Chapter 1: Equations of state of the high-pressure phases of a natural peridotite and implications for the Earth’s lower mantle

Abstract. To help determine the chemical composition of the Earth’s mantle, we characterized an undepleted natural peridotite—thought to be representative of the Earth’s upper-mantle—to 107 GPa using high-resolution x-ray diffraction. At lower-mantle conditions, the peridotite transforms to the assemblage 76 (± 2)% (Mg$_{0.88}$Fe$^{2+}_{0.03}$Fe$^{3+}_{0.05}$Al$_{0.12}$Si$_{0.94}$)O$_3$ orthorhombic perovskite by volume (at zero pressure), 17 (± 2)% (Mg$_{0.80}$Fe$_{0.20}$)O magnesiowüstite and 7 (± 1)% CaSiO$_3$ perovskite. The measured room-temperature bulk properties of this high-pressure assemblage, together with a range of estimates of thermal properties of the constituent minerals, are inconsistent with seismological constraints on the density and bulk modulus of the lower mantle. Therefore, we propose that the lower mantle differs in bulk composition (e. g., richer in iron, Mg$\# \sim 0.85$) from current estimates for the upper mantle, requiring some amount of segregation between the upper and lower mantle over geological history.
Introduction

Geochemists, geodynamicists, seismologists, and mineral physicists have long debated the nature of the Earth’s mantle which comprises more than three-quarters of the Earth’s volume and thus dictates the thermal and chemical evolution of the Earth [1-12]. The global discontinuities in seismic-wave velocities at 410 and 660 km depths are attributed to high-pressure transformations of upper-mantle minerals into lower-mantle phases [13-16]. However, recent studies suggest that there may be large-scale compositional variations near the base of the lower mantle, and there are reasons for suspecting that the mantle is not entirely uniform in bulk composition [8, 10, 17].

To assess the similarity in composition of the deep mantle to that at shallower levels, we compressed a natural peridotite—an upper-mantle rock—to lower-mantle pressures in a laser-heated diamond-anvil cell, and measured the lattice parameters and compressibility of the various mineral phases by high-resolution synchrotron and laboratory-based x-ray diffraction. If the mantle is homogeneous, the density and elasticity of the upper-mantle rock composition once transformed to the relevant mineral phases at lower-mantle conditions, should agree with the seismologically-observed properties of the lower mantle.

Methods

The starting material for our experiment, BN-35 [18-20], is a garnet-spinel lherzolite xenolith and thought to be a good proxy for relatively primitive and fertile upper-mantle rock. With an Mg# \( \approx 0.89 \) and consisting of \( \sim 45\% \) olivine, 25% orthopyroxene, 15% clinopyroxene, and 15% garnet by volume [18, 21], our sample is a
natural analog of pyrolite, a model intended to represent the upper mantle: see Table 1-1 (an Mg#, molar Mg/(Mg+Fe) ratio, of 0.90 (± 0.05) is the estimated value for the bulk composition of the uppermost mantle) [1]

Angle-dispersive x-ray diffraction patterns collected at high pressure, before and after laser heating, as well as after decompression confirm the identity of the phases, and show that their observed compressions are compatible with the known equations of state of the individual mineral phases (see Section 4, High-Pressure, Room-Temperature Measurements). Two independent sets of experiments were carried out. In the first, samples were compressed and transformed under quasi-hydrostatic conditions (argon pressure medium) in a laser-heated diamond-anvil cell (Nd-YAG laser, $\lambda = 1064$ nm or Nd-YLF laser, $\lambda = 1053$ nm), and characterized at room temperature by synchrotron x-ray diffraction using image plates at beamline 10-2 at the Stanford Synchrotron Radiation Laboratory ($\lambda = 0.7277$ Å) and the GSECARS 13-IDD beamline at the Advanced Photon Source ($\lambda = 0.4246$ Å). In the second set of experiments, the same sample material was loaded without a pressure medium and patterns were collected using laboratory sources with Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation (high-pressure diffraction) and Cu $K\alpha$ ($\lambda = 1.5418$ Å) radiation (zero-pressure diffraction) [20]. Ruby grains were added as a pressure calibrant in all experiments [22]. In some of the experimental runs, additional laser heating (at pressures of 41, 47, 66, 78 and 87 GPa) was applied to thermally relax the sample of any non-hydrostatic stresses. All 300 K measurements (synchrotron- and laboratory-based) are mutually compatible and are used to compile a whole-rock equation of state. More detailed experimental procedures have been described elsewhere [19, 20].
Experimental Results

Upon compression to lower-mantle pressures (P > 24 GPa) and laser heating to ~2000 K in a diamond anvil cell, the peridotite transforms into a new assemblage consisting of 64 (± 2) mol% orthorhombic perovskite (opv), 31 (± 2) mol% magnesiowüstite (mw), and 5 (± 1) mol% calcium perovskite (cpv). The identification and abundances of the high-pressure phases is determined by x-ray diffraction and through modeling the bulk composition of the starting material [19]. Twenty-five x-ray diffraction patterns were taken of the sample at pressures between 25 and 107 GPa at room temperature, before and after heating, and upon subsequent decompression (see Fig. 1-1).

Additional in-situ high-pressure, high-temperature experiments confirm that the opv, mw, and cpv phases exist at high temperatures (Fig. 1-1). Due to potential systematic errors, however, such measurements do not yield sufficiently reliable density values to allow a direct and independent comparison of the whole-rock assemblage at lower-mantle conditions with the seismologically-observed properties of the mantle; therefore, the measurements obtained in-situ, at simultaneously high pressures and temperatures, are not included here. The high-pressure and high-temperature data shown in the inset of Fig. 1-1 are nevertheless entirely consistent with our thermal equation of state.
Major-element Partitioning

Major-element partitioning was determined from the observed ambient-pressure unit-cell volume $V_0$ of opv and mw, as well as analysis of the bulk (starting) composition of the rock assuming conservation of cations and charge. In the absence of other minor elements, Mg and Fe partitioning into these high-pressure phases has been reasonably well documented [23-25], but the multi-variate partitioning of elements between the three phases found in the present natural assemblage is not well constrained by prior work [23, 26, 27]. No systematic trends in $V_0$, and thus no systematic trends in individual phase compositions, were observed among our samples, despite different loading and synthesis conditions (e. g., pressure and temperature, see [19]). Therefore, the following assumptions were made in our analysis: the calcium perovskite is pure CaSiO$_3$, incorporating all of the Ca in the multi-phase assemblage [27]; the Fe concentration in magnesiowüstite is determined by $V_0$ [14], with the remaining Fe assumed to be in orthorhombic perovskite; and all of the Al$^{3+}$ cations are distributed between the Mg and Si sites in orthorhombic perovskite for charge balance. With the above constraints, it is possible to balance all major elements yielding the assemblage composition: 64 (± 2) mol% orthorhombic perovskite ($\text{Mg}_{0.88}\text{Fe}^{2+}_{0.05}\text{Fe}^{3+}_{0.01}\text{Al}_{0.12}\text{Si}_{0.94})\text{O}_3$, 31 (± 2) mol% magnesiowüstite ($\text{Mg}_{0.80}\text{Fe}_{0.20})\text{O}$, and 5 (± 1) mol% calcium perovskite CaSiO$_3$. We note that the final values of whole-rock density remain unchanged, within quoted uncertainties, regardless of the validity of these assumptions [19].

High-Pressure, Room-Temperature Measurements
Orthorhombic Perovskite

Orthorhombic perovskite has long been recognized as the most abundant phase in the Earth’s mantle (e.g., [28, 29]), probably making up more than 75% of the lower mantle and more than 50% of the Earth’s volume. Except for a few early experiments on natural samples [20, 21, 29] and some recent experiments on Al-bearing perovskites [30-32], much of the focus has been on the Mg-endmember MgSiO$_3$ (e.g., [33]) and (Mg, Fe)SiO$_3$ (e.g., [34]) (see Table 1-2). At all pressures in our experimental range, we observe orthorhombic perovskite and measure its unit-cell volume as a function of pressure (Fig. 1-2). Despite a variety of synthesis-pressure and -temperature conditions, we do not find a systematic difference in Fe partitioning between opv and mw [19]. Using a 3$^{rd}$ order Birch-Murnaghan equation of state, we determined a compression curve for our opv that is comparable to previous equations of state (Table 1-2, Fig. 1-2). The relatively large $V_0$ that we measure for orthorhombic perovskite (~1% larger than pure endmember MgSiO$_3$) is consistent with the results of past studies on Fe- and Al-bearing silicate perovskites [14, 30, 31], and the compressibility is compatible with that documented by [31] (~2% smaller than pure endmember MgSiO$_3$).

Magnesiowüstite

The next most dominant phase of the lower mantle is expected to be magnesiowüstite. Extensive work has been done on the pure Mg (e.g., [35-37]) and Fe (e.g., [38]) endmembers, as well as on a variety of solid solutions between the two (e.g., [39, 40]). Magnesiowüstite is observed at all experimental pressures, as well as on quench, except at pressures of 70.6 and 84.4 GPa where the overlap of opv diffraction
peaks obscures mw identification. The equation of state we determine is compatible with those of former studies as is shown in Table 1-2 and Fig. 1-3.

**Calcium Perovskite**

Calcium perovskite is thought to be the least abundant of the major phases in the Earth’s lower mantle [41]. Due to the consequently weak diffraction peaks of calcium perovskite and overlap of diffraction peaks with those of the more abundant phases, cpv was not detected above \( \sim 70 \) GPa, even though its stability has been documented to much higher pressures [42, 43] (Fig. 1-4). Calcium perovskite also does not quench to ambient conditions [42, 43]. Although there is some spread in the reported compressibility of cpv [42, 44, 45], its low abundance (~5 mol%) means that any resulting uncertainties make little difference to the assemblage’s bulk properties (< 0.5%). Because of these difficulties, and the fact that our measurements are in agreement with it, the equation of state of [43] was used to determine the volume of the calcium perovskite portion of the assemblage in the modeling that we describe below.

**Whole-Rock Assemblage**

As we are able to track the structural changes of individual phases (see Table 1-2, 1-3), we are able to determine a high-pressure assemblage volume and density at each pressure, \( V_{RVV-35} = \sum x_i V_i \), from the molar ratios \( x_i \) of the three phases and the respective unit-cell volumes \( V_i \) (see Fig. 1-5). The derivative of the pressure–volume relation for the high-pressure assemblage yields the isothermal bulk modulus of the rock as a function of pressure (therefore depth) in the mantle.

Other methods of determining the bulk properties of composite materials include the Reuss (all grains equally stressed) and Voigt (all grains equally strained)
approximations (see [46] for a review); these provide a measure of the uncertainty associated with averaging the moduli (Table 1-3). The arithmetic mean of the Voigt and Reuss bounds, the Voigt-Reuss-Hill average, has also been suggested as another approximation to the moduli of composite materials. Whichever approximation is invoked (they all are very similar and lie within mutual uncertainties), none of our conclusions regarding the density and bulk composition of the lower mantle is affected. Also dispersion of seismic waves is known to affect the seismologically-observed moduli, which are only partly relaxed, whereas our approach yields fully relaxed values. Therefore our calculated bulk modulus represents a lower bound for comparison with the mantle, and may systematically underestimate the seismologically observed modulus. In combination with the effects of averaging moduli for a poly-phase aggregate, the resultant offset can amount to as much as 3% increased stiffness at lower-mantle conditions.

**Birch-Murnaghan Equation of State**

The individual-phase isothermal bulk modulus, $K_{0T}$, and its pressure derivative, $K_{0T}'$, are determined using the Birch-Murnaghan formulism [47], a good approximation for Earth materials, which is based on a Taylor expansion of the Helmholtz free energy in the Eulerian strain measure, $f$:

$$f = \frac{1}{2} \left[ \left( \frac{V}{V_0} \right)^{-2/3} - 1 \right]$$  \hspace{1cm} (1)

where $V/V_0$ is the ratio of the high-pressure volume $V$ to the room-pressure volume $V_0$. The pressure $P$ can be normalized to give an effective derivative of the equation of state:

$$F = \frac{P}{3f(1 + 2f)^{3/2}}$$  \hspace{1cm} (2)
Expanding to fourth order of Eulerian strain,

\[ F = K_{0T} (1 + f \left( \frac{3}{2} K_{0T} - 6 \right) + f^2 \left( \frac{3}{2} K_{0T} K_{0T}'' + \frac{3}{2} K_{0T} \left( K_{0T}' - 7 \right) + \frac{143}{6} \right) + ...) \]  

(3)

Routinely the Birch-Murnaghan formulism is truncated to third order (before the \( f^2 \) term), hence an \( F \) vs. \( f \) plot yields \( K_{0T} \) (intercept) and \( K_{0T}' \) (via the slope) (see Insets of Figs. 1-2 through 1-5).

**High-Temperature Analysis**

*Whole-rock assemblage at High Pressure and Temperature*

To compare our whole-rock, room-temperature data with seismic observations of the Earth’s interior, we applied a Mie-Grüneisen-Debye model to determine a thermal equation of state for each phase as well as for the whole-rock assemblage at temperatures of 1000 K, 1500 K, 2000 K, 2500 K and 3000 K (Fig. 1-6) (see following Section, High-Temperature Analysis: Thermal Equation of State). Because the temperature variation is expected to be small (thus negligible) across the bulk of the lower mantle (~500 K from about 700-2700 km depth), an isotherm is a reasonable approximation for the actual temperature variation throughout much of the deep interior [48, 49]. Two sets of thermal parameters are used to compare our thermally-corrected data with the Preliminary Reference Earth Model (PREM) [50] (Table 1-4): the “Standard” set [39, 45, 51] is supported by a reanalysis of the gold pressure standard [52], whereas the “Low” set is illustrative of prior analyses yielding relatively low values of thermal expansion [6].

**Thermal Equation of State**

A Mie-Grüneisen thermal equation of state adds a thermal pressure to the room-temperature pressure at a given volume, yielding a total pressure at temperature \( T \) [6, 53]:
\[ P_{\text{total}}(V, T) = P(V, 300 \, K) + P_{\text{thermal}}(V, T) \]  

(4)

where,

\[ P_{\text{thermal}} = \left( \frac{\gamma}{\Theta} \right) \left[ E_{\text{thermal}}(T, \Theta_D) - E_{\text{thermal}}(300 \, K, \Theta_D) \right] \]  

(5)

where the Grüneisen parameter, \( \gamma \), is,

\[ \gamma = \gamma_0 \left( \frac{V^q}{V_0^q} \right) = -\frac{\partial \ln \Theta_D}{\partial \ln V} \]  

(6)

and with a Debye model for the internal energy, \( E_{\text{thermal}} \),

\[ E_{\text{thermal}} = 9nRT \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} x^3 \exp \left( \frac{\gamma_0 - \gamma}{q} \right) dx \]  

(7)

and

\[ \Theta_D = \Theta_{D0} \exp \left( \frac{\gamma_0 - \gamma}{q} \right), \]  

(8)

where \( \Theta_D \) is the Debye temperature. Subscript 0 indicates the value at zero pressure and 300 K. The correction from isothermal to adiabatic (subscript S) bulk modulus, \( K_S = K_T (1 + \alpha \gamma T) \), is performed in a self-consistent manner using the same model and individual phase parameters (\( \alpha \) is the volumetric thermal-expansion coefficient). \( K_T \) is determined from the fourth-order Birch-Murnaghan equation of state (3) [47]. For the whole-rock assemblage we use \( \gamma_{\text{rock}} = \sum a_i \gamma_i \), where \( a_i \) is the volume percent of each phase and \( \gamma_i \) is the phase Grüneisen parameter. As thermal expansion depends on both pressure and temperature, we solved for \( \alpha_{\text{rock}} \) directly by solving for the volume of the rock (as stated above) for a small interval (± 1K) around the temperature of interest and using

\[ \alpha = \frac{\partial \ln V}{\partial T} \bigg|_p \]  

(Table 1-4).
High-Temperature Error Analysis

Representative error bars for the final pressure at a given volume and temperature are derived from the uncertainties in the 300 K compression measurements and in the correction to high temperature. The uncertainty in compression is determined via Bell et al.’s analysis [54], while the uncertainty in the thermal correction is based on the difference between the Standard and Low thermal-expansion models (Fig. 1-6, Table 1-4). This determination of uncertainty is probably generous, as the thermal portion (~2 times the compression part of the uncertainty) encompasses the full range of possible temperature corrections (“Standard” and “Low” Thermal Expansion Parameters, Table 1-4).

In general, at a given pressure an increase in temperature increases the uncertainty in the thermal portion; conversely, at a given temperature an increase in pressure decreases the uncertainty in the thermal portion of the equation of state. The reason for this is that the absolute magnitude of the thermal correction to the 300 K pressure (at a given volume) increases with increasing temperature and decreases with increasing pressure, the latter mitigating the increase in relative uncertainty of the thermal correction with increasing pressure.

Discussion

We apply our results by first testing the hypothesis that the entire mantle is uniformly mixed, and consists of a pyrolite-like composition. Comparison of experimentally observed phase transformations with the corresponding depths of seismic
discontinuities within the transition zone yields a temperature of 1900-2000 K for the top of the lower mantle, rising toward 2500 K at the bottom assuming an adiabat [14-16, 55].

It is evident from Fig. 1-6A, however, that the density of our natural peridotite is incompatible with such high temperatures. Even accounting for uncertainties in the thermal properties, the density can only be matched by temperatures between 1000-1500 K across the depth of the lower mantle: about 1000 K too cold, and below typical eruption temperatures at mid-ocean ridges [56]. Indeed, analysis of the bulk modulus also suggests lower-mantle temperatures in the range of 2000-3000 K (Fig. 1-6B).

One way to satisfy the observed properties of the lower mantle with a peridotite-like composition close to that which we studied is to invoke a higher iron content at depth, rather than the preferred value for the upper mantle (Mg# ≈ 0.90, see Table 1-1). If some region of the deep mantle differs in bulk composition from the shallower mantle, however, then temperatures are expected to be increased by about 500-1000 K due to the presence of thermal boundary layers at the interface at which the bulk composition changes, across which mixing is suppressed [49]. Thus, temperatures of about 2500-3000 (± 500) K are reasonable for a layer within the lower mantle that differs in composition from shallower depths (e.g., [8]).

As varying the Fe/Mg ratio has essentially no effect on the bulk modulus of the high-pressure, perovskite-dominated assemblage (e.g., [34]), Fig. 1-6B shows that such high temperatures are in good accord with our measurements. The density deficit of ~1-4% obtained from Fig. 1-6A can then be “fixed” by an increased abundance of iron, to an Mg# ≈ 0.85 (± 0.02). The result is non-unique, however, as there are tradeoffs between
temperature and composition (e. g., including Si, Al and Ca abundances) for satisfying the observed properties of the lower mantle [51].

Nevertheless, the intrinsic density difference between the observed density profile for the lower mantle and the lower-mantle density predicted for the current (pyrolite-like) estimate of upper-mantle bulk composition is sufficient to stabilize layered convection over geological time [57-60]. Thus geochemical, geophysical and—now—mineral physical observations point to complex structure and dynamics of the Earth’s mantle [8].
References


[22] H.K. Mao, P.M. Bell, J.W. Shaner, et al., Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of the ruby R1 fluorescence pressure gauge from 0.06 to 1 Mbar, Journal of Applied Physics 49(6), 3276-83, 1978.


[34] H.K. Mao, R.J. Hemley, Y. Fei, et al., Effect of pressure, temperature, and composition on lattice parameters and density of (Fe,Mg)SiO$_3$-Perovskites to 30 GPa, Journal of Geophysical Research 96(B5), 8069-79, 1991.


### Table 1-1. Composition comparison of BN-35 and pyrolite.

<table>
<thead>
<tr>
<th>Element</th>
<th>BN-35&lt;sup&gt;a&lt;/sup&gt; cations per 12 O</th>
<th>Pyrolite&lt;sup&gt;b&lt;/sup&gt; cations per 12 O&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Pyrolite&lt;sup&gt;c&lt;/sup&gt; cations per 12 O</th>
<th>Upper estimate&lt;sup&gt;d&lt;/sup&gt; cations per 12 O&lt;sup&gt;e&lt;/sup&gt;</th>
<th>Mantle estimate&lt;sup&gt;d&lt;/sup&gt; cations per 12 O&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>3.291 (0.094)</td>
<td>3.251 (0.084)</td>
<td>3.252</td>
<td>3.243 (0.101)</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.014 (0.008)</td>
<td>0.011 (0.011)</td>
<td>0.010</td>
<td>0.010 (0.003)</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.367 (0.112)</td>
<td>0.391 (0.073)</td>
<td>0.375</td>
<td>0.382 (0.127)</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.503 (0.072)</td>
<td>0.474 (0.101)</td>
<td>0.526</td>
<td>0.458 (0.102)</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.009 (0.002)</td>
<td>0.006 (0.002)</td>
<td>0.007</td>
<td>0.007 (0.003)</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>4.010 (0.128)</td>
<td>4.094 (0.235)</td>
<td>4.137</td>
<td>4.125 (0.215)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.256 (0.012)</td>
<td>0.239 (0.065)</td>
<td>0.271</td>
<td>0.255 (0.077)</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.042 (0.010)</td>
<td>0.056 (0.021)</td>
<td>0.057</td>
<td>0.057 (0.028)</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.0 (-)</td>
<td>0.002 (0.007)</td>
<td>0.001</td>
<td>0.001 (0.009)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.014 (-)</td>
<td>0.012 (0.003)</td>
<td>0.013</td>
<td>0.013 (0.003)</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.017 (0.018)</td>
<td>0.017 (0.006)</td>
<td>0.023</td>
<td>0.023 (0.006)</td>
<td></td>
</tr>
</tbody>
</table>

Mg# = Mg/(Mg+Fe) = 0.89

<sup>a</sup> Uncertainties are given in parentheses and are determined by taking the difference of element values from an independent measurement of the starting sample [18, 20].

<sup>b</sup> An average pyrolite from Table 5-2, column 8 of [1]. Uncertainties are determined from the standard deviation of columns 1-7 of Table 5-2.

<sup>c</sup>A simplified model based on the 5 major oxide components [61].

<sup>d</sup>From [62].

<sup>e</sup>Uncertainties are given in parentheses.

<sup>f</sup>Fe<sup>2+</sup> and Fe<sup>3+</sup> totals are combined.
Table 1-2. Comparison of equation of state parameters of lower-mantle minerals using a 3\textsuperscript{rd} order Birch-Murnaghan equation of state [47].

<table>
<thead>
<tr>
<th>Study</th>
<th>Composition</th>
<th>( V_0 ) (Å(^3))</th>
<th>( K_0T ) (GPa)</th>
<th>( K_0T' )</th>
<th>( P ) range (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Orthorhombic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perovskite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This Study</td>
<td>( \text{Mg}<em>{0.88}\text{Fe}^{2+}</em>{0.05}\text{Fe}^{3+}<em>{0.01}\text{Al}</em>{0.12}\text{Si}_{0.94}\text{O}_3 )</td>
<td>163.90 (0.67)</td>
<td>269 (14)</td>
<td>4.06 (0.66)</td>
<td>24-107</td>
</tr>
<tr>
<td>Fiquet et al., 2000</td>
<td>( \text{MgSiO}_3 )</td>
<td>162.27 (0.01)</td>
<td>253 (9)</td>
<td>3.9 (0.2)</td>
<td>39-94</td>
</tr>
<tr>
<td>Knittle &amp; Jeanloz, 1987</td>
<td>( \text{Mg}<em>{0.88}\text{Fe}</em>{0.12}\text{Si}_3 )</td>
<td>162.77 (0.39)</td>
<td>266 (6)</td>
<td>3.9 (0.4)</td>
<td>25-127</td>
</tr>
<tr>
<td>Mao et al., 1991</td>
<td>( \text{Mg}<em>{1.00-0.80}\text{Fe}</em>{0.00-0.20}\text{Si}_3 )</td>
<td>162.49 (0.07)</td>
<td>261 (4)</td>
<td>4.0(^a)</td>
<td>&lt;  29, synthesis at 40 GPa</td>
</tr>
<tr>
<td>Zhang &amp; Weidner, 1999</td>
<td>( \text{Al}<em>{0.10}(\text{MgSi})</em>{0.95}\text{O}_3 )</td>
<td>163.2 (0.2)</td>
<td>234 (4)</td>
<td>4.0(^a)</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Daniel et al., 2001</td>
<td>( \text{Al}<em>{0.154}(\text{MgSi})</em>{0.923}\text{O}_3 )</td>
<td>163.52 (0.03)</td>
<td>229 (4)</td>
<td>2.5 (0.4)</td>
<td>&lt; 32</td>
</tr>
<tr>
<td>Andrault et al., 2001</td>
<td>( \text{AlFe}<em>{0.05}(\text{MgSi})</em>{0.95}\text{O}_3 )</td>
<td>163.2 (0.2)</td>
<td>265.0 (3.7)</td>
<td>4.0(^a)</td>
<td>26-58</td>
</tr>
<tr>
<td>Andrault et al., 2001</td>
<td>( \text{Al}<em>{0.08}\text{MgSi}</em>{0.95}\text{O}_3 )</td>
<td>163.3 (0.2)</td>
<td>266.7 (2.8)</td>
<td>4.0(^a)</td>
<td>26-56</td>
</tr>
<tr>
<td>Andrault et al., 2001</td>
<td>( \text{Al}<em>{0.22}(\text{MgSi})</em>{0.89}\text{O}_3 )</td>
<td>163.5 (0.4)</td>
<td>275.5 (6.0)</td>
<td>4.0(^a)</td>
<td>26-68</td>
</tr>
<tr>
<td><strong>Magnesiowüstite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This Study</td>
<td>( \text{Mg}<em>{0.80}\text{Fe}</em>{0.20}\text{O} )</td>
<td>76.09 (0.60)</td>
<td>175 (9)</td>
<td>3.75 (0.46)</td>
<td>24-107</td>
</tr>
<tr>
<td>Jackson &amp; Niesler, 1982</td>
<td>( \text{MgO} )</td>
<td>74.69 (0.2)</td>
<td>162.5 (0.2)</td>
<td>4.13 (0.09)</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>Duffy et al., 1995</td>
<td>( \text{MgO} )</td>
<td>74.7(^a) (0.1)</td>
<td>177 (4)</td>
<td>4.0 (0.1)</td>
<td>&lt; 227</td>
</tr>
<tr>
<td>Dewaele et al., 2000</td>
<td>( \text{MgO} )</td>
<td>74.71(^a) (0.2)</td>
<td>161(^a) (0.2)</td>
<td>3.94 (0.2)</td>
<td>&lt; 53</td>
</tr>
<tr>
<td>Richet et al., 1989</td>
<td>( \text{Mg}<em>{0.40}\text{Fe}</em>{0.60}\text{O} )</td>
<td>78.43 (0.02)</td>
<td>149 (4)</td>
<td>4.0(^a)</td>
<td>&lt; 50</td>
</tr>
<tr>
<td>Richet et al., 1989</td>
<td>( \text{Mg}<em>{0.20}\text{Fe}</em>{0.80}\text{O} )</td>
<td>79.26 (0.03)</td>
<td>148 (10)</td>
<td>4.0(^a)</td>
<td>&lt; 49</td>
</tr>
</tbody>
</table>

\(^a\) fixed.
Table 1-3. Equation of state data for the three high-pressure phases and the whole-rock assemblage observed for a peridotite composition at lower-mantle pressures\(^a\). Listed are the measured \(V_0\), \(K_{0T}\), \(K_{0T}^\prime\) and mol\% of each of the three lower-mantle phases, as well as the whole-rock bulk properties obtained by four methods for calculating the properties of multi-phase assemblages [46]. We assume that the given phases keep a constant mol\% abundance throughout the mantle, which yields \(K_{0T} = 247 (\pm 21)\) GPa and \(K_{0T}^\prime = 4.01 (\pm 0.67)\). The other methods (Reuss, Voigt, and Voigt-Reuss-Hill) all yield values that fall within quoted uncertainties of our assumption of constant molar abundance.

<table>
<thead>
<tr>
<th>Phase</th>
<th>(V_0 (\text{Å}^3))</th>
<th>(K_{0T} \text{ (GPa)})</th>
<th>(K_{0T}^\prime)</th>
<th>mol%, (x_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>opv</td>
<td>163.90 (0.67)</td>
<td>269 (14)</td>
<td>4.06 (0.66)</td>
<td>64 (2)</td>
</tr>
<tr>
<td>mw</td>
<td>76.09 (0.60)</td>
<td>175 (9)</td>
<td>3.75 (0.46)</td>
<td>31 (2)</td>
</tr>
<tr>
<td>cpv(^b)</td>
<td>45.37 (0.08)</td>
<td>281 (4)</td>
<td>4.0</td>
<td>5 (1)</td>
</tr>
<tr>
<td>Whole rock</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constant mol%</td>
<td>247 (21)</td>
<td>4.01 (0.67)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reuss</td>
<td>247 (15)</td>
<td>4.13 (0.48)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voigt</td>
<td>254 (11)</td>
<td>4.00 (0.51)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voigt-Reuss-Hill</td>
<td>251</td>
<td>4.07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Uncertainties in parentheses are 2 standard deviations.

\(^b\) Values taken from [43], where \(K_{0T}^\prime\) is constrained to 4.0.
Table 1-4. Thermal parameters used in or obtained from the Mie-Grüneisen-Debye equation of state.

<table>
<thead>
<tr>
<th>Thermal Parameters</th>
<th>opva</th>
<th>mw</th>
<th>cpvc</th>
<th>rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta_D$ (K)</td>
<td>1017</td>
<td>500</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>1.96</td>
<td>1.5</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>$q$</td>
<td>2.5</td>
<td>1.1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{300 , K, , 0 , GPa , (10^{-5} , K)}$</td>
<td>2.4</td>
<td>3.1</td>
<td>3.0</td>
<td>2.6</td>
</tr>
<tr>
<td>$\alpha_{2000 , K, , 0 , GPa , (10^{-5} , K)}$</td>
<td>6.8</td>
<td>5.0</td>
<td>3.4</td>
<td>6.3</td>
</tr>
<tr>
<td>$\alpha_{2000 , K, , 25 , GPa , (10^{-5} , K)}$</td>
<td>3.3</td>
<td>2.9</td>
<td>2.3</td>
<td>3.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermal Parameters</th>
<th>opve</th>
<th>mw</th>
<th>cpvc</th>
<th>rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta_D$ (K)</td>
<td>1000</td>
<td>673</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>1.31</td>
<td>1.41</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>$q$</td>
<td>1</td>
<td>1.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{300 , K, , 0 , GPa , (10^{-5} , K)}$</td>
<td>1.6</td>
<td>3.1</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$\alpha_{2000 , K, , 0 , GPa , (10^{-5} , K)}$</td>
<td>3.0</td>
<td>4.8</td>
<td>3.4</td>
<td>3.3</td>
</tr>
<tr>
<td>$\alpha_{2000 , K, , 25 , GPa , (10^{-5} , K)}$</td>
<td>2.1</td>
<td>2.6</td>
<td>2.3</td>
<td>2.2</td>
</tr>
</tbody>
</table>

$^{a}$ From [9].

$^{b}$ From [39].

$^{c}$ From [45].

$^{d}$ Calculated values (see Section 5.2, High-Temperature Analysis: Thermal Equation of State).

$^{e}$ From [6].
**Fig. 1-1.** Rietveld refinement applied to the powder-diffraction pattern of BN-35 at 59.5 (± 1.4) GPa and 300 K collected with synchrotron x-ray (\(\lambda = 0.7277\) Å) radiation [19]. The raw data (dots) and the refinement (solid curve) are consistent with 3 phases: opv, mw, cpv (tick marks in descending order). The unassigned diffraction peak at ~2.5 Å is attributed to ruby (internal pressure standard). The goodness of the fit is shown in the residuals (% difference between observed and Rietveld fit) plotted below the data. **Inset:** *In-situ* high-pressure and high-temperature energy-dispersive x-ray diffraction pattern show the same phases to be present at 36 (± 2) GPa and T~1500 (± 150) K. Vertical lines denote the gold pressure calibrant, and diffraction peaks from the individual phases are labeled.

**Fig. 1-2.** Volume versus pressure for orthorhombic perovskite at room temperature, based on data collected both on compression with laser-annealing at each pressure (black) and decompression (white). Gray symbols are measurements done without laser-annealing after initial synthesis heating. The circles are data collected from monochromatic (\(\lambda = 0.7277\) Å) synchrotron radiation and the squares are from laboratory-based sources [19]. The heavy solid line through the data points is calculated from the Birch-Murnaghan equation of state. The dashed line is the Birch-Murnaghan equation of state of [34]. **Inset:** A more sensitive representation of the same data, an \(F\) vs. \(f\) plot (see Section 4.5, High-Pressure, Room-Temperature Measurements: Birch-Murnaghan Equation of State). The intercept of the line is the \(K_{0T}\) (269 ± 14 GPa) of orthorhombic perovskite, while the slope is related to \(K_{0T}'\) (4.06 ± 0.66). The shaded area is the extrapolated uncertainty.
**Fig. 1-3.** Volume versus pressure for magnesiowüstite at room temperature. Symbol identification is the same as in Figure 1-2. The heavy solid line through the data points is calculated from the Birch-Murnagahan equation of state. The dashed line is the Birch-Murnagahan equation of state of [39]. **Inset:** An $F$ vs. $f$ plot, as in Figure 1-2. The intercept of the line is the $K_{0T}$ ($175 \pm 9$ GPa) of magnesiowüstite, while the slope is related to $K_{0T}'$ ($3.75 \pm 0.46$).

**Fig. 1-4.** Volume versus pressure for calcium perovskite at room temperature. Symbol identification is the same as in Figure 1-2. The heavy solid line through the data points is calculated from the Birch-Murnagahan equation of state of [43] (used in this study). For comparison, the dashed line is the equation of state measured by [44]. **Inset:** An $F$ vs. $f$ plot, as in Figure 1-2.

**Fig. 1-5.** Volume versus pressure for the transformed peridotite assemblage at room temperature, based on data collected both on compression and decompression. The circles are data collected from synchrotron radiation and the squares are from laboratory-based sources [19]. The solid shapes represent diffraction patterns in which all 3 phases are present, while the open shapes include extrapolation due to unobserved phases. The curve through the data points is calculated from the Birch-Murnaghan equation of state of the whole-rock assemblage. **Inset:** An $F$ vs. $f$ plot, as in Figure 1-2. The intercept of the line is the $K_{0T}$ ($247 \pm 21$ GPa) of the rock, while the slope is related to $K_{0T}'$ ($4.01 \pm 0.67$).
Fig. 1-6. Comparison of lower-mantle assemblage with PREM [50]. Two scenarios are plotted which give a range of possibilities for mantle thermal expansivities: Standard (solid) and Low (dash) thermal expansion parameters (see Table 1-4). The isothermal temperatures used in the model are 1000 K (blue), 1500 K (purple), 2000 K (green), 2500 K (orange), and 3000 K (red). Representative error bars at 65 GPa (~1500 km depth) and 2000 K are given (see Section 5.3, High-Temperature Analysis: High-Temperature Error Analysis). (A) At temperatures relevant to the lower mantle of the Earth (2000-3000 K), the density of the whole-rock assemblage is lower than that of PREM by 1-4%. (B) The adiabatic bulk modulus $K_s$ also differs from PREM by up to ~3% for relevant lower-mantle temperatures.
Fig. 1-1
Orthorhombic Perovskite

$\text{Mg}_{0.88}\text{Fe}^{2+}_{0.05}\text{Fe}^{3+}_{0.01}\text{Al}_{0.12}\text{Si}_{0.94}\text{O}_3$
Magnesiowüstite
(Mg$_{0.80}$Fe$_{0.20}$)O

Fig. 1-3
Fig. 1-4
Fig. 1-5
Fig. 1-6