polycrystalline ice. The resulting textures were then measured by neutron diffraction, and the measured pole figures were used to calculate orientation distribution functions for the samples. Finally, microstructures in the samples were investigated using low temperature scanning electron microscopy, optical microscopy, and replication techniques. As an example, one study used the new low-temperature neutron-diffraction setup to identify phase and structure of polycrystalline D_2O ice I under shock load as would occur during meteorite bombardment of the icy satellites. Five synthetic, uniform grain size D_2O ice specimens were shock-loaded at temperatures near 100 K using a two-stage light gas gun that was fitted with a cryogenic tank and achieved peak pressures up to 5.0 GPa. The phase of the metastable shock-loaded specimens was subsequently identified at 100 K in a neutron powder diffractometer as crystalline ice I. Optical microscopy of the shocked ice surfaces revealed the grain structure in its original structure and had not recrystallized. Findings from this work have many geological and geophysical implications for the icy bodies of the outer solar system.

As problems in elastic/anelastic behavior, rocks have long presented experimental and theoretical challenges that arise from their complex mechanical and chemical structure and their interaction with fluids. A new theoretical framework for the description of linear and nonlinear elasticity has been developed to explain the behavior of such consolidated materials. The objective of this work is to develop the theoretical tools (analytic and computational) to implement a new approach to the elastic behavior of rock. The rock is assumed to be composed of many mechanical features, e.g., cracks and pores, each of which behave in a possibly nonlinear and hysteretic fashion. The new

approach is based on an abstract pressure space (Preisach-Mayergoyz or PM space) in which the number density ρ_{PM} of the mechanical features is tracked as a function of external pressure P on the rock. Given the number density ρ_{PM} , it is possible to predict the stress-strain equation of state (which exhibits hysteresis and discrete memory), the ratio of static to dynamic modulus, and the cubic and quartic nonlinear coefficients characterizing the rock's pressure dependence. This represents a complete description of the linear and nonlinear elastic behavior.

Three computational schemes for extracting ρ_{PM} from uniaxial stress-strain data on rock were developed. The numerical procedures are termed (a) the method of simulated annealing, (b) the method of normal modes, and (c) the method of decaying exponentials. All three give similar results when applied to stress-strain data on sandstone. These inversion methods are listed in order of increasing imposed prior knowledge or bias, and in order of decreasing computational memory and time consumption. The normal mode analysis is preferred as a compromise inversion technique.

These inversion techniques were tested on three uniaxial stress-strain data sets: a) Berea sandstone measured at New England Research, b) another Berea sandstone measured at the University of California, Berkeley, and c) Castlegate sandstone measured at Schlumberger-Doll Research. Descriptions of the three inversion techniques and the results when applied to the three data sets are given in manuscripts published and in review. In all three cases, the PM space extracted from a subset of the data allowed prediction of the complete set of stress-strain data, the quasistatic elastic modulus, the dynamic elastic modulus and the coefficients of nonlinear elastic response of the rock. As shown in Figure 5, samples were subjected to complicated stress protocols beyond those that gave the data set used to determine ρ_{PM} . In each case it was possible to reliably predict the strain response to these stress tests. This result and its progeny are of basic importance for problems from earthquake engineering to waste isolation. The approach is a large step toward establishing a very powerful/useful theoretical framework for the description of linear and nonlinear elastic behavior of rocks (and other consolidated materials such as concrete).

It would be a matter of striking significance for understanding the dynamics of mantle convection if there were a way to verify that some material is transported from Earth's core all the way to the surface. The moderately siderophile elements (W, Mo, As, and Sb) have several properties that are important for understanding problems involving

the evolution of the Earth and the Moon (e.g., core formation on the Earth and the Moon, origin of the Moon, origin of mantle plumes). For instance, molybdenum is geochemically well behaved and is correlated with the light rare earth elements in every measured terrestrial reservoir [Newsom and Sims, *Origin of the Earth*, 1991]. In order to evaluate the depletion of Mo (and other moderately siderophile elements), the abundance of the siderophile element is normalized to the abundance of a refractory lithophile element and the siderophile/lithophile element ratio is compared with the chondritic (solar system) ratio. By using a refractory lithophile element that has the same incompatibility as the siderophile element, the effect of igneous fractionation is diminished.

Progress was made in publication of data for the depletion of tungsten in the Earth's silicate mantle. Depletion of W in the bulk silicate Earth due to core formation provides clues to the formation and early evolution of the Earth. Tungsten is a highly incompatible element, whose absolute concentrations vary because of igneous processes. Therefore, the abundance of W is normalized to the highly incompatible lithophile element Th, to correct for igneous fractionation since the end of core formation. Similar W/Th ratios are observed in several terrestrial reservoirs (Figure 6), including the depleted mantle (nodules and Mid-Ocean Ridge Basalts), the old continental crust (upper continental sediments and Archean granulites), and the young continental crust (continental and oceanic arcs). Use of Th as a normalizing element is inappropriate, however, in the case of granulite xenoliths from the lowermost continental crust. These samples have higher W/Th ratios due to loss of Th (and U) compared to other incompatible elements including Ba and W. Similarly, the few investigated komatiite samples (cooled from dense, very hot magmas most abundant early in Earth history) have high ratios of W to the normalizing elements, possibly due to loss of the normalizing elements during alteration. Depletion of W in the bulk silicate Earth was determined by using a mass balance calculation based on the W/Th ratios of mantle and crustal reservoirs, including the uncertainty in the initial abundance of W in the Earth as based on W abundances in chondritic meteorites. The resulting depletion of W relative to the refractory lithophile element Th is 0.06, with a range from 0.03 to 0.1. The depletion range for W overlaps the depletions of the compatible siderophile elements Co and Ni, which is consistent with the heterogeneous accretion theory for the origin of the Earth.

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Figure 1. Unit cell volumes $V(P,T)$ of jadeite $\text{NaAlSi}_2\text{O}_6$. The curves are isothermal compressions calculated from the fitted thermoelastic parameters. Isotherms are at temperature steps $\Delta T=200$ K above 300 K up to 1273 K. Error bars are smaller than the symbols.

Figure 2. Pressure-dependent acoustic velocities obtained by ISBS measurements on H_2O at 25°C .

Figure 3. Compressional velocities at room temperature for upper mantle silicates. The top curve is for a pyrope-rich garnet. The middle (dot-dash) curve is San Carlos olivine. The long curving solid line is Kilbourne Hole orthopyroxene. The lower (dotted) curve is bronzite as measured by Webb. The solid short line segment is the "conventional wisdom" for orthopyroxene as reported in several papers.

Figure 4. (100) Pole figures of olivine showing calculated orientation distributions of 1000 olivine grains within the aggregate at each node point in the buoyant (bottom) and passive (top) models. The aggregates are undeformed at 100 km depth. The deformation of grains in the aggregate is tracked as it moves along a streamline and is subjected to gradients in flow velocity.

Figure 5. Stress-strain curves for a sample of Berea sandstone. The density ρ_{PM} was determined from the outer perimeter loop and then applied to predict the extremely complex behavior seen in the inner loops as in the expanded inset.

Figure 6. W/Th (tungsten/thorium) ratio in samples from different terrestrial reservoirs can be compared to the W/Th ratio in chondritic meteorites to determine the depletion of W in the bulk silicate earth. Depletion of W (about a factor of 20) relative to depletion of nickel and cobalt provides a constraint on core formation in the Earth and is consistent with the heterogeneous accretion theory.