LA-UR-00-5438

97814

Approved for public release; distribution is unlimited

Title: **Earth Materials and Earth Dynamics**

Author(s):
Kristin A. Bennett* (LANSCE-12)
Thomas J. Shankland (EES-4)
Yusheng Zhao, (LANSCE-12)
David Schiferl (CST-6)
Carlos N. Tomé (MST-8)
U. Fred Kocks (CMS)
Malcolm Nicol (UCLA)
J. M. Brown (Univ. Washington)
J. Zaug (Univ. Washington)
Wei Li, (LANSCE-12)
Hans -R. Wenk (UC Berkeley)
John R. Baumgardner (T-4)
Ricardo Lebensohn, (Univ. Rosario, Rosario, Argentina)
Luca Lutterotti (Univ. Trento, Italy)
I. Shimizu (Univ. Tokyo)
M. Montagnat (UC Berkeley),
Bryan J. Travis (EES-5)
Barbara Dutrow (Louisiana State University)
Carl W. Gable (EES-5)
C. T. Foster, Jr. (Univ. Iowa)
Connie Christensen (Louisiana State University)
R. Dean Taylor (MST-10)
Raymond Jeanloz (UC-Berkeley)
Moshe P. Pasternak, (MST-10 and Tel Aviv University
Jeff Nguyen (UC Berkeley)
Paul A. Johnson (EES-4)
Katherine. R. McCall (University of Nevada at Reno)
Richard. A. Guyer (University of Massachusetts at Amherst)
Albert Migliori (MST-10)
Timothy W. Darling (MST-10)
James A. TenCate (EES-4)
Koen A.-E. Van Den Abeele (University of Leuven, Belgium)
Eric Smith (University of Texas at Austin)
Vijayashree Kari (University of Nevada at Reno)
Timothy J. Ulrich (University of Nevada at Reno)
Eric L. Chronister (UC Riverside)
Michael McIntire (UC Riverside)
Harry W. Green, II (UC Riverside)
Larissa Dobrzhinetskaya (UC Riverside and Cal State Fullerton)

Submitted to: DOE Office of Scientific and Technical Information (OSTI)

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Earth Materials and Earth Dynamics LDRD Final Full Report - (97814) 1997-1999

RECEIVED
DEC 13 2000
OSTI

Author List/ Contributors

Kristin A. Bennett* (LANSCE-12), Thomas J. Shankland (EES-4), Yusheng Zhao, (LANSCE-12), David Schiferl (CST-6), Carlos N. Tomé (MST-8), Fred Kocks (CMS), Malcolm Nicol (UCLA), J. M. Brown (Univ. Washington), J. Zaug (Univ. Washington), Wei Li, (LANSCE-12), Hans -R. Wenk (UC Berkeley), John R. Baumgardner (T-4), Ricardo Lebensohn, (Univ. Rosario, Rosario, Argentina), Luca Lutterotti (Univ. Trento, Italy), I. Shimizu (Univ. Tokyo), M. Montagnat (UC Berkeley), Bryan J. Travis (EES-5), Barbara Dutrow (Louisiana State University), Carl W. Gable (EES-5), C. T. Foster, Jr. (Univ. Iowa), Connie Christensen (Louisiana State University), R. Dean Taylor (MST-10), Raymond Jeanloz (UC-Berkeley), Moshe P. Pasternak, (MST-10 and Tel Aviv University), Jeff Nguyen (UC Berkeley), Paul A. Johnson (EES-4), Katherine. R. McCall (University of Nevada at Reno), Richard. A. Guyer (University of Massachusetts at Amherst), Albert Migliori (MST-10), Timothy W. Darling (MST-10), James A. TenCate (EES-4), Koen A.-E. Van Den Abeele (University of Leuven, Belgium), Eric Smith (University of Texas at Austin), Vijayashree Kari (University of Nevada at Reno), Timothy J. Ulrich (University of Nevada at Reno), Eric L. Chronister (UC Riverside), Michael McIntire (UC Riverside), Harry W. Green, II (UC Riverside), Larissa Dobrzhinetskaya (UC Riverside and Cal State Fullerton)

Abstract

In the project 'Earth Materials and Earth Dynamics' we linked fundamental and exploratory, experimental, theoretical, and computational research programs to shed light on the current and past states of the dynamic Earth. Our objective was to combine different geological, geochemical, geophysical, and materials science analyses with numerical techniques to illuminate active processes in the Earth. These processes include fluid-rock interactions that form and modify the lithosphere, non-linear wave attenuations in rocks that drive plate tectonics and perturb the earth's surface, dynamic recrystallization of olivine that deforms the upper mantle, development of texture in high-pressure olivine polymorphs that create anisotropic velocity regions in the convecting upper mantle and transition zone, and the intense chemical reactions between the mantle and core. We measured physical properties such as texture and nonlinear elasticity, equation of states at simultaneous pressures and temperatures, magnetic spins and bonding, chemical permeability, and thermal-chemical feedback to better characterize earth materials. We artificially generated seismic waves, numerically modeled fluid flow and transport in rock systems and modified polycrystal plasticity theory to interpret measured physical properties and integrate them into our understanding of the Earth. This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL).

*Principal Investigator, e-mail: bennett@lanl.gov

Background and Research Objectives

Study of Earth materials and Earth dynamics are essential areas of investigation for understanding and interpreting the composition and evolution of the solid Earth. Through a broadly based, interdisciplinary approach that combined measurement and theory we investigated the current state of the earth and the processes by which it was formed and modified. We used a combination of experimental techniques including neutron and x-ray diffraction, high-precision mass spectrometry, transient optical grating and conventional geochemistry (including electron microprobe, x-ray fluorescence, scanning electron microscope, and ion probe) to better characterize anisotropic physical properties within the Earth. Simultaneously we developed analytical tools such Constant Strain Analysis (CSA) and Resonance-Template Matched Filtering (RTMF) and Resonant Ultrasound Spectroscopy (RUS), and modified existing codes such as MOR3D, RITA (Rietveld Integrated Texture Analysis) and GSAS (General Structure Analysis System) for better interpreting data (see Publications list). We modeled dynamic processes such as fluid and chemical transport, deformation-based recrystallization, mantle convection and seismicity. The strength of this work is based on the combination of measurement and numerical techniques to address specific problems within the lithosphere mantle and core of the earth.

The Lithosphere

- To quantitatively understand the effects of coupling thermal, chemical and mechanical processes active during the evolution of hydrothermal fluid-rock systems and how this coupling affects the lithosphere, we studied system dynamics and resultant mineralogy and chemistry of various rock systems. Our objective was to investigate through field, laboratory and numerical analysis how variations in the fluid phase alter the system's behavior and how these effects would be manifested in the rock record. By linking thermal modeling studies with textural modeling studies, we quantitatively predicted the textural and chemical evolution of contact metamorphic systems as a function of the fluid flow/thermal field. These goals were achieved primarily by numerical experimentation utilizing a computer code, MOR3D developed by scientists at Los Alamos, coupled with field and laboratory investigations of fluid infiltrated rocks.

- Through new analytical and computational research we are pioneering understanding of non-linear elastic behavior of rocks [10][11]. We studied nonlinear hysteretic behavior of earth systems and developed resonant mode inversion techniques for rock characterization [13]. One of the most dramatic observations made recently has been slow dynamics in the non-linear elastic response of rocks during resonant bar measurements. When a rock is subjected to high amplitude continuous-wave drive, it remembers this state of high dynamic strain for a substantial period of time after the high dynamic strain has been terminated. One way to observe this behavior is to monitor the resonance frequency with a linear probe, i.e., conduct a resonance sweep at very low drive level before and after the sample has been subjected to a high dynamic strain. The frequency of the linear resonance peak is monitored as a function of time, by making repeated low-drive amplitude frequency sweeps. The linear resonance peak position recovers from the value it had at high dynamic strain to its initial value on a time scale of order ~1000 s or greater. Slow dynamics uniquely reveals that non-linear resonant response of a rock is sensitive to physical processes that cannot be observed by other means. Thus slow dynamics has prompted new directions for experimental work and invites a more sophisticated theoretical analysis. Our objective was to develop data analysis tools for transcription of the experimental strain data [6].

The Mantle

- To understand seismic properties of the mantle we investigated mantle mineral physics at simultaneous high temperature and high pressure. The transition zone is rich in phase transformations associated with pyroxene structures and compositions. Complex phase relations in the pressure and temperature range of the transition zone are the direct results of mantle mineralogy [12][4]. Densities and acoustic velocities of mantle minerals can be modeled in their volume fraction and chemical compositions for comparison with seismological observations. Previous efforts to establish density-velocity-composition relations have concentrated on ferro-magnesian silicates [5][16][17][18]. However, for pyroxenes, there is lack of experimental data on the high-pressure form of clinopyroxene $(Mg_{1-x}Fe_x)_2Si_2O_6$ (x=0.12) due to experimental difficulties [9]. Starting from a basis of thermoelastic equations of state involving "minor" chemical compositions, such as Na, Ca, and Al, we can investigate the effects of Fe-Mg substitution on pyroxenes of complex structure and chemistry.

- In particular, the study of unit cell dimensional change and structural variation of clinopyroxenes at high P-T conditions offers a unique opportunity for delineating the causes for mantle anisotropy in the transition zone. Our goal was to investigate pyroxenes equation of states, the second most abundant minerals (after olivine) that constitute about 35% of the volume of Earth's upper mantle to evaluate depth dependence of seismic properties in the upper mantle.

- To understand anisotropy in the upper mantle and transition zone dynamics we investigated lattice preferred orientation (texture) during deformation and phase transformation. It is well-established that the seismic anisotropy of the shallow upper mantle beneath the oceans is a result of texture of olivine crystals produced by plastic deformation occurring during corner flow as asthenospheric mantle upwells at mantle ridges [3] [14]. Experimental deformation of peridotite has shown that this preferred orientation is caused by preferential flow of olivine by movement of dislocations on the (010) plane in the [100] direction. The rotations that take place during plastic deformation by generation and movement of dislocations on this slip system naturally lead to the [010] direction standing approximately normal to a planar foliation, and the [100] direction aligning approximately parallel to the lineation. Little is known about the texture that might be produced by corresponding plastic flow of the high pressure polymorphs of olivine in the transition zone because natural samples never are transported untransformed to the surface. Experimental apparatus to induce large strains in the laboratory at the extreme pressures required to stabilize wadsleyite (>13 GPa) and ringwoodite (>15GPa) are only now being developed [12]. Our aim was to determine the texture developed in flow of wadsleyite by dislocation creep and during transformation from olivine to wadsleyite. The results can be compared to measurements of seismic anisotropy in the mantle transition zone to determine indirectly the flow mechanisms (and therefore flow properties) of that region of the mantle. Such information is crucial for improved modeling of mantle circulation. In general the transition zone appears to display much less anisotropy than the shallower mantle, suggesting that flow may not be by dislocation processes, but in places anisotropy has been inferred. We believe that the observed decrease in seismic anisotropy at the transition zone may be due to phase transformation when a lattice preferred orientation is erased. Our goal was to experimentally deform and transform olivine to wadsleyite and measure the resulting lattice preferred orientations by neutron diffraction. These experiments were the first to deform a polycrystalline beta-phase (wadsleyite) structure in stress and measure the developing texture.

Our results will contribute significantly to the timely debate as to the causes of decreased anisotropy in the deeper upper mantle . Our goal was to use and the high-pressure deformation at the University of California Riverside to deform and transform olivine and wadsleyite and to measure the resulting textures at Los Alamos Neutron Scattering Center (LANSCE).

- In addition to understand anisotropy development in the upper mantle during convection, we developed new microscopic deformation based recrystallization models and introduced them into conventional macroscopic convection models. While crystal rotations during deformation are well understood, processes during dynamic recrystallization remain enigmatic. Within the Earth's mantle, large cells of convection are induced by thermal instability and maintained by temperature and density gradients. In modeling this convective flow Los Alamos has played a prominent role. The models have been based on the assumption that the material is a viscous fluid with neither internal structure nor directional properties. In reality most of the Earth (except the outer core and some small portions of the upper mantle) are composed of solid crystals that deform according to laws of polycrystal plasticity. Furthermore in many parts of the Earth, and particularly at temperatures in the mantle and core, simultaneous dynamic recrystallization occurs [15]. We sought to develop a deformation-based model for dynamic recrystallization that is based on a balance between preferential grain growth and nucleation due to the strain energy accumulated in individual grains [19]. Experiments by Karato et al. (see Publications list) have shown that in simple shear deformation of olivine at low strains an asymmetric texture develops with a [100] maximum rotated away from the shear direction against the sense of shear. At large strain where recrystallization is pervasive, the pattern is symmetrical and [100] is parallel to the shear direction. We attempted to model this with a viscoplastic self-consistent polycrystal plasticity theory largely developed at Los Alamos. We have extended the model to olivine and have predicted its deformation and recrystallization in simple shear.

<u>The Core</u>

- To quantify mantle-core interactions, we investigated magnetic spin and bonding properties in FeO. Seismological, geodynamic, geomagnetic, geodetic and mineral physics evidence indicate that the core–mantle boundary is among the most dynamically active regions of the planetary interior, apparently due to the occurrence of intense chemical reactions between the mantle and core. It is now recognized that FeO is an important model compound for characterizing the nature of chemical bonding deep inside the Earth [8]. The present studies of $Fe_{0.94}O$ to 120 GPa and $T \leq 300$ K show that there is a high spin (magnetic) to low spin (diamagnetic) transition. The relative abundance of the two species is T and P dependent. The molar volume changes gradually with P at room temperature. Our goal was to show via high- pressure research that the magnetic collapse of $Fe_{1-x}O$ is an isochoric, second-order transition resulting from a gradual increase in the crystal-field with increasing pressure. This would greatly enhance our understanding of the dynamics of the core-mantle boundary.

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

Just as important to understanding solid earth dynamics, this research is at the center of significant defense programmatic efforts; for instance, maintaining the capability to characterize materials at high pressures and temperatures, monitoring and predicting constitutive responses of nuclear stockpile materials, and predicting strong ground motion for earthquake hazard analysis. Los Alamos has recently taken the lead in studying strong ground motion events by non-linear wave dynamics techniques [6]. This project involved forefront research in non-linear wave studies. In addition Los Alamos houses the most powerful peak flux accelerator of protons in the world, the Los Alamos Neutron Science Center (LANSCE). This project developed pioneering Time-of-Flight (TOF) data analysis techniques and neutron diffraction in anticipation of the new instrument 'HIPPO' at LANSCE.

The work proposed here complements Science and Technology Base and National Research & Development needs within the institution of Los Alamos.
Isotopic studies uncover aspects of geological and atmospheric evolution, a background to atmospheric studies; they are necessary for understanding global climate change in the Earth's past and processes relating to retention of wastes in soils and rocks. Computational modeling applies to near-surface studies of environmental hazards and volcanism. The work creates a better understanding of the causes and distribution of earthquakes and contributes to efforts to reduce the hazards from earthquakes and is related to verification and non-proliferation issues. In particular, an enhanced understanding of lateral and vertical velocity heterogeneities in Earth's crust and mantle is important in efforts to detect, recognize, and monitor nuclear testing. Environmental restoration is another area that is affected by this work. Studies of fluid-flow processes, as well as efforts to develop numerical models of soil formation, have direct application to environmental restoration

projects, and will potentially increase the efficiency of restoration efforts. Moreover new experimental and data analysis techniques in this work are used to measure texture in tantalum, plutonium and beryllium important for the Science Based Stockpile Stewardship Program and maintaining the integrity of the Nation's nuclear stockpile.

Scientific Approach and Accomplishments

Through a broadly based, interdisciplinary approach, we investigated the current state of the Earth and the processes by which it is formed and modified. Strength of this work is the integration of techniques to address specific problems. We used a combination of practical techniques including neutron and x-ray diffraction, high-precision mass spectrometry, transient optical grating and conventional geochemistry (including electron microprobe, x-ray fluorescence, scanning electron microscope, and ion probe), Mössbauer spectroscopy; and numerical techniques including modeling and data analysis such as Constant Strain Analysis (CSA) and Resonance-Template Matched Filtering (RTMF) and Resonant Ultrasound Spectroscopy (RUS) seismic techniques, fluid flow models, RITA and GSAS (General Structure Analysis System). We investigated mantle mineral physics at simultaneous high temperature and high pressure. We investigated anisotropy development during deformation in the Earth by property characterization and quantitative modeling. We investigated microscopic characteristics of mantle-core interactions. We performed detailed analysis of coupled fluid flow and chemical transport for implications for mineral chemistry, permeability evolution and thermal-chemical feedback effects. We studied nonlinear hysteretic behavior in earth materials. We measured preferred orientations in experimentally deformed upper minerals.
We measured magnetic bonding in iron oxides as a function of pressure to elucidate what is thought to be one of the most dynamically active regions of the earth.

The Lithosphere

- To understand fluid-rock interactions in the earth we performed detailed analysis of coupled fluid flow and chemical transport via mineral chemistry, permeability evolution and thermal-chemical feedback effects. These goals were achieved primarily by utilizing a computer code, MOR3D that incorporates diffusion, advection, and dispersion, and it has options to include salinity-driven flows, chemical reaction, silica precipitation and dissolution, cooling intrusives, and particle tracking, all in three dimensions. In this work we added new modules to account for the heats of reaction. MOR3D's utility derives from the completeness of the code. Thermal and flow field calculations constrain temperatures and quantify mass transfer responsible for producing the observed mineral assemblages. Effects of latent heat on the host rocks were analyzed. Maximum temperatures and fluid flux in the host rocks are sensitive to the latent heat term and to the method to calculate its release.

This result affects the isograds observed in the host rocks as well as the timing of isograd advance and heating rates of surrounding rocks. Two differing crustal domains were analyzed. Both were for sill-like intrusions, but the depth and size of intrusion varied dramatically; a "deep" domain, 50x50x50 km with a 2-km wide pluton centered at 15 km depth; and a "shallow" high-resolution domain, 30x40 meters with an intrusion at 650 bars pressure. In addition, initially thermal modeling studies were completed for 2D, in order to more quickly evaluate the effects of various parameters. Once this was completed, the modeling was extended to 3D for a 50x50x50-km system. Variations in temperatures at the end of the pluton were not dramatic; that is, they were within errors of geothermometric data. Maximum fluid fluxes were somewhat smaller for specific positions within the system and were above the pluton (See Publications for more details).

- To investigate non-linear elasticity in rocks we developed two data analysis tools termed, Constant Strain Analysis (CSA) and Resonance-Template Matched Filtering (RTMF). The essential property of both of these tools is that they deliberately avoid assumptions about models; they are in effect methods for the transcription of experimental strain data into a convenient analysis form.
  As a consequence, these tools provide a robust characterization of non-linear properties for practical purposes, e.g., tables of rock properties, etc., and will help to unravel the mechanisms of nonlinear response. In addition we developed a Resonant Ultrasound Spectroscopy (RUS) is a method whereby the elastic tensor of a sample is extracted from measured resonance frequencies. Typically, a rectangular parallelepiped sample is placed between two piezoelectric transducers, a source and a detector. The sample is driven at constant voltage as the frequency is swept through multiple resonances. The measured resonance frequencies are the input to an iterative inversion algorithm that finds the best match between the data and a set of resonances generated from a model. RUS has been used successfully to determine the elastic properties of single crystals of minerals found in the earth's mantle. We are extending the applicability of RUS to macroscopic samples of rock. Rocks are potentially difficult samples on which to

apply RUS, because of their high acoustic attenuation (low Q), inhomogeneity, anisotropy, and the difficulty preparing suitable samples. Our study has an experimental component and a theoretical component.

In preliminary measurements, we analyzed a variety of rock types to determine optimal sample sizes and aspect ratios (length/diameter), the minimum number of resonances necessary for obtaining an accurate inversion, the sensitivity of RUS to anisotropy in rock samples, and the precision of measurements on samples of varying sizes and aspect ratios. Assuming isotropy, we have found that RUS provides reliable results for relatively high Q materials such as basalt, primarily because a large number of resonance frequencies can be accurately determined. For example, application of RUS to a sample of basalt with an aspect ratio of 4 yields an RMS error of 0.31% in the fit between the predicted and measured resonance frequencies, and the elastic constants c_{11} and c_{44} change by 0.54% and 0.12% respectively with a χ^2 increase of 2%. Application of RUS to low Q materials such as sedimentary rock is considerably more difficult, and it remains unclear if RUS is viable for such materials. We are exploring the effects of inhomogeneity on the variational calculated resonanaces in the RUS technique. We have solved a sequence of one-dimensional problems that illustrates the principles involved in implementing the variational technique for inhomogeneous materials. These results can be compared to analytic results. We find that inhomogeneity can be modeled using the variational method, although the number of modes necessary for an accurate solution is much higher than for the homogeneous case.

The Mantle

Jadeite and diopside are two major components of the clinopyroxene minerals; which have the chemical composition of $NaAlSi_2O_6$ and $CaMgSi_2O_6$, respectively. For understanding material properties in the deep mantle we measured equation of states for these two pyroxenes. The thermoelastic equation of state, specifically, the temperature derivatives of elastic moduli and the pressure derivative of thermal expansion, are the important parameters for evaluating depth dependence of seismic properties [1]. These thermoelastic parameters have never been investigated for the clinopyroxenes due to significant experimental difficulties associated with low crystal symmetry. We presented the first measurement to derive a thermoelastic equation of state at simultaneous high pressure and high temperature conditions of clinopyroxene minerals namely, jadeite and diopside. This resulted from separating heavily overlapped diffraction spectra using GSAS together with the le Bail refinement technique, which permitted us to simultaneously obtain peak positions and lattice parameters. For jadeite and diopside, we have measured unit cell parameters at pressures up to 8.2 GPa and temperatures up to 1280 K, thus mapping the compression and thermal expansion and their pressure and temperature derivatives of the clinopyroxene structure in P-V-T space. Thermoelastic parameters for $NaAlSi_2O_6$ and $CaMgSi_2O_6$ were derived by fitting the P-V-T data to the high-T Birch-Murnaghan equation of state. We obtained isothermal bulk modulus K_{T0} along with the pressure and temperature derivatives. We also obtained volumetric thermal expansivity α for both minerals. The isothermal compression lines calculated from the fitted thermoelastic parameters clearly shows that the thermoelastic parameters produce good fits to the P-V-T, as shown in Fig. 1. The thermal expansivity α at extreme conditions is required for modeling mantle dynamics. From Fig. 2, which illustrates the decrease of α with pressure, it is clear that parameters such as Rayleigh number will be functions of depth even in the upper mantle. From this information we predicted a set of internally consistent thermoelastic EOS parameters for the clinopyroxene $(Mg_{0.88}Fe_{0.12})_2Si_2O_6$ using a systematic crystal chemistry approach. The effect of these new observations is to favor an olivine-like (pyrolite) stoichiometry for the upper mantle. See resulting papers listed in Publications).

- To understand Earth materials and transition zone dynamics we investigated lattice preferred orientation (texture) during deformation and phase transformation. At Los Alamos Neutron Scattering Center (LANSCE) and the University of California Riverside we used a combination of high-pressure experimental deformation and neutron diffraction techniques to deform and transform olivine analogs through its α, β phase and into a true γ spinel phase, quantitatively extracting the changing lattice orientations. Phase transformation induced anisotropy has been suggested as a possible cause of the observed seismic low velocity zones at 540-and 670–km depth in the upper mantle. Experiments are related to seismic anisotropy's simulated from lattice orientations.

An indirect procedure to examine various aspects of mineralogy and flow in the transition zone is use of germanate analogues. We investigated quantitatively the texture in undeformed and deformed Mn_2GeO_4 olivine, and in 2 specimens partially transformed to the β-phase. Quantitative texture analysis of these materials was performed by neutron diffraction on the High Intensity Powder Diffractometer (HIPD) at the Lujan Center at LANSCE. The resulting textures were measured by time-of-flight neutron diffraction using a generalized spherical harmonic method combine with Rietveld analysis to calculate complete pole figures. This method of neutron diffraction was especially important in this texture study because the coarse-grained multi-phase samples contained low symmetry phases and multiple peak overlaps so that the traditional method of x-ray diffraction would be impossible. With the Rietveld method we were able to extract textures and complete pole figures from any number of reflections from all phases in the bulk (3 mm-diameter sample). Weight percent and the pole figures for both phases were successfully extracted from the data even when one phase constituted only 20% of the total of these small specimens were nearly random (without preferred orientation). Figure 3 shows a neutron diffraction pattern of the two phases. Pole figures from the transformed and deformed samples (Figures 4 and5) showed strong preferred orientation with $(100)_\alpha \parallel (001)_\beta \parallel$ max compression; $(010)_\alpha \parallel (100)_\beta$ and $(001)_\alpha \parallel (010)_\beta$ perpendicular to compression. These preliminary results demonstrate the power of this technique to obtain complete texture determinations from very small amounts of material. These are the firsts quantitative texture measurements of a polycrystalline high-pressure olivine polymorph.

- We investigated anisotropy development during deformation in the Earth by property characterization and quantitative modeling. A defining characteristic of Earth Materials is their deformation state. Rocks deform by mechanisms similar to those in man-made materials where processes are better understood. We borrowed methodology from materials science to characterize quantitatively deformation features at all scales (using electron microscopy, neutron and x-ray diffraction, and advanced methods of data processing) and interpreted results with the help of polycrystal plasticity theory. We studied the development of a model to simulate dynamic recrystallization that so far has been restricted to deformation and it is likely that in the deep interior (mantle and core) dynamic recrystallization is pervasive. The model of recrystallization was based on a self-consistent deformation model and predicts texture pattern as a balance of nucleation and growth processes, both driven by internal strain. See Publications. We introduced polycrystal plasticity into the Los Alamos Terra code applied this three-dimensional finite element approach to predict development of seismic anisotropy in the upper mantle and inner core of the Earth. See resulting papers in Publications. We developed a new method RITA that combines the crystallographic Rietveld technique with discrete methods of quantitative texture analysis to extracted quantitative information about texture from complex neutron diffraction patterns. With this method (tested for calcite, quartz and copper-iron composites) it will be possible to determine preferred orientation from olivine xenoliths that derive from the upper mantle and thus to reconstruct some features of their deformation history.

The Core

- To characterize mantle-core interactions we investigated the magnetic spin and bonding properties of FeO at the pressures of the Earth's core–mantle boundary through a combination of Mössbauer spectroscopy and synchrotron-based x-ray diffraction. The present studies of $Fe_{0.94}O$ to 120 GPa and $T \leq 300$ K show that there is a high spin (magnetic) to low spin (diamagnetic) transition. The relative abundance of the two species is T and P dependent. The molar volume changes gradually with P at room temperature. We conclude that the magnetic collapse of $Fe_{1-x}O$ is an isochoric, second-order transition resulting from a gradual increase in the crystal-field with increasing pressure. Earlier results showed that the Néel temperature T_N of $Fe_{1-x}O$ rose to well above room temperature at a pressure of 60 GPa and resulted in a six-line magnetic hyperfine Mössbauer spectrum. As the pressure was increased further, a non-magnetic component grew at the expense of the magnetic component and suggested that full transformation might occur at 300K by 120 GPa. During this period we have completed a series Mössbauer spectra at $P \geq 80$ GPa and $T \leq 300$ K. These are the first studies of Mössbauer spectroscopy to pressures above 100 GPa to be reported. Thus, the magnetic state of $Fe_{0.94}O$ was investigated to 120 GPa at $T \leq 300$ K. At 300 K a diamagnetic low-spin (LS) state of Fe^{2+} is detected at 90 GPa; its abundance increases with P. The gap between the $^5T_{2g}$ high-spin (HS) ground state and the $^1A_{1g}$ LS excited state decreases with increasing P and at 120 GPa the LS species, first observed at 70 K, is fully converted at ~450 K. The magnetic collapse of $Fe_{1-x}O$ is an isochoric second-order transition resulting from a gradual increase in crystal-field strength with increasing pressure. Typical Mössbauer data are given in Figure 6. For more information see resulting papers in Publications.

Publications

1. Abramson, E. H., J. M. Brown, L. J. Slutsky, and J. Zaug, "Elasticity of San Carlos olivine to 17 Gpa", J. Geophys. Res., **102**, 12,253-12,263, (1997).

2. Baer, B.J., O. Berg, E.L. Chronister, "Picosecond Photon Echo and Coherent Raman Studies of Vibrational Dynamics in Molecular Solids under Pressure," in High Pressure Science and Technology - 1999, Proceedings of AIRAPT-17, July (1999).

3. Baer, B., J. M. Brown, J. M. Zaug, D. Schiferl, and E. L. Chronister, "Impulsive stimulated scattering in ice VI and ice VII", J. Chem. Phys., **108**, 4540-4544, (1998).

4. Bennett, K., R. B. Von Dreele and H.-R. Wenk, "HIPPO, a new high intensity neutron diffractometer for characterization of bulk materials", Proceedings of the Twelfth International Conference on Textures of Materials, **1**, 129-134 (1999).

5. Boness, D.A., and J.M. Brown, "Heat capacity of shocked alkali halides", in Shock Compression of Condensed matter-1995, edited by S.C. Schmidt and W. C. Tao, American Institute of Physics, New York, 85-88, (1996).

6. Chai, M. and J. M. Brown, "Effects of static non-hydrostatic stress on the R lines of ruby single crystals", Geophys. Res. Lett., **23**, 3539-3542, (1997).

7. Chai, M., J. M. Brown, and L. J. Slutsky, "The elastic constants of a pyrope-grossular-almandine garnet to 20 Gpa", Geophys. Res. Lett., **24**, 523-526, (1997).

8. Chai, M., J. M. Brown, and L. J. Slutsky, "The elastic constants of an aluminous orthopyroxene to 12.5 Gpa", J. Geophys. Res., **102**, 14,779-14,785, (1997).

9. Chai, M., J. M. Brown, and Y. Wang, "Yield strength, slip systems and deformation induced phase transition of San Carlos olivine up to transition zone pressure at room temperature", in Properties of Earth and Planetary Materials at High Pressure and Temperature, ed. by M.H. Manghnani and T. Yagi, American Geophysical Union, 483-494, (1998).

10. Dutrow, B.L., Henry, D., Christensen, C., Gable, C, Travis, B, and Heydari, E., "Blackened Smackover: Thermal evolution and mass transfer adjacent to a subsurface alkalic igneous dike in Northern, Louisiana", Gulf Coast Assoc. Geol. Socs. Trans., **47**, 131-139, (1997).

11. Dutrow, B. L., D.J. Henry, and C.T. Foster, Jr. "Tourmaline-rich pseudomorphs after staurolite: Demarcation of an infiltration front", Am. Mineralogist, **84**,794-805, (1999).

12. Guyer, R. A. and K. R. McCall, "Superfluid avalanches", Journal of Low Temperature Physics, **111**, 841, (1998).

13. Guyer, R. A., K. R. McCall, K. Van Den Abeele, "Slow elastic dynamics in a resonant bar of rock", Geophys. Res. Lett., **25**, 1585 (1998).

14. Guyer, R. A., and P. A. Johnson, "The astonishing case of mesoscopic elastic nonlinearity", Physics Today, **52**, 30-35, (1999) [Invited].

15. Guyer, R. A., K. R. McCall, G. N. Boitnott, L. B. Hilbert, Jr., and T. J. Plona, "Quantitative implementation of Preisach-Mayergoyz space to find static and dynamic elastic moduli in rock", J. Geophys. Res., **102**, 5281-5293 (1997).

16. Guyer, R. A., P. A. Johnson, and J. N. TenCate, "Hysteresis and the Dynamic Elasticity of Consolidated Granular Materials", Phys Rev. Lett, **82**, 3280-3283, (1999).

17. Hearn, E., G. Humphreys, M. Chai, and J. M. Brown, "The effect of anisotropy on the development of oceanic asthenosphere", J. Geophys. Res., **102**, 11,943-11,956, (1997).

18. Holdaway, M., Mukhopadhyay, B., Dyar, M.D., Guidotti, C., and Dutrow, B., "Garnet-biotite geothermometry revisited: New Margules parameters and a natural specimen data base from Maine", Am. Mineralogist, **82**, 582-595, (1997).

19. Kadish, A., "On the Problem of Source Identification from Far-Field Observations in Hysteretic Materials", J. Acoust. Soc. Am., **103**, 3196-3202, (1998).

20. Kadish, A., "Static friction threshold effects on hysteresis and frequency spectra in rocks", J. Acoustical Society of America, **105**, 3097-107, (1999).

20. Lebensohn, R. A., H.-R. Wenk, and C. Tomé, "Modelling deformation and recrystallization textures in calcite", Acta Mater., **46**, 2683-2693, (1998).

21. Lutterotti, L., S. Matthies, H.-R. Wenk, A.J. Schultz, and J.W. Richardson, "Combined texture and structure analysis of deformed limestone from time-of-flight neutron diffraction spectra", J. Appl. Phys, **81**, 594-600, (1997).

22. Masuda, K., O. L. Anderson, and D. Erskine, "Differential laser interferometer apparatus for measuring the thermal expansivity of minerals at high temperatures", Bull. Geol. Surv. Japan, **48**, 257-261, (1997).

23. Matthies, S., L. Lutterotti, and H.-R. Wenk, "Advances in texture analysis from diffraction spectra", J. Appl. Cryst., **30**, 31-42 (1997).

25. Pasternak, M.P., G.Kh. Rozenberg, A.P. Milner, M. Amanowicz, T. Zhou, U. Schwarz, K. Syassen, R.D. Taylor, M. Hanfland, and K. Brister, "Pressure-Induced Concurrent Transformation to an Amorphous and Crystalline Phase in Berlinite-Type $FePO_4$", Phys. Rev. Letters, **79**, 4409 (1997).

26. Pasternak, M.P.; Taylor, R.D.; Jeanloz, R.; Li, X.; Nguyen, J.H.; McCammon, C.A., "High pressure collapse of magnetism in Fe{sub 0.94}O: Mossbauer spectroscopy beyond 100 Gpa', Phys.Rev.Letters,**79**,5046-9, (1997).

25. Pasternak, M.P. and R.D. Taylor, "Atomic-Scale Properties of Structure, Valence, and Magnetism in Pressure-Induced Amorphized Materials", Rev. High Pressure Sci. Technol. **7**, 362 (1998), [Invited].

27. Pasternak, M.P., G. Kh. Rozenberg, A.P. Milner, M. Amanowicz, K.E. Brister, and R.D. Taylor, "Pressure Induced Amorphization of Antiferromagnetic $FePO_4$-, J. Magnetism and Magnetic Materials, **183**, 185 (1998).

28. Pasternak, M.P., M. Amanowicz, A.P. Milner, G.Kh. Rozenberg , R.D Taylor, G.R. Hearne, and K.E. Brister, "High-Pressure p-p band Closure of the Negative-Δ Sr_2FeO_4 Perovskite", J. Magnetism and Magnetic Materials, **177**, 1377 (1998).

29. Pearson, A., F. Heidelbach, and H.-R. Wenk, "Texture analysis of quartz in a granite mylonite by EBSP-orientation imaging microscopy", Textures and Microstructures, **29**, 185-199, (1997).

30. Roberts, J.J.; Duba, A.G.; Mathez, E.A.; Shankland, T.J.; Kinzler, R., "Carbon-enhanced electrical conductivity during fracture of rocks", J. Geophys. Res., **104**, 737-47, (1999).

30. Rozenberg, G.Kh., M.P. Pasternak, A.P. Milner, M. Amanowicz, K. Syassen, K.E. Brister, M. Hanfland, and R.D. Taylor, "Pressure Induced Amorphization of Antiferromagnetic $FePO_4$ and $Fe(OH)_2$", Rev. High Pressure Sci. Technol . **7**, 356 (1998).

26. Shankland, T. J., A. G. Duba, E. A. Mathez, C. Peach, "Increase of Electrical Conductivity with Pressure as an Indicator of Conduction through a Solid Phase in Mid-Crustal Rocks", J. Geophys. Res., **102**, 14741-14750 (1997).

27. Schiferl, D.; Nicol, M.; Zaug, J.M.; Sharma, S.K.; Cooney, T.F.; Wang, S.-Y.; Anthony, T.R.; Fleischer, J.F., "The diamond {sup 13}C/{sup 12}C isotope Raman pressure sensor system for high-temperature/pressure diamond-anvil cells with reactive samples", J. Appl. Phys., **82**, 3256-65, (1997).

27. Topor, L., A. Navrotsky, Y. Zhao, & D.J. Weidner, "Thermochemistry of Fluoride Perovskites: Heat Capacity, Enthalpy of Formation, and Phase Transition of $NaMgF_3$", J. Solid State Chem., **132**, 131-138, (1997).

28. Takeshita, T, Wenk, H.-R., Lebensohn, R., "Development of preferred orientation and microstructure in sheared quartzite; comparison of natural data and simulated results", Tectonophysics , **312**,133-155, (1999).

28. Van Den Abeele, K. E.-A., P. A. Johnson, R. A. Guyer, and K. R. McCall, "On the quasi-analytic treatment of hysteretic nonlinear response in elastic wave propagation", J. Acoust. Soc. Am., **101**, 1885, (1997).

29. Van Den Abeele, K. E.A. J. Carmeliet, J. A. TenCate and P. A. Johnson "Single Mode Nonlinear Resonant Acoustic Spectroscopy (SIMONRAS) for damage detection in quasi-brittle materials." 2nd International conference "Emerging Technologies in NDT", Athens, May (1999).

31. Wenk, H.-R., G. Canova, and Y. Brechet, "A deformation-based model for recrystallization", Acta Mater., **45**, 3283-3296, (1997).

32. Wenk, H.-R., S. Matthies, J. Donovan and D. Chateigner, BEARTEX, " A Windows-based program system for quantitative texture analysis", J. Appl. Cryst., **31**, 262-269, (1998).

33. Wenk, H.-R., "A voyage through the deformed Earth with the self-consistent model", Modelling and Simulation in Materials Science and Engineering, **7**, 699-722 (1999).

34. Wenk, H.R, Tome, C.N., "Modeling dynamic recrystallization of olivine aggregates deformed in simple shear", J. Geophy. Res.,**104**, 25513-2, (1999).

33. Wiryana, S., L. J. Slutsky, and J. M. Brown, "The equation of state of water to 200° C and 3.5 Gpa: Model potentials and the experimental pressure scale", Earth Planet. Sci. Lett,. **163**, 123-130, (1998).

34. Zhao, Y., R. B. Von Dreele, J. Zhang, and D. J. Weidner, "Thermal Equation of State of Monoclinic Pyroxene: CaMgSi2O6 Diopside," Review of high Pressure Science & Technology, (special issue), **V6**, 181, (1997).

36. Zhao, Y.; Von Dreele, R.B.; Shankland, T.J.; Weidner, D.J.; Zhang, J.; Wang, Y.; Gasparik, T., " Thermoelastic equation of state of jadeite $NaAlSi_2O_6$: an energy-dispersive Reitveld refinement study of low symmetry and multiple phases
diffraction", Geophys.Res. Letts., **24**, 5-8, (1997).

Other Publications (unfunded by LDRD)

1. Kocks, U.F., C. Tomé and H.-R. Wenk, Texture and Anisotropy. Preferred Orientations in Polycrystals and Their Effect on Materials Properties. Cambridge University Press, Cambridge, (1998).

Ph. D. Thesis

1. Chai, Mu, Ph.D. Thesis, Physical properties of mantle silicates under upper mantle pressures, Univ. of Washington, December 1996.

References

[1] Bassett, W. A., T.-C. Wu, I-M. Chou, H. T. Haselton, Jr., J. Frantz, B. O.Mysen, W.-L. Huang, S. K. Sharma, and D. Schiferl, "The Hydrothermal Diamond Anvil Cell (HDAC) and Its Applications", The Geochemical Society, Special Publication #5, 1996, edited by M. D. Dyar, C. McCammon & M. W. Schaefer, pp. 261-272, (1996).

[2] Bennett, K., H.-R. Wenk, W.B. Durham, L.A. Stern and S.H. Kirby, "Preferred crystallographic orientation in the ice I—II transformation and the flow of ice II", Phil. Mag. A, **76**, 413-435, (1997).

[3] Blackman, D.K., J.-M. Kendall, P.R. Dawson, H.-R. Wenk, D. Boyce, and J.P. Morgan, "Teleseismic imaging of subaxial flow at mid-ocean ridges: travel-time effects of anisotropic mineral texture in the mantle", Geoph. J. Internat. **127**, 415-426, (1996).

[4] Chai, M., J. M. Brown, and L. J. Slutsky, "Thermal diffusivity of mantle minerals", Phys. Chem. Min., **23**, 470-475, (1996).

[5] Cyan, H., J. D. Carnes, and O. L. Anderson, "Thermal properties of forsterite, including C_V, calculated from αK_T through the entropy", J. Phys. Chem. Solids, **57**, 1593-1599, (1996).

[6] Field EH, Johnson PA, Beresnev IA, Zeng YH, "Nonlinear ground-motion amplification by sediments during the 1994 Northridge earthquake", Nature, **390**, 599-602, 1997.

[7] Ferrari, M., L. Lutterotti, S. Matthies, P. Polonioli, and H.-R. Wenk, "New opportunities in the texture and stress field by whole pattern analysis", Mater. Sci. Forum, **228-231**, 83-88, (1996).

[8] Hearne, G.R., M.P. Pasternak, and R.D. Taylor, "Selected Studies of Magnetism at High Pressure", International Conference on the Applications of the Mössbauer Effect-95, Il Nuovo Cimento, **18D**, 145, (1996).

[9] Hearne, G.R., M. P. Pasternak, G. Rozenberg, E. Milner, and R.D. Taylor, "Mössbauer Studies of Sr_2FeO_4 to Pressures of 20 Gpa", Il Nuovo Cimento Conference Proceedings, **50**, 541, (1996).

[10] Kadish, A., P. A. Johnson, and B. Zinszner, "Evaluating Hysteresis in Earth Materials Under Dynamic Resonance", J. Geophys. Res., **101**, 25,139, (1996).

[11] McCall, K. R., R. A. Guyer, L. Zhu, G. N. Boitnott, L. B. Hilbert, Jr., T. J. Plona, "Experimental determination of dynamic elastic properties of rock from quasistatic measurements", in Rock Mechanics: Tools and Techniques, eds. M. Aubertin, F. Hassani, and H. Mitri, 147, (1996).

[12] Karato S, Rubie D. C, "Toward an experimental study of deep mantle rheology: A new multianvil sample assembly for deformation studies under high pressures and temperatures", J. Geophs. Res., **109**, 20111-20122, (1997).

[13] McCall, K. R. and R. A. Guyer, "A new theoretical paradigm to describe hysteresis, discrete memory and nonlinear elastic wave propagation in rock", Nonlin. Proc. in Geophys., **3**, 89, (1996).

[14] Nicolas, A., Bouchez, J.L., Boudier, F. & Mercier, J.-C. , "Textures, structures and fabrics due to solid state flow in some european lherzolites", Tectonophysics, **12**, 55-86 (1971).

[15] Nicolas, A., and Christensen, N. I., " Formation of anisotropy in upper mantle peridotites; a review in: Composition, structure and dynamics of the lithosphere-asthenosphere system (eds. Fuchs, K.; Froidevaux, C.) Geodynamics, **16**,111-123, (1987).

[16] Ragan, D. D., D. R. Clarke and D. Schiferl, "Silicone Fluid as a High Pressure Medium in Diamond-Anvil Cells", Rev. Sci. Instrum., **67**, 494, (1996).

[17] Rozenberg, G.Kh., G.R. Hearne, M.P. Pasternak, P.A. Metcalf, and J.M. Honig, "The Nature of the Verwey Transition in Magnetite (Fe_3O_4) to Pressures of 16 Gpa", Phys. Rev., **B53**, 6482, (1996).

[18] Taylor, R.D., G.R. Hearne, and M.P. Pasternak, "Pressure-Induced Transformation in Molecular Crystals", Il Nuovo Cimento Conference Proceedings, **50**, 880, (1996).

[19] Wenk, H.-R., "A deformation-based model of dynamic recrystallization applied to quartz, in Tectonics and Metamorphism (The Hara Volume), . Soubun Co., Ltd., Tokyo, 280-286 (1996).

[20] Wenk, H.-R., D. Chateigner, M. Pernet, J. Bingert, E. Hellstrom, and B. Ouladdiaf, "Texture analysis of Bi-2212 and 2223 tapes and wires by neutron diffraction", Physica, **C272**, 1-12, (1996).
[21] Bennett, K. R. B. Von Dreele and H.-R. Wenk, "HIPPO, a new high intensity neutron diffractometer for characterization of bulk materials", Proceedings of the Twelfth International Conference on Textures of Materials, **1**, 129-134 (1999).

Figure Captions

Figure 1. The cell volumes V(P,T) of diopside vs temperature. Empty circles represent raw P-V-T data and filled solid symbols are the corrected cell volumes V(P,T) for corrected pressure P_c of 1.5, 3.0, 4.5, 6.0, and 7.5 GPa, respectively. Data points in between any two P_cs are corrected twice via compression and decompression.

Figure 2. Thermal expansion of diopside as a function of pressure. Slope of the fitted straight line represents the pressure derivative of thermal expansion $\Delta\alpha_V/\Delta P$. Width of the line shows the confidence interval and predicted error of the fit.

Fig 3. Evolution of thermal field for a sheet-like intrusion at 10 km depth. Intrusion is 2 km thick, intruded at a temperature of 875°C (red box) into homogeneous sediments with a permeability of 10^{-15} or 10^{-16}. Note the difference in the fluid flow fields and temperatures as a function of permeability differences.

Figure 4. Neutron Diffraction patterns showing Intensity versus d-spacing for an experimentally deformed α–β Mn2GeO4 olivine. Red marks represent diffraction peaks from the α-phase; blue marks represent those from the β-phase. Purple curve represents the difference curve between the calculated ideal pattern (green) and the measured data (red points). Neutrons have the advantages of 'seeing' coarse grains, bulk texture, and using Rietveld refinement, texture and structure of overlapping peaks can be analyzed.

Figure 5. (100), (010) and (001) pole figures in experimentally deformed α–β Mn2GeO4 olivine measured by neutron diffraction at Los Alamos Neutron Scattering Center (LANSCE). Equal area projection. Direction of stress in center. We measured 20% a phase and 80% b phase in the sample. The phase change from α–b Mn_2GeO_4 is a directional process. Those α grains with (010) orientations transform first. There is an orientation relationship between α-olivine a-axes and β phase b-axes.

Fig. 6. Mössbauer spectra of $Fe_{0.94}O$ measured at P ≥ 60 GPa at 300 K. The solid line is a least-square-fit to the experimental points assuming magnetic- and quadrupole-split components with varying intensities. The inset depicts the variation of the relative abundance of the non-magnetic (LS) component with pressure, a transition that is almost complete by 120 GPa.