

High-Temperature Phase Transition and Dissociation of (Mg,Fe)SiO₃ Perovskite at Lower Mantle Pressures

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To study the crystallography of Earth's lower mantle, techniques for measuring synchrotron x-ray diffraction from a laser-heated diamond anvil cell have been developed. Experiments on samples of (Mg,Fe)SiO₃ show that silicate perovskite maintains its orthorhombic symmetry at 38 gigapascals and 1850 kelvin. Measurements at 65 and 70 gigapascals provide evidence for a temperature-induced orthorhombic-to-cubic phase transition and dissociation to an assemblage of perovskite and mixed oxides. If these phase transitions occur in Earth, they will require a significant change in mineralogical models of the lower mantle.

Comparisons between seismological models and equation-of-state measurements on orthorhombic (Mg,Fe)SiO₃ perovskite have led to the conclusion that this compound is the predominant phase of the lower mantle and the most abundant mineral in Earth (1, 2). However, this result is largely untested under deep mantle conditions. Most of the elasticity measurements have been conducted near 300 K or outside the thermodynamic stability field of perovskite (3, 4). To address this problem, we carried out high-temperature x-ray diffraction measurements on minerals in a laser-heated diamond cell. We describe here the results for (Mg,Fe)SiO₃ perovskite synthesized from a natural enstatite. At lower mantle pressures, these data document a high-temperature phase transformation and dissociation to an assemblage of perovskite and mixed oxides.

We measured synchrotron energy-dispersive x-ray diffraction spectra during laser heating of diamond cell samples. Whereas the methods for laser heating (5, 6) and high-pressure x-ray diffraction (7) are well developed, it has not been possible to combine these techniques until the recent development of dedicated high-intensity synchrotron x-ray sources for high-pressure research. In these experiments, we focused a 120-W CO₂ laser spot 50 to 75 μ m in diameter onto a sample as it was illuminated with polychromatic synchrotron x-rays collimated to a beam of 15 to 20 μ m (at beamline X17C of the National Synchrotron Light Source) (8). The sample was viewed continuously through a video system, and the thermal radiation was focused onto a spectrograph with a silicon diode array for spectroradiometric temperature measurements. The composition of this sample (9) corresponds to Mg/(Mg + Fe) =

0.864 on an atomic basis, and it is comparable to the composition of earlier models of lower mantle chemistry [that is, it is enriched in iron and silicon relative to the upper mantle (1, 2)]. We measured the x-ray diffraction from the sample before, during, and after multiple cycles of laser heating.

These experiments are at the technical limits for the simultaneous control of high-temperature CO₂ laser heating and high-precision synchrotron powder x-ray diffraction. Although the experiments offer an opportunity to examine crystal structures under lower mantle conditions, there are limitations to the quantitative interpretation of the data. Specifically, quantitative measurement of thermal expansion is limited by changes in sample pressure associated with the high-temperature conditions. Indeed, we observed large variability in the apparent thermal expansion between different samples during laser heating. This phenomenon also prohibited quantitative measurements of the volume change (ΔV) across phase transitions, although the sign of these measurements (positive or negative) appears to be correct.

We carried out successful diffraction experiments at 38 (± 2), 64 (± 3), and 70 (± 3) GPa (10). At each pressure, we examined a separate crystal loaded in a new sample assembly. The pressures were determined from room temperature volume measurements in NaCl and perovskite. The accuracy is limited by stress gradients across the sample, secular changes in pressure due to laser heating, and uncertainties in the equations of state of NaCl (11) and perovskite (3). We measured spectroradiometric temperatures only at 38 GPa. Equipment failures during the synchrotron runs precluded measurements at 64 and 70 GPa. Consequently, these data place only weak constraints on the thermoelastic properties of perovskite at high temperatures.

Room temperature x-ray diffraction measurements show that all of the samples are fully transformed to orthorhombic perov-

skite after the initial laser heating. The x-ray diffraction pattern for orthorhombic silicate perovskite consists of groups of lines that are split in response to the distortion away from the ideal cubic perovskite structure (12). The triplet of 020, 112, and 200 lines is the strongest and most informative because it constrains the unit cell volume and the magnitude of the orthorhombic distortion. For a cubic perovskite, these lines collapse to a single diffraction peak that is indexed to the 110 line of the high-symmetry phase.

In the experiment at 38 GPa, we measured the average spectroradiometric temperature across the region exposed to x-rays as 1850 (± 200) K (Fig. 1). Over the heating cycle there was an increase in the relative intensity of the 020 line, presumably due to recrystallization of the sample at high temperatures. Overall, there was little change in the splitting of the peaks during or after the laser heating, an indication that perovskite maintained its orthorhombic symmetry throughout this experiment. [Similar results have been obtained from x-ray diffraction measurements on MgSiO₃ composition under comparable pressures and temperatures (13).] The pressure and temperature for this run were lower than the estimated geotherm at the corresponding depth in the lower mantle (greater than 2100 K at 900 km) (14).

At 64 GPa, we observed a reversible transition in the diffraction pattern between the triplet of 020, 112, and 200 lines at room temperature and a single diffraction peak at

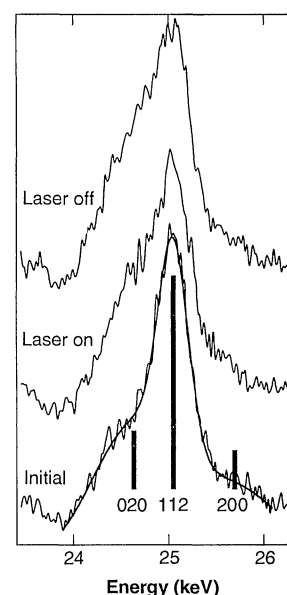


Fig. 1. Details of the diffraction spectra near the 020, 112, 200 triplet collected before, during, and after laser heating of perovskite at 38 (± 2) GPa. The positions of the individual peaks and the least squares fit to the data are indicated on the initial spectrum at ambient conditions. The average spectroradiometric temperature measured across the laser-heated spot was 1850 $\pm$ 200 K. The total duration of the laser heating was 10 min.

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high temperatures over the cycle of laser heating (Fig. 2, A through C). In this sample, the diffraction lines shifted to lower energies, indicating larger volumes under high temperatures. Analysis of such data for this particular sample shows that the mineral expanded along the *a* and *c* directions more than along *b* and that there was a small decrease in the orthorhombic distortion (that is, $c/a \rightarrow \sqrt{2}$ and $a/b \rightarrow 1$). These data are consistent with earlier thermal expansion studies at lower pressures and temperatures (3, 13).

For the run at 64 GPa, simultaneous diffraction from the surrounding NaCl showed a continuous increase in the thermal strain after the laser was turned on. The observation of thermal dilation in NaCl confirmed that we were measuring diffraction from the laser-heated portion of the sample. The time scale for the dilation depended on the relative positioning of the laser and the x-ray beam and fluctuations in the power and mode structure of the laser. After 5 min of laser heating, the strain in the NaCl approached a maximum and the individual peaks of the 020, 112, 200 triplet in the orthorhombic perovskite were no longer distinguishable. To characterize the subsequent diffraction spectra, we fit the remaining perovskite line to a single Gaussian peak (Fig. 2B). Initially, this peak was quite broad; however, it sharpened considerably with time. At its minimum, the width was comparable to the diffraction peaks from the adjacent NaCl [0.33 (perovskite) versus 0.32 (NaCl) keV]. The resolution of our spectra under these conditions (in energy and intensity) clearly shows that the single peak is not derived from broadening of the 020, 112, and 200 lines due to fluctuations or gradients in

pressure or temperature.

When the laser was turned off, the thermal strain in the NaCl reversed. Within 1 min of quenching, broadening of the perovskite peak indicated a distortion of the crystal structure. After 3 min, the breadth of the line was consistent with two closely spaced diffraction lines. At 8 min, the 020, 112, 200 triplet can be identified. Once the single diffraction peak formed at high temperatures, all of the lines corresponding to the orthorhombic structure (for example, splitting of the 202 and 022 lines and the 220 and 004 lines) and the tilting of the SiO_6 octahedra (for example, the 132 and 312 lines) disappeared. On cooling, these lines reappeared along with the 020, 112, 200 triplet. We observed this reversible transition reproducibly in four heating and cooling cycles at this pressure. Observations of the diffracted linewidths and intensities suggest that all of the runs at this pressure were carried out well below the solidus temperature for perovskite.

To reproduce the observations at 64 GPa, we carried out an experiment on a separate crystal in a new sample assembly at 70 GPa. In this run, we also observed the formation of a single diffraction line near the 020, 112, 200 triplet (Fig. 3A). Accompanying this transition was a loss of the 122 and 113 lines that originate from the octahedral tilting in the orthorhombic structure (12). In the high-temperature structure the remaining diffraction occurs at an interatomic spacing $d = 2.295 \pm 0.001$ and 1.623 ± 0.001 Å. These two lines differ by a factor of $\sqrt{2}$, indicating that they can be indexed as the 110 and 200 lines of the cubic perovskite structure. When the sample cooled, the 020, 112, 200 triplet was once again

observed in the spectra along with the 122 and 113 lines. We reproduced these observations five times at this pressure.

The results at 64 and 70 GPa are consistent with an increase in symmetry associated with a temperature-induced phase transition to a cubic-structure perovskite. Similar phase transformations are common in a wide range of perovskite-structured materials. Studies of such transitions at elevated pressures and shear stresses have often showed broad hysteresis and a wide interval of temperature or pressure for the phase transformation (15, 16). Such behavior is qualitatively consistent with our observations (Fig. 2). In our experiments, we infer that the 020, 112, 200 triplet merged with the 110 line of the cubic structure and that the ΔV of the transition was negative. Our observations cannot be the result of texturing or recrystallization because such processes are not reversible with changes in temperatures. Similarly, the merging of the triplet cannot be accounted for by anisotropic thermal expansion because of the time scales for recovering the orthorhombic phase on quenching the laser.

After the sample had been heated at 70 GPa for more than 1 hour, new diffraction lines formed at the expense of the perov-

Fig. 2. Time-resolved x-ray diffraction spectra for silicate perovskite during laser heating in the diamond cell at 64 (± 3) GPa. (A) Diffraction spectra near the 020, 112, 200 triplet accumulated over 1-min intervals. All spectra are normalized to the same relative intensity. The numbers indicate the time in minutes since the start of laser heating, and they are equivalent to the time scale of (B) and (C). The laser was turned off between spectra 8 and 9. (B) Full width at half maximum for Gaussian fits to the single diffraction peak in the perovskite spectrum in (A). (C) Volume strain in the surrounding NaCl ($\Delta V/V$) referenced to the volume at time $t = 0$.

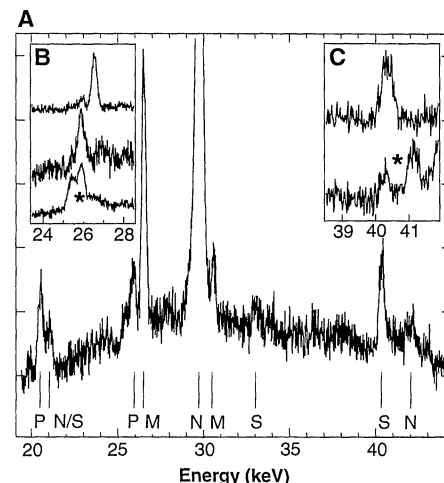
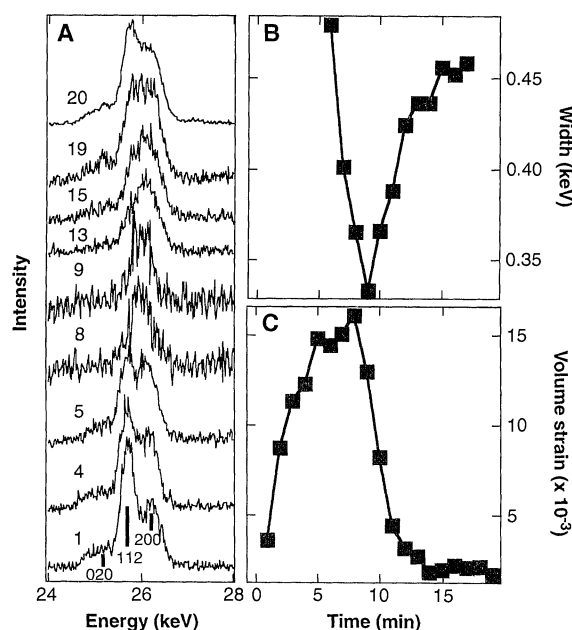


Fig. 3. (A) X-ray diffraction spectra during laser heating of the sample at 70 (± 3) GPa accumulated for 10 min. Under high-temperature conditions, diffraction lines corresponding to (Mg,Fe)O (M) and SiO_2 stishovite (S) are formed at the expense of perovskite (P). Under laser-heating conditions, the volumes of the phases are 8.83 cm^3/mol [(Mg,Fe)O], 12.47 cm^3/mol (SiO_2), and 20.73 cm^3/mol (perovskite). Lines corresponding to NaCl are shown as N. (B) Changes in the region of the 020, 112, 200 triplet. Room temperature conditions are indicated by a *. The overlying spectra during laser heating show the evolution to a single diffraction line (indexed as the 110 line of the cubic phase) (middle) and then to a combination of lines from (Mg,Fe)O and cubic perovskite (top). (C) (top) The 211 line of stishovite during laser heating splits on cooling to room temperature (*, bottom).

skite spectra (Fig. 3, B and C). The new peaks were sharp; often their widths were below the resolution limit of our Ge detector (~ 0.22 keV full width at half maximum). Such conditions are characteristic of reduced shear stresses (due to low sample strengths), and they suggest that the sample temperatures are higher than that associated with the orthorhombic-to-cubic transformation. The new peaks can be indexed as a mixture of (Mg,Fe)O (magnesiowüstite) and rutile-structured SiO_2 (stishovite). That is, our sample appears to have dissociated to mixed oxides and perovskite after prolonged laser heating at high temperatures. Although we cannot rule out the possibility of small amounts of partial melting during the formation of magnesiowüstite and stishovite, large-scale melting seems unlikely because of the strong intensity of the diffraction lines. The oxide lines remained after the sample was quenched, an indication that the transition is irreversible over the time scales of cooling in these experiments. Close inspection of the 211 line of stishovite shows a splitting on cooling, however (Fig. 3C). This distortion is consistent with the formation of the CaCl_2 phase at room temperature, as observed in diffraction and spectroscopic experiments at comparable pressures (17).

In general, our results are consistent with earlier diamond cell studies showing orthorhombic silicate perovskite as the primary phase in quench experiments after moderate laser heating at pressure ≥ 25 GPa for samples with comparable iron contents (1). Our data indicate that cubic silicate perovskite could have been synthesized in earlier experiments, but it would not have been observed because of the reversibility on quenching to room temperature conditions. Our results are in contrast with conclusions of recent LAPW (18) and pseudopotential (19) calculations for MgSiO_3 compositions that orthorhombic perovskite (*Pbnm*) is thermodynamically favored over cubic and tetragonal structures for the entire pressure range of the lower mantle. In both of these studies, the free energy of the perovskite structure is particularly sensitive to the rotations of the SiO_6 octahedra. We infer that the substitution and site occupancy of iron in perovskite may alter the energetics of these distortions and thereby stabilize the high-symmetry phase. Because these reactions appear to involve a finite change in volume, they would require a significant change in compositional models of the lower mantle if they are geologically possible within Earth.

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8. For each synchrotron run, we compressed a single crystal of a natural bronzite in a NaCl medium in a diamond anvil cell. The NaCl served as an infrared window for the CO_2 laser and as a thermal insulator between the sample and the diamond anvil. The crystals were polished to a thickness of ~ 7 μm to minimize the vertical temperature gradients. Micropositioning motors allowed alignment of the x-ray beam with a spatial resolution of ± 1 μm within the sample [J. Hu, H. K. Mao, J. F. Shu, R. J. Hemley, in *High Pressure Science and Technology*, S. C. Schmidt, Ed. (American Institute of Physics, Washington, DC, 1994), pp. 441–444]. Because the CO_2 laser is able to heat the entire crystal and we visually observed the sample throughout the experiment, we were assured that x-ray diffraction was obtained from the laser-heated region. All diffraction measurements were carried out at the smallest scattering angle (2θ) that was feasible for our optical system (12°) to allow maximum dispersion in energy of the diffraction spectra. For the spectroradiometric measurements, the laser-heated spot was imaged through an aperture onto the spectrograph. We determined the temperatures by fitting the blackbody spectra to Wien's law [D. Heinz and R. Jeanloz, in *High Pressure Research in Mineral Physics*, M. H. Manghnani and Y. Syono, Eds. (Terra Scientific, Tokyo, and American Geophysical Union, Washington, DC, 1987), pp. 113–127]. Because we imaged the entire laser-heated region, we determined an average temperature over the heated portion of the sample.
9. Electron microprobe analysis shows that the composition of our sample by mole fraction is SiO_2 , 49.65%; MgO , 40.67%; FeO , 6.39%; CaO , 1.73%; and Al_2O_3 , 1.54%.
10. The pressures and their uncertainties are derived from room-temperature volume measurements across the sample. Elastic models of samples in the laser-heated diamond cell indicate that the thermal pressure for perovskite at temperatures above 1300 K may be 3 to 5 GPa [D. L. Heinz, *Geophys. Res. Lett.* **17**, 1161 (1990)].
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20. We thank D. George for help with the electron microprobe analysis. We have enjoyed helpful discussions with and comments from R. Cohen, T. Duffy, L. W. Finger, R. Jeanloz, C. T. Prewitt, M. Walter, and T. Yagi. This work was supported by NSF and the Carnegie Institution of Washington.

17 February 1995; accepted 17 April 1995

ILR1, an Amidohydrolase That Releases Active Indole-3-Acetic Acid from Conjugates

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In plants, the growth regulator indole-3-acetic acid (IAA) is found both free and conjugated to a variety of amino acids, peptides, and carbohydrates. IAA conjugated to leucine has effects in *Arabidopsis thaliana* similar to those of free IAA. The *ilr1* mutant is insensitive to exogenous IAA-Leu and was used to positionally clone the *Arabidopsis ILR1* gene. *ILR1* encodes a 48-kilodalton protein that cleaves IAA-amino acid conjugates in vitro and is homologous to bacterial amidohydrolase enzymes. DNA sequences similar to that of *ILR1* are found in other plant species.

IAA, the most widespread and abundant auxin, is a signaling molecule that modulates division and elongation of plant cells. IAA regulates developmental events including embryo symmetry establishment (1), root initiation, and apical dominance, as well as environmental responses such as gravitropism and phototropism (2). Most IAA in plants is found conjugated through its carboxyl group to a variety of amino acids, peptides, and carbohydrates (3). These con-

jugates represent $\sim 95\%$ of the IAA pool, and they are postulated to inactivate excess IAA, allow rapid alteration of free IAA concentration, and transport IAA through the plant (3). Although conjugation and deconjugation are likely control mechanisms in the modulation of free IAA concentrations during development and growth, the enzymes involved in these processes are only beginning to be characterized. The maize *iaglu* gene, which encodes an enzyme that esterifies IAA to glucose, has recently been cloned (4), and enzymes that hydrolyze IAA-glucose (5) or IAA-Ala have been partially purified (6). To determine the role of IAA conjugates in vivo, we isolated *Arabidopsis* mutants with defects in deconjugation.

More than 80% of the IAA pool in *Arabidopsis* is in an amide-linked form (7), but

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