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LETTER

Mössbauer spectroscopy of mantle transition zone phases and determination of minimum Fe^{3+} content

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ABSTRACT

We report Mössbauer spectra of γ-Fe_2SiO_4, γ-$Mg_{1.8}Fe_{0.2}SiO_4$, β-$Mg_{1.8}Fe_{0.2}SiO_4$, and $Mg_{0.85}Fe_{0.15}SiO_3$ garnet synthesized in equilibrium with excess Fe metal and SiO_2 at high pressure and high temperature in a multianvil press. Spectra of γ-Fe_2SiO_4 and γ-$Mg_{1.8}Fe_{0.2}SiO_4$ show one Fe^{2+} doublet corresponding to the single octahedral site in the spinel structure and one Fe^{3+} doublet with Fe^{3+}/Fe_{tot} = 0.06 and 0.04 for γ-Fe_2SiO_4 and γ-$Mg_{1.8}Fe_{0.2}SiO_4$, respectively. The spectrum for β-$Mg_{1.8}Fe_{0.2}SiO_4$ includes two Fe^{2+} doublets tentatively assigned to the $^{[6]}$M1-M3 and $^{[6]}$M2 sites and one Fe^{3+} doublet with Fe^{3+}/Fe_{tot} = 0.03. The spectrum of $Mg_{0.85}Fe_{0.15}SiO_3$ garnet shows two Fe^{2+} doublets corresponding to the dodecahedral and octahedral sites and one Fe^{3+} doublet with Fe^{3+}/Fe_{tot} = 0.07. No Fe^{3+} was present in the starting materials within the limits of detection, and the amounts of Fe^{3+} measured in the experimental products represent the minimum possible for these phases at the given *P-T* conditions and Fe-Mg composition. The ability of transition zone phases to accommodate significant Fe^{3+} in equilibrium with Fe metal implies that, in an isochemical mantle, the f_{O_2} of the transition zone must be lower than that of the upper mantle.

INTRODUCTION

Mössbauer studies of minerals derived from the upper mantle have been crucial for estimating the oxidation state of the upper mantle (e.g., Wood et al., 1990, and references therein). Recently O'Neill et al. (1993) argued that the relatively high f_{O_2} of the upper mantle (near QFM) is a consequence of Fe^{3+} concentration in the modally minor phases clinopyroxene and spinel, so changes in mantle mineralogy probably could cause changes in the oxidation state of the mantle. Below 400 km in the Earth's mantle, the assemblage olivine + pyroxenes ± spinel ± garnet transforms to β-$(Mg,Fe)_2SiO_4$ + $(Mg,Fe)SiO_3$-rich garnet and, at ~550 km, to γ-$(Mg,Fe)_2SiO_4$ + $(Mg,Fe)SiO_3$-rich garnet (e.g., Takahashi and Ito, 1987). This region of the mantle, known as the transition zone, constitutes about 13% of the mantle by volume. Although no samples have been obtained from this region of the mantle, synthesis of these phases in the laboratory is possible and provides important information on structure, crystal chemistry, and physical properties. In this study we synthesized transition zone phases from ^{57}Fe-enriched compositions in the system MgO-SiO_2-Fe-O at their low f_{O_2} stability limits, in equilibrium with excess Fe metal and SiO_2, and used ^{57}Fe Mössbauer spectroscopy to determine the crystal chemistry of Fe and the minimum Fe^{3+}/Fe_{tot} in these high-pressure phases.

EXPERIMENTAL PROCEDURE

We synthesized starting materials of olivine and pyroxene in a gas-mixing furnace under controlled mixtures of CO and CO_2 at 1100–1300 °C from mixtures of MgO, SiO_2, ^{57}Fe-enriched Fe_2O_3 (94% ^{57}Fe), and isotopically normal Fe metal. No Fe^{3+} could be detected in any of the starting materials by Mössbauer spectroscopy. Excess SiO_2 and fine-grained Fe metal (20 wt% of each) were mixed in with the starting materials (with the exception of fayalite in experiment 170) and loaded into Fe capsules. The samples were synthesized at the conditions listed in Table 1 using a split-sphere multianvil apparatus. We used Toshiba F-grade tungsten carbide anvils with a truncation edge length of 5 mm and MgO octahedral sample assemblies (edge length 10 mm) containing a $LaCrO_3$ heater. We calibrated pressure at room temperature using transitions in Bi, ZnS, and GaAs and at 1200 and 1600 °C using the transitions olivine to β-phase and β-phase to spinel for Mg_2SiO_4 compositions (Akaogi et al., 1989). Temperatures were monitored using a $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple. Experimental products

TABLE 1. Experimental synthesis conditions

Expt.	Starting materials	*P* (GPa)	*T* (°C)	*t* (h)	Products*
170	Fa_{100}	8.0(5)	1000(50)	9.0	γ (+ Cfs + Fe)
519	Fs_{15} + SiO_2 + Fe	18.0(5)	1700(50)	0.25	γ + St + Fe (+ Gt)
526	Fs_{15} + SiO_2 + Fe	18.0(5)	1900(50)	0.10	Gt + St + Fe (+ γ)
549	Fs_{10}	15.0(5)	1600(50)	0.33	Cpx
578	Fs_{10} + SiO_2 + Fe	16.0(5)	1600(50)	0.17	β + St + Fe

Note: Fa = fayalite; Fs = ferrosilite; γ = γ-$(Mg,Fe)_2SiO_4$; Cfs = clinoferrosilite; Fe = Fe metal; St = stishovite; Gt = $(Mg,Fe)SiO_3$ garnet; β = β-$(Mg,Fe)_2SiO_4$; Cpx = clinopyroxene.
* Phases listed in parentheses occur in trace amounts (<3%).

(typically 1–2 mg) were mounted on plastic foil for powder X-ray diffraction analysis and Mössbauer spectroscopy. X-ray diffraction data showed extremely sharp lines, which allowed accurate determination of lattice parameters. Electron microprobe analysis indicated homogeneous chemical composition within each phase, and no evidence for glass or impurities was found using backscattered electron imaging. Transmission Mössbauer spectra were recorded at room temperature on a triangular-velocity constant-acceleration Mössbauer spectrometer with a nominal 50-mCi ^{57}Co source in a 6-μm Rh matrix. The velocity scale was calibrated with respect to 25-μm Fe foil.

EXPERIMENTAL RESULTS

Room-temperature Mössbauer spectra of the experimental products listed in Table 1 are illustrated in Figure 1. The spectra were fitted to quadrupole doublets with Lorentzian line shape where individual component widths and areas were constrained to be equal; results are listed in Table 2. Because sample thicknesses varied up to ~30 mg Fe/cm^2 (unenriched), corrections based on calculations of Rancourt (1989) were applied to relative area ratios to determine site distributions. We also considered the effects of differing recoil-free fractions for Fe^{3+} and Fe^{2+} in the same site (DeGrave and Van Alboom, 1991). Although such corrections do not replace the complex fitting analysis required for thick absorbers, they provide a more realistic estimate of site distributions than does the common assumption of zero correction. We compared our correction to Fe^{2+}(i) (M1) and Fe^{2+}(ii) (M2) site distributions in clinopyroxene with the experimental results of Skogby et al. (1992), which are based on extrapolation to zero thickness; both methods gave identical corrections.

γ-$(Mg,Fe)_2SiO_4$

Mössbauer spectra of γ-Fe_2SiO_4 and γ-$Mg_{1.8}Fe_{0.2}SiO_4$ were each fitted to one Fe^{2+} and one Fe^{3+} quadrupole doublet, corresponding to Fe in the single octahedral site in both phases. Mössbauer parameters for Fe^{2+} in γ-Fe_2SiO_4 are identical to those reported earlier by Suito et al. (1984) and Choe et al. (1992). An additional quadrupole doublet was fitted to the γ-$Mg_{1.8}Fe_{0.2}SiO_4$ spectrum to account for a small amount (<5%) of $(Mg,Fe)SiO_3$ garnet in the sample (see Fig. 1). Although no Fe^{3+} was found in the olivine starting material, measurable amounts of Fe^{3+} were present in both high-pressure phases. The

TABLE 2. The ^{57}Fe Mössbauer parameters of phases quenched from high pressure

Expt. no.	170	519	526	549	578	578
Phase	γ-Fe_2SiO_4	γ-$Mg_{1.7}Fe_{0.3}SiO_4$	$Mg_{0.85}Fe_{0.15}SiO_3$ garnet	$Mg_{0.9}Fe_{0.1}SiO_3$ clinopyroxene	β-$Mg_{1.8}Fe_{0.2}SiO_4$ (*T* = 298 K)	β-$Mg_{1.8}Fe_{0.2}SiO_4$ (*T* = 80 K)
Fe^{2+}(i)						
Shift (mm/s)*	1.09(1)	1.05(1)	1.26(1)	1.14(1)	1.06(1)	1.15(1)
ΔE_Q (mm/s)	2.62(1)	2.78(1)	3.60(1)	2.09(1)	2.76(1)	2.91(1)
FWHM (mm/s)	0.33(3)	0.32(3)	0.29(3)	0.27(3)	0.33(3)	0.36(3)
Fe^{2+}(ii)						
Shift (mm/s)*	—	—	1.11(3)	1.16(1)	1.09(3)	1.17(3)
ΔE_Q (mm/s)	—	—	1.39(3)	2.60(1)	2.29(3)	2.54(3)
FWHM (mm/s)	—	—	0.35(5)	0.29(3)	0.32(5)	0.31(5)
Fe^{3+}						
Shift (mm/s)*	0.18(5)	0.27(5)	0.31(3)	—	0.27(5)	0.28(5)
ΔE_Q (mm/s)	0.37(5)	0.00**	0.48(3)	—	0.37(5)	0.17(5)
FWHM (mm/s)	0.46(10)	0.78(10)	0.37(7)	—	0.38(10)	0.37(5)
Area ratio $Fe^{2+}(ii)/Fe^{2+}_{tot}$	—	—	0.89	0.39	0.20	0.17
Area ratio Fe^{3+}/Fe_{tot}	0.07	0.06	0.10	—	0.04	0.03
Adjusted $Fe^{2+}(ii)/Fe^{2+}_{tot}$†	—	—	0.93(2)	0.36(2)	0.16(2)	0.13(2)
Adjusted Fe^{3+}/Fe_{tot}†	0.06(2)	0.04(2)	0.07(2)	—	0.03(1)	0.02(1)

Note: All measurements were made at room temperature unless otherwise noted.
* Relative to Fe metal at 298 K.
** Fixed for determination of Fe^{3+}/Fe_{tot}.
† Estimated from calculations of Rancourt (1989).

Fe^{3+} content of γ-Fe_2SiO_4 determined by Mössbauer spectroscopy is consistent with the amount calculated by comparing the measured lattice parameter (8.236 ± 0.001 Å) with the linear relation of lattice parameter and composition in the γ-Fe_2SiO_4-Fe_3O_4 solid solution (O'Neill and Canil, 1992). Fe^{3+} is also found in γ-$Mg_{1.8}Fe_{0.2}SiO_4$, despite the lowering of the minimum f_{O_2} stability of spinel caused by the addition of Mg.

Our experiments approached Fe^{3+} equilibrium from the lower boundary because the starting materials contained no Fe^{3+} within the limits of measurement. This implies that the measured Fe^{3+}/Fe_{tot} values represent the minimum possible for these phases at the given Fe/(Fe + Mg) content and experimental *P-T* conditions. It is therefore important to explain why γ-Fe_2SiO_4 synthesized at the same *P-T* conditions by Suito et al. (1984) appears to contain less Fe^{3+} than our sample. They heated α-Fe_2SiO_4 at 8 GPa and 1000 °C for 10 min in a graphite capsule and heater, also approaching Fe^{3+} equilibrium from the lower boundary. High-pressure experiments that we performed on γ-Fe_2SiO_4 at 1000 °C for periods of 5.25, 6.5, and 9 h in graphite capsules always produced more Fe^{3+} (Fe^{3+}/Fe_{tot} ~ 0.07) than Suito et al. (1984) observed, so it is possible that they did not reach Fe^{3+} equilibrium in the relatively short time scale of their experiment. Assuming ideal mixing of Fe_2SiO_4-Fe_3O_4 spinels (O'Neill and Canil, 1992), thermodynamic calculations predict Fe^{3+} concentrations of a few mol% along the Fe_2SiO_4-Fe-$FeSiO_3$ boundary, although an exact calculation also requires data for high-pressure clinoferrosilite, which are not available. Even though we cannot prove that equilibrium was achieved in our experiments, our approach from minimum Fe^{3+} content and the presence of excess clinoferrosilite and Fe metal in the experimental products indicates that f_{O_2} did not exceed that along the Fe-γ-Fe_2SiO_4-$FeSiO_3$ boundary during the experiment, and that our reported Fe^{3+}/Fe_{tot} values truly represent minimum estimates.

β-$(Mg,Fe)_2SiO_4$

The best empirical fit to the Mössbauer spectrum of β-$Mg_{1.8}Fe_{0.2}SiO_4$ consists of two quadrupole doublets [Fe^{2+}(i) and Fe^{2+}(ii)] with similar isomer shifts and different quadrupole splittings, where parameters are effectively constrained by a shoulder on the low velocity peak (see Fig. 1). We also fitted a magnetic sextet to account

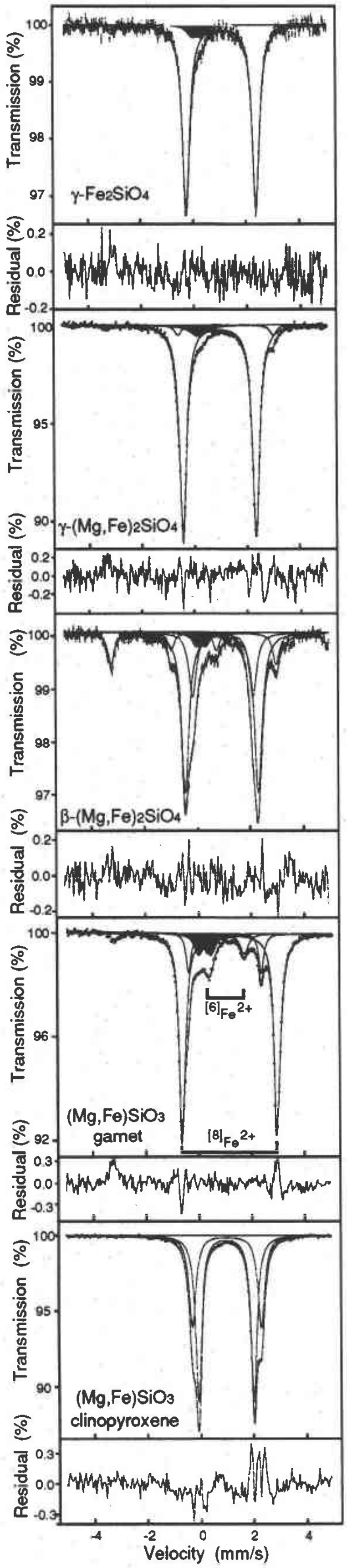

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Fig. 1. Room temperature ^{57}Fe Mössbauer spectra of phases quenched from high pressure. The velocity scales are relative to ^{57}Fe in Rh; add 0.114 mm/s for conversion to metallic Fe. Peaks corresponding to Fe^{3+} are shaded black in all spectra. There is a small doublet corresponding to $(Mg,Fe)SiO_3$ garnet in the γ-$Mg_{1.7}Fe_{0.3}O_4$ spectrum and a small doublet corresponding to γ-$(Mg,Fe)_2SiO_4$ in the $Mg_{0.85}Fe_{0.15}SiO_3$ garnet spectrum; four lines of the sextet corresponding to metallic Fe are visible in the β-$Mg_{1.8}Fe_{0.2}SiO_4$ spectrum.

for Fe metal and a single quadrupole doublet corresponding to Fe^{3+}. Sawamoto and Horiuchi (1990) reported that Fe^{2+} prefers the M1 and M3 sites (39 and 43%, respectively) over the M2 site (18%) in β-$Mg_{1.8}Fe_{0.2}SiO_4$, on the basis of single-crystal refinement results. This would imply assignment of the Fe^{2+}(i) doublet to the M1 and M3 sites and the Fe^{2+}(ii) doublet to the M2 site on the basis of the observed relative areas (see Table 2), but this assignment is speculative in the absence of other evidence. Fei et al. (1992) reported a spectrum from β-$Mg_{1.68}Fe_{0.32}SiO_4$ synthesized at 15.5 GPa and 1800 °C, which they fitted to one Fe^{2+} and one Fe^{3+} doublet, where the hyperfine parameters of their Fe^{2+} doublet are closest to our Fe^{2+}(i) (Table 2). The absence of a second doublet in the data of Fei et al. (1992) may indicate a variation in Fe site distribution with Fe^{2+}/Mg ratio, but this possibility is extremely speculative until further data are available. Although it is not possible to determine Fe^{3+} site assignments from our Mössbauer data, the amount of Fe^{3+} (Fe^{3+}/Fe_{tot} = 0.03) is effectively constrained by the area difference between high- and low-velocity peaks. The sample of Fei et al. (1992) contained significantly more Fe^{3+} (Fe^{3+}/Fe_{tot} = 0.08) than our sample synthesized at minimum f_{O_2}.

$(Mg,Fe)SiO_3$ garnet

We fitted the Mössbauer spectrum of $Mg_{0.85}Fe_{0.15}SiO_3$ garnet to two Fe^{2+} doublets and one Fe^{3+} doublet [also present were small amounts of γ-$(Mg,Fe)_2SiO_4$ and Fe metal; these were modeled with a quadrupole doublet and a magnetic sextet, respectively]. Even though spectral features effectively constrain the positions of Fe^{2+}(i) peaks and the relative abundance of all species, the positions of Fe^{2+}(ii) and Fe^{3+} peaks are not well defined. Fe^{2+}(i) is assigned to the dodecahedral site, since the hyperfine parameters fall within the range reported for $^{[8]}Fe^{2+}$ in garnets by Amthauer et al. (1976) (and outside the range for any other coordination or valence state). Fe^{2+}(ii) is assigned to the octahedral site on the basis of the center shift, which falls within the range reported by Kühberger et al. (1989) for sites of similar size. The quadrupole splitting of the Fe^{2+}(ii) doublet is unusually small, which might be explained by the low distortion of this site in the garnet structure (Ingalls, 1964; Angel et al., 1989). The large temperature dependence of Fe^{2+}(ii) quadrupole splitting is also consistent with this explanation ($\Delta E_{Q\,298\,K} - \Delta E_{Q\,80\,K}$ = 0.43 mm/s, from unpublished data of Geiger et al. for $Mg_{0.9}Fe_{0.1}SiO_3$ garnet synthesized at the same P-T conditions in a Mo capsule). Fe^{2+} is strongly partitioned into the dodecahedral site compared with Mg, suggesting that the exchange $(Mg,Fe^{2+}) + Si \leftrightarrow 2Al$ on the octahedral sites might be inhibited with increasing Fe^{2+}/Mg ratio in garnets at high pressure. Because of the uncertainty in hyperfine parameters, it is not possible to assign the site for Fe^{3+}. We suggest occupation of the octahedral sites, however, on the basis that Fe^{3+} occupies the octahedral site in common grospydite garnets and in $Fe_3Al_2Si_3O_{12}$-$Fe^{2+}_3Fe^{3+}_2Si_3O_{12}$ garnets at high pressure (Woodland and O'Neill, in preparation). We observed the highest minimum Fe^{3+}/Fe_{tot} ratio in $(Mg,Fe)SiO_3$ garnet compared with all other phases and note that even higher Fe^{3+} contents were found in samples synthesized at unbuffered f_{O_2} conditions (O'Neill et al., 1993).

$(Mg,Fe)SiO_3$ clinopyroxene

We equilibrated $Fe_{0.1}Mg_{0.9}SiO_3$ clinopyroxene at conditions similar to other experiments to provide a comparison with upper mantle phases. We obtained a typical pyroxene spectrum and fitted two Fe^{2+} doublets, corresponding to octahedrally coordinated M1[Fe^{2+}(i)] and M2 [Fe^{2+}(ii)] sites. In sharp contrast to the three transition zone phases, we found no Fe^{3+} within the limits of detection. This is consistent with the constraint of f_{O_2} during our experiments to minimum Fe^{3+}, since the extensive solubility of Fe^{3+} in clinopyroxene (e.g., Huckenholz et al., 1966) implies a significant Fe^{3+} content at conditions of higher f_{O_2}. Intracrystalline Fe^{2+}/Mg partitioning in the high-pressure clinopyroxene is much more disordered than in orthopyroxenes prepared at atmospheric pressure (Skogby et al., 1992) and may be an important factor in stabilizing high-pressure clinopyroxene at intermediate Mg/Fe^{2+} ratios.

DISCUSSION

The low f_{O_2} stability limit of a ferromagnesian silicate $(Mg,Fe^{2+})_nSiO_{(2+n)}$ in the simplified mantle system MgO-SiO_2-Fe-O is given by

$$\underset{\text{silicate}}{Fe^{2+}_nSiO_{2+n}} = \underset{\text{metal}}{nFe} + \underset{\text{stishovite}}{SiO_2} + (n/2)O_2. \tag{1}$$

The amount of Fe^{3+} in the silicate is controlled by reactions such as

$$\underset{\text{spinel or }\beta\text{-phase}}{3Fe^{2+}_2SiO_4} + O_2 = \underset{\text{spinel or }\beta\text{-phase}}{2Fe^{2+}Fe^{3+}_2O_4} + \underset{\text{stishovite}}{3SiO_2} \tag{2}$$

$$\underset{\text{garnet}}{2.5Fe^{2+}_4Si_4O_{12}} + O_2 = \underset{\text{garnet}}{2Fe^{2+}_3Fe^{3+}_2Si_3O_{12}} + \underset{\text{stishovite}}{4SiO_2}. \tag{3}$$

The combination of Equation 1 with Equation 2 or Equation 3 shows that the minimum amount of Fe^{3+} in a ferromagnesian silicate, at given Mg/(Mg + Fe), P, and T, occurs at the phase's lower limit of f_{O_2} stability, i.e., in equilibrium with excess Fe metal and SiO_2.

The minimum Fe^{3+} contents of transition zone phases (Table 2) are large compared with the small amounts of Fe^{3+} that the dominant upper mantle phases, olivine and orthopyroxene, can accommodate (e.g., Nakamura and Schmalzried, 1983). The concentration of Fe^{3+} in the modally minor phases of clinopyroxene and spinel results in a relatively high f_{O_2} of the upper mantle (near QFM): if Fe^{3+}/Fe_{tot} were evenly distributed among all upper mantle phases, then the upper mantle f_{O_2} would be reduced by approximately 3 log units, i.e., to a point close to metal saturation (O'Neill et al., 1993). If the transition zone is assumed to be isochemical (including Fe^{3+}/Fe_{tot}) with the upper mantle ($Fe^{3+}/Fe_{tot} \sim 0.02$), then we calculate the f_{O_2} of the transition zone to be close to metal saturation. The substantially lower f_{O_2} of the transition zone relative to the upper mantle is a consequence of the ability of all the dominant phases in the transition zone to accommodate amounts of Fe^{3+} that are comparable with, or greater than, the bulk Fe^{3+} content of the upper mantle. The inevitable presence of Fe^{3+} in transition-zone minerals is likely to have significant effects on physical properties such as electrical conductivity and should also be taken into account in the accurate determination of phase boundaries.

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