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# Chemical composition of the lower mantle inferred from the equation of state of $\text{MgSiO}_3$ perovskite

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The chemical composition of the lower mantle is estimated based on the most reliable equation of state for  $\text{MgSiO}_3$  perovskite, obtained by an *in situ* X-ray diffraction study up to 29 GPa and 2000 K. The density profile and temperature gradient of various compositions are compared with those of the preliminary reference Earth model (PREM). Assuming that the lower mantle consists of a mixture of  $(\text{Mg}_{1-x}, \text{Fe}_x)\text{SiO}_3$  perovskite and  $(\text{Mg}_{1-y}, \text{Fe}_y)\text{O}$  magnesiowüstite, the mixing ratio (in molar ratio), which is in harmony with the PREM, is in the range from 2:1 to 3:1 of perovskite and magnesiowüstite when the total iron content,  $\text{Fe}/(\text{Mg} + \text{Fe})$ , is about 0.11. If the iron content is higher than this, the amount of magnesiowüstite decreases. An iron content less than 0.11 implies too low temperature compared to the geotherm, while if it is 0.15 or more, too high temperature is required.

## 1. Introduction

Silicate perovskite is believed to be the most important constituent of the lower mantle. Knowledge of its stable structure and equation of state in the lower mantle is crucial for discussions of the deep interior of the Earth. High-pressure and high-temperature *in situ* X-ray diffraction provides a useful method for acquiring such information and we have made many efforts to develop improved experimental techniques for *in situ* X-ray observations of silicate perovskite at lower mantle conditions. By adopting sintered diamond as an anvil material and using synchrotron radiation as an intense X-ray source, we have succeeded in extending the pressure and temperature limit of *in situ* X-ray studies (Yagi 1994) and we have clarified the following properties of  $\text{MgSiO}_3$  perovskite.

(1) The orthorhombic form of  $\text{MgSiO}_3$  perovskite is stable up to at least 1900 K and 36 GPa, which corresponds to the conditions of the uppermost part of the lower mantle. The distortion from cubic symmetry decreases only slightly with increasing temperature (Funamori & Yagi 1993; Funamori *et al.* 1994).

(2) Thermal expansion has been measured based on  $P$ - $V$ - $T$  data obtained from 5 to 29 GPa. Data were collected from room temperature to 800 K between 5 and 17 GPa, and up to 1200 K at 20 GPa (Utsumi *et al.* 1995). Above 25 GPa, observations were made up to 2000 K (Funamori *et al.* 1996). In these pressure and temperature ranges, the temperature dependence of thermal expansion was smaller than was reported at atmospheric pressure (Knittle *et al.* 1986).

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(3) Thermal expansion decreases with increasing pressure. The degree of decrease however, is not as large as that indicated by the equation of state proposed by Mao *et al.* (1991) (Utsumi *et al.* 1995; Funamori *et al.* 1996).

(4) Using the  $P$ – $V$ – $T$  data on pure  $\text{MgSiO}_3$  perovskite from atmospheric pressure to 29 GPa collected by Wang *et al.* (1994), Utsumi *et al.* (1995) and Funamori *et al.* (1996), an equation of state which can be applied over a wide range of pressure and temperature was obtained. (The measurements of Wang *et al.* (1994) were made using a cubic-anvil-type apparatus up to 11 GPa. The experimental techniques are very similar to those used in our study (Utsumi *et al.* 1995), except for the pressure range.) However, the uncertainty of the derived equation of state is still large, considering the many possible systematic errors in the measurements, although the accuracy is much higher than that of previous studies (Funamori *et al.* 1996).

So far, many studies have been made to estimate the chemical composition of the lower mantle using various analytical methods (see, for example, Jeanloz & Knittle 1989; Bina & Silver 1990; Hemley *et al.* 1992; Wang *et al.* 1994; Zhao & Anderson 1994). However, our newly obtained, more accurate, equation of state for perovskite (Funamori *et al.* 1996) enables us to make a better estimate of the density at lower mantle conditions for use in such discussions. Taking into account though the uncertainties of the equation of state mentioned previously along with that of the Earth model, it is still difficult to place strong constraints by comparing the density and/or bulk modulus. In spite of the difficulties, it is still important to consider the chemical composition of the lower mantle that can be inferred from the most plausible parameters obtained for the equation of state. The purpose of this paper then is to consider the chemical composition of the lower mantle, inferred from the most reliable equation of state available at present.

## 2. Analysis

As a first approximation, the chemical composition of the lower mantle can be simplified as a mixture of  $(\text{Mg}_{1-x}, \text{Fe}_x)\text{SiO}_3$  perovskite and  $(\text{Mg}_{1-y}, \text{Fe}_y)\text{O}$  magnesiowüstite. Recent high-pressure and high-temperature quench experiments on peridotite and pyrolite strongly suggest that, among other elements, Al is included in the magnesian perovskite while Ca crystallizes into another unquenchable perovskite structure under lower mantle conditions (O'Neill & Jeanloz 1990; Irifune 1994). Since the density and the elastic properties of these perovskites containing Ca and Al are reported to be similar to those of the  $(\text{Mg}, \text{Fe})\text{SiO}_3$  perovskite (Yagi *et al.* 1989; Mao *et al.* 1989; Wang & Weidner 1994; Yusa *et al.* 1995), this simple model is expected to represent the elastic properties of the lower mantle as a first approximation.

The analysis here is made by comparing the densities of various mixtures of perovskite and magnesiowüstite, calculated from the equations of state of each material, with the density profile of the preliminary reference Earth model (PREM) (Dziewonski & Anderson 1981), which is based on seismic observations. There are many factors other than the equations of state which affect the density calculation: the mixing ratio of perovskite and magnesiowüstite, the temperature, the total iron content, and the partition coefficient of iron between perovskite and magnesiowüstite. If the latter two parameters are held fixed, the density at a given depth can be calculated as a function of the mixing ratio and the temperature. The absolute temperature in the lower mantle, however, is not well determined, which results in a large uncertainty



in the mixing ratio. Therefore, in order to narrow the possible compositional range, additional considerations are made using information from the geothermal gradient.

### (a) Equations of state

Our previous calculation of the equation of state of  $\text{MgSiO}_3$  perovskite (Funamori *et al.* 1996) was made using the Birch–Murnaghan equation of state. For the high-temperature equation of state however, the Mie–Grüneisen equation of state has also been used. This equation is based on the Debye model of solids and is known to explain well the observed thermoelastic properties of many minerals. In the present paper, we first analyse the  $P$ – $V$ – $T$  data using the Mie–Grüneisen equation of state. However, in order to see the effect of the different equations of state, additional analyses are made using the Birch–Murnaghan equation of state as before.

In the Mie–Grüneisen equation of state, isothermal bulk modulus and its pressure derivative,  $K_0$  and  $K'_0$ , are required to specify a compression curve at a given temperature,  $T_0$ . The thermal pressure is then calculated by the Mie–Grüneisen relation

$$P_{\text{th}} = (\gamma/V)[E(T, \theta_D) - E(T_0, \theta_D)],$$

where  $E$ ,  $\theta_D$  and  $\gamma$  are the thermal internal energy, the Debye temperature and the Grüneisen parameter, respectively. The thermal internal energy is expressed as

$$E = 9nRT(T/\theta_D)^3 \int_0^{\theta_D/T} t^3 dt / (e^t - 1),$$

where  $n$  and  $R$  are the number of atoms in the chemical formula and gas constant, respectively. The volume dependences of  $\theta_D$  and  $\gamma$  are expressed as

$$\theta_D = \theta_{D0}(V/V_0)^{-\gamma}$$

and

$$\gamma = \gamma_0(V/V_0)^q,$$

where  $q$  is a fit parameter. Therefore, in total, five parameters,  $K_0$ ,  $K'_0$ ,  $\theta_{D0}$ ,  $\gamma_0$  and  $q$ , are required to specify the Mie–Grüneisen equation of state. For the least-squares fitting calculations, a third-order Birch–Murnaghan equation of state at room temperature was used to specify the compression curve. The bulk modulus was fixed at  $K_0 = 261$  GPa (Mao *et al.* 1991), as in the previous study (Funamori *et al.* 1996). The pressure derivative of the bulk modulus,  $K'_0$ , was fixed at either 4 or 3.75, as will be discussed later. The Debye temperature of  $\text{MgSiO}_3$  perovskite has been estimated by Akaogi & Ito (1993) based on heat capacity measurement. Calculations were made using either their proposed value ( $\theta_{D0} = 1030$  K), or treated  $\theta_{D0}$  as a free parameter. The two other parameters,  $\gamma_0$  and  $q$ , were always treated as free parameters. In total, six different parameter sets were determined by the combination of  $K'_0$ ,  $\theta_{D0}$  and equation of state.

At first, a total of 122 data, based on the NaCl pressure scale (Wang *et al.* 1994; Utsumi *et al.* 1995; Funamori *et al.* 1996), were used for calculating the free parameters. These data are represented by the circles in figure 9 of Funamori *et al.* (1996). This is the most consistent data set based on a single pressure scale to date. However, this excludes many of the high-temperature data obtained by using either Au or MgO as a pressure marker, represented by the diamonds in the same figure. There was no meaningful difference between the results when these additional 78 data were included. In this paper, only the results obtained using all 200 data are shown. In



order to show the range of the scatter however, one analysis was made using two data sets, 122 data and 200 data (which will be shown in figure 3).

Densities of the lower mantle, for given chemical compositions, were then calculated based on the equation of state parameters thus obtained. The density is affected by the assumption of the total iron concentration in the lower mantle and by the partition coefficient of iron between perovskite and magnesiowüstite. At the beginning, the total iron concentration,  $\chi_{\text{Fe}} = \text{Fe}/(\text{Mg} + \text{Fe})$ , and the partition coefficient,  $k = (\text{Fe}_{\text{Mw}}/\text{Mg}_{\text{Mw}})/(\text{Fe}_{\text{Pv}}/\text{Mg}_{\text{Pv}})$  were fixed to be 11% and 4%, respectively; however, the analyses were repeated later with these parameters varying.

Although the perovskite in the mantle contains some iron, the equation of state of pure  $\text{MgSiO}_3$  was used because, in many oxides and silicates with geophysical importance, the equation of state is relatively insensitive to the iron content, as long as the structure remains the same (Anderson *et al.* 1992). For the perovskite structure, it has been reported that there is no meaningful difference in the compression curves of  $\text{MgSiO}_3$  and  $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ , at room temperature (Mao *et al.* 1991).

For magnesiowüstite, the effect of iron on the bulk modulus is also small. Throughout the present analysis, the equation of state parameters for  $(\text{Mg}_{0.6}\text{Fe}_{0.4})\text{O}$  determined by Fei *et al.* (1992) were used. The chemical compositions considered in the present study are from a pure perovskite to a mixture of perovskite and magnesiowüstite in the molar ratio of  $1:\frac{2}{3}$ . Even in the most magnesiowüstite-rich composition, the amount of magnesiowüstite is less than a third of perovskite by volume. Thus, even though the equation of state of magnesiowüstite may be changed slightly, it only affects the final result a little.

A perovskite and magnesiowüstite lower mantle consists of two phases which have distinctly different bulk modulus. In a mixture of these two phases, because of the stress inhomogeneity, the average density obtained from the seismic observation is different from the average expected for a mixture under purely hydrostatic compression (see Zhao & Anderson 1994). In the present analysis, the density of the two-phase mixture was calculated using the Hill average (Watt *et al.* 1976).

### (b) The density at 26 GPa (721 km depth)

An example of the fitted parameters of the Mie–Grüneisen equation of state of  $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$  perovskite is summarized, together with those of  $(\text{Mg}_{1-y}\text{Fe}_y)\text{O}$  magnesiowüstite, in table 1. In the present least-squares calculations for perovskite, the parameters  $\gamma_0$  and  $q$  took the values of  $\gamma_0 = 1.4 \pm 0.1$  and  $q = 1.0 \pm 0.5$ , depending on the assumptions of other parameters. Even though these values are relatively unconstrained, there were no meaningful differences among the resulting volumes. The densities of pure perovskite with a composition  $(\text{Mg}_{0.89}\text{Fe}_{0.11})\text{SiO}_3$  and a  $1:\frac{2}{3}$  mixture of perovskite  $(\text{Mg}_{0.94}\text{Fe}_{0.06})\text{SiO}_3$  and magnesiowüstite  $(\text{Mg}_{0.81}\text{Fe}_{0.19})\text{O}$  are calculated at the pressure corresponding to 721 km (26.0 GPa) using these parameters. They are shown in figure 1 as a function of temperature, together with the density given by the PREM at 721 km. This pressure is within the pressure region of our experiments on pure  $\text{MgSiO}_3$ . Therefore, the upper curve (Pv0.11) reflects the measured density of perovskite, taking into consideration that the calculations here were made assuming that  $\chi_{\text{Fe}} = 11\%$ . This figure shows, if the error bars of the equation of state and the PREM are ignored, that the temperature at this depth should be *ca.* 2400 K in order for pure perovskite to explain the PREM density. On the other hand, a temperature of 1700 K is required if magnesiowüstite exists in a molar amount of about  $\frac{2}{3}$  that of perovskite. Although the temperature in the Earth's



Table 1. Equation of state parameters of  $(\text{Mg}_{1-x}, \text{Fe}_x)\text{SiO}_3$  perovskite and  $(\text{Mg}_{1-y}, \text{Fe}_y)\text{O}$  magnesiowüstite

	$(\text{Mg}_{1-x}, \text{Fe}_x)\text{SiO}_3$ perovskite	$(\text{Mg}_{1-y}, \text{Fe}_y)\text{O}$ magnesiowüstite <sup>a</sup>
Parameters for room-temperature third-order Birch–Murnaghan equation of state		
$K_0$ (GPa)	261	157
$K'_0$	3.75	4
$T_0$ (K)	300	300
$V_0$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$24.46 + 1.03x$	$11.25 + 1.00y$
Parameters for Mie–Grüneisen relation		
$\theta_{\text{D}0}$ (K)	1030	500
$\gamma_0$	1.37 (3)	1.50
$q$	0.6 (4)	1.1

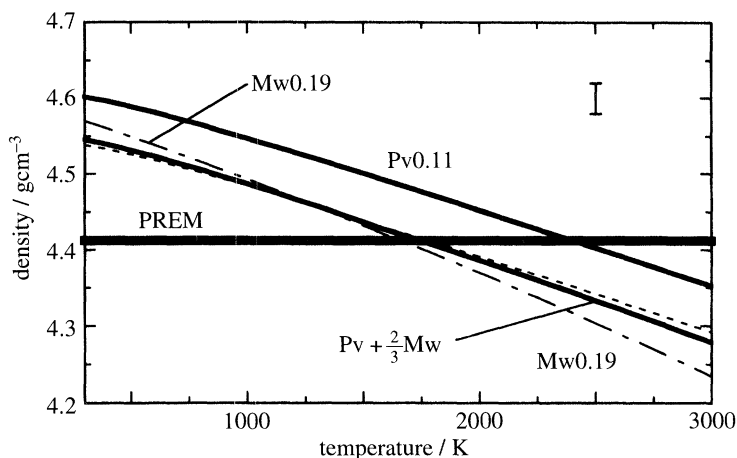
<sup>a</sup>Fei *et al.* (1992).

Figure 1. Densities calculated at 26 GPa (721 km) as a function of temperature for pure perovskite with 11% iron (Pv0.11) and a  $1:\frac{2}{3}$  mixture of perovskite and magnesiowüstite with 6% and 19% iron ( $\text{Pv} + \frac{2}{3}\text{Mw}$ ), respectively (total iron,  $\chi_{\text{Fe}} = 11\%$ ). Dashed curves are for the individual perovskite and magnesiowüstite phases. The error bar indicates the *ca.* 95% confidence level of the density of perovskite at 2000 K, calculated from Funamori *et al.* (1996). The density derived from the PREM (Dziewonski & Anderson 1981) at this depth is also shown.

deep interior has a large uncertainty, it is estimated at this depth to be between about 1900 K and 2700 K (see, for example, Anderson & Sumino 1980; Jeanloz & Morris 1986) depending on the model. Therefore, it can be concluded that, within this temperature range, it is difficult to accommodate magnesiowüstite in as much as  $\frac{2}{3}$  of perovskite, assuming that  $\chi_{\text{Fe}} = 11\%$ . If the temperature at this depth were better estimated, we could narrow the possibilities of the chemical composition. At present however, any combination of temperature, within the estimated limits, and corresponding chemical composition can explain the PREM density.



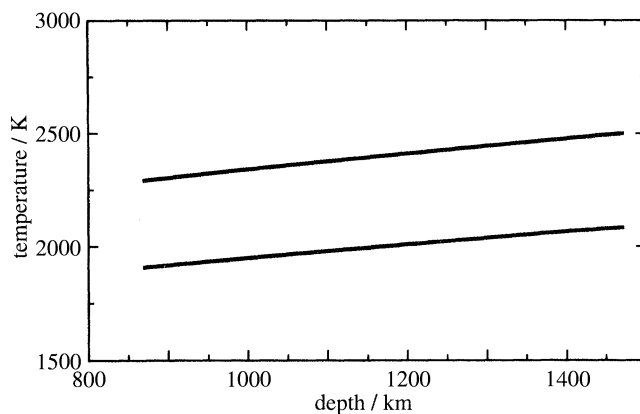


Figure 2. Adiabatic temperature profiles in the lower mantle calculated by the method of Brown & Shankland (1981), using the parameters of the PREM. The two curves were obtained by giving two different temperatures, 2000 and 2400 K, at 1171 km.

(c) *Comparisons of the temperature profile*

In order to get further constraints, calculations were made for comparison with the temperature profile of the Earth. Sometimes the chemical composition of the lower mantle is argued using density and bulk modulus as constraints. However, these two parameters are not independent in the adiabatic geothermal models. Moreover, the isothermal bulk modulus is very sensitive to the small systematic errors of the  $P$ - $V$ - $T$  measurements. For the discussions using density and bulk modulus, an adiabatic bulk modulus is required. Additional uncertainties are introduced in the conversion from isothermal to adiabatic bulk modulus.

If the comparison of the density in the previous section is made at several different depths, the temperature profile which satisfies a particular chemical composition can be obtained. We then assume that the temperature profile thus obtained should be in harmony with the temperature distribution expected from the PREM, to determine the best fit chemical composition.

In deriving the PREM, a uniform and adiabatic temperature distribution was assumed as a starting model and the resulting density profile has a nearly adiabatic temperature profile; in another words the inhomogeneity parameter,  $\eta$ , is close to unity (Dziewonski & Anderson 1981). Therefore, it is natural to expect that the lower mantle model which is in harmony with the PREM should have an adiabatic temperature distribution. There are several different methods to obtain an adiabatic temperature distribution and we have used the method of Brown & Shankland (1981) which is based on a Debye model with two cut-off frequencies. Parameters used for the calculation are density, compressional and shear velocities, mean atomic weight, and the starting temperature at a given depth. The first three parameters were obtained from the PREM while the mean atomic weight was calculated from the assumed chemical composition. However, even when the mean atomic weight is varied from 20.77 (pure perovskite) to 21.26 ( $1\frac{2}{3}$  mixture of perovskite and magnesiowüstite), the temperature effect is less than 1 K. Figure 2 is a temperature profile obtained through this calculation assuming two different starting temperatures, 2000 and 2400 K, at 1171 km depth.

There are many ways to calculate the temperature profile within the Earth, assuming either an adiabatic or non-adiabatic distribution. In table 2, the previous works are compared at 1171 km. The authors referenced in table 2 argued that the actual



Table 2. Parameters for adiabatic geothermal gradient at 1171 km

(Calculations were made assuming  $K_s = 380.2$  GPa (Dziewonski *et al.* 1975) and  $\gamma$  independent of temperature.)

	$T$ (K)	$\gamma$	$\gamma T/K_s$ (K GPa <sup>-1</sup> )	$(\gamma T/K_s)_{T=2255}$ (K GPa <sup>-1</sup> )
Stacy (1977)	2445	0.997	6.41	5.91
Anderson & Sumino (1980)	2255	1.138	6.75	6.75
Brown & Shankland (1981)	2034	1.23	6.58	7.30

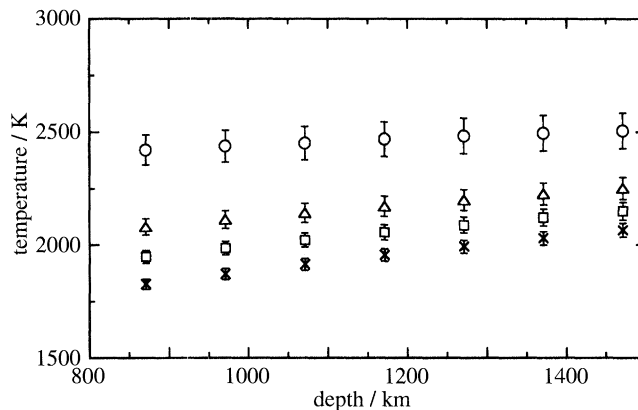


Figure 3. Temperatures which satisfy the PREM density for four different mixtures of perovskite and magnesiowüstite, calculated at every 100 km. Circles, triangles, squares, and crosses represent the mixtures in the following molar ratio of perovskite and magnesiowüstite, respectively; 1:0, 1:1/3, 1:1/2, and 1:2/3. Error bars are calculated based on one standard deviation of the results obtained through various equation of state parameters.

distribution would be superadiabatic while Jeanloz & Morris (1987) proposed a sub-adiabatic temperature profile, although no numerical values were given. It is clear from table 2 that the present estimate of the adiabatic gradient,  $\gamma T/K_s$ , gives the steepest geothermal gradient for the lower mantle, when it is calculated at the same temperature. As will be shown in the next section, the use of a shallower gradient suggests a smaller amount of magnesiowüstite.

It is desirable to make comparisons with geothermal gradients over as wide a range as possible. However, the  $P$ - $V$ - $T$  data on silicate perovskite used in the present analysis are only up to 29 GPa and, as was discussed in the previous paper (Funamori *et al.* 1996), a large extrapolation of the equation of state is dangerous. On the other hand, near the discontinuity between the lower mantle and the transition zone, the density and the temperature derived from the PREM may have a high degree of uncertainty. Considering all these factors, we have made comparisons in an area of the lower mantle from 871 to 1471 km, which corresponds to 32 to 61 GPa.

The difference between temperatures calculated from the seismic adiabatic gradient (figure 2, but giving different temperatures at 1171 km) and those derived from the cross point in a plot similar to figure 1 were calculated at every 100 km. In figure 3, an average of the latter temperatures calculated for four different mixtures of perovskite and magnesiowüstite, using the various equation of state parameters, is



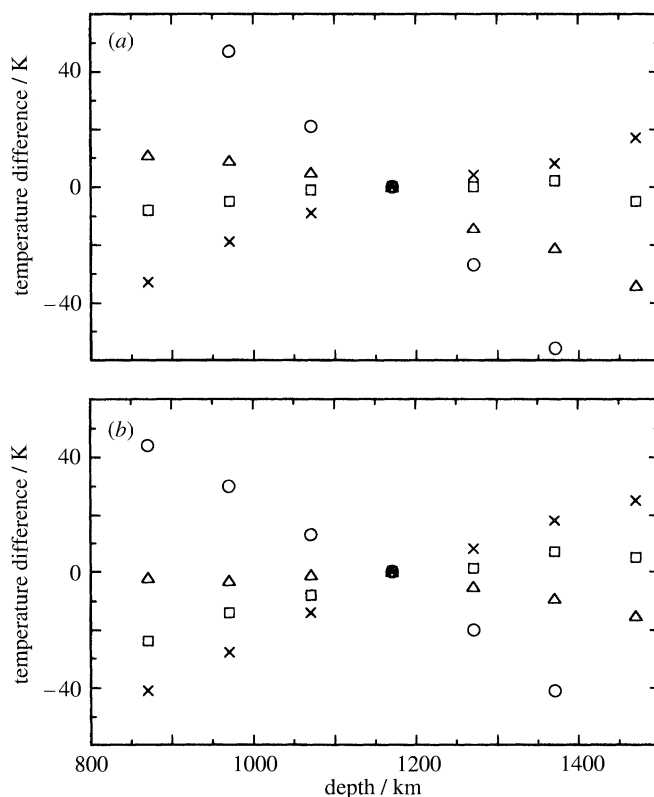


Figure 4. Differences between the adiabatic seismic temperature and those which are calculated based on the equations of state to satisfy the PREM density. Four different mixtures of perovskite and magnesiowüstite are compared in the depth from 871 to 1471 km. Symbols are the same as those used in figure 3. Four different adiabatic temperature profiles were used so that the temperature difference at 1171 km becomes zero for each mixture. The Mie–Grüneisen equation of state was used assuming (a)  $K'_0 = 4$  and  $\theta_{D0} = 1030$  K, and (b)  $K'_0 = 4$  and treated  $\theta_{D0}$  as a free parameter in the least-squares calculation.

shown. Error bars in this figure represent the scatter (one  $\sigma$ ) of the results when the calculation was made using the various parameters. In figures 4–7, the differences of the temperatures calculated using the methods for figures 2 and 3 are plotted with depth. Calculations were made by giving the temperature at the centre of the compared area (1171 km) in figure 2 so that the temperature difference for each mixture at that depth becomes zero. Comparisons were made using the various values for the equation of state parameters, which were obtained under different assumptions through the least-squares calculations, so that the uncertainty could be estimated. In figures 4a, b, the results obtained by fixing for perovskite,  $K'_0 = 4$  and  $\theta_{D0} = 1030$  K, and by fixing  $K'_0 = 4$  but letting  $\theta_{D0}$  be a free parameter, respectively, are shown. Four different mixtures of perovskite and magnesiowüstite, in molar ratios of 1:0,  $1:\frac{1}{3}$ ,  $1:\frac{1}{2}$ , and  $1:\frac{2}{3}$ , are compared.

The composition which satisfies the adiabatic gradient should be expressed by a horizontal straight line. It became clear, as seen in the figures, that as long as  $K'_0$  is fixed to 4, all the lines had some curvature. Ignoring this slight curvature, the composition which satisfies the gradient requirements is a mixture between  $1:\frac{1}{3}$  and  $1:\frac{1}{2}$ .



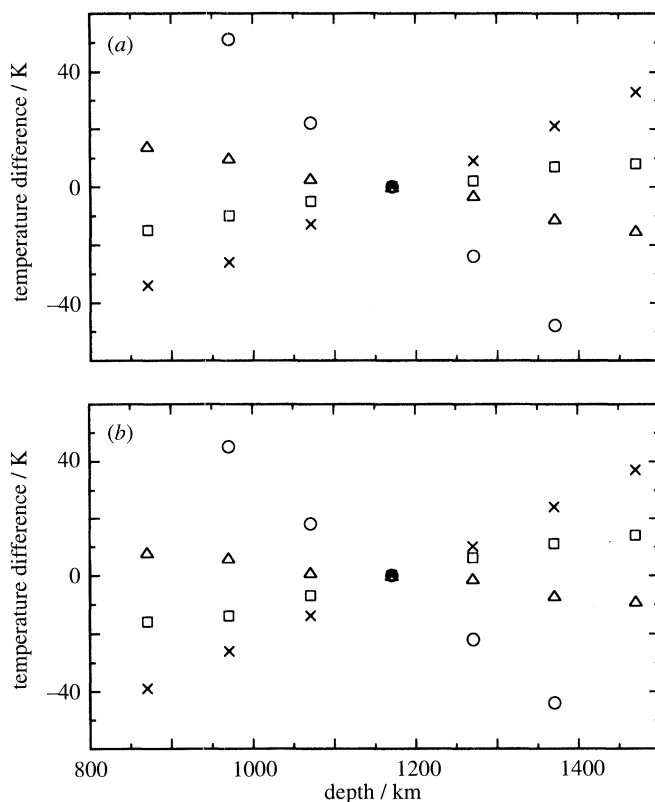


Figure 5. Difference of the temperatures calculated with  $K'_0 = 3.75$ : (a)  $\theta_{D0} = 1030$  K; (b)  $\theta_{D0}$  treated as a free parameter. All other conditions are the same as those in figure 4.

Figures 5a, b are obtained by setting  $K'_0 = 3.75$ , with  $\theta_{D0} = 1030$  K and as a free parameter, respectively. In this case all the lines are close to straight and compositions between  $1:\frac{1}{3}$  and  $1:\frac{1}{2}$  mixture satisfy the adiabatic temperature gradient.

The results obtained using the Birch–Murnaghan equation of state are shown in figures 6a, b, with  $K'_0 = 4$  and  $3.75$ , respectively. There are no meaningful differences compared to the results obtained by the Mie–Grüneisen equations of state and the conclusion that the compositions between  $1:\frac{1}{3}$  and  $1:\frac{1}{2}$  mixture satisfy the adiabatic gradient remains unchanged.

The effect of the partition coefficient of iron is shown in figures 7a, b, which were obtained assuming  $k = 2$  and  $6$ , respectively. All other parameters are the same as those in figure 5a, in which  $k$  was assumed to be  $4$ . As is clear from this figure, the partition coefficient does not much affect the temperature difference. On the other hand, the total iron content considerably affects the temperature at which the density matches the PREM density, and thus the difference from the seismic adiabatic thermal gradient. The result obtained by assuming  $\chi_{Fe} = 14\%$ , compared to  $11\%$  in all other calculations, is shown in figure 7c. In this case, the horizontal line is in the composition range between pure perovskite and  $1:\frac{1}{3}$  mixture.

The total iron content affects the estimated temperature as well. Figure 8 shows the temperatures at  $1171$  km of the four different mixtures of perovskite and magnesiowüstite for two different iron contents,  $\chi_{Fe} = 11\%$  (figure 5a) and  $\chi_{Fe} = 14\%$  (figure 7c). The solid line in figure 8 represents the temperature of the mixture which



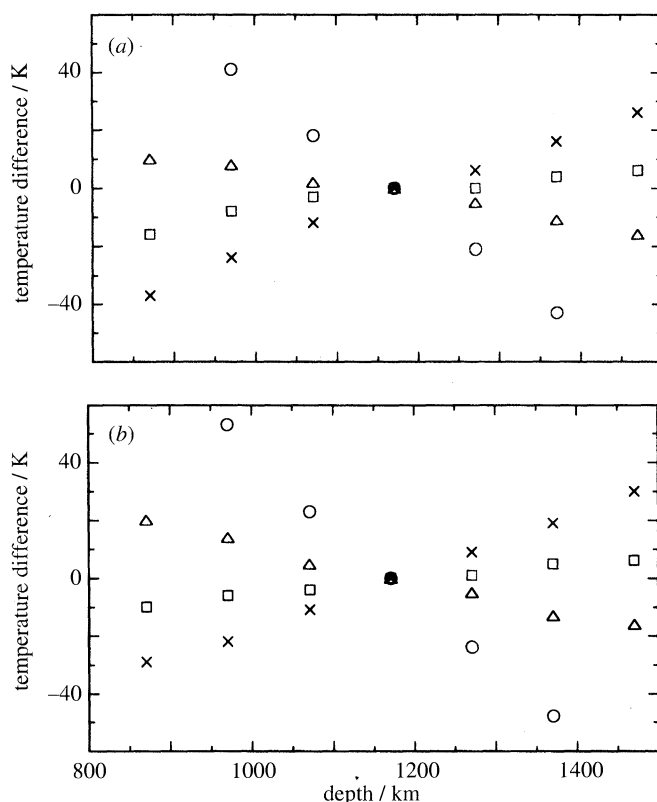


Figure 6. Difference of the temperatures calculated using the Birch–Murnaghan equation of state with (a)  $K'_0 = 4$  (B-HEOS), and (b)  $K'_0 = 3.75$  (B-MEOS).

best satisfies the requirements of the seismic geothermal gradient, i.e. a mixture having a horizontal slope in the previous figures, assuming that the temperature varies linearly with  $\chi_{\text{Fe}}$ . As seen here, this is a mixture between  $1:\frac{1}{3}$  and  $1:\frac{1}{2}$  for  $\chi_{\text{Fe}} = 11\%$ , and between pure perovskite and a  $1:\frac{1}{3}$  mixture, but closer to the later, for  $\chi_{\text{Fe}} = 14\%$ . The estimated temperature, according to various models, at this depth is between 2000 and 2800 K (see, for example, Anderson & Sumino 1980; Jeanloz & Morris 1986). It is clear from this figure that if the iron content in the lower mantle is 10% or less, or if it is 15% or more, it is difficult to satisfy the requirement of both temperature gradient and absolute temperature, even though the mixing ratio of perovskite and magnesiowüstite is varied.

#### (d) *Magnesiowüstite in the lower mantle*

Based on the considerations in the previous section, it can be concluded that if the amount of magnesiowüstite in the lower mantle exceeds one half (by molar ratio) of the perovskite, or if the amount of iron is less than *ca.* 11% or more than *ca.* 14%, it is difficult to explain the density and temperature profile of the PREM. The greatest concern in discussions of the lower mantle is whether it is chemically homogeneous with the upper mantle or not. This is an important issue relating to many fundamental geophysical problems such as mantle convection, and the evolution of the Earth.

Experimental studies on rocks, however, indicate that the amount of magne-



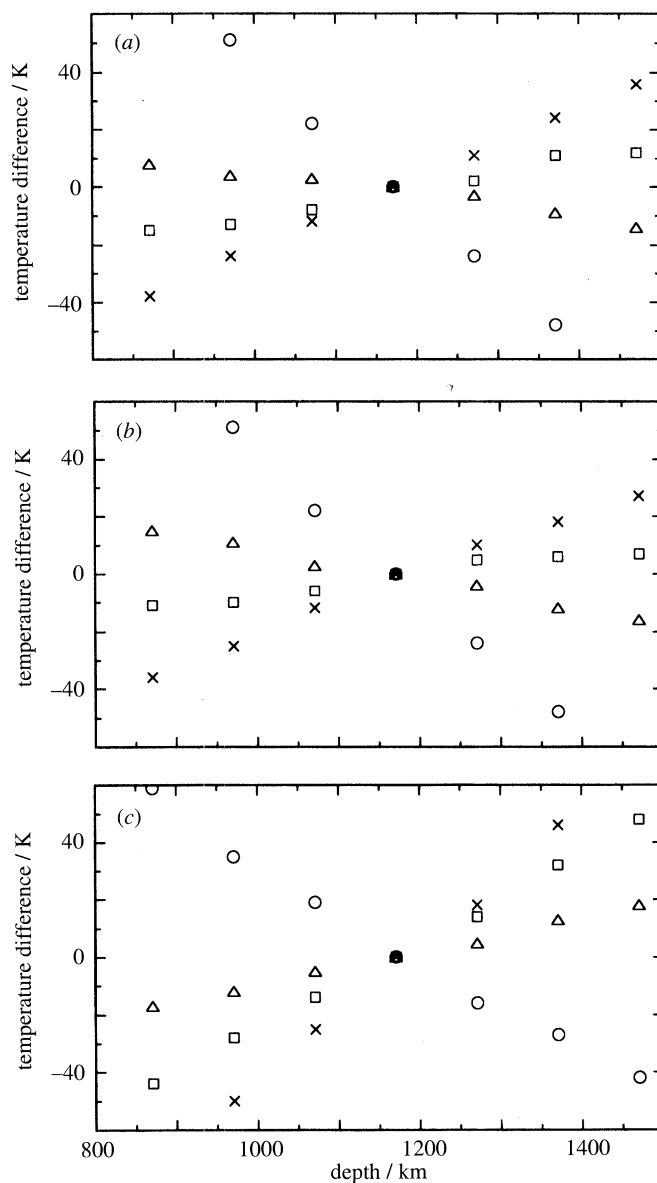


Figure 7. Difference of the temperatures calculated based on the Mie–Grüneisen equation of state using the parameters in figure 5a. The effects of total iron content,  $\chi_{\text{Fe}}$ , and the partition coefficient of iron between perovskite and magnesiowüstite,  $k$ , are compared. The iron contents are calculated assuming (a)  $\chi_{\text{Fe}} = 11\%$ ,  $k = 2$ , (b)  $\chi_{\text{Fe}} = 11\%$ ,  $k = 6$ , and (c)  $\chi_{\text{Fe}} = 14\%$  and  $k = 4$ .

siowüstite expected to form from upper mantle materials are still not certain. In a system composed of  $\text{MgO-FeO-SiO}_2$ , magnesiowüstite is formed through the decomposition of olivine. If a 1:1 mixture of olivine and pyroxene (approximately 60% olivine by volume) is taken to lower mantle conditions, a  $1:\frac{1}{2}$  mixture of perovskite and magnesiowüstite is expected to form, in which the volume of magnesiowüstite is about 19%. As mentioned above, this is the upper limit expected for the lower mantle. Experimental results using a pyrolite composition, in which the olivine content



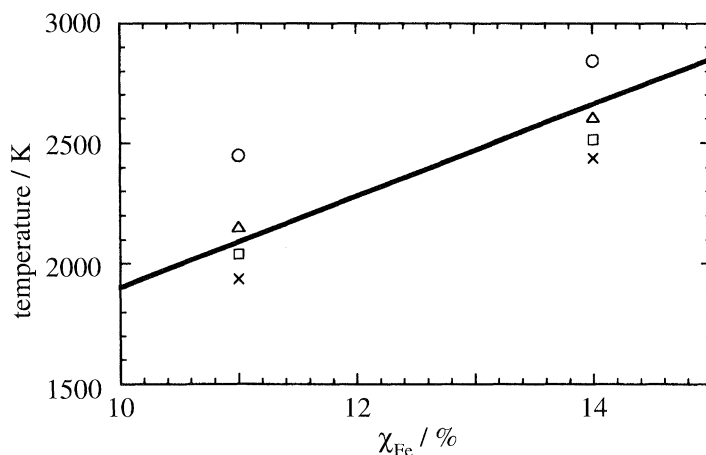


Figure 8. The temperatures at 1171 km depth calculated for the four different mixtures shown in figures 5a ( $\chi_{\text{Fe}} = 11\%$ ) and 7c ( $\chi_{\text{Fe}} = 14\%$ ). Symbols for the different mixtures are the same as before. As discussed in the text, the solid line represents the best-fit mixture. This figure also shows that the limitations on the total iron content can be placed at *ca.* 11% and 14% (see discussion in text).

was about 60% by volume, indicates that only 15–16% magnesiowüstite is formed (Irifune 1995), which is slightly less than that expected from the simple system considered above. O'Neill & Jeanloz (1990) reported the formation of a similar amount of magnesiowüstite, although the peridotite they used contained less olivine (approximately 45% by volume). Even though the present result implies that the amount of magnesiowüstite expected to exist in the lower mantle is less than half of perovskite, it is still difficult to conclude whether this result implies a chemically homogeneous mantle or not. Further experiments to clarify the amount of magnesiowüstite formed from the various chemical compositions will be required to address this question.

### 3. Conclusion

The chemical composition of the lower mantle has been estimated by comparing the density and temperature profiles calculated from the equations of state of the component minerals with those derived from the PREM. Assuming that the lower mantle consists of a mixture of  $(\text{Mg}_{1-x}, \text{Fe}_x)\text{SiO}_3$  perovskite and  $(\text{Mg}_{1-y}, \text{Fe}_y)\text{O}$  magnesiowüstite, a mixing ratio inferred from the most plausible equation of state is from a 2:1 to 3:1 mixture (by molar ratio) of perovskite and magnesiowüstite when the total iron content,  $\chi_{\text{Fe}} = 11\%$ . Increase in iron content suggests silica-rich lower mantle. When  $\chi_{\text{Fe}}$  is less than 11%, the temperature becomes too low compared to the geotherm, while if it is 15% or more, the temperature gets too high. The ambiguity of this conclusion was examined by changing various parameters used in the calculations, and although they affect the details of the discussions, the conclusion described above is unchanged.

However, as was discussed in detail in the previous paper (Funamori *et al.* 1996), the reliable limit of the equation of state of perovskite, and magnesiowüstite, is not high enough to take these conclusions as a 'constraint'. Further efforts should be made to increase the reliable limits of the equations of state, and to clarify the



amount of magnesio-wüstite formed at lower mantle conditions through high-pressure and temperature experiments.

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