Pressure-volume-temperature equation of state of MgSiO$_3$ perovskite from molecular dynamics and constraints on lower mantle composition

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Abstract
The composition of the lower mantle can be investigated by examining densities and seismic velocities of compositional models as functions of depth. In order to do this it is necessary to know the volumes and thermoelastic properties of the compositional constituents under lower mantle conditions. We determined the thermal equation of state (EOS) of MgSiO$_3$ perovskite using the nonempirical variational induced breathing (VIB) interatomic potential with molecular dynamics simulations at pressures and temperatures of the lower mantle. We fit our pressure-volume-temperature results to a thermal EOS of the form $P(V, T) = P_0(V, T_0) + \Delta P_{th}(T)$, where $T_0 = 300$ K and $P_0$ is the isothermal Universal EOS. The thermal pressure $\Delta P_{th}$ can be represented by a linear relationship $\Delta P_{th} = a + bT$. We find $V_0 = 165.40$ Å$^3$, $K_{T_0} = 273$ GPa, $K_{\prime T_0} = 3.86$, $a = -1.99$ GPa, and $b = 0.00664$ GPa K$^{-1}$ for pressures of 0-140 GPa and temperatures of 300-3000 K. By fixing $V_0$ to the experimentally determined value of 162.49 Å$^3$ and calculating density and bulk sound velocity profiles along a lower mantle geotherm we find that the lower mantle cannot consist solely of (Mg,Fe)SiO$_3$ perovskite with $X_{Mg}$ ranging from 0.9-1.0. Using pyrolitic compositions of 67 vol % perovskite ($X_{Mg} = 0.93-0.96$) and 33 vol % magnesiowüsite ($X_{Mg} = 0.82-0.86$), however, we obtained density and velocity profiles that are in excellent agreement with seismological models for a reasonable geotherm.
1. Introduction

By comparing density and seismic velocity profiles of compositional models with seismological models it is possible to investigate the composition of the Earth’s lower mantle. Therefore an understanding of the high pressure, high temperature properties, and equation of state (EOS) of (Mg,Fe)SiO$_3$ perovskite is vital to our understanding of the lower mantle, as this mineral accounts for perhaps two thirds of the mineralogy of this region [Bina, 1998] and one third of the volume of the entire planet. Experiments have been performed up to pressures approaching those found at the base of the mantle, but direct coverage of the high pressure, high temperature properties, and thermodynamic stability of perovskite in the lower mantle is an open question and has been studied with experimental and theoretical methods. Work by Meade et al. [1995], Saxena et al. [1996, 1998], and Dubrovinsky et al. [1998] indicate that perovskite will break down to oxides under lower mantle conditions. The thermodynamic analysis of Stixrude and Bukowinski [1992] and the experimental work of Serghiou et al. [1998], however, suggest that it will not.

We used MD simulations using the nonempirical variational induced breathing (VIB) model, similar to the model of Wolf and Bukowinski [1988], to investigate the properties and EOS of Mg-pv at pressures (0-140 GPa) and temperatures (300-3000 K) that cover the bulk of the conditions found in the lower mantle. Newton’s equations of motion are solved as functions of time, and equilibrium properties are obtained as time averages over a sufficiently long interval. This accounts for all orders of anharmonicity but not for quantum lattice dynamics effects. Thus our results are more appropriate at high temperatures above the Debye temperature (1076 K [Anderson, 1998]) and are entirely suitable for the Earth’s mantle. We then used our results, combining them with data for other components and phases where appropriate, to calculate density and seismic velocity profiles along a geothermal gradient for different compositional models. These profiles were then compared with profiles from a reference Earth model in order to test the compositional models’ fitness for the lower mantle.

2. Method

MD simulations were performed on supercells of 540-2500 atoms of orthorhombic (Pbnm) Mg-pv using the nonempirical VIB potential. VIB is a Gordon-Kim type model [Gordon and Kim, 1972], where the potential is obtained by overlapping ionic charge densities which are computed using the local density approximation (LDA) [Hedin and Lundqvist, 1971]. The total energy is a sum of (1) the self-energy of each atom, (2) the long-range electrostatic energy computed using the Ewald method, and (3) the short-range interaction energy, i.e., the sum of the kinetic, short-range electrostatic, and exchange-correlation overlap energies from the LDA. Free oxygen ions are not stable and are stabilized in VIB by surrounding them with Watson spheres with charges equal in magnitude but opposite in sign to the ions, e.g., 2+ spheres for O$^{2-}$. Interactions are obtained
for overlapping ion pairs at different distances with different Watson sphere radii for each oxygen. The
interactions are fit with a 23-parameter analytical expression as functions of the interatomic distance \( r \)
and \( U_i = z_i/R_i \), where \( U_i \), \( z_i \), and \( R_i \) are the Watson sphere potential, charge, and radius for atom \( i \).
For each oxygen \( i \), \( R_i \) is adjusted to minimize the total energy at each time step. This gives an effective
many-body potential. The oxygen ions respond to changes in their environment. For example, they
are compressed at high pressures relative to low pressures. Previous work on Mg-pv using the related PIB model
gave an equation of state in excellent agreement with experiment [Cohen, 1987]. Also, work using VIB on
MgO has shown that this model accurately predicts EOS and thermal properties [Inbar and Cohen, 1995].

Nominally charged ions give semiquantitative, but less accurate, results than desired for Mg-pv. This
is due to a small degree of covalent bonding relative to ionic bonding as revealed by electronic structure
calculations of cubic \((Pm\overline{3}m)\) Mg-pv performed using the first principles LAPW method [Cohen et
al., 1989]. These calculations show that while the Mg is nearly a perfectly spherical Mg\(^{2+}\) ion, there
is some charge transfer from O to Si and a small covalent bond charge (involving \( \approx 0.1 \) electrons) between Si and O. By varying the ionic charges on Si \((3.1+ \text{ to } 3.55+)\) and O \((1.70\text{ to } 1.85-)\) to account for the covalency, but otherwise using the same methods as before, we compared the resulting zero temperature pressure-volume data to the LAPW results of Stixrude and Cohen [1993]. The best agreement was found with Si\(^{3.4+}\) and O\(^{1.8-}\). Using these charges, the resulting potential gives excellent agreement with the octahedral rotation energetics obtained using the LAPW method [Stixrude and Cohen, 1993; Hemley and Cohen, 1996] (Figure 2).

MD runs were performed for 20 ps with a 1 fs time step using a sixth-order Gear predictor-corrector scheme [Gear, 1971] in the constant pressure-temperature ensemble using the thermostat and barostat of Martyna et al. [1994]. Initial atomic positions for the genesis run were the same as those for the unrotated octahedra of Stixrude and Cohen [1993]. Subsequent runs at higher pressures or temperatures used the positions generated by a previous run. Statistical ensembles were obtained in \(~2000\) iterations for the genesis run and in \(<1000\) iterations for subsequent runs.

We fitted pressure-volume-temperature \((P\text{-}V\text{-}T)\) data obtained from the MD simulations to a thermal
EOS of the form

\[
P(V, T) = P_0(V, T_0) + \Delta P_{th}(T)
\]

with a reference temperature \( T_0 = 300 \text{ K} \) and the thermal pressure \( \Delta P_{th} \) relative to the 300 K isotherm.
We analyzed our results using the third-order Birch-Murnaghan isothermal EOS [Birch, 1952]

\[
P_0 = 3K_{T_0}f(1 + 2f)^{5/2}(1 - \xi f),
\]

with the Eulerian strain variable \( f \) and the coefficient \( \xi \) given by

\[
f = \frac{1}{2} \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right], \quad \xi = \frac{3}{2} (K'_{T_0} - 4),
\]

and the Universal EOS [Vinet et al., 1987]

\[
P_0 = 3K_{T_0}(1 - x) x^{-2} \exp \left[ \frac{3}{2} \left( K'_{T_0} - 1 \right)(1 - x) \right],
\]

where \( x = (V/V_0)^{1/3} \), \( K_T \) is the isothermal bulk modulus, and \( K'_{T} \) is its pressure derivative.

\[
\Delta P_{th} \text{ is given by}
\]

\[
\Delta P_{th} = \int_{T_0}^{T} \left( \frac{\partial P}{\partial T} \right)_V dT = \int_{T_0}^{T} (\alpha K_T) d\tilde{T},
\]

where \( \alpha \) is the volume coefficient of thermal expansion. If \( \alpha K_T \) is independent of \( T \), then the thermal pressure can be represented by a linear relationship [Anderson, 1980, 1984; Anderson and Suzuki, 1983]

\[
\Delta P_{th} = a + bT,
\]

which applies to a wide range of solids at high \( T \), including minerals, alkali metals, and noble gas solids [Anderson, 1984]. The linearity of \( \Delta P_{th} \) in \( T \) starts at 300 K [Masuda and Anderson, 1993] in minerals. There should be a small anharmonic correction at high \( T \), which results in an additional \( cT^2 \) term in (6), which is often sufficiently small so that it can be neglected [Anderson, 1984]. Indeed, including the \( cT^2 \) term did not statistically improve our fits. Likewise, our fits were not improved by including volumetric compression terms [e.g., Jackson and Rigden, 1996].

Once the P-V-T data were fit, other parameters, such as \( \alpha \),

\[
\alpha = \left( \frac{\partial \ln V}{\partial T} \right)_P,
\]
its volume dependence, the Anderson-Grüneisen parameter,
\[ \delta_T = \left( \frac{\partial \ln \alpha}{\partial \ln V} \right)_T, \tag{8} \]
the Grüneisen parameter,
\[ \gamma = \frac{\alpha K_T V}{C_V}, \tag{9} \]
and its volume dependence,
\[ q = \left( \frac{\partial \ln \gamma}{\partial \ln V} \right)_T, \tag{10} \]
were obtained by numerical differentiation. \( C_P \) was found by calculating enthalpy \((U + PV)\) at each MD run point and differentiating with respect to \(T\). Using the relation \( C_P = C_V(1 + \alpha T) \), equation (9) can be rewritten as
\[ \gamma = \left( \frac{C_P}{\alpha K_T V - T \alpha} \right)^{-1}. \tag{11} \]

3. Results

MD calculations were performed at 46 pressure-temperature (P-T) points, ranging from 0-140 GPa and 300-3000 K, thus covering the P-T conditions of the lower mantle (Table 1). Axial ratios \( b/a \) and \( c/a \) follow smooth trends at lower mantle pressures (Figures 3a-3b), with deviations away from the \( Pbnm \) structure seen at \( P \leq 12 \) GPa and \( T \geq 2400 \) K. At 3000 K and 12 GPa the structure can be observed to move towards cubic lattice parameters \((b/a \rightarrow 1, c/a \rightarrow \sqrt{2})\). This point, in particular, is close to the melting curve of Mg-pv [Heinz and Jeanloz, 1987, Knittle and Jeanloz 1984, Porrier, 1985], and such temperature-induced phase transitions have been predicted for Mg-pv by MD [Wolf and Bukowinski, 1987] and lattice dynamics [Matsui and Price, 1991]. In addition, it has been found for RbCaF\(_3\) and KMnF\(_3\) perovskites by MD simulations [Lewis and Lépine, 1989, Nosé and Klein, 1988] and observed experimentally in the fluoride perovskite neighborite (NaMgF\(_3\)) [Chao et al., 1961]. Regardless of these changes, the volumes are well behaved as functions of pressure and temperature (Figure 3c), and no other structural anomalies or melting was encountered during runs at other P-T points.

The resulting P-V-T EOS fits and their reduced \( \chi^2 \) values are given in Table 2. Both the Birch-Murnaghan and Universal EOSs are in excellent agreement with experimental results. As for the accuracy of our thermal pressure expression, RMS differences between volumes found using equation (1) for either EOS and those found using isothermal EOSs are of the order of \( 10^{-3} \) \( \AA^3 \). As for the differences between the two equation of state forms, Jeanloz [1988] compared them over moderate compressions and found that they are quite similar. More recent work by Cohen et al. [2000] supports this, but they found that for large \((>30\%)\) strains and for determining parameters such as \( V_0, K_{T_0} \), and \( K_{T_0}' \), the Universal EOS works best. So, for the rest of our analyses we use that here. However, given that under the pressure range studied, compressions will be no greater than 25\%, so we can confidently compare our results with those of others that were found with the Birch-Murnaghan EOS.

Once we determined the EOS parameters, we determined volumes for Mg-pv over a wide P-T range (-10-150 GPa, 0-3300 K). Using this extended data set, we determined the isostructural bulk modulus \([K_T = -V(\partial P/\partial V)_T] \) at those points and \( \alpha, \delta_T, \gamma, \) and \( q \) using equations (7), (8), (11), and (10). We found \((\partial K/\partial T)_{P=0} = -0.0251 \) GPa K\(^{-1}\), close to those found experimentally, -0.023 GPa K\(^{-1}\) [Wang et al., 1994] and -0.027 GPa K\(^{-1}\) [Fiquet et al., 1998], as well as one found by the inversion of multiple experimental data sets, -0.021 GPa K\(^{-1}\) [Jackson and Rigden, 1996].

Figure 4 shows \( \alpha \) at pressures from 0 to 140 GPa. Experimental results shown have higher \( T \) slopes, as well as higher extrapolated values for most temperatures, though an average value found by Jackson and Rigden [1996] at zero GPa of \( 2.6 \times 10^{-5} \) K\(^{-1}\) over 300-1660 K matches our value over the same \( T \) range exactly. Kato et al. [1995] found an average value of \( 2.0 \pm 0.4 \times 10^{-5} \) K\(^{-1}\) over 298-1473 K and 25 GPa, close to our average value of \( 1.89 \times 10^{-5} \) K\(^{-1}\) at the same conditions. The lack of quantum effects in our MD results can be seen at low temperatures; instead of tending toward zero at zero temperature, \( \alpha \) remains large. The \( \delta_T \) increases with \( T \), but decreases as \( P \) increases (Figure 3). The dependency of \( \delta_T \) on \( T \) decreases as a function of \( P \), with convergence to a value of 2.87 at \(~)130 \) GPa, similar to the high-pressure behavior in MgO found by the same MD method [Ishii and Cohen, 1995]. Our value of \( \delta_T = 3.79 \) at ambient conditions is in excellent agreement with the experimentally derived value of Wang et al. [1994] of 3.73, though it is lower than the value of 4.5, found by Masuda and Anderson [1995] from the experimental data of Utsumi et al. [1995]. Other theoretical determinations of \( \delta_T \) are much higher, however. Hama
Ahrens and Suito [1998a] found a value of 5.21, on the basis of calculations using the LAPW results of Stixrude and Cohen [1993] and the Debye approximation for lattice vibration. Using MD and semiempirical potentials [Matsui, 1988], Belonoshko and Dubrovinsky [1996] found $\delta_T = 5.80$, and Patel et al. [1996] found $\delta_T = 7.0$ using the same potentials, combining MD with lattice dynamics. Anderson [1998], using Debye theory, calculated zero pressure values ranging from 4.98 at 400 K to $\sim 4$ at 1000 K $\leq T \leq 1800$ K, coming close to our values at those temperatures.

The Gruneisen parameter also increases as a function of $T$ and decreases as a function of $P$ and approaches a value of 1 at pressures of 130-140 GPa (Figure 5). Our value of 1.33 at zero $P$ and 300 K matches well with Wang et al.’s [1994] value of 1.3 and Utsumi et al.’s [1995] and Masuda and Anderson’s [1995] value of 1.45. Stixrude et al. [1992], using the experimental data of Mao et al. [1991], found a higher value of $\gamma = 1.96$. Values determined by the inversion of multiple experimentally determined P-V-T data sets match well also: 1.5 [Bina, 1995], 1.33 [Jackson and Rigden, 1999], and 1.42 [Shim and Duffy, 2000]. Two shock wave studies find a value of 1.5 [Duffy and Ahrens, 1999; Akins and Ahrens, 1999] on the basis of limited data sets: four for the former (with $q$ fixed equal to 1) and two for the latter. Values of $\gamma$ from theoretical studies range from very close to ours, 1.279 [Hama and Suito, 1998a] and 1.44 [Hemley et al., 1987], to 1.97 [Belonoshko and Dubrovinsky, 1996; Patel et al., 1996]. Anderson’s [1998] zero pressure, 300 K value of 1.52 is somewhat higher than ours, but at 400-1800 K his values of $\sim 1.4$ are very close to ours.

The volume dependence of $\gamma$, $q$, is 1.03 at 300 K (Figure 5). Our equation of state form, with $\Delta P_{th}$ linear in $T$ and independent of volume, constrains $q = 1$ if the isochoric heat capacity $C_V = 3nR$, the classical harmonic value. As $T$ increases, we find that $q$ increases to a value of 1.07 at 3000 K owing to anharmonicity. Values from inverted experimental data sets range from 1.0 [Bina, 1995] to 2.0 [Shim and Duffy, 1991]. Stixrude et al. [1992] found a high $q$ value of 2.5 to go along with their value for $\gamma$. Akins and Ahrens’s [1999] value was even higher, $q = 4.0 \pm 1.0$ with $C_V = 5nR$, but these are preliminary conclusions based on limited data. Patel et al. [1996] found a value of 3.0 at 0 GPa, decreasing to 1.7 at 100 GPa using a combination of molecular and lattice dynamics. Anderson’s [1998] Debye calculations gave values close to unity at $T \geq 1000$ K, with $q$ decreasing slightly with increasing $T$, to 0.82 at 1800 K.

### 4. Discussion and Conclusions

Taking sets of experimental P-V-T data, we fit the high temperature data [Fiquet et al., 1998, 2000; Stixrude et al., 1999] and available experimental MgSIO$_3$ data to our thermal Universal EOS form (Table 2) in order to have consistent bases for comparison. The resulting fits have higher statistical uncertainties but compare well with our results. Volumes calculated along the lower mantle geothermal gradient of Brown and Shankland [1981], which has a starting $T$ of 1873 K at 670 km (Figure 1), show that those calculated from our EOS are 3 to 4 $A^3$ per unit cell larger, $\sim 2.5\%$, than those calculated from the inverted experimental data sets (Figure 8). This corresponds to density differences of $\sim 0.1$ g cm$^{-3}$. This is the opposite of the typical error of the local density approximation to density functional theory, on which our method is based. The larger volume is due to the choice of ionic charges and other model assumptions. If we fix $V_0$ to the experimentally determined value of 162.49 A$^3$ [Mao et al., 1991] but otherwise use our EOS parameters, our calculated volumes are very close, within 1%, to the volumes derived from the inverted experimental data sets. The comparisons also improve as pressure increases. To compare our model with other zero temperature theoretically derived EOSs, we calculated volumes at 0 K from 0-140 GPa and fit an isothermal Universal EOS to them (Table 3).

Compositional models of the lower mantle can be tested against seismological models by examining densities and seismic wave velocities as functions of depth. Candidates include pyrolite [Ringwood, 1975] and chondritic or pure perovskite models. Studies support both the former [Bina and Silver, 1990; Stacey, 1996] and latter [Butler and Anderson, 1978; Stixrude et al., 1992], though uncertainties in the thermodynamic parameters of the constituent minerals make it difficult to resolve this question with certainty. Indeed, several studies have been able to support both models depending on whether high (pure perovskite) or low (pyrolite) values of $\alpha$ and $\delta_T$ or $\gamma$ and $q$ are used [Zhao and Anderson, 1994; Anderson et al., 1995; Karki and Stixrude, 1999].

Calculating the densities of Mg-pv along a geothermal gradient [Brown and Shankland, 1981] (Figure 4), we see that they are $\sim 0.2-0.3$ g cm$^{-3}$ ($\sim 4-5\%$) too low compared with those from the Prelim-
The calculated bulk sound velocities, \( V_0 = \sqrt{K_S/\rho} \), where \( K_S = K_T(1 + \gamma \alpha T) \), are, in turn, \(~0.4-0.6 \text{ km s}^{-1} \) too high compared to the ak135+ seismological model [Kennett et al., 1993; Montagner and Kennett, 1996] (Figure 9b). Using the experimentally determined value of \( V_0 = 162.49 \text{ km s}^{-1} \) [Mao et al., 1995] in place of our calculated value does increase the densities somewhat, but not enough to match the PREM values.

As the perovskite found in the lower mantle should be a solid solution of the Mg and Fe end-members, we added iron by adjusting density by [Jeanloz and Thompson, 1983],

\[
\rho (X_{Fe}) = \rho (0)/(1 + 0.269 X_{Fe})
\]

but we did not change the bulk moduli [Mao et al., 1993]. Including 10 mol % Fe does cause densities to agree somewhat with the PREM values (Figure 10a), but the bulk sound velocities are still much too high (Figure 10b). Consequently, we find that the lower mantle cannot consist solely of (Mg,Fe)SiO\(_3\) perovskite.

We also tested pyrolitic compositions consisting of mixtures of perovskite and magnesiowüstite (mw). Densities of mw were calculated using the thermodynamic data set of Fei et al. [1991], as well as \( K_T \)s for the Mg end-member. \( K_T \)s were then calculated using the relation

\[
\alpha(P, T) = \alpha(P_0, T) \left[ \frac{V(P, T)}{V(P_0, T)} \right]^{\gamma_T},
\]

with \( \delta_T \) and \( \gamma \) from Inbar and Cohen [1995]. Iron was accounted for in \( K_S \) via the relationship [Jeanloz and Thompson, 1983]

\[
K_S (X_{Fe}) = K_S (0) + 17 X_{Fe}.
\]

Experimental evidence suggests that for such a bulk composition, \( K^\text{pv-mw}_{Fe-Mg} \) should increase in the mantle from \(~0.20 \) (660 km) to \(~0.35 \) (1500 km), with \( X^\text{pv}_\text{Fe} \) decreasing and \( X^\text{mw}_{\text{Fe-Mg}} \) increasing with depth [Mao et al., 1997]. Compositional models with high Fe content of pv and low Fe content of mw (and vice versa) fall inbetween the results of those shown in Figure 11. Given the range of Fe-Mg partitioning between perovskite and magnesiowüstite under the appropriate pressure and temperature conditions, we find pyrolite to be the most likely compositional model for the lower mantle.

Given that other components (Al, Fe\(^{3+}\)) and phases (CaSiO\(_3\) perovskite) should be present in the lower mantle, we do not expect exact agreement of a simplified pyrolite model with any seismological model. It is believed that, under lower mantle conditions, Al\(_2\)O\(_3\) is mainly incorporated into the Mg-pv structure [Irihune, 1994; Wood, 2000]. Generally, the effect of the incorporation of Al into Mg-pv on its physical properties has been considered small [e.g., Weidner and Wang, 1998]. However, Al, unlike Fe, causes significant distortion in the Mg-pv lattice [O’Neil and Jeanloz, 1994], which may affect the compressibility. Recent experimental work by Zhang and Weidner [1999], at pressure of up to 10 GPa and temperatures of up to 1073 K, indicates that compared with MgSiO\(_3\), Mg-pv with 5 mol % Al has a smaller \( K_T \) value (232-236 GPa) and a \((\partial K_T/\partial T)_P \) value more than double that in magnitude. The values for \( \alpha_0 \), \((\partial\alpha/\partial T)_P \), and \( \delta_T \) are also larger. Smaller bulk moduli and the higher density (0.2% at 300 K and 0 GPa) would cause seismic velocities to decrease. In addition, the presence of Al tends to equalize the partitioning of Fe into perovskite and magnesiowüstite and may allow garnet to coexist with perovskite in the uppermost \(~100 \text{ km} \) of the lower mantle [Wood and Rubie, 1996; Wood, 2000]. These partitioning experiments, however, were done at high \( f_{O_2} \), so it is uncertain how applicable they are to the mantle. The effect of the presence of Fe\(^{3+}\) in Mg-pv on the EOS and elasticity, while known for defect concentrations and electrostatic charge balance [McCammon, 1997; 1998], is unknown. As for CaSiO\(_3\) perovskite (Ca-pv), experimental data suggest that its elastic properties are in excellent agreement with seismological models and thus would be invisible in the lower mantle [Wang et al., 1990; Hama and Suito, 1998].

Performing MD calculations over the range pressures and temperatures found in the Earth’s mantle, we find a thermal EOS that is in excellent agreement.
with experimental results. Thermodynamic parameters can be derived that agree well with experimentally determined values and that can be confidently interpolated to conditions found in the lower mantle. Moreover, no solid-solid phase transitions or melting was found during the runs under lower mantle conditions, so orthorhombic MgSiO$_3$ perovskite should be stable to the core-mantle boundary. Using these results, we find that pyrolite with $K_{Fe-Mg}^{PV}$ = 0.26-0.34 is the most likely compositional model for the lower mantle.

**Acknowledgments.** We thank Iris Inbar, Russell Hemley, Stephen Gramsch, Joe Akins, Mark Woods, Sheila Coleman, and Lars Stixrude for helpful discussions and comments. We acknowledge the support of the National Science Foundation through grant EAR-9870328. The computations were performed on the Cray SV1 at the Geophysical Laboratory, with the support of NSF grant EAR-9975753 and the W. M. Keck Foundation.

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Received March 29, 2000; revised September 28, 2000; accepted December 5, 2000.

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Figure 1. Experimental pressure-temperature coverage of (Mg,Fe)SiO$_3$ perovskite. Open symbols are for static experiments on $X_{\text{Mg}} = 1.0$, solid symbols are for $X_{\text{Mg}} = 0.9$, and open symbols with crosses are shock wave data. Hexagons, Kudoh et al., [1987]; right-facing triangles, Ross and Hazen, [1990]; left-facing triangles, Wang et al., [1994]; upward pointing triangles, Fiquet et al., [1998]; downward pointing triangles, Fiquet et al., [2000]; diamonds, Saxena et al., [1999]; open circles, Utsumi et al., [1995]; solid circles, Knittle and Jeanloz, [1987]; squares, Funamori et al., [1996]; stars, Mao et al., [1991]; pentagons, Kato et al., [1995]; circle with cross, Duffy and Ahrens, [1993]. Solid curve is the lower mantle geothermal gradient of Brown and Shankland [1981]. Static experimental work has direct coverage of approximately the upper one third. The shock wave data point that falls near the geotherm is perovskite plus magnesiowüstite.
Figure 2. Energetics of octahedral rotations: calculated total energies relative to the cubic structure (Pm3m) using VIB (curves) and LAPW [Stixrude and Cohen, 1993; Hemley and Cohen, 1996] (symbols) as a function of (left) $R$ and (right) $M$ point rotation angles as represented by the fractional change in the oxygen coordinate ($\delta_R$ and $\delta_M$). The orthorhombic structure ($Pbnm$) occurs at $\delta_R = 0.0912$ and $\delta_M = 0.0766$ at $P = 0$ GPa.
Figure 3. Structural parameters and volumes of MD results: (a) $b/a$ axis ratio and (b) $c/a$ axis ratio. At low pressures and high temperatures the structure begins to deviate from orthorhombic $Pbnm$, but no phase transitions, with the possibility of the structure heading toward cubic at 12 GPa and 3000 K. (c) Volume. Symbols are MD results and curves are Universal EOS fits every 300 K.
Figure 4. Volume coefficient of thermal expansion. Solid curves are from this work. Other symbols, from experimental work as follows: dashed curve (0 GPa), Wang et al. [1994]; circle (0 GPa), Fiquet et al. [1998]; square (0 GPa) and dashed-dotted line (25 GPa), Funamori et al. [1996]
Figure 5. Anderson-Grüneisen parameter as a function of temperature. The circle is the experimentally determined value from Wang et al. [1994]. The square is the value determined by Masuda and Anderson [1995] from the experimental data of Utsumi et al. [1995]. Open circles are $\delta_T$s determined from Debye theory by Anderson [1998].
Figure 6. Grüneisen parameter as a function of temperature. The solid circle is the experimentally determined value from Wang et al. [1994], and the square is the value determined by Masuda and Anderson [1995] from the experimental data of Utsumi et al. [1995]. Other symbols are from inversion of multiple experimentally determined data sets: triangle, Bina [1995]; inverted triangle, Jackson and Rigden [1996]); and diamond, Shim and Duffy [2000]. Open circles are $\gamma$s determined from Debye theory by Anderson [1998].
Figure 7. The $\ln \gamma$ versus $\ln V$. The slope of each curve gives $q$: solid curve and squares, 300 K; dashed curve and circles, 1200 K; dotted curve and triangles, 2100 K; dash-dotted curve and inverted triangles, 3000 K. The lower temperatures are all close to 1, with a slight rise to 1.07 at 3000 K.
Figure 8. Volumes of MgSiO$_3$ perovskite along the geothermal gradient of Brown and Shankland [1981].Dash-dotted curve is volume from our Universal EOS fit. Dashed curve is from our Universal fit with $V_0$ fixed to 162.49 Å$^3$ [Mao et al., 1991]. Dotted curve is for experimental data sets with $V_0$ fixed to 162.49 Å$^3$ (see Table 2). Both high temperature (F98+F00+S99) and all MgSiO$_3$ data sets fall on the same line. Shaded areas indicate the uncertainties in the fits of the experimental data sets.
Figure 9. (a) Densities and (b) bulk sound velocities of MgSiO$_3$ perovskite calculated along the lower mantle geotherm of Brown and Shankland [1981] using the thermal Universal EOS. Solid curve is for uncorrected volumes and dashed curve is for $V_0$ set to the experimental value of Mao et al., [1991]. Squares are densities from PREM [Dziewonski and Anderson, 1981]. Circles are velocities from the ak135-f seismological model [Kennett et al., 1995; Montagner and Kennett, 1996].
Figure 10. (a) Densities and (b) bulk sound velocities of (Mg,Fe)SiO$_3$ perovskite calculated along the geotherm of Brown and Shankland [1981] using the experimental value of $V_0$ Mao et al., [1991] for $X_{pv}^{Fe} = 0.00$ (solid curve), 0.05 (dashed curve), and 0.10 (dotted curve). Squares are densities from PREM [Dziewonski and Anderson, 1981]. Circles are velocities from the ak135-f seismological model [Kennett et al., 1995; Montagner and Kennett, 1996].
Figure 11. (a) Densities and (b) bulk sound velocities of two simplified pyrolite models (67 vol % pv, 33 vol % mw) along the geotherm of Brown and Shankland [1981]. Solid curve is \(X_{\text{Mg}}^{\text{pv}} = 0.93\), \(X_{\text{Mg}}^{\text{mw}} = 0.82\). Dashed curve is \(X_{\text{Mg}}^{\text{pv}} = 0.96\), \(X_{\text{Mg}}^{\text{mw}} = 0.86\). Squares are densities from PREM [Dziewonski and Anderson, 1981]. Circles are velocities from the ak135-f seismological model [Kennett et al., 1995; Montagner and Kennett, 1996].
Table 1. MD P-V-T Data Used in EOS Fits

| P, GPa | T, K  | a, Å  | b, Å  | c, Å  | V, Å³ |
|--------|-------|-------|-------|-------|-------|
| 0      | 300   | 4.8166| 4.9283| 6.9649| 165.33|
| 0      | 600   | 4.8299| 4.9397| 6.9787| 166.50|
| 0      | 900   | 4.8439| 4.9519| 6.9944| 167.77|
| 0      | 1200  | 4.8586| 4.9648| 7.0107| 169.11|
| 0      | 1500  | 4.8732| 4.9769| 7.0289| 170.48|
| 0      | 1800  | 4.8886| 4.9901| 7.0455| 171.87|
| 0      | 2100  | 4.9109| 5.0145| 7.0578| 173.20|
| 0      | 2400  | 4.9311| 5.0354| 7.0688| 175.52|
| 0      | 2700  | 4.9525| 5.0538| 7.0831| 177.28|
| 0      | 3000  | 4.9672| 5.0633| 7.1076| 178.76|
| 12     | 900   | 4.7790| 4.8856| 6.8895| 160.86|
| 12     | 1200  | 4.7917| 4.8951| 6.9024| 161.90|
| 12     | 1500  | 4.8036| 4.9051| 6.9165| 162.97|
| 12     | 1800  | 4.8169| 4.9157| 6.9288| 164.06|
| 12     | 2100  | 4.8295| 4.9256| 6.9441| 165.18|
| 12     | 2400  | 4.8429| 4.9367| 6.9586| 166.36|
| 12     | 2700  | 4.8628| 4.9539| 6.9690| 167.88|
| 12     | 3000  | 4.9035| 4.9531| 6.9695| 169.27|
| 25     | 300   | 4.6971| 4.8093| 6.7728| 152.99|
| 25     | 600   | 4.7073| 4.8169| 6.7830| 153.80|
| 25     | 900   | 4.7181| 4.8250| 6.7948| 154.68|
| 25     | 1200  | 4.7285| 4.8330| 6.8055| 155.53|
| 25     | 1500  | 4.7390| 4.8409| 6.8166| 156.38|
| 25     | 1800  | 4.7497| 4.8487| 6.8291| 157.27|
| 25     | 2100  | 4.7609| 4.8572| 6.8408| 158.19|
| 25     | 2400  | 4.7728| 4.8658| 6.8514| 159.11|
| 25     | 2700  | 4.7850| 4.8736| 6.8645| 160.08|
| 25     | 3000  | 4.8015| 4.8859| 6.8773| 161.34|
| 50     | 900   | 4.6194| 4.7307| 6.6445| 145.20|
| 50     | 1200  | 4.6280| 4.7366| 6.6531| 145.84|
| 50     | 1500  | 4.6366| 4.7414| 6.6632| 146.48|
| 50     | 1800  | 4.6450| 4.7474| 6.6726| 147.14|
| 50     | 2100  | 4.6545| 4.7524| 6.6821| 147.81|
| 50     | 2400  | 4.6627| 4.7589| 6.6920| 148.49|
| 50     | 2700  | 4.6728| 4.7644| 6.7014| 149.20|
| 50     | 3000  | 4.6814| 4.7700| 6.7129| 149.90|
| 140    | 300   | 4.3572| 4.5023| 6.2698| 123.00|
| 140    | 600   | 4.3627| 4.5046| 6.2768| 123.35|
| 140    | 900   | 4.3687| 4.5076| 6.2839| 123.74|
| 140    | 1200  | 4.3747| 4.5097| 6.2903| 124.10|
| 140    | 1500  | 4.3806| 4.5121| 6.2967| 124.46|
| 140    | 1800  | 4.3867| 4.5146| 6.3027| 124.82|
| 140    | 2100  | 4.3923| 4.5164| 6.3104| 125.18|
| 140    | 2400  | 4.3986| 4.5186| 6.3170| 125.55|
Table 1. (continued)

| P, GPa | T, K | a, Å  | b, Å  | c, Å  | V, Å³ |
|--------|------|-------|-------|-------|-------|
| 140    | 2700 | 4.4048| 4.5209| 6.3235| 125.92|
| 140    | 3000 | 4.4109| 4.5230| 6.3309| 126.31|
## Table 2. Equation of State Parameters

|                     | $V_0$, Å$^3$ | $K_{T_0}$, GPa | $K'_{T_0}$ | a, GPa | b, GPa K$^{-1}$ | $\chi^2$, GPa |
|---------------------|--------------|----------------|------------|--------|----------------|--------------|
| **This work**       |              |                |            |        |                |              |
| Birch-Murnaghan EOS | 165.40(6)    | 274(1)         | 3.73(2)    | -2.00(2) | 0.00667(5)     | 0.08561      |
| Universal EOS       | 165.40(5)    | 273(1)         | 3.86(2)    | -1.99(1) | 0.00664(5)     | 0.06712      |
| **Experimental results** |          |                     |            |        |                |              |
| M91                 | 162.49(7)    | 261(4)         | 4$^b$      |        |                |              |
| F98                 | 162.65(15)   | 262(6)         | 3.41(22)   | -1.79(21) | 0.00597(70)   | 1.47438      |
|                     | 162.49$^c$   | 267(3)         | 3.25(10)   | -1.79(21) | 0.00597(70)   | 1.41566      |
|                     | 162.60(9)    | 264$^d$        | 3.33(2)    | -1.79(21) | 0.00596(69)   | 1.41333      |
|                     | 162.49$^c$   | 264$^d$        | 3.41(3)    | -1.80(35) | 0.00601(73)   | 1.36143      |
| F00                 | 162.74(56)   | 239(8)         | 4.41(18)   | -1.85(6) | 0.00618(20)   | 0.61052      |
|                     | 162.49$^c$   | 245(4)         | 4.29(11)   | -1.85(6) | 0.00618(20)   | 0.59369      |
|                     | 161.68(18)   | 264$^d$        | 3.88(2)    | -1.85(6) | 0.00617(20)   | 0.60570      |
|                     | 162.49$^c$   | 264$^d$        | 3.52(4)    | -1.73(8) | 0.00577(28)   | 1.23307      |
| S99                 | 163.25(63)   | 242(6)         | 4.45(10)   | -1.72(1) | 0.00574(2)    | 0.26719      |
|                     | 162.49$^c$   | 256(5)         | 4.20(10)   | -1.72(1) | 0.00572(2)    | 0.26227      |
|                     | 161.10(28)   | 264$^d$        | 4.06(4)    | -1.71(1) | 0.00572(2)    | 0.26645      |
|                     | 162.49$^c$   | 264$^d$        | 3.89(2)    | -1.75(2) | 0.00584(7)    | 0.31819      |
| F98 + F00 + S99     | 162.93(33)   | 235(6)         | 4.72(13)   | -1.85(12) | 0.00618(38)   | 1.56307      |
|                     | 162.49$^c$   | 244(4)         | 4.52(13)   | -1.86(12) | 0.00621(40)   | 1.55478      |
|                     | 161.69(22)   | 264$^d$        | 4.08(1)    | -1.87(12) | 0.00622(38)   | 1.61901      |
|                     | 162.49$^c$   | 264$^d$        | 3.75(2)    | -1.73(15) | 0.00577(7)    | 2.22349      |
| **All**             | 162.31(10)   | 249(6)         | 4.40(20)   | -1.92(10) | 0.00639(32)   | 0.60337      |
|                     | 162.49$^c$   | 243(8)         | 4.55(28)   | -1.90(10) | 0.00635(34)   | 0.61628      |
|                     | 162.01(22)   | 264$^d$        | 3.92(8)    | -1.88(10) | 0.00628(38)   | 0.67860      |
|                     | 162.49$^c$   | 264$^d$        | 3.75(2)    | -1.67(20) | 0.00557(65)   | 1.04352      |

$^a$MD are best fit EOS parameters to molecular dynamics P-V-T data. Experimental results are the best fit Universal EOS parameters to experimental data sets, except data taken from Mao et al. [1991] (M91). Remaining experimental results are F98, Fiquet et al. [1998] (27 data points); F00, Fiquet et al. [2000] (38 data points); S99, Saxena et al. [1999], (37 data points); All, all $X_{Mg} = 1.0$ data (363 data points; see Figure 1). Values in parentheses are standard deviations.

$^b$Fixed equal to 4.

$^c$Fixed to $V_0$ from Mao et al. [1991].

$^d$Fixed to $K_{T_0}$ from Yeganeh-Haerati [1994].
Table 3. Zero Temperature Equation of State Parameters

|       | V, Å³  | K, GPa | K'   |
|-------|--------|--------|------|
| This work<sup>a</sup> | 164.22 | 280    | 3.84 |
| PIB<sup>b</sup>         | 164.78 | 252    | 4.05 |
| LAPW<sup>c</sup>        | 160.74 | 266    | 4.2  |
| PWPP<sup>d</sup>        | 157.50 | 259    | 3.9  |

<sup>a</sup>Universal fit. Other theoretical fits are third-order Birch-Murnaghan fits.

<sup>b</sup>Cohen [1987].

<sup>c</sup>Stixrude and Cohen [1993].

<sup>d</sup>Wentzcovitch et al. [1995].