Stability of MgSiO₃ Perovskite in the Lower Mantle

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As it is expected to be the dominant phase in the lower mantle, any pressure-induced phase changes in MgSiO₃ could require significant modifications in current models of the dynamics and structures of Earth's deep mantle. Studies to date have yielded discrepant results regarding the high-pressure stability of MgSiO₃ perovskite. Understanding the source of discrepancy is essential, both to resolving the stability of perovskite and to developing more reliable techniques for understanding the Earth's deep interior. In this report, we give an overview of previous studies on the stability of MgSiO₃ perovskite and recent observations on the post-perovskite transition. We also summarize our measurements on MgSiO₃ perovskite to core–mantle boundary pressure–temperature (P–T) conditions using in-situ X-ray diffraction. Major peaks in our diffraction patterns are best explained by those of MgSiO₃ perovskite at 1200–2500-km depth conditions. No evidence of dissociation to MgO + SiO₂ and a transition to a cubic perovskite structure has been found to core–mantle boundary P–T conditions. We have also observed a new peak at 2.62–2.57 Å at 88–145 GPa, the existence of which may be relevant to a modification in perovskite crystal structure. However, the possibility that this peak may be from a chemical reaction among gasket, anvil materials, and sample cannot be ruled out. More significant changes are observed during heating above 2500 K at 135–145 GPa: appearance of new peaks, splitting of a peak, and intensity changes of some diffraction peaks. The recently proposed post-perovskite phase explains dominant new diffraction features. Based on the results available as of May 2005, the post-perovskite transition appears to be relevant to the D″ seismic discontinuity. Furthermore, depth of the post-perovskite transition may be very sensitive to variations in chemical composition as well as temperature.

1. INTRODUCTION

The paucity of the samples directly originating from the lower mantle and instability of most lower-mantle phases at ambient conditions make laboratory measurements at high pressures (P) and high temperatures (T), along with first-principles calculations, important means to understanding the properties of the Earth's deep mantle. The pioneering work of Liu [1975] and Liu and Ringwood [1975] revealed that the major elements of the mantle, i.e., O, Si, Mg, Fe, and Ca, are hosted in perovskite-type structures at lower-mantle P–T conditions. In recent years, lines of evidence have been reported for their possible natural occurrences in meteorites [Tomioka and Fujino, 1997; Langenhorst and Poirier, 2000; Tomioka and Kimura, 2003] and xenoliths [Collerson et al., 2000].

As a dominant mineral in the lower mantle, the phase relations and physical properties of magnesium silicate (MgSiO₃) perovskite have been of prime interest for understanding
seismically observed structures and computationally predicted dynamics of the Earth's interior: Possible crystal structure changes in mantle minerals could play roles as seismic interfaces or flow regulators in the mantle, as is the case for the post-spinel boundary between the upper and lower mantle [Ito and Takahashi, 1989; Ito et al., 1990; Tackley et al., 1993; van der Hilst et al., 1997; Chudinovskikh and Boehler, 2001; Fukao et al., 2001; Shim et al., 2001a; Lebedev et al., 2002; Fei et al., 2004b]. However, experimental and theoretical results of the past decade have yielded discrepant findings regarding the stability of MgSiO$_3$ perovskite [Knittle and Jeanloz, 1987; Meade et al., 1995; Saxena et al., 1996, 1998; Mao et al., 1997; Serghiou et al., 1998; Fiquet et al., 2000; Andraut1, 2001; Shim et al., 2001b, 2004]. Furthermore, a significant change in the crystal structure of (Mg,Fe)SiO$_3$ has been recently reported by several groups [Murakami et al., 2004, 2005; Shim et al., 2004; Oganov and Ono, 2004; Itaka et al., 2004; Mao et al., 2004; Tsuchiya et al., 2004a, b].

The phase relations for silicate perovskites are important issues to be resolved, owing to recent inferences about deep-mantle structures [e.g., Lay et al., 1998; Gurnis et al., 1998; Sidorin et al., 1999; Kellogg et al., 1999; van der Hilst and Kára, 1999; Albarède and van der Hilst, 1999; Trampert et al., 2004], and to the expected enhancement in resolution of seismic tomography for the lower mantle by the deployment of dense seismic arrays, e.g., USArray, J-array, and GEOSCOPE [Levander et al., 1999; Fischer and van der Hilst, 1999]. In fact, developments in experimental techniques in the last decade [Shen et al., 2001; Andraut and Fiquet, 2001; Yogi et al., 2001; Watanuki et al., 2001] enable experimentalists to study directly the phase relations at in-situ deep-mantle P–T conditions [e.g., Fiquet et al., 1998, 2000; Dewaele et al., 2000; Shim et al., 2000, 2001b, 2004; Murakami et al., 2003, 2004; Oganov and Ono, 2004; Mao et al., 2004; Shieh et al., 2005].

In this paper, we review recent experimental results for the stability and crystal structure of MgSiO$_3$ at mid- to lowermost mantle P–T conditions. Important issues in experimental technique at this extreme P–T condition are briefly introduced in order to discuss possible sources of discrepancy in the stability of MgSiO$_3$. A summary of our results [refer to Shim et al., 2001b, 2004, for details] is presented in order to demonstrate experimental data used to examine the stability and crystal structure of MgSiO$_3$. We also consider potential implications of the observed changes in MgSiO$_3$ for the structure and dynamics of the lowermost mantle.

2. A BRIEF REVIEW

This section is not intended to provide a detailed technical review of all data bearing on the controversial issue of the stability of MgSiO$_3$ perovskite. Instead, we limit ourselves to a few important experimental issues for a general audience. Detailed technical reviews are available in the literature [e.g., Dubrovinsky et al., 1999; Serghiou et al., 1999; Boehler, 2000]. Knowledge about the post-perovskite transition is quickly growing at this moment. This summary for the post-perovskite transition is based on the results published in the literature as of May 2005.

2.1. Experimental Results

The data reported for pure MgSiO$_3$ so far in the literature are summarized in Figure 1. To facilitate the discussion, synthetic X-ray diffraction patterns of MgSiO$_3$ with different perovskite crystal structures are shown in Figure 2 (the method used to produce the synthetic diffraction patterns is presented in Appendix 1).

The first data relevant to the stability of (Mg,Fe)SiO$_3$ perovskite at deep-mantle pressures were reported by Knittle and Jeanloz [1987]. They observed the synthesis of (Mg,Fe)SiO$_3$ perovskite from enstatite starting materials to 127 GPa by performing X-ray diffraction measurements for temperature-quenched samples. The first in-situ study for (Mg,Fe)SiO$_3$ perovskite was carried out by Meade et al. [1995] (Figure 1a). They interpreted a decrease in peak width of the triplet (compare Pv3 in Figures 2a and b) during heating at 65 GPa as evidence of the phase transition from an orthorhombic (Pbnm space group) to a cubic structure in (Mg,Fe)SiO$_3$ perovskite. However, the method they used, energy-dispersive diffraction, does not provide sufficient resolution to resolve splitting of the triplet: Its disappearance could result from preferred orientation, in which diffraction peaks are observable only in certain directions for one-dimensional detectors, e.g., the solid-state detector. Later studies using two-dimensional detectors, which enable the recording of full diffraction rings, showed that the triplet splitting is still resolvable in this pressure range [e.g., Fiquet et al., 2000]. Meade et al. [1995] also reported that (Mg,Fe)SiO$_3$ perovskite dissociates to (Mg,Fe)O + SiO$_2$ after heating for 1 h at 70 GPa.

On the basis of X-ray diffraction of heated products of two different crystalline starting materials (i.e., forsterite and enstatite) at high pressure, Saxena et al. [1996] reported that Mg end-member silicate perovskite (MgSiO$_3$) dissociates to MgO + SiO$_2$ at the similar conditions (Figure 1a). They claimed that longer heating (72 h) was required to observe the dissociation at 80 GPa and 1250 K, which is lower than the temperature normally reached in laser heating (>1500 K).

In contrast, Mao et al. [1997] confirmed the stability of MgSiO$_3$ perovskite to 85 GPa and 2000 K, using the energy-dispersive diffraction technique. They proposed that the
Figure 1. Pressure and temperature conditions for the data points reported for pure MgSiO$_3$: (a) previous measurements [Meade et al., 1995; Saxena et al., 1996, 1998; Fiquet et al., 1998, 2000; Serghiou et al., 1998; Murakami et al., 2004] and (b) our measurements [Shim et al., 2001b, 2004]. A representative error bar of our data is shown for pressure and temperature. A geotherm is obtained from Brown and Shankland [1981]. Different symbols in (a) represent data from different studies and different phases observed during or after heating. Different symbols in (b) represent different starting materials and phases observed during and after heating [Pv: perovskite, CPv: cubic perovskite, Oxs: MgO + SiO$_2$, PPv: post-perovskite, En: (Mg$_{0.5}$Fe$_{0.5}$)SiO$_3$ enstatite, Gl: MgSiO$_3$ glass].

 earlier observation of dissociation by Meade et al. [1995] may be due to incongruent melting or diffusion of MgSiO$_3$ perovskite in large thermal gradients.

Serghiou et al. [1998] published Raman spectra measured at 300 K and high pressure for heated products of MgSiO$_3$ glass, periclase (MgO) + quartz (SiO$_2$) mixtures, and MgSiO$_3$ enstatite. They confirmed the stability of MgSiO$_3$ perovskite to 100 GPa and 3000 K. They proposed that the possible existence of steep thermal and pressure gradients in the earlier experiments by Meade et al. [1995] and Saxena et al. [1996] might result in the dissociation of MgSiO$_3$ perovskite. In contrast, Dubrovinsky et al. [1999] argued that the glass and periclase + quartz mixture starting materials could lead to the synthesis of a metastable phase. They also claimed that pressure during heating could be significantly lower than the pressure measured after heating. Later, in-situ angle-dispersive X-ray diffraction patterns of MgSiO$_3$ perovskite were reported by Fiquet et al. [2000] to 90 GPa and 2000 K, and post-heating diffraction patterns of (Mg,Fe)SiO$_3$ (Fe $\leq$ 18 mol%) to 120 GPa and 2300 K were reported by Andrault [2001]. Both studies confirmed the stability of (Mg,Fe)SiO$_3$ perovskite within their $P-T$ range.

In the recent in-situ X-ray measurements by Murakami et al. [2004], the pressure and temperature range has been extended to 134 GPa and 2600 K for pure MgSiO$_3$. The stability of MgSiO$_3$ perovskite was confirmed to 113 GPa and 2300 K. Above 126 GPa, they observed significant changes in diffraction patterns. To explain the observed changes, they proposed a phase transition in MgSiO$_3$ to a new phase with the CaIrO$_3$-type (Cmcm) structure at the base of the lower mantle. This result is confirmed in measurements carried out by two different groups [Shim et al., 2004; Oganov and Ono, 2004].

2.2. Important Technical Issues

The key technical issues in this controversy include thermal gradients in the laser-heated diamond-cell samples, stress conditions of the samples, pressure determinations, transformation kinetics, and the possibility of incongruent...
melting. Pressure variations in the diamond-anvil cell during laser heating is affected by several factors [Andrault et al., 1998], including thermal pressure [Heinz, 1990] and thermal relaxation of the cell [Kavner and Duffy, 2001]. Whereas the thermal pressure increases total pressure, the thermal relaxation of the cell results in a pressure decrease.

Thus, the pressure change in the diamond cell is difficult to predict and this makes in-situ pressure measurement essential at high $P-T$. In fact, Dubrovinsky et al. [1999] argued that pressure during heating can be lower than what is measured after heating in Serghiou et al. [1998]'s experiments and thus their measurement conditions are not high enough to

Figure 2. Calculated diffraction patterns of MgSiO$_3$ perovskite at 100 GPa and 300 K. (a) Cubic ($Pm\bar{3}m$) structure. (b) Orthorhombic ($Pbnm$) structure, which is a stable structure to at least 1800-km depth conditions, and (c) orthorhombic structure ($Pbnm$) without shift of Mg atom positions at the dodecahedral site centers. (d) Monoclinic ($P2_1/m$), (e) orthorhombic ($Pmmn$), and (f) tetragonal ($P4_{2}mnc$) structures, which are proposed to explain the new peak (New1) observed above 88 GPa (indicated by heavy arrows). The box in (b) and (c) highlights the intensity changes induced by the position shift of Mg atoms. Expected peak positions are shown as bars below the diffraction patterns for individual structures. "Pv1", "Pv2", "Pv3", and "Pv4" indicate a doublet (002+110), a singlet (111), a triplet (020+112+200), and a doublet (103+211), respectively—diagnostic diffraction features of perovskite. These notations are used throughout this paper. The calculation method is described in Appendix 1.
observe the dissociation. While in the earlier experiments pressure was determined after heating [Saxena et al., 1996; Serghiou et al., 1998], more recent in-situ X-ray diffraction measurements [Fiquet et al., 2000; Shim et al., 2001b, 2004; Murakami et al., 2004] determine pressure during heating by using the equation of state for platinum [Holmes et al., 1989], which was heated and compressed together with samples, at in-situ conditions.

One of the critical issues has been the stability of heating. Two different techniques have been used in previous studies: laser and resistance heating. Laser heating can generate temperatures directly relevant to the lower mantle (2000–4000 K). However, due to the limited size of laser beams, only a portion of the sample can be heated (typically 20–40 μm in diameter). This can introduce very steep thermal gradients radially in the sample. The other problem is the thermal gradients along the loading axes of the diamond-anvil cells due to the high thermal conductivity of diamond anvils. Several techniques have been developed to decrease the thermal gradients: Insulation materials, e.g., inert noble gases, can be loaded to separate the samples from diamond anvils (Figure 3). By directing laser beams on both sides of the sample, temperature gradients along the loading axis can be reduced [Shen et al., 2001] (Figure 3). Temporal fluctuation of temperature in the samples can also be a source of the instability (Figure 4c).

Better temperature homogeneity is generally assumed for the resistance heating. In this technique, micro-heaters are placed near the sample chamber of the diamond-anvil cell. More precise temperature measurements are expected since thermocouples can be attached near the sample chamber. A major limitation of this technique is that temperatures are limited to 1200 K, which is much lower than those in the mantle. Also at this lower temperature, kinetics becomes important during phase transitions. It has been also suggested that high heat conduction through the diamond anvils can induce an extreme thermal gradient along the loading axis of the diamond-anvil cell in some type of resistance heating [see Serghiou et al., 1999; Dubrovinskaia and Dubrovinsky, 2003, for a detailed discussion].

Figure 3. Experimental setup for the double-sided laser-heated diamond-anvil cell with synchrotron X-ray diffraction.
Radial and Axial Thermal Gradients

<table>
<thead>
<tr>
<th>Rad</th>
<th>Weight</th>
<th>T1(K)</th>
<th>T2(K)</th>
</tr>
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<tbody>
<tr>
<td>-4.219</td>
<td>0.121</td>
<td>1981(12)</td>
<td>2033(9)</td>
</tr>
<tr>
<td>-2.531</td>
<td>0.267</td>
<td>2102(11)</td>
<td>2159(9)</td>
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<tr>
<td>-0.844</td>
<td>0.112</td>
<td>2151(10)</td>
<td>2243(9)</td>
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<tr>
<td>0.844</td>
<td>0.112</td>
<td>2139(10)</td>
<td>2239(9)</td>
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<tr>
<td>2.531</td>
<td>0.267</td>
<td>2122(10)</td>
<td>2215(10)</td>
</tr>
<tr>
<td>4.219</td>
<td>0.121</td>
<td>2092(10)</td>
<td>2195(11)</td>
</tr>
</tbody>
</table>

**Averages**

- Min-Max: 2066(85) to 2138(105)
- Simple: 2098(61) to 2180(79)
- Weighted: 2101(48) to 2182(63)

**Overall Averages**

- Max-Min: 2112(131)
- Simple: 2140(80)
- Weighted: 2141(69)

Figure 4. Temperature measurements at 100 ± 8 GPa and 2204 ± 78 K. (a) Schematic view of the heated spot (cylindrical symmetry is assumed), and radial thermal gradients for both sides of the sample (T1 and T2). A table is also shown, presenting temperatures measured along the solid line. The numbers in parentheses are 1σ uncertainties. The X-ray-probed area is indicated with a rectangle. Different areas represented by different temperature measurements are shown in different shades of gray. The numbers on those areas indicate the area fractions in the X-ray-probed region. (b) Fitting of a measured thermal radiation spectrum (thin line) to gray-body radiation (thick curve). (c) Temporal fluctuation of temperature during a diffraction pattern measurement. A temporal average and its uncertainty are shown by a gray area (refer to Appendix 3 for details).
There have been some reports that the thermal gradients can in fact result in element partitioning between the hot and cold spots of the samples [e.g., Fei et al., 1996; Andrault and Fiquet, 2001]. Furthermore, Kesson et al. [1995] reported that (Mg,Fe,Al)(Si,Al)O₃ perovskite melts incongruently to SiO₂ and oxides in unevenly hot regions during laser heating. More technical development is warranted to ensure the stability and homogeneity of heating at lower-mantle P-T conditions. Use of the insulation media and larger homogeneous laser modes are among the methods that have been implemented.

Formation of a metastable phase has been observed in some high P-T measurements. For example, metastable (Ca,Mg)SiO₃ perovskite has been synthesized by heating glass starting material below 1300 K [Kim et al., 1994]. Later, Irifune et al. [2000] found that (Ca,Mg)SiO₃ perovskite transforms to a stable phase assemblage (CaSiO₃ and MgSiO₃ perovskites) at sufficiently high temperature (>1500 K). A similar observation has also been made in (Ca,Mg,Fe,Al)SiO₃ [Asahara et al., 2005]. Thus, it is very important to carry out measurements for different starting materials, such as glass, crystalline, and oxide component mixtures, and to heat samples to sufficiently high temperatures. Serghiou et al. [1998] confirmed the stability of MgSiO₃ perovskite by conducting experiments of different types of starting materials. A remaining issue is whether using quartz for the MgO + SiO₂ mixture starting materials is appropriate [Serghiou et al., 1998]. Dubrovinsky et al. [1999] argued that the use of a low-pressure polymorph of SiO₂, i.e., quartz, as a starting material could result in a synthesis of a metastable phase at high P-T where quartz is unstable.

Saxena et al. [1998] reported that longer heating is required to observe the dissociation. However, this was at lower temperature (1200 K), where kinetics may also play an important role and insufficient heating can cause synthesis of a metastable phase [Irifune et al., 2000]. Furthermore, in their earlier experiment, Saxena et al. [1996] reported that they were able to observe the dissociation below 1500 K even with 10–15 min of laser heating above 83 GPa. This heating duration is similar or even less than those in other laser-heating studies [Serghiou et al., 1998; Fiquet et al., 2000; Shim et al., 2001b, 2004; Murakami et al., 2004]. Thus, it is unlikely that heating duration is the major factor to cause the discrepancy.

3. EXPERIMENTAL OBSERVATIONS

In this section, we summarize our observations (some of these results are published in Shim et al. [2001b, 2004]). We used three different starting materials: (Mg₀.₉,Fe₀.₀⁹)SiO₃ enstatite, MgSiO₃ glass, and an equimolar MgO + SiO₂ mixture. The composition of the glass is very close to MgSiO₃ with a slight enrichment of Si (Table 1).

### Table 1. Chemical Compositions of the Starting Materials, Expressed as the Molar Cation Fractions for a Formula Based on 3 Oxygens.

<table>
<thead>
<tr>
<th></th>
<th>Enstatite⁷</th>
<th>Glass⁹</th>
</tr>
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<tbody>
<tr>
<td>Mg</td>
<td>0.91</td>
<td>0.98</td>
</tr>
<tr>
<td>Fe</td>
<td>0.09</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Si</td>
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<td>1.01</td>
</tr>
<tr>
<td>Na</td>
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<td></td>
</tr>
<tr>
<td>Total</td>
<td>2.00</td>
<td>1.99</td>
</tr>
</tbody>
</table>

⁷Chemical analysis of enstatite obtained by energy-dispersive spectroscopy at Princeton Material Institute.

⁹Electron microprobe analyses of a glass starting material performed by J. Akins and T. Ahrens at Caltech.

In-situ X-ray diffraction was conducted at the GeoSoilEnviroCARS sector of the Advanced Photon Source with a double-sided laser-heating system (Figure 3 and Shen et al. [2001]). To minimize the temperature inhomogeneity in the X-ray–probed area, the X-ray beam was focused on less than 10 × 10 µ m² on the sample and co-linearity was ensured among the incident lasers, X-ray beam, and diamond-anvil cell rotation axis. Nd:YLF laser beams with a TEM₉₀ mode were focused on both sides of the sample in the diamond-anvil cells while diffraction patterns were recorded (Figure 4). Thermal radiation spectra, which are corrected for the system response, were fitted to Planck’s equation in order to measure temperature [Jephcoat and Besedin, 1996; Bohler, 2000]. Including radial and axial thermal gradients, temporal fluctuations during the X-ray exposure, and fitting residual (e.g.), the temperature uncertainty is 100–300 K in these measurements (Figure 4, refer to Appendix 3 for details). The samples were heated for 30–45 min during a heating cycle.

Pressure is determined using the P-V-T relations in platinum [Holmes et al., 1989] and argon [Finger et al., 1981; Ross et al., 1986], which are loaded together with the starting materials. The estimated uncertainty is ±5 GPa at 300 K and ±10 GPa at high temperature. The most significant error source is the overlap of diffraction peaks for platinum and argon above 70 GPa. Shear stresses and temperature uncertainty also contribute to this uncertainty. Detailed descriptions about the experimental technique can be found in Shim et al. [2001b, 2004].

3.1. Stability of MgSiO₃ Perovskite

From three different starting materials, we observe major diffraction peaks of perovskite during and after laser heating, including a triplet (Pv3) and two doublets (Pv1 and Pv4) at
50–120 GPa (Figure 5). Although the most intense diffraction peak of MgSiO₃ perovskite, Pᵥ³ (Figure 2), is severely overlapped by a diffraction peak from the rhenum gasket, two weak shoulders of Pᵥ³ are observed aligned off of the rhenum diffraction peak. A second doublet at a higher angle, Pᵥ⁴, and a singlet, Pᵥ², are more readily observed throughout our experiments. No major diffraction peak from the gasket material, pressure standard, pressure medium, any proposed high-pressure silica phase [Teter et al., 1998], or MgO overlaps these peaks (Figure 5). Furthermore, as shown in Figure 2a, Pᵥ² should have zero intensity for cubic perovskite and thus its presence can be diagnostic of lower-symmetry perovskite structures.

The stability of MgSiO₃ perovskite is thus confirmed at 50–118 GPa and 1500–2900 K (corresponding to 1200–2500-km depth) from the fact that the positions and intensities of major diffraction peaks remain consistent with those expected for MgSiO₃ perovskite without major changes (Figure 1b). The P–T conditions of our observations are close to the expected geotherm [e.g., Brown and Shankland, 1981] for the lower mantle and cover the entire P–T conditions expected for this region (Figure 1b).

A phase transition has been proposed for MgSiO₃ perovskite from orthorhombic to cubic structures at 65 GPa [Meade et al., 1995]. However, we were able to resolve two or three of the distinct peaks of the perovskite triplet (Pᵥ³) below 78 GPa (Figure 5a). Furthermore, Pᵥ², which is diagnostic of noncubic perovskite, is continuously observed. These suggest that MgSiO₃ perovskite has an orthorhombic unit cell and that no phase transition to a higher symmetry phase (tetragonal or cubic) exists to 78 GPa and 2100 K. Above this to core–mantle boundary P–T conditions, our angle-dispersive patterns contain Pᵥ² peaks during heating and the shoulder peaks of Pᵥ³, which are diagnostic of noncubic perovskite structure (Figure 5). Thus, in our study there is no evidence for a phase transition to a cubic perovskite to the core–mantle boundary.

3.2. Possible Modifications in MgSiO₃ Perovskite Structure at 88 GPa

We observe a new peak at 2.62–2.57 Å (New1 in Figure 5) from 88 to 144 GPa in the patterns that also contain diffraction peaks of MgSiO₃ perovskite both during and after heating. This new peak appears in the runs with different starting materials (MgSiO₃ glass and MgO + SiO₂ oxide mixture) and in subsequent heating of materials already transformed to perovskite. This peak cannot be identified as arising from MgO, the CaCl₂-type SiO₂, or any other theoretically proposed post-stishovite phases, but this new peak is found to be indexed as a perovskite diffraction line. The pressure-induced shift of the New1 peak agrees well with the expected shift for peaks of MgSiO₃ perovskite. This observation associates New1 peak with MgSiO₃ perovskite or another material with very similar compressibility (refer to Shim et al. [2004] for details). From systematic absence of this peak in Pbnm (orthorhombic) perovskite and forward modeling, we have proposed that appearance of this peak may indicate a modification in crystal structure of MgSiO₃ perovskite to P2₁/m (monoclinic), Pmnm (orthorhombic), or P4₂/nmc (tetragonal) above 88 GPa (Figure 6; refer to Appendix 2 for details).

We calculated diffraction patterns of these three possible perovskite structures and compared them with our observed diffraction patterns (Figure 2). We found that the intensity ratio between New1 and Pᵥ⁴ is 1.3 ± 0.3 and its sensitivity to pressure and temperature is minor at 88–144 GPa and 1500–2800 K from our angle-dispersive measurements. In Figure 2, except for the case of P4₂/nmc, the new peak intensity predicted by the space groups considered here is significantly lower than the observed peak intensity (Figure 2d,e,f).

However, direct comparison between observed and synthetic intensities is difficult in this case. Knowledge of atomic
3.3. Post-Perovskite Transition in MgSiO$_3$

When the sample was heated at 135–145 GPa, we held the temperature below 2500 K for the first 20 min of heating. No significant changes were observed other than the diffraction peaks of MgSiO$_3$ perovskite and New1 at this condition. However, when the sample was heated above 2500 K, we observed several changes in the diffraction patterns: the appearance of other new features at 2.42 Å (New2), 2.93 Å (New3), and 2.75 Å (near Pv2) and intensity changes in the peaks near 13.7° and 14.1°, and more diffraction peaks in Pv4 (Figure 7). It is notable that major diffraction peaks of perovskite and the new peak observed from 88 GPa (New1) are retained during this change. These features remain after temperature quench.

We examined the possibility of diffraction from materials other than the sample, such as platinum (pressure standard), argon (pressure medium), and rhenium (gasket). None

positions is needed in order to calculate X-ray peak intensities. However, our forward modeling does not constrain the position shift of the cations from the dodecahedral site centers (e.g., Mg in MgSiO$_3$ perovskite) and the distortions of the octahedra (e.g., SiO$_6$ in MgSiO$_3$ perovskite) and these were not included in the calculation of Figure 2. To estimate the uncertainty in the calculated diffraction intensities in Figure 2, we calculate X-ray diffraction patterns of Pbnm perovskite with and without the cation shifts from the center of dodecahedral sites. For some peaks, e.g., Pv2, the intensity is very sensitive to the cation shifts, whereas other peaks do not show significant changes in intensities. This indicates that the ignored factors could have a significant effect on the intensity of the new peak. Therefore, at this moment, the measured intensity does not provide sufficient information to distinguish the space group of the possible high-pressure phase of MgSiO$_3$ perovskite.

![Figure 6. Crystal structure of (a) P21/m and (b) Pmmn perovskites, proposed for the observations above 88 GPa, and (c) the post-perovskite phase (Cmcm) of MgSiO$_3$ above 120 GPa, proposed by Murakami et al. [2004]. For perovskite structures, projections along three pseudo-cubic axes are shown for comparison. The crystal structures of P21/m and Pmmn have same tilting senses as Pbnm and P42/nmc, respectively. The octahedra and the balls represent the SiO$_6$ structural units and Mg atoms, respectively. The unit cell is shown by solid lines. (a) and (b) have also been presented in Shim et al. [2001b]](image)

![Figure 7. A diffraction pattern measured at 138 ± 4 GPa and 300 K after laser heating (bottom) together with calculated diffraction patterns of orthorhombic MgSiO$_3$ perovskite (OPv), the post-perovskite phase (CaIrO$_3$ type with a Cmcm space group) proposed by Murakami et al. [2004], the $\alpha$-PhO$_2$-type silica, and MgO. Inset (a) shows the observed peak-splitting of Pv2. Inset (b) shows the observed peak-splitting of a peak at 13.5°. The major diffraction peaks of MgSiO$_3$ perovskite and the post-perovskite phase are identified with black arrows and grey arrows, respectively. Notations are the same as in Figures 2 and 5.](image)
of these materials can explain the newly observed peaks. Furthermore, none of the three possible perovskite structures can explain the new peak observed above 88 GPa predict peaks near New2 (Figure 2). Interestingly, the splitting of singlet Pv2 in Pbnm perovskite is predicted by all the candidate space groups we considered for New1 (Figure 2). However, the splitting has not been observed below 130 GPa. A possible explanation is that the splitting is induced by the transition at 88 GPa, and its magnitude becomes sufficiently large with compression that it can be observed at this higher pressure. We have also applied to New2 the geometrical modeling that we implemented for analysis of New1. However, no perovskite structure can explain the appearance of New2 merely with octahedral tilting.

A phase transition from perovskite to the CaIrO$_2$-type structure (Cmmm) at 120 GPa has been recently proposed by Murakami et al. [2004]. The peak position and intensity of New2 are very consistent with what is expected for the post-perovskite phase observed by Murakami et al. [2004] (Figure 7). Furthermore, the intensity increases in the peaks at 14–15° and the appearance of weak diffraction peaks at the higher angle side of Pv4 can be explained by the post-perovskite phase. Unlike MgSiO$_3$ perovskite, the post-perovskite phase has a relatively intense peak at 13.7° (Figure 7). However, the post-perovskite structure cannot explain New1 and New3. New1 appears above 88 GPa and remains even after the change at 145 ± 10 GPa. The fact that the major diffraction peaks observed in Figure 7 can be assigned to those of the modified MgSiO$_3$ perovskite and the post-perovskite phase may indicate that the observed pattern is due to an incomplete transition from the modified perovskite to the post-perovskite phase in our experiments.

We also investigate the possibility of a dissociation of MgSiO$_3$ during the heating run at 135–145 GPa. The peak positions of the new peaks do not match those of the CaC$_2$-type Si$_2$ diffraction peaks. We also calculate diffraction patterns of the α-PbO$_2$-type SiO$_2$ based on the unit-cell parameters reported by Murakami et al. [2003] (Figure 7). Although the most intense peak of the α-PbO$_2$-type SiO$_2$ is very close to New2, the most intense peak of the post-perovskite phase shows better agreement in position with New2. A new peak at 13.7° is quite close to one of the α-PbO$_2$-type SiO$_2$ peaks. However, the post-perovskite phase has a peak that better matches the observed peak position. New3 (8.36°) is very close to the second most intense peak of the α-PbO$_2$-type SiO$_2$ (8.42°). However, New3 appears to be a doublet, whereas a singlet is expected at this position for the α-PbO$_2$-type SiO$_2$. A structure (at 10.2°) between New2 and a weak peak of the post-perovskite phase at 10.4° may be assigned to the most intense peak of the α-PbO$_2$-type SiO$_2$ at 10.3° (Figure 7). However, if indeed these structures are the

diffraction from the α-PbO$_2$-type SiO$_2$, their intensities are very close to the background and significantly smaller than the intensities of the post-perovskite phase diffraction peaks. Furthermore, no significant evidence above noise level are observed for the presence of MgO. In summary, the observed diffraction patterns at 135–145 GPa are better explained by the mixture of the modified MgSiO$_3$ perovskite and the post-perovskite phase.

3.4. Observation of SiO$_2$

After heating MgSiO$_3$ perovskite at 107 GPa, in a pattern recorded for an area 10 μm away from the heated spot, we found a weak peak that can be assigned to the most intense diffraction peak of the CaCl$_2$-type silica phase (Figure 8). One possible interpretation of this is that the steep thermal gradients existing at the edge of the hot spot induce unstable conditions for MgSiO$_3$ perovskite, resulting in a dissociation as previously proposed [Serghiou et al., 1998]. In fact, some of the previous studies [Serghiou et al., 1999; Boehler, 2000] have proposed that steep thermal gradients in the laser-heated

![Figure 8](image-url)
sample may be a source of discrepancy about the stability of MgSiO$_3$ perovskite in earlier studies. Unfortunately, diagnostic peaks of MgO overlap those of MgSiO$_3$ perovskite at this condition. We also note that excess SiO$_2$ has been widely observed in MgSiO$_3$ perovskite synthesis experiments at lower pressure [e.g., O’Neill and Jeanloz, 1994]. More study is needed before drawing further conclusions, as this was observed only once in our measurements and has yet to be reproduced.

4. DISCUSSION

4.1. Possible Sources for Discrepancy on the Stability

Comparison of the experimental techniques between our study and the other studies [Meade et al., 1995; Saxena et al., 1996; Serghiou et al., 1998; Fiquet et al., 1998, 2000; Murakami et al., 2004] may provide some insights on the sources of the discrepancy on the stability. The main differences are: (1) Diffraction measurements are performed at in-situ high-$P$-$T$ conditions relevant to those in the mantle. (2) The samples are loaded together with an inert pressure medium, argon, which insulates the sample from the very efficient thermal conductors, diamond anvils. Thus, the argon insulation layers surrounding the samples may reduce the axial thermal gradients in the diamond-anvil cell. (3) The TEM$_{01}$ mode of Nd:YLF laser beams in the laser heating system [Shen et al., 2001] used in our study provides a large homogeneous heating spot. Heating of both sides of the sample in this study may also reduce the thermal gradients along the loading axis of the diamond-anvil cells. These technical improvements provide a better sample environment for examining the stability of MgSiO$_3$ perovskite. In addition, the observation of SiO$_2$ diffraction at a spot 10 $\mu$m away from the center of the heated spot (20 $\mu$m in diameter) suggests that strong thermal gradients can lead to a dissociation of MgSiO$_3$ perovskite.

4.2. Uncertainty Associated With the New Peaks With MgSiO$_3$

It is worth discussing the uncertainties in the observation of the new peaks at 88 $\pm$ 5 GPa (Newl). The Newl peak was not observed in recent measurements by Murakami et al. [2004]. Whereas Murakami et al. [2004] used only a gel starting material, we have confirmed the appearance of Newl when different crystalline starting materials were used. As shown in the case of (Mg,Fe)SiO$_3$ [Kim et al., 1994; Irfune et al., 2000], use of amorphous starting materials could result in different heating products. To insulate the sample + platinum foil, Murakami et al. [2004] separate their sample + platinum mixture from diamond anvils by using pure sample foils. However, X-rays are scattered at both the sample + platinum foil and the pure sample foils, which are directly in contact with diamond anvils. Therefore, the measured diffraction is from both the sample with relatively less thermal gradients and the sample with extreme thermal gradients. Thus, the contamination with extreme thermal gradients in the sample cannot be ruled out in their experiments. However, we used argon to insulate the sample + platinum mixture foils throughout our experiments. This Newl peak also was not observed in Mao et al. [2004]. However, the difference in chemical composition between their starting materials, (Mg,Fe)SiO$_3$, and our starting materials, MgSiO$_3$, could result in the different observations.

The Newl peak was observed in Oganov and Ono [2004]. However, they assign the peak to platinum carbide, which is proposed to be a product of chemical reaction between diamond anvil and platinum. Interestingly, we do not observe the Newl peak in our CaSiO$_3$ perovskite measurements [Shim et al., 2000], which were performed at similar $P$-$T$ conditions with platinum in the diamond cell. If the Newl is from a reaction between platinum and diamond anvil, the Newl peak should have been observed in this experiment. Nevertheless, we note that there still exist uncertainties in evaluating the possibility of chemical reaction. More studies are warranted to resolve the problem.

4.3. Geophysical Implications of the Post-Perovskite Transition

Because the knowledge of the post-perovskite transition is rapidly growing and many more results are appearing in the literature, it may be too early to discuss implications of the post-perovskite transition at this moment. Yet it may be useful to summarize current knowledge for a general audience and discuss possible implications for the structure and dynamics near the core–mantle boundary. The discussion in this section is based on the results published as of May 2005.

The expected transition depth of the post-perovskite boundary is very close to the depth of the D$''$ discontinuity existing 200–300 km above the core–mantle boundary [Lay and Helmberger, 1983; Wyssession et al., 1998; Sidorin et al., 1999]. According to measurements by Murakami et al. [2004] and Oganov and Ono [2004], the phase boundary may exist between 114 and 126 GPa at 2000–2500 K, which corresponds to 400 and 200 km above the core–mantle boundary in the preliminary reference Earth model (PREM) [Dziewonski and Anderson, 1981], respectively (Figure 1). The post-perovskite phase was observed at even higher pressure in our measurements, 140 GPa (Figure 1). With regard to a gap in our data set between 118 and 140 GPa, an appropriate interpretation
is that the phase boundary exists in this range. Therefore, our data are not inconsistent with the results of Murakami et al. [2004] and Oganov and Ono [2004]. Furthermore, we found that the post-transition is very sluggish, which could result in overestimation of the transition pressure. This was confirmed in more recent measurement by Mao et al. [2004].

Note that uncertainties in the measured pressure and temperature are significant at these extreme experimental conditions. In synchrotron X-ray measurements, pressure is normally determined from the measured temperature and volume of the internal pressure standards (e.g., platinum and gold) using their equations of state. Volume can be precisely determined from the diffraction peak positions. Temperature uncertainty in typical laser heating [Boehler, 2000] is $\pm 200$–300 K at pressures greater than 100 GPa. Including these measurement uncertainties, $\pm 5$–10 GPa uncertainty in pressure (i.e., $\pm 100$–200 km uncertainty in depth) may be a reasonable estimation at 100–140 GPa and high temperature.

Uncertainties in the equations of state of the standard materials should also be considered. Including uncertainties in thermoelastic parameters, such as bulk modulus, pressure derivative of bulk modulus, and Grüneisen parameters, $\pm 5$ GPa uncertainty is a reasonable estimate for the pressure scales at 100–140 GPa and high temperature. However, as recently demonstrated by Shim et al. [2001a] and Fei et al. [2004a], different pressure scales may not be consistent with each other. The measurements performed by Murakami et al. [2004], Shim et al. [2004], and Oganov and Ono [2004] are based on the platinum scale [Holmes et al., 1989; Jamieson et al., 1982]. However, the accuracy of the platinum scale is not well known at core-mantle boundary $P$–$T$ conditions. The gold pressure scale is one of the best studied among the existing internal standards [Jamieson et al., 1982; Heinz and Jeanloz, 1984; Anderson et al., 1989; Shim et al., 2002; Okabe et al., 2002; Tsuchiya, 2003; Matsui and Shima, 2003]. As demonstrated by Shim et al. [2002], however, even the existing gold pressure scales are discrepant by about 10 GPa corresponding to 200 km in depth near core-mantle boundary $P$–$T$ conditions (Figure 9).

First-principles calculations have provided constraints on the depth of the post-perovskite transition [Oganov and Ono, 2004; Tsuchiya et al., 2004a]. Depending on used method, the value ranges from 108 to 125 GPa, which is comparable to the experimental results. Thus, a reasonable estimation of the transition depth based on the published data is 200–400 km above the core-mantle boundary in pure magnesium silicate (MgSiO$_3$) with an uncertainty of $\pm 200$ km.

Considering the chemical composition models of the lower mantle [e.g., Ringwood, 1975; Taylor and McLennan, 1985; Anderson, 1989], the post-perovskite phase should contain some amount of iron (maybe 5–15%). The effect of iron on the transition pressure has been studied by Mao et al. [2004], who found that the post-perovskite transition occurs at 100 GPa in 10% iron ferromagnesian silicate, (Mg$_{0.9}$Fe$_{0.1}$)SiO$_3$. This is about 700 km above the core-mantle boundary. In other words, incorporation of 10% iron decreases the post-perovskite transition pressure by 15–25 GPa and elevates the height of the transition from the core-mantle boundary by 300–500 km. The sensitivity of the post-perovskite transition depth to iron is very high compared with that for the olivine-wadsleyite and the post-spinel transitions (both decrease by less than 1 GPa with 10% iron [Akaogi et al., 1989; Ito and Takahashi, 1989]). There is some degree of uncertainty in comparing the results of Mao et al. [2004] with the data for pure MgSiO$_3$, as these two different sets of results are tied to different pressure scales (NaCl and platinum), for which the consistency is not well constrained at this pressure range.

Murakami et al. [2005] performed X-ray measurements for a pyrolitic starting material to 126 GPa and 2450 K and observed the post-perovskite transition between 103 and 113 GPa, i.e., 600 km and 400 km, respectively, above the core-mantle boundary. A direct comparison with the data that constrain the post-perovskite transition pressure in pure MgSiO$_3$ is difficult, because consistency between the gold (used in pyrolite measurements by Murakami et al. [2005]) and the platinum pressure scales (used in pure MgSiO$_3$ measurements by Murakami et al. [2004]; Oganov and Ono [2004]; Shim et al. [2004]) is not well known. Murakami et al. [2005] reported that the post-perovskite phase contains only 3% iron. From Mao et al. [2004], however, a 3% iron concentration is associated with a 5–8 GPa decrease in transition pressure. Thus, the decrease in the transition pressure measured in Murakami et al. [2005] can be mainly explained by the effect of iron. The effect of aluminium is not well understood yet. However, it is generally expected that aluminium may increase the post-perovskite transition pressure [Caracas and Cohen, 2005]. In summary, these two results demonstrate that the post-perovskite transition pressure may be very sensitive to minor elements, and the degree of the sensitivity may be much higher than those of the phase transitions that occur at the transition zone.

It is also important to note that the post-perovskite phase may have different element partitioning with magnesiowustite compared to perovskite. As pointed out by Murakami et al. [2005], changes in iron partitioning could affect the viscosity [Durham et al., 1979] and electrical conductivity [Li and Jeanloz, 1991; Peyronneau and Poirier, 1989] of the lowermost mantle. Murakami et al. [2005] reported that iron is still preferentially partitioned into magnesiowustite after the post-perovskite transition; moreover, they observed that magnesiowustite is more enriched in iron when it coexists with the post-perovskite than when it coexists with perovskite.
However, Mao et al. [2004] have proposed that iron is preferentially partitioned into the post-perovskite phase than into perovskite during the phase transition and predicted that the post-perovskite phase may have higher capacity for iron than any other phases at the lowermost mantle. This discrepancy may be related to the fact that the starting materials of Mao et al. [2004]'s contain only Mg, Fe, Si, and O, whereas Murakami et al. [2005] used starting materials having a pyroclitic composition with minor elements (e.g., aluminum and calcium), which may be more relevant to the chemical composition of the mantle. More measurements are necessary in order to understand element partitioning at the base of the mantle. Notably, both of the above results demonstrated that the iron partitioning among different phases in the lowermost mantle may be significantly different from that in the rest of the lower mantle.

Another important effect of iron observed in recent experiments [Mao et al., 2004] is that iron increases the width of the post-perovskite transition significantly: the width of the transition for 10% iron is approximately 10 GPa, i.e., 200 km. This is a remarkably large width compared to the olivine-wadsleyite and post-spinel transitions (both less than 1 GPa for 10% iron [Akaogi et al., 1989; Ito and Takahashi, 1989]). Assuming that 10% iron is a reasonable estimate in perovskite, this width seems rather large when compared to a seismically constrained transition width of the D" discontinuity (less than 50–75 km [Wysession et al., 1998]). However, there are many other factors to consider when comparing the laboratory measurements to the seismic observations. For example, as shown in the case of the olivine-wadsleyite transition [Irfune and Isshiki, 1998], transition width can be strongly affected by element partitioning with other phases, such as magnesio-wadsleyite and CaSiO₃ perovskite. Furthermore, more precise in-situ measurements are necessary.

The Clapeyron slope of a phase transition is important for understanding the effect of the phase transition with regard to the mantle convection, as is well demonstrated for the phase boundaries at the transition zone [e.g., Tackley et al., 1993]. If the post-perovskite transition exists above the core–mantle boundary, it will likely affect the mantle convection in the lowermost mantle. This is particularly interesting because the D" layer has been believed to be the source region of the
mantle plumes and the graveyard of the subducting slabs according to some models [e.g. Morgan, 1971; Christensen and Hofmann, 1994; Garnermo and Lay, 2003].

Currently available measurements cannot constrain the sign and the magnitude of the Clapeyron slope of the post-perovskite boundary (Figure 1). Some first-principles calculations provide constraints on the slope: +9.56–9.85 MPa/K [Oganov and Ong, 2004] and +7.5 ± 0.3 MPa/K [Tsuchiya et al., 2004a]. The sign and magnitude of the slope is comparable to a seismologic estimation for the D" discontinuity, i.e., +6 MPa/K [Sidorin et al., 1999]. It is notable that the magnitude of the slope is factor of 2-4 greater than those of the phase boundaries in the transition zone: +3.6 MPa/K for the olivine-wadsleyite transition [Morishima et al., 1994], +2 MPa/K for the post-garnet transition [Hirose et al., 2001], and −2.8 MPa/K for the post-spinel transition [Ito and Takahashi, 1989; Irifune et al., 1998]. This makes the transition depth of the post-perovskite boundary very sensitive to temperature. For example, a 500 K decrease in temperature may elevate the transition depth by 100 km. At this moment, the effect of minor elements on the sign and magnitude of the slope has not been studied. However, from the high sensitivity of the transition depth to chemical composition and temperature, the post-perovskite boundary may develop significant topography if lateral variations in temperature and chemical composition exist near the core–mantle boundary. Interestingly, seismic studies have revealed that there exist lateral heterogeneities in the lowermost mantle [e.g., Gaherty and Lay, 1992; Liu and Dziewonski, 1998; Kuo et al., 2000; Garnermo and Lay, 2003; Thomas et al., 2004a] and that the D" discontinuity height varies laterally from 100 km to 450 km above the core–mantle boundary [Wysession et al., 1998].

The effect of a phase transition with a positive Clapeyron slope near the core–mantle boundary has been studied in computer simulations by Nakagawa and Tackley [2004]. They showed that a positive slope boundary destabilizes the thermal boundary layer at the core–mantle boundary and will result in more vigorous plume activity. In future simulations, the finite transition width of the post-perovskite and the depth variation by lateral variations in chemical composition should be considered. Most of all, more knowledge about the post-perovskite transition is necessary to understand its effect on the mantle convection.

It is interesting to note that the estimated slope of the post-perovskite transition may be very close to the temperature gradient in the thermal boundary layer at the lowermost mantle. Although the lower-mantle geotherm is expected to be close to adiabatic and the gradient may be 0.3 K/km [Brown and Shankland, 1981; Duffy and Hemley, 1995], the mantle side of the core–mantle boundary should be strongly super-adiabatic, compared with the rest of the mantle, due to vertical heat transfer across the core–mantle boundary. It is very difficult to estimate the temperature gradient in this layer because the necessary parameters are not well constrained, including the melting temperature of iron [Williams et al., 1987; Saxena et al., 1994; Boehler, 1993; Williams et al., 1998; Shen et al., 1998]. Using the PREM model [Dziewonski and Anderson, 1981], Stacey and Loper [1983] estimated that the thermal boundary layer extends to 73 km above the core–mantle boundary with a maximum thermal gradient of 11.2 K/km. However, according to seismic observations, the thickness of the thermal boundary layer could be much larger, i.e., 200–250 km [Wysession et al., 1998]. Including existing uncertainties in important parameters, temperature increase across the D" layer may lie in a range of 1000–2000 K [Jeanlos and Morris, 1986; Boehler et al., 1995; Williams et al., 1998]. Therefore, the temperature gradient of 5–10 K/km in the D" layer would not be an unreasonable estimate. According to these estimations, the temperature gradient in the thermal boundary layer may be very close to the estimated Clapeyron slope of the post-perovskite boundary, i.e., 5–7 K/km. This similarity in slopes may result in very interesting changes in mineralogy in response to lateral variations in temperature and chemical composition at the lowermost mantle (Figure 10). We will demonstrate a few possible cases, but this discussion remains qualitative because uncertainties are not resolved for the post-perovskite boundary and the temperature gradient in the thermal boundary layer. To simplify the discussion, we shall treat the post-perovskite transition as a sharp boundary; however, as has been shown in some recent measurements [e.g., Mao et al., 2004], minor elements, such as iron and aluminum, can increase the transition width. Also, although we represent the super-adiabatic thermal gradient in the thermal boundary layer with a line in Figure 10d, the gradient may be highly non-linear [e.g., Stacey and Loper, 1983].

Figure 10a shows a case where the post-perovskite transition exists above the thermal boundary layer. However, if the thermal boundary layer is extended to a higher elevation from the core–mantle boundary and/or if the post-perovskite boundary exists at a deeper depth (possibly due to the effect of minor elements), it is possible that perovskite is still stable to the core–mantle boundary and that the post-perovskite transition does not occur in the lowermost mantle (Figure 10b). If the post-perovskite transition exists in the thermal boundary layer with a higher slope than the temperature gradient in the thermal boundary layer (Figure 10c), the transition depth will be deeper than one expected for a mantle geotherm.

Very interesting changes in mineralogy at the lowermost mantle can be predicted when the temperature gradient in the thermal boundary layer is higher than the Clapeyron slope of the post-perovskite boundary and when the post-
Figure 10. Schematic models of the post-perovskite (PPv) boundary and the mantle geotherm near the thermal boundary layer at the bottom of the mantle. (a) The post-perovskite transition exists above the thermal boundary layer. (b) The post-perovskite transition does not occur in the mantle. This is possible if minor elements move the boundary to a deeper depth and/or the temperature in the thermal boundary is sufficiently high. (c) The post-perovskite transition occurs in the thermal boundary layer. (d) The post-perovskite boundary crosses the geotherm more than once. This could result from more gentle slope of the post-perovskite boundary or a non-linear geotherm in the thermal boundary layer. This will result in alternating layers of perovskite (Pv) and the post-perovskite.

A similar result is expected when the temperature gradient in the D" layer is highly non-linear and the slope changes from lower to higher than the slope of the post-perovskite boundary. In fact, Stacey and Loper [1983] predicted that temperature in the thermal boundary layer exponentially increases with depth.

These models remain schematic due to the uncertainties discussed above. More precise determinations on the sensitivity of the post-perovskite transition to temperature and chemical composition will enable us to include or exclude some of these cases. In addition, although mantle geotherm and the post-perovskite boundary are assumed to be independent of each other in these schematic models, latent heat from the phase transition may perturb the geotherm near the transition boundary, as shown for the phase boundaries in the transition zone [e.g., Agee, 1998].

Nevertheless, these models may have some implications for seismic observations. An important point from these schematic models is that the expected sensitivity of the post-perovskite transition to temperature and chemical composition, a steep temperature gradient at the lowermost mantle, and lateral variations in temperature and chemical composition at the lowermost mantle as indicated in some seismic studies [e.g., Gaherty and Lay, 1992; Liu and Dziewonski,
1998; Kuo et al., 2000; Garnero and Lay, 2003; Thomas et al., 2004a) may result in significant lateral variations in the transition depth and mineralogy. For example, the D" discontinuity becomes observable and not observable over distances of 10–100 km, and the discontinuity is sometimes coherently observed over a distance of 1000 km [Wysession et al., 1998]. Furthermore, using seismic observations of beneath Eurasia [Thomas et al., 2004b] and Caribbean [Thomas et al., 2004a], Hernlund et al. [2005] has proposed that, depending on local temperature profile near the core–mantle boundary, the post-perovskite boundary can be crossed twice by the geotherm, which results in observation of a pair of seismic discontinuities near the core–mantle boundary.

According to the proposed crystal structure (CaIrO$_3$ type) for the post-perovskite phase [Murakami et al., 2004; Iitaka et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004a], SiO$_6$ octahedra form layers in the post-perovskite structure, whereas they form a 3-dimensional network in perovskite (Figure 6c). This fundamental difference in the crystal structures may result in significantly different physical and chemical properties of the post-perovskite phase.

However, the post-perovskite phase is stable only at extreme $P$–$T$ conditions and does not appear to be quenchable, which makes measurements of the physical properties of the post-perovskite phase difficult. First-principles calculations provide constraints on some of important physical properties of the post-perovskite phase. A density increase of 1.0–1.5% has been reported for the post-perovskite transition [Murakami et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004a]. Compared to other transitions related to seismic discontinuities in the transition zone, e.g., 4–6% for the post-spinel transition, this density increase is very moderate.

At this moment, elastic properties of the post-perovskite phase are constrained only by the first-principles calculations. The bulk modulus of the post-perovskite phase at 0 GPa is 221–232 GPa [Oganov and Ono, 2004; Tsuchiya et al., 2004b], which is smaller than that of perovskite, i.e., 260 GPa. However, what makes the post-perovskite phase slightly more incompressible at the transition pressure is a higher pressure derivative of bulk modulus: 4.2–4.4 for the post-perovskite versus 3.7–4.0 for perovskite. Whereas $P$-wave velocity change is expected to be small [0.3%, Oganov and Ono, 2004] during the transition, $S$-wave velocity change is expected to be much higher (1.5% [Tsuchiya et al., 2004b]). The magnitudes of the velocity changes in the post-perovskite transition are smaller than seismic estimation of the changes at the D" discontinuity, which are approximately 3% for both $P$ and $S$ waves [Wysession et al., 1998].

Shear-wave splitting has been observed in D" below several regions, e.g., Caribbean [e.g., Kendall and Silver, 1996] and Alaska/North Pacific [e.g., Lay and Young, 1991], and has been attributed to anisotropy in D". Kendall and Silver [1998] reviewed the possibility of lattice-preferred orientation as the cause of the anisotropy. However, no satisfactory explanation was found from lattice-preferred orientation of most mantle minerals. The D" anisotropy can be described as transverse isotropy with a symmetry axis along the vertical direction. Because of the 2-dimensional layered structure of the post-perovskite, some have proposed that the post-perovskite may be responsible for the observed D" anisotropy with an expectation that a slip plane may be developed parallel to the SiO$_6$ octahedral layers, which are perpendicular to the $b$-axis, in the post-perovskite phase [Figure 6c, Iitaka et al., 2004; Oganov and Ono, 2004]. First-principles calculations of Iitaka et al. [2004] have shown that the post-perovskite phase is elastically more anisotropic than is perovskite.

Oganov and Ono [2004] proposed that the shear-wave splitting with $V_{SH} > V_{SV}$ may be explained by the texturing of the post-perovskite phase. Tsuchiya et al. [2004b] argued that vertical alignment of the $c$-axis, which is parallel to the octahedral layers in the post-perovskite phase, could also explain the observed $V_{SH} > V_{SV}$. Stackhouse et al. [2005] studied the effect of temperature on the elastic anisotropy of perovskite and the post-perovskite and proposed that the elastic anisotropy of the post-perovskite phase is much less sensitive to temperature change than is perovskite, and $R_{S/P} (\equiv \partial \ln V_s/\partial \ln V_p)$ of the post-perovskite is much lower than that of perovskite and the seismically measured value of the lowermost mantle. Note that these calculations were performed for pure MgSiO$_3$; the effect of minor elements, e.g., Fe, Al, Ca, remains to be studied. Another important physical property change that may be related to the post-perovskite phase is a transition from high-spin to low-spin state of iron in (Mg,Fe)SiO$_3$ [Badro et al., 2004] and aluminum bearing (Mg,Fe)SiO$_3$ [Li et al., 2004] above 70 GPa. These investigators proposed that the transition will increase the intrinsic radiative thermal conductivity of this major mantle mineral and that this transition may increase contributions from radiative heat transfer.

Many other properties are yet to be determined for the post-perovskite phase, including the effect of minor elements, melting curve, element partitioning, rheology, elasticity, and chemical reaction with iron. This is particularly important for understanding the physical and chemical processes in the lowermost mantle, given that the post-perovskite phase seems to be the dominant phase in this region.

5. CONCLUSION

Although some earlier measurements [Meade et al., 1995; Saxena et al., 1996, 1998] have proposed a dissociation of
MgSiO$_3$ perovskite at mid-mantle $P$-$T$ conditions, more recent measurements by many different groups [Mao et al., 1997; Serghiou et al., 1998; Fiquet et al., 2000; Andrault, 2001; Shim et al., 2001b, 2004] have shown that MgSiO$_3$ perovskite is stable to at least 118 GPa and 2900 K (2500-km depth). For example, in our in-situ X-ray diffraction measurements on MgSiO$_3$ at 50–144 GPa and 1400–2900 K, the dominant features observed in diffraction patterns during and after heating are identified as those of perovskite. This confirms the stability of MgSiO$_3$ perovskite at 1200–2500-km depth in the mantle.

However, a modification in the crystal structure of perovskite in deep mantle remains a viable explanation for our observation of a new peak that appears at 88 GPa. The source of this new peak remains inconclusive because of the possibility of alternative interpretations, such as chemical reaction or impurity.

A significant change in the crystal structure of MgSiO$_3$ has recently been observed by several groups, i.e., post-perovskite transition near core–mantle boundary $P$-$T$ conditions [Murakami et al., 2004; Shim et al., 2004; Oganov and Ono, 2004]. According to recent studies, the post-perovskite transition depth is likely very sensitive to variations in chemical composition and temperature, which may be related to the observed large variation in depth of the D'' discontinuity. Furthermore, the proposed slope of the post-perovskite boundary seems very similar to the expected temperature gradient of the thermal boundary layer in the lowermost mantle. This may also result in a high sensitivity of mineralogy to variations in temperature and chemical composition. However, more studies are necessary to further investigate implications of the post-perovskite transition to the structure and dynamics of the lowermost mantle. The important measurements to be conducted include the transition depth, the Clapeyron slope, and the transition width in pure MgSiO$_3$ and “dirty” systems (the effect of minor elements). Interactions between the post-perovskite phase and other phases in the lowermost mantle are important: element partitioning between the post-perovskite phase and other major mantle minerals, and chemical reaction with iron and iron alloys. Elastic parameters, thermodynamic parameters, rheology, and transport properties of the post-perovskite are among the important parameters that should be measured.

APPENDIX 1: CALCULATION OF X-RAY DIFFRACTION PATTERNS

We calculate the expected positions and intensities for the diffraction peaks of MgSiO$_3$ perovskite, Cmcm-structured MgSiO$_3$, MgO, and SiO$_2$ phases for phase identification (e.g., Figures 2, 5, 7, and 8). Crystal-structure parameters of MgSiO$_3$ perovskite (orthorhombic, Pbnm) are obtained from recent X-ray measurements by Fiquet et al. [2000]. We calculate the diffraction pattern of the post-perovskite phase by using the CaIrO$_3$-type (Cmcm) structure proposed by Murakami et al. [2004]. Diffraction patterns of SiO$_2$ are calculated for all the phases proposed, based on recent experiments [Dubrovinsky et al., 1997; Andrault et al., 1998; Murakami et al., 2003] and a first-principles calculation [Teter et al., 1998], including the CaCl$_2$ and $\alpha$-PbO$_2$ type structures. Pressure and temperature variations of unit-cell parameters are determined by using the published equations of state [Fiquet et al., 2000; Speziale et al., 2001; Murakami et al., 2004]. We assume that the equations of state for all high-pressure forms of SiO$_2$ are the same as that for stishovite [Hemley et al., 1994]. The predicted peak positions of the $\alpha$-PbO$_2$-type SiO$_2$ under this assumption agree with those reported by Murakami et al. [2003].

To calculate X-ray diffraction patterns, it is necessary to know the space group, the unit-cell parameters, atomic positions, temperature factors for each atom, and other experimental parameters. To obtain unit-cell parameters at 100 GPa, we first calculate the expected volume of MgSiO$_3$ perovskite, using its equation of state [Mao et al., 1991; Jackson and Rigden, 1996]. For non-cubic structures we need to know the axial ratios to obtain unit-cell parameters from the volume. For the Pbnm structure, we chose the axial ratios reported by Fiquet et al. [2000] at 79.7 GPa and 1681 K. For the proposed structures above 88 GPa, i.e., $P2_1/m$, P4$_2$/nmc, and Pmmm, the axial ratios are obtained from a geometric model (refer to Appendix 2).

Atomic positions are obtained from Fiquet et al. [2000] for Pbnm structure and from the geometrical modeling for $P2_1/m$, P4$_2$/nmc, and Pmmm structures. Temperature factors were assumed to be the same as those measured by the single-crystal X-ray diffraction study at lower pressure by Ross and Hazen [1990]. We assumed that Mg atoms are at the center of dodecahedral sites and that the SiO$_6$ octahedra are rigid and not distorted in P2$_1/m$, P4$_2$/nmc, and Pmmm structures, since no constraints are available for these. In fact, in Pbnm perovskite, the positions of Mg atoms are shifted from the center of the dodecahedral sites, and the SiO$_6$ octahedra are distorted [Fiquet et al., 2000]. To demonstrate the effect of Mg atoms shifting from the dodecahedral site center, we calculate X-ray diffraction pattern for Pbnm structure with Mg atoms at the center (Figure 2c). For some of the peaks, e.g., Pvi2, significant intensity changes are observed. Thus, there exists some degree of ambiguity in the calculated intensity of MgSiO$_3$ perovskite. However, peak positions are not affected by the Mg atom shifts. X-ray diffraction patterns were calculated with the GSAS program [Larson and Dreele, 1988].
APPENDIX 2: GEOMETRICAL MODELING FOR PEROVSKITE STRUCTURES

To investigate the possibility of associating the Newl peak observed above 88 GPa with perovskite, we performed geometrical calculations. We first assume that the distortion of perovskite is induced only by the tilting of SiO$_6$ octahedra and that the octahedra behave as rigid units. This distortion mechanism permits only a few modifications of the perovskite structures [Glazer, 1972; Woodward, 1997]. The constraints we implemented in the model are listed in Shim et al. [2001b]. We found that only three space groups can satisfy the constraints: $P2_1/m$ (monoclinic), $Pmmn$ (orthorhombic), and $P4_2/nmc$ (tetragonal).

The POPATO [Woodward, 1997] program enables us to calculate the atomic positions in the perovskite structures distorted only by the rigid octahedral tilting. The input parameters are unit-cell parameters and the distances between Si and O sites. We obtained the Si–O distance at 100 GPa from the equation of state, the axial compressibility of MgSiO$_3$ perovskite, and atomic positions reported at 79.7 GPa and 1681 K. Unit-cell parameters were obtained such that they can reproduce both the new peak (Newl) and the observed perovskite diffraction peaks. The atomic positions obtained from this method are used for our X-ray diffraction calculations. The unconstrained parameters in this model are the atomic positions of Mg and the distortion of the SiO$_6$ octahedra.

APPENDIX 3: AVERAGING SCHEME FOR TEMPERATURE OF THE SAMPLE

In the double-sided laser heating system at GSECARS, two imaging spectrometers with charge-coupled devices measure thermal radiation spectra (Figure 4b) across the sample. These thermal radiation spectra are fitted to a gray-body equation after correcting for system response (Figure 4). As a result of this, a line profile of temperature can be obtained for both sides of the sample.

In each run, there exist several temperature determinations across the sample volume for which diffraction measurements are collected (rectangle in Figure 4a). Assuming cylindrical symmetry for the temperature distribution in the sample, each temperature measurement represents a different area, as shown in the schematic diagram of Figure 4a. Using this area as a weight for each data point, a weighted average can be calculated. In this particular case, the weighted averages for both sides (2101±48 K for T1 and 2182±63 K for T2) are not significantly different from simple averages (2098±61 K for T1 and 2180±79 K for T2) within the uncertainties. Axial thermal gradients can be estimated by taking the difference between the averages for both sides. The thermal profiles are measured several times during X-ray diffraction measurements (Figure 4c). The uncertainty of measured temperature includes temporal fluctuations, axial and radial thermal gradients, and uncertainty in gray-body fitting.

It is important to note that the uncertainty calculated in this procedure should be viewed as an estimation of precision rather than absolute accuracy. The measured thermal gradients are contaminated by the interference of thermal radiation from different locations in the sample and by the transparency of the sample. Also, the wavelength-dependent emissivity of the sample is unknown at high $P$–$T$.

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