

Maximum solubility of FeO in (Mg, Fe)SiO₃-perovskite as a function of temperature at 26 GPa: Implication for FeO content in the lower mantle

Yingwei Fei

Center for High Pressure Research, Geophysical Laboratory, Carnegie Institution of Washington, D.C.

Yanbin Wang

Center for High Pressure Research, Department of Earth and Space Sciences
State University of New York at Stony Brook

Larry W. Finger

Center for High Pressure Research, Geophysical Laboratory, Carnegie Institution of Washington, D.C.

Abstract. We have explored phase relations in the fundamental ternary system MgO-FeO-SiO₂ at lower mantle pressure (26 GPa) via synthesis experiments on the join MgSiO₃-FeSiO₃. The maximum solubility of FeO in (Mg,Fe)SiO₃ perovskite as a function of temperature has been determined in the multianvil apparatus in the temperature range of 1150-1740°C. Pure perovskites with 10 and 15 mol % FeSiO₃ can only be synthesized above 1525°C and 2072°C, respectively, at 26 GPa. Synthesis experiments were also conducted in a laser-heated diamond anvil cell to resolve a previous discrepancy concerning the maximum solubility of FeO in (Mg,Fe)SiO₃ perovskite determined by different high-pressure apparatus. Both Mössbauer spectroscopic and X ray diffraction studies revealed that laser-heated samples with more than 10 mol % FeSiO₃ invariably contained magnesiowüstite. The coexistence of magnesiowüstite with relatively lower FeO content perovskite results from chemical disequilibrium process caused by the large temperature gradient in the laser-heated samples. Finally, we conclude that the maximum FeO content at the top of the lower mantle is about 12 mol % for a perovskite-dominated lower mantle, along a 2000-K lower mantle geotherm.

Introduction

High-pressure experiments in the system MgO-FeO-SiO₂ have shown that the rock-forming minerals, (Mg,Fe)SiO₃ pyroxene and (Mg,Fe)₂SiO₄ olivine, transform to assemblages, (Mg,Fe)SiO₃ perovskite and (Mg,Fe)SiO₃ perovskite plus (Mg,Fe)O magnesiowüstite, respectively, in the Mg-rich region at Earth's lower mantle conditions [Liu, 1975; Ito *et al.*, 1984]. Comparison of seismic observation of the lower mantle with measured physical properties of mantle minerals suggests that silicate perovskite and magnesiowüstite are likely the dominant lower mantle minerals. However, the chemical composition of the lower mantle, in terms of the Fe/(Mg+Fe) and Si/Mg ratios, is the subject of considerable debate [Jeanloz and Knittle, 1989; Bina and Silver, 1990; Stixrude *et al.*, 1992; Wang *et al.*, 1994]. The arguments on either Fe and Si enrichment in the lower mantle relative to the upper mantle or identical upper and lower mantle compositions largely rely, in part, on accurate measurements of thermoelastic properties of silicate perovskite. Alternatively, compositional constraints of the lower mantle can be derived from phase equilibrium studies at high pressure and temperature.

In this study, we report experimental determination of the maximum solubility of FeO in (Mg,Fe)SiO₃ perovskite as a function of temperature at lower mantle pressure. The results provide the upper bound of the FeO content for a perovskite-dominated (perovskitic) lower mantle.

The (Mg,Fe)SiO₃ pyroxene transforms to (Mg,Fe)SiO₃ perovskite or a three-phase assemblage of (Mg,Fe)SiO₃ perovskite, (Mg,Fe)O magnesiowüstite, and SiO₂ stishovite, at high pressure and temperature, depending on the Mg #, the atomic ratio Mg/(Mg+Fe). These phase relations were studied by using the laser-heating diamond anvil cell techniques [Liu, 1975; Yagi *et al.*, 1979; Fei *et al.*, 1991] and the multianvil apparatus [Ito and Yamada, 1982; Ito *et al.*, 1984; Ito and Takahashi, 1989]. However, the maximum solubility of FeO in (Mg,Fe)SiO₃-perovskite and its dependence on temperature and pressure are not well constrained. For example, the maximum solubility of FeO was 11 mol % at 26 GPa and 1600°C, obtained by using the multianvil apparatus [e.g., Ito and Takahashi, 1989], whereas perovskites with 21 mol % FeSiO₃ were synthesized at similar pressure with the laser-heating diamond anvil technique, according to Yagi *et al.* [1979]. In this study, we reexamine the perovskite stability field in the MgSiO₃-FeSiO₃ system, using both high-pressure apparatus. The synthesized samples will be characterized by multiple analytic techniques, including Mössbauer spectroscopy, high-resolution X ray diffraction, and electron microprobe.

Copyright 1996 by the American Geophysical Union.

Paper number 96JB00408.
0148-0227/96/96JB-00408\$09.00

Experimental Procedure

Synthetic orthopyroxenes with compositions, $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$ (En95), $(\text{Mg}_{0.90}\text{Fe}_{0.10})\text{SiO}_3$ (En90), $(\text{Mg}_{0.87}\text{Fe}_{0.13})\text{SiO}_3$ (En87), $(\text{Mg}_{0.85}\text{Fe}_{0.15})\text{SiO}_3$ (En85), and $(\text{Mg}_{0.80}\text{Fe}_{0.20})\text{SiO}_3$ (En80), were used as starting materials. They were synthesized from oxide mixtures in gold capsules at 1000°C and 1.5 GPa, using the piston-cylinder apparatus [Fei *et al.*, 1991]. All the starting materials were ^{57}Fe -enriched (92% enrichment). The synthesized samples were examined optically and by X ray diffraction. The compositions were confirmed by electron microprobe. To avoid any other Fe-bearing phase, the orthopyroxenes were synthesized with about 2 wt % excess SiO_2 .

To reach into the stability field of $(\text{Mg,Fe})\text{SiO}_3$ perovskite, we used the multianvil high-pressure device installed at State University of New York at Stony Brook (USSA-2000) [Remsberg *et al.*, 1988; Gasparik, 1989; Liebermann and Wang, 1992]. The experiments were conducted by using a 7-mm MgO octahedron cell assembly described by Wang *et al.* [1992]. The powdered starting materials were loaded into a rhenium capsule which also served as a heater. A lanthanum chromite sleeve outside the heater was used as a thermal insulator. The sample assembly was fitted into an octahedral cavity formed by eight corner-truncated tungsten carbide cubes. Pyrophyllite gaskets were used between the cubes. In all the experiments, we first slowly compressed the sample to a pressure of 26 GPa at room temperature and then increased electrical power to achieve the desirable temperatures. Temperatures were measured with a W3%Re-W25%Re thermocouple, looped around the outer surface of the cylindrical heater. The run duration varied from 10 to 320 min. Samples were quenched by turning off the power supply.

The recovered samples were examined by Mössbauer spectroscopy, X ray diffraction, and electron microprobe analysis to identify stable phases and their chemical compositions. Mössbauer spectroscopy is an ideal tool for studying the oxidation state and site occupancy of Fe in the structure of Fe-bearing phases and for identifying multiple Fe-bearing phases in the sample. Detailed sample characterization by this technique was described by Fei *et al.* [1994]. The molar $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the Fe-bearing silicate perovskite synthesized in this study is $0.12(\pm 0.02)$, determined by fitting the Mössbauer spectra.

High-resolution synchrotron X ray powder diffraction data were collected at beamline X7A of the National Synchrotron Light Source, Brookhaven National Laboratory. A detailed description of the beamline is given by Cox *et al.* [1988]. The experiments were conducted using a single-crystal Si(111) monochromator and a position-sensitive detector [Jephcoat *et al.*, 1992]. Samples with diameters of about 150 μm were mounted on a glass fiber, aligned to the highly collimated beam. An adjustable slit system was designed to optimize the peak-to-background ratio. The X ray diffraction pattern was analyzed by Rietveld structural refinement. The cell parameters of the silicate perovskites were obtained by the final refinement. The typical precision of unit-cell volume is $\pm 0.01 \text{ \AA}^3$ from such a refinement. Cell parameters for a few perovskite samples were obtained by energy-dispersive X ray diffraction measurements. A least squares fit of the energy spectrum yielded a typical uncertainty of $\pm 0.05 \text{ \AA}^3$.

All the recovered samples were prepared for obtaining backscattered electron image and chemical composition map, using a JEOL-SUPERPROBE JXA-8800L electron microprobe installed at the Geophysical Laboratory, Carnegie Institution of Washington. These images were used to identify phase

assemblages and to examine the homogeneity of the sample. The compositions of the perovskites were determined by averaging at least five analyses for each sample. To avoid amorphization induced by electron beam, the beam current was reduced to 10 nA, one fifth of the normal current. A highly focused spot beam was used to analyze the small perovskite grains, ranging from 1 to 7 μm .

Fe-bearing silicate perovskites were also synthesized by laser-heating technique in the diamond anvil cell. The experimental procedure used in this study is similar to that described by Fei *et al.* [1991]. The powdered starting material was compressed in a diamond anvil cell without pressure medium to about 35 GPa at room temperature. Pressures were measured by the ruby pressure scale for nonhydrostatic compression [Mao *et al.*, 1978]. The sample was then heated by a yttrium/aluminum/garnet (YAG) laser beam. We scanned the sample with the laser beam until the entire sample changes to brown color, the characteristic color of perovskite in the diamond cell. In order to obtain sufficient sample for Mössbauer spectroscopic study, at least 10 samples were synthesized for each composition under similar synthesis conditions. Each sample is about 250 μm in diameter and 5 μm in thickness.

Results and Discussion

The maximum solubility of FeO in $(\text{Mg,Fe})\text{SiO}_3$ perovskite as a function of temperature at 26 GPa was determined by measuring the composition of the perovskite coexisting with magnesiowüstite and stishovite. The estimates of the perovskite composition obtained from three different methods (Mössbauer spectroscopy, X ray diffraction, and electron microprobe) are used to test the internal consistency of the determinations. Experimental conditions and results are summarized in Table 1. Note that the phase assemblages identified by the three techniques are different (Table 1a). Mössbauer spectroscopy is only sensitive to phases that contain iron; therefore it cannot detect the presence of stishovite. In the X ray composition images obtained by electron microprobe, magnesiowüstite could not be seen. The reason became apparent in detailed analysis of the X ray diffraction spectra in which the grain size was seen to be of the order of 300 Å . However, the presence of magnesiowüstite can be inferred by the iron deficit in perovskite compared to that of the starting material. It was also difficult to see the presence of a trace amount of stishovite in the compositional images. Chemical compositions of perovskite were determined by electron microprobe analysis and by X ray diffraction using the relationship between cell parameters and composition (Table 1b). Quantitative analysis of the sample was also obtained from the powder diffraction data.

Mössbauer spectroscopy was used to determine the number of iron-bearing phases, and to quantify the amount of ferrous and ferric iron in each of them. Because Fe^{2+} preferentially partitions into magnesiowüstite in preference to perovskite [Yagi *et al.*, 1979; Ito *et al.*, 1984; Fei *et al.*, 1991], the presence of a very small amount of the former phase may be seen in the Mössbauer spectra. Figure 1 shows the spectra of two samples quenched from 1490°C and 1650°C with 10 mol % FeSiO_3 in the starting materials. The spectrum of the sample quenched from higher temperatures represents the Mössbauer resonance absorption spectrum of single-phase perovskite, whose spectrum has been interpreted by Fei *et al.* [1994]. The intense absorption envelop is due to Fe^{2+} with a superimposed, partially resolved quadrupole

Table 1a. Experimental Run Conditions and Results

Run	P, GPa	T, °C	Time, min	Starting Materials	Mössbauer	Phase Present* Probe	X Ray
1727	26	1150	60	En95	Pv	Pv	Pv+trace St
1572	26	1600	120	En95	Pv	Pv	Pv+trace St
1573	26	1200	320	En90	Pv+Mw	Pv+Mw+St	Pv+Mw+St
1605	26	1350	20	En90	Pv+Mw	Pv+Mw+St	Pv+Mw+St
1619	26	1490	60	En90	Pv+Mw	Pv+Mw+St	Pv+Mw+St
1620	26	1650	10	En90	Pv	Pv	Pv+trace St
0975	26	1700	60	En90	Pv	Pv	Pv+trace St
1900	26	1740	15	En87	Pv+Mw	Pv+Mw+St	Pv+Mw+St

*Pv, perovskite; Mw, magnesiowüstite; and St, stishovite.

Table 1b. Iron Contents in Perovskites Determined by X Ray Diffraction and Electron Microprobe

Run	T, °C	Starting Materials	a, Å	b, Å	c, Å	V, Å ³	X _{Fe} [*]	
							X Ray	Probe
1727	1150	En95					0.050	0.050
1572	1600	En95	4.7840(1)	4.9306(1)	6.9016(1)	162.80(1)	0.050	0.050
1573	1200	En90	4.7865(1)	4.9301(1)	6.9021(1)	162.88(1)	0.064(2)	0.076(5)
1605	1350	En90	4.7880(4)	4.9318(6)	6.9040(11)	163.03(5)	0.090(8)	0.083(5)
1619	1490	En90	4.7885(5)	4.9317(7)	6.9054(10)	163.07(5)	0.097(8)	0.097(5)
1620	1650	En90	4.7888(1)	4.9322(1)	6.9048(1)	163.09(1)	0.100	0.100
0975	1700	En90					0.100	0.100
1900	1740	En87	4.7905(5)	4.9330(6)	6.9059(14)	163.20(6)	0.119(9)	0.125(5)

*The iron contents were calculated from $V = 162.51 + 5.80X_{Fe}$.

split doublet due to Fe³⁺. By contrast, the spectrum of the sample quenched from 1490°C contains an additional absorption peak due to the presence of magnesiowüstite. Electron microprobe analysis of this sample showed that an FeO content of the perovskite less than that of the starting material, confirming the presence of magnesiowüstite. Deconvolution of the Mössbauer spectrum with lines of Lorentzian shape yielded a molar Fe³⁺/ΣFe ratio of 0.12 for the single-phase perovskite sample. Perovskite coexisting with magnesiowüstite contains substantially less Fe³⁺, indicating redistribution of ferric iron between perovskite and magnesiowüstite.

The relationship between perovskite unit cell parameters and composition has been reviewed by *Kudoh et al.* [1990] and *Hemley and Cohen* [1992], but these data do not have the internal consistency required to provide precise composition determination. In this study we calibrated the relationship using the unit cell for MgSiO₃ measured by *Mao et al.* [1991] and two iron-bearing samples in which magnesiowüstite was absent. Figure 2 shows the relationship between cell parameters and FeO content for (Mg,Fe)SiO₃ perovskite determined using high-resolution X ray diffraction data and Rietveld structural refinement. Using this calibration, the FeO contents of perovskite determined from the X ray diffraction data are found to be consistent with those from electron microprobe analysis (Table 1, also see below). The uncertainty in the FeO mole fraction X_{Fe} determined from the unit cell volume is ±0.003. Samples were synthesized under similar environments, and the data were analyzed in a consistent way, so that any uncertainties related to sample synthesis history and data process were avoided.

Figure 3 illustrates the stability field of single-phase perovskite in the system MgSiO₃-FeSiO₃ at 26 GPa. Single-phase

perovskites, (Mg_{0.95}Fe_{0.05})SiO₃ and (Mg_{0.9}Fe_{0.1})SiO₃, were synthesized at 1150°C and 1650°C, respectively. However, we were unable to convert starting material pyroxenes with either 13 or 15 mol % FeSiO₃ to single-phase perovskite, even at 1750°C. Composition analyses of the perovskite coexisting with magnesiowüstite and stishovite yielded the maximum solubility of FeO in perovskite, which increases with increasing temperature (Figure 3). The FeO content in perovskite determined by electron microprobe is generally in a good agreement with that derived from the cell volume-composition relationship by X ray diffraction. The relatively large uncertainty in the FeO content determined by electron microprobe was due to small grain size. Uncertainty in temperature was caused by thermal gradient within the furnace assembly [cf. *Ito et al.*, 1984; *Liebermann and Wang*, 1992]. We only used samples close to the thermocouple for X ray and electron microprobe analysis. The temperature uncertainty was estimated to be less than ±75 °C. The best fit of our experimental data to a linear function yielded $X_{Fe} = -0.043(9) + 9.5(8) \times 10^{-5} T(^{\circ}C)$.

We compare our results with that of *Ito et al.* [1984] and *Ito and Takahashi* [1989], who determined phase relations in the system Mg₂SiO₄-Fe₂SiO₄ to 26 GPa at 1100°C and 1600°C, using olivines as starting materials. Our results are in a good agreement with their FeO-solubility data at 1600°C but about 1% lower than their data at 1100°C (Figure 3). This discrepancy could be explained by the use of different volume-composition calibrations [cf. *Ito and Yamada*, 1982; this study].

Experiments conducted in the multianvil apparatus indicate that the maximum solubility of FeO in perovskite is 11 mol % at 1600°C and 26 GPa [*Ito and Takahashi*, 1989; this study]. However, perovskite with 21 mol % FeSiO₃ was synthesized at

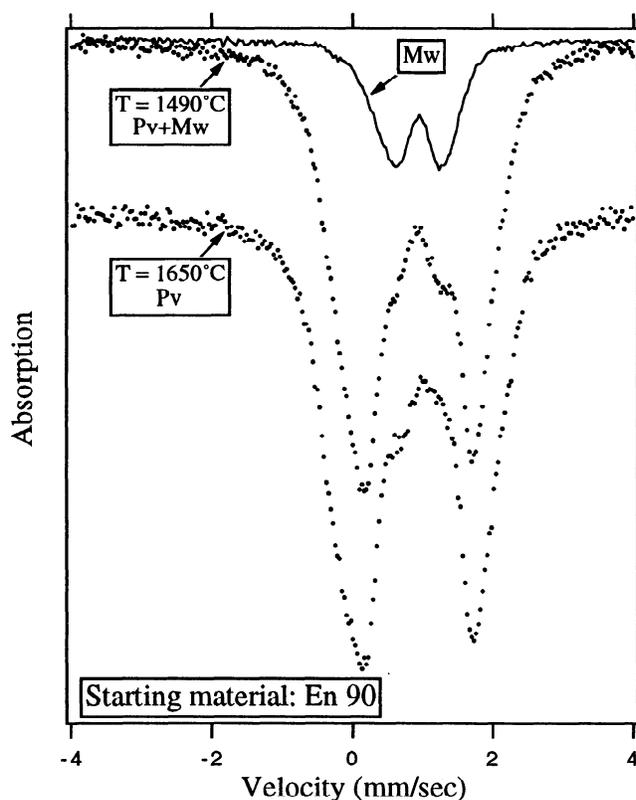


Figure 1. Mössbauer spectra of samples synthesized from starting material $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ pyroxene (En90) in the multianvil apparatus at 26 GPa and at 1650°C (lower spectrum) and 1490°C (middle spectrum). The sample synthesized at higher temperature is single-phase perovskite, whereas the sample synthesized at lower temperature contains magnesiowüstite. The spectrum of $(\text{Mg}_{0.2}\text{Fe}_{0.8})\text{O}$ magnesiowüstite (upper most spectrum) is shown for comparison.

similar pressure using a laser heated diamond anvil cell technique [Yagi *et al.*, 1979]. In order to resolve this discrepancy, we also synthesized perovskites using the laser-heated diamond anvil cell technique similar to that described by Yagi *et al.* [1979]. In the experiments, we used pyroxenes, $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ and $(\text{Mg}_{0.8}\text{Fe}_{0.2})\text{SiO}_3$, as starting materials. The synthesized perovskite samples invariably contained magnesiowüstite as seen in the Mössbauer spectra (Figure 4). The presence of magnesiowüstite in the laser-heated samples was also confirmed by the X ray diffraction data, which indicated that the FeO content in the synthesized perovskite was lower than that of the starting material. On the basis of our multianvil results (Figure 3), $(\text{Mg}_{0.8}\text{Fe}_{0.2})\text{SiO}_3$ pyroxene would transform to the three-phase assemblage at any temperature below melting. The synthesized perovskite from $(\text{Mg}_{0.8}\text{Fe}_{0.2})\text{SiO}_3$ pyroxene contains about 17 mol % FeSiO_3 , determined from the cell volume-composition relationship (Figure 2), indicating that the peak temperature of the synthesis could be as high as 2300°C. On the other hand, the synthesized perovskite from $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ pyroxene contained only about 6 mol % FeSiO_3 , which would imply a synthesis temperature is only about 1200°C. The inconsistency can be partly explained by the large temperature gradient which drives the chemical diffusion [cf. Campbell and Heinz, 1992] and produces inhomogeneous sample. For example, each laser-heating spot could produce a single-phase perovskite center with

a ring of three-phase assemblage. Under this scenario, the presence of magnesiowüstite in a laser-heated sample is unavoidable above a certain FeO content, even when the peak temperature is well within the stability field of perovskite.

Geophysical Implications

Chemical composition models of Earth's lower mantle, based on comparison between the measured physical properties of the lower mantle minerals and the seismic data, have to be consistent with the phase equilibrium relations in the system MgO-FeO-SiO_2 . Our experimentally determined maximum FeO solubility in perovskite as a function of temperature at lower mantle pressure

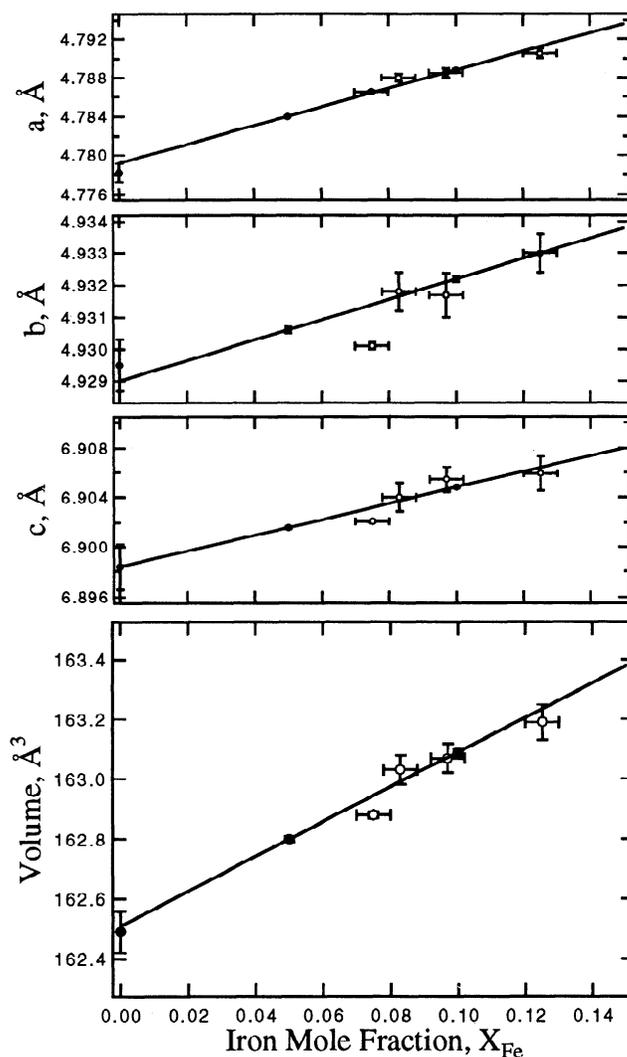


Figure 2. Unit cell parameters of silicate perovskite as a function of mole fraction of FeSiO_3 component. The solid circles represent single-phase perovskites with FeO mole fractions $X_{\text{Fe}} = 0.0, 0.05,$ and 0.10 . The cell parameters of end-member MgSiO_3 perovskite were determined by Mao *et al.* [1991]. The solid lines are the linear expressions of the cell parameters of $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$ and $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ perovskites. The open circles represent perovskites coexisting with magnesiowüstite, synthesized at different temperatures. The compositions were determined with electron microprobe.

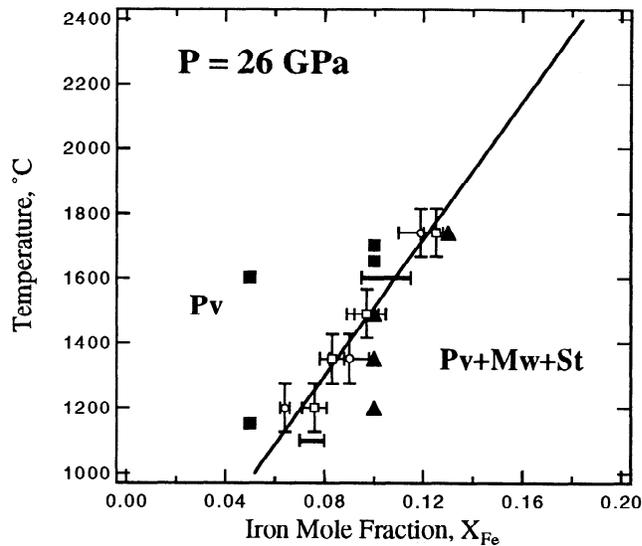


Figure 3. The maximum solubility of FeO in perovskite as a function of temperature at 26 GPa. The solid squares indicate synthesis of single-phase perovskite, whereas the solid triangles represent the three-phase assemblage (perovskite + magnesiowüstite + stishovite). The compositions of perovskite in the three-phase assemblage were determined by X ray diffraction (open circles) and with electron microprobe (open squares). Data from Ito *et al.* [1984] and Ito and Takahashi [1989] are shown for comparison (horizontal bars). The solid line is the best fit $X_{\text{Fe}} = -0.0394 + 9.14 \times 10^{-5} T (^{\circ}\text{C})$.

provides an upper limit on the FeO content in a perovskitic lower mantle.

For a simplified model mantle composition, the focus of the argument is on the $\text{Fe}/(\text{Fe}+\text{Mg})$ and $(\text{Mg}+\text{Fe})/\text{Si}$ ratios for the lower mantle, which indicate whether Earth's mantle is compositionally stratified. The upper limit of the $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio in the lower mantle is constrained by the stable mineral assemblage, controlled by the $(\text{Mg}+\text{Fe})/\text{Si}$ ratio, and the mantle temperature. If the lower mantle is perovskitic, where the $(\text{Mg}+\text{Fe})/\text{Si}$ ratio is 1.0, for a given geotherm, the upper bound of the FeO content is defined by the maximum FeO solubility in perovskite. Figure 5 illustrates the maximum $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio along the geotherm of Stacey [1992] at the top of the lower mantle. If the temperature at the top of the lower mantle is less than 2000 K, the maximum FeO content in the lower mantle is about 12%. A model with higher FeO content in the lower mantle has to adopt a higher geotherm to be consistent with our experimental results on the maximum solubility of FeO in perovskite.

Because iron strongly partitions into magnesiowüstite when perovskite and magnesiowüstite coexist [Yagi *et al.*, 1979; Ito *et al.*, 1984; Fei *et al.*, 1991], the maximum $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio in a perovskite-magnesiowüstite lower mantle, where the $(\text{Mg}+\text{Fe})/\text{Si}$ ratio is greater than 1.0, could be much higher than the maximum FeO solubility in perovskite. To argue the presence of stishovite in the lower mantle, the $(\text{Mg}+\text{Fe})/\text{Si}$ ratio has to be less than 1.0 or the $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio of perovskite is greater than the maximum FeO solubility in perovskite for a perovskitic lower mantle ($[\text{Mg}+\text{Fe}]/\text{Si}$ ratio = 1.0).

The above discussion is based on our experiments carried out at a single pressure. The experimental results only provide

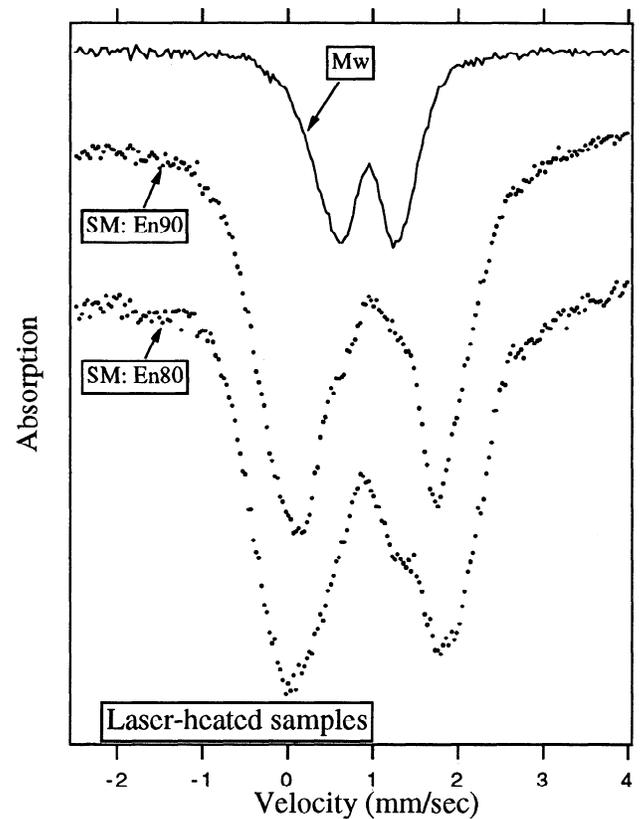


Figure 4. Mössbauer spectra of samples synthesized from starting materials $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ pyroxene (En90) and $(\text{Mg}_{0.8}\text{Fe}_{0.2})\text{SiO}_3$ pyroxene (En80) using laser-heated diamond anvil cell technique. Both samples indicate the presence of magnesiowüstite in addition to silicate perovskite (see text for discussion). The spectrum of $(\text{Mg}_{0.2}\text{Fe}_{0.8})\text{O}$ magnesiowüstite is also shown for comparison.

constraint on the upper limit of FeO content at the top of the lower mantle. The maximum solubility of FeO in perovskite as a function of pressure needs to be determined to provide further compositional constraints at the deeper parts of the lower mantle.

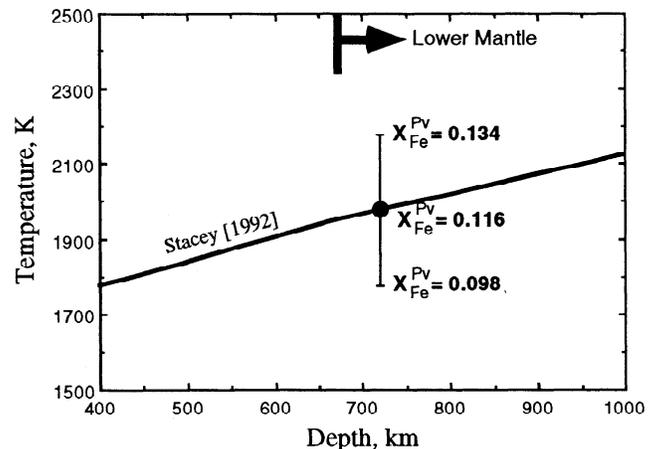


Figure 5. The maximum FeO content in a perovskitic lower mantle along the geotherm [Stacey, 1992]. Error bar range represents the composition limits at 200°C above and below the geotherm.

Acknowledgments. We thank D. E. Cox, Brookhaven National Laboratory for his assistance with the X ray powder diffraction measurements. This work was supported by the NSF Science and Technology Center for High Pressure Research and the Carnegie Institution of Washington.

References

- Bina, C. R., and P. Silver, Constraints on lower mantle composition and temperature from density and bulk sound velocity profiles, *Geophys. Res. Lett.*, **17**, 1153-1156, 1990.
- Campbell, A. J., and D. L. Heinz, Material transport in laser-heated diamond anvil cell melting experiments, *Geophys. Res. Lett.*, **19**, 1061-1064, 1992.
- Cox, D. E., B. H. Toby, and M. M. Eddy, Acquisition of powder diffraction data with synchrotron radiation, *Aust. J. Phys.*, **41**, 117-131, 1988.
- Fei, Y., H. K. Mao, and B. O. Mysen, Experimental determination of element partitioning and calculation of phase relations in the MgO-FeO-SiO₂ system at high pressure and high temperature, *J. Geophys. Res.*, **96**, 2157-2169, 1991.
- Fei, Y., D. Virgo, B. O. Mysen, Y. Wang, and H. K. Mao, Temperature dependent electron delocalization in (Mg,Fe)SiO₃-perovskite, *Am. Mineral.*, **79**, 826-837, 1994.
- Gasparik, T., Transformation of enstatite-diopside-jadeite pyroxenes to garnet, *Contrib. Mineral. Petrol.*, **102**, 389-405, 1989.
- Hemley, R. J., and R. E. Cohen, Silicate perovskite, *Annu. Rev. Earth Planet Sci.*, **20**, 553-600, 1992.
- Ito, E., and E. Takahashi, Postspinel transformations in the system Mg₂SiO₄-Fe₂SiO₄ and some geophysical implications, *J. Geophys. Res.*, **94**, 10,637-10,646, 1989.
- Ito, E., and H. Yamada, Stability relations of silicate spinel ilmenites and perovskites, in *High-Pressure Research in Geophysics*, edited by S. Akimoto and M. H. Manghnani, pp. 405-419, Cent. for Acad. Publ. Jpn., Tokyo, Japan, 1982.
- Ito, E., E. Takahashi, and Y. Matsui, The mineralogy and chemistry of the lower mantle: An implication of the ultrahigh-pressure phase relations in the system MgO-FeO-SiO₂, *Earth Planet. Sci. Lett.*, **67**, 238-248, 1984.
- Jeanloz, R. and E. Knittle, Density and composition of the lower mantle, *Philos. Trans. R. Soc. London A* **328**, 377, 1989.
- Jephcoat, A. P., L. W. Finger, and D. E. Cox, High pressure, high resolution synchrotron x-ray powder diffraction with a position-sensitive detector, *High Pressure Res.*, **8**, 667-676, 1992.
- Kudoh, Y., C. T. Prewitt, L. W. Finger, A. Darovskikh, and E. Ito, Effect of iron on the crystal structure of (Mg,Fe)SiO₃ perovskite, *Geophys. Res. Lett.*, **17**, 1481-1484, 1990.
- Liebermann, R. C., and Y. Wang, Characterization of sample environment in a multianvil split-sphere apparatus, in *High-Pressure Research in Mineral Physics* edited by Y. Syono and M. H. Manghnani, pp. 19-31, AGU, Washington, D. C., 1992.
- Liu, L. G., Post-oxide phases of forsterite and enstatite, *Geophys. Res. Lett.*, **2**, 417-419, 1975.
- Mao, H. K., P. M. Bell, J. W. Shaner, and D. J. Steinberg, Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of the ruby R₁ fluorescence pressure gauge from 0.06 to 1 Mbar, *J. Appl. Phys.*, **49**, 3276-3283, 1978.
- Mao, H. K., R. J. Hemley, Y. Fei, J. Shu, L. Chen, A. Jephcoat, Y. Wu, and W. A. Bassett, Effect of pressure, temperature, and composition on lattice parameters and density of (Fe,Mg)SiO₃-perovskites to 30 GPa, *J. Geophys. Res.*, **96**, 8069-8079, 1991.
- Remsberg, A. R., J. N. Boland, T. Gasparik, and R. C. Liebermann, Mechanism of the olivine-spinel transformation in Co₂SiO₄, *Phys. Chem. Miner.*, **15**, 498-506, 1988.
- Stacey, F. D., *Physics of the Earth*, 513 pp., Brookfield Press, Kenmore, Queensland, Australia, 1992.
- Stixrude, L., R. J. Hemley, Y. Fei, and H. K. Mao, Thermoelasticity of silicate perovskite and magnesiowüstite and stratification of the Earth's mantle, *Science*, **257**, 1099-1101, 1992.
- Wang, Y., F. Guyot, and R. C. Liebermann, Electron microscopy of (Mg,Fe)SiO₃ perovskite: Evidence for structural phase transitions and implications for the lower mantle, *J. Geophys. Res.*, **97**, 12,327-12,347, 1992.
- Wang, Y., D. J. Weidner, R. C. Liebermann, and Y. Zhao, *P-V-T* equation of state of (Mg,Fe)SiO₃ perovskite: constraints on composition of the lower mantle, *Phys. Earth Planet. Inter.*, **83**, 13-40, 1994.
- Yagi, T., P. M. Bell, and H. K. Mao, Phase relations in the system MgO-FeO-SiO₂ between 150 and 700 kbar at 1000 °C, *Year Book, Carnegie Inst. Washington*, **78**, 614-618, 1979.

Y. Fei and L. W. Finger, Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, N. W., Washington, DC 20015. (e-mail: fei@gl.ciw.edu; finger@gl.ciw.edu)

Y. Wang, Department of Earth and Space Sciences, State University of New York at Stony Brook, Stony Brook, NY 11794.

(Received August 14, 1995; revised January 24, 1996; accepted January 31, 1996.)