

LETTER

Mössbauer spectroscopy of mantle transition zone phases and determination of minimum Fe³⁺ content

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ABSTRACT

We report Mössbauer spectra of γ -Fe₂SiO₄, γ -Mg_{1.8}Fe_{0.2}SiO₄, β -Mg_{1.8}Fe_{0.2}SiO₄, and Mg_{0.85}Fe_{0.15}SiO₃ garnet synthesized in equilibrium with excess Fe metal and SiO₂ at high pressure and high temperature in a multianvil press. Spectra of γ -Fe₂SiO₄ and γ -Mg_{1.8}Fe_{0.2}SiO₄ show one Fe²⁺ doublet corresponding to the single octahedral site in the spinel structure and one Fe³⁺ doublet with Fe³⁺/Fe_{tot} = 0.06 and 0.04 for γ -Fe₂SiO₄ and γ -Mg_{1.8}Fe_{0.2}SiO₄, respectively. The spectrum for β -Mg_{1.8}Fe_{0.2}SiO₄ includes two Fe²⁺ doublets tentatively assigned to the ¹⁶M1-M3 and ¹⁶M2 sites and one Fe³⁺ doublet with Fe³⁺/Fe_{tot} = 0.03. The spectrum of Mg_{0.85}Fe_{0.15}SiO₃ garnet shows two Fe²⁺ doublets corresponding to the dodecahedral and octahedral sites and one Fe³⁺ doublet with Fe³⁺/Fe_{tot} = 0.07. No Fe³⁺ was present in the starting materials within the limits of detection, and the amounts of Fe³⁺ 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 Fe³⁺ in equilibrium with Fe metal implies that, in an isochemical mantle, the *f*_{O₂} 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*_{O₂} of the upper mantle (near QFM) is a consequence of Fe³⁺ 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)₂SiO₄ + (Mg,Fe)SiO₃-rich garnet and, at ~550 km, to γ -(Mg,Fe)₂SiO₄ + (Mg,Fe)SiO₃-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 ⁵⁷Fe-enriched compositions in the system MgO-SiO₂-Fe-O at their low *f*_{O₂} stability limits, in equilibrium with excess Fe metal and SiO₂, and used ⁵⁷Fe Mössbauer spectroscopy to de-

termine the crystal chemistry of Fe and the minimum Fe³⁺/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 CO₂ at 1100–1300 °C from mixtures of MgO, SiO₂, ⁵⁷Fe-enriched Fe₂O₃ (94% ⁵⁷Fe), and isotopically normal Fe metal. No Fe³⁺ could be detected in any of the starting materials by Mössbauer spectroscopy. Excess SiO₂ 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 LaCrO₃ 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 Mg₂SiO₄ compositions (Akaogi et al., 1989). Temperatures were monitored using a W₉₇Re₃-W₇₅Re₂₅ 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)₂SiO₄; Cfs = clinoferrosilite; Fe = Fe metal; St = stishovite; Gt = (Mg,Fe)SiO₃ garnet; β = β-(Mg,Fe)₂SiO₄; 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 back-scattered electron imaging. Transmission Mössbauer spectra were recorded at room temperature on a triangular-velocity constant-acceleration Mössbauer spectrometer with a nominal 50-mCi ⁵⁷Co 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/cm² (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 Fe³⁺ and Fe²⁺ 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 Fe²⁺(i) (M1) and Fe²⁺(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)₂SiO₄

Mössbauer spectra of γ-Fe₂SiO₄ and γ-Mg_{1.8}Fe_{0.2}SiO₄ were each fitted to one Fe²⁺ and one Fe³⁺ quadrupole doublet, corresponding to Fe in the single octahedral site in both phases. Mössbauer parameters for Fe²⁺ in γ-Fe₂SiO₄ 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}SiO₄ spectrum to account for a small amount (<5%) of (Mg,Fe)SiO₃ garnet in the sample (see Fig. 1). Although no Fe³⁺ was found in the olivine starting material, measurable amounts of Fe³⁺ were present in both high-pressure phases. The

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

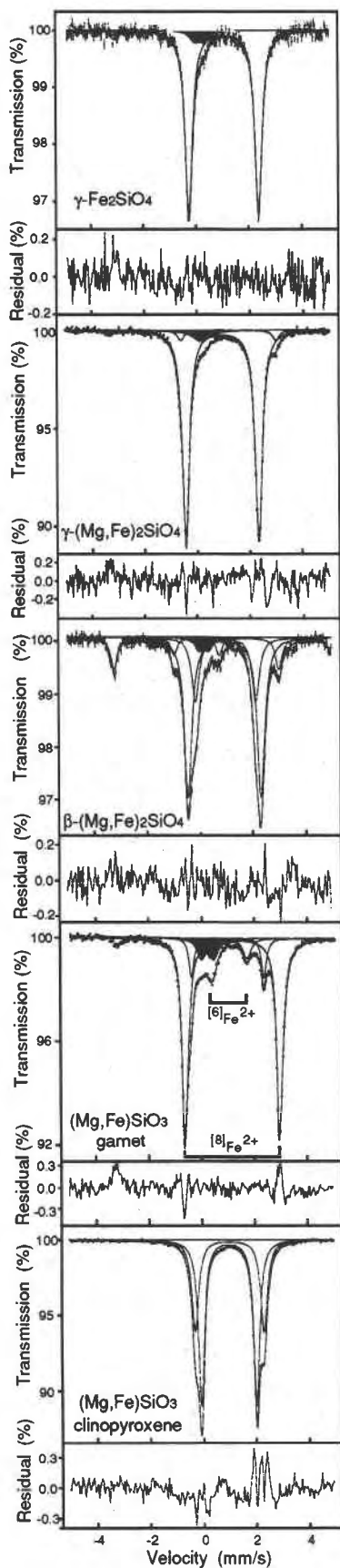
Expt. no.	170	519	526	549	578	578
Phase	γ-Fe ₂ SiO ₄	γ-Mg _{1.7} Fe _{0.3} SiO ₄	Mg _{0.85} Fe _{0.15} SiO ₃ garnet	Mg _{0.9} Fe _{0.1} SiO ₃ clinopyroxene	β-Mg _{1.8} Fe _{0.2} SiO ₄ (T = 298 K)	β-Mg _{1.8} Fe _{0.2} SiO ₄ (T = 80 K)
			Fe²⁺(i)			
Shift (mm/s)*	1.09(1)	1.05(1)	1.26(1)	1.14(1)	1.06(1)	1.15(1)
ΔE ₀ (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)
			Fe²⁺(ii)			
Shift (mm/s)*	—	—	1.11(3)	1.16(1)	1.09(3)	1.17(3)
ΔE ₀ (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)
			Fe³⁺			
Shift (mm/s)*	0.18(5)	0.27(5)	0.31(3)	—	0.27(5)	0.28(5)
ΔE ₀ (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⁺ (i)	—	—	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 _{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 Fe³⁺/Fe_{tot}.

† Estimated from calculations of Rancourt (1989).



Fe³⁺ content of γ -Fe₂SiO₄ 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 -Fe₂SiO₄-Fe₃O₄ solid solution (O'Neill and Canil, 1992). Fe³⁺ is also found in γ -Mg_{1.8}Fe_{0.2}SiO₄, despite the lowering of the minimum f_{O_2} stability of spinel caused by the addition of Mg.

Our experiments approached Fe³⁺ equilibrium from the lower boundary because the starting materials contained no Fe³⁺ within the limits of measurement. This implies that the measured Fe³⁺/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 -Fe₂SiO₄ synthesized at the same P - T conditions by Suito et al. (1984) appears to contain less Fe³⁺ than our sample. They heated α -Fe₂SiO₄ at 8 GPa and 1000 °C for 10 min in a graphite capsule and heater, also approaching Fe³⁺ equilibrium from the lower boundary. High-pressure experiments that we performed on γ -Fe₂SiO₄ at 1000 °C for periods of 5.25, 6.5, and 9 h in graphite capsules always produced more Fe³⁺ (Fe³⁺/Fe_{tot} ~ 0.07) than Suito et al. (1984) observed, so it is possible that they did not reach Fe³⁺ equilibrium in the relatively short time scale of their experiment. Assuming ideal mixing of Fe₂SiO₄-Fe₃O₄ spinels (O'Neill and Canil, 1992), thermodynamic calculations predict Fe³⁺ concentrations of a few mol% along the Fe₂SiO₄-FeFeSiO₃ 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 Fe³⁺ 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 -Fe₂SiO₄-FeSiO₃ boundary during the experiment, and that our reported Fe³⁺/Fe_{tot} values truly represent minimum estimates.

β -(Mg,Fe)₂SiO₄

The best empirical fit to the Mössbauer spectrum of β -Mg_{1.8}Fe_{0.2}SiO₄ consists of two quadrupole doublets [Fe²⁺(i) and Fe²⁺(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 ⁵⁷Fe Mössbauer spectra of phases quenched from high pressure. The velocity scales are relative to ⁵⁷Fe in Rh; add 0.114 mm/s for conversion to metallic Fe. Peaks corresponding to Fe³⁺ are shaded black in all spectra. There is a small doublet corresponding to (Mg,Fe)SiO₃ garnet in the γ -Mg_{1.7}Fe_{0.3}O₄ spectrum and a small doublet corresponding to γ -(Mg,Fe)₂SiO₄ in the Mg_{0.85}Fe_{0.15}SiO₃ garnet spectrum; four lines of the sextet corresponding to metallic Fe are visible in the β -Mg_{1.8}Fe_{0.2}SiO₄ spectrum.

for Fe metal and a single quadrupole doublet corresponding to Fe³⁺. Sawamoto and Horiuchi (1990) reported that Fe²⁺ prefers the M1 and M3 sites (39 and 43%, respectively) over the M2 site (18%) in β -Mg_{1.8}Fe_{0.2}SiO₄, on the basis of single-crystal refinement results. This would imply assignment of the Fe²⁺(i) doublet to the M1 and M3 sites and the Fe²⁺(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}SiO₄ synthesized at 15.5 GPa and 1800 °C, which they fitted to one Fe²⁺ and one Fe³⁺ doublet, where the hyperfine parameters of their Fe²⁺ doublet are closest to our Fe²⁺(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 Fe²⁺/Mg ratio, but this possibility is extremely speculative until further data are available. Although it is not possible to determine Fe³⁺ site assignments from our Mössbauer data, the amount of Fe³⁺ (Fe³⁺/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 Fe³⁺ (Fe³⁺/Fe_{tot} = 0.08) than our sample synthesized at minimum f_{O_2} .

(Mg,Fe)SiO₃ garnet

We fitted the Mössbauer spectrum of Mg_{0.85}Fe_{0.15}SiO₃ garnet to two Fe²⁺ doublets and one Fe³⁺ doublet [also present were small amounts of γ -(Mg,Fe)₂SiO₄ and Fe metal; these were modeled with a quadrupole doublet and a magnetic sextet, respectively]. Even though spectral features effectively constrain the positions of Fe²⁺(i) peaks and the relative abundance of all species, the positions of Fe²⁺(ii) and Fe³⁺ peaks are not well defined. Fe²⁺(i) is assigned to the dodecahedral site, since the hyperfine parameters fall within the range reported for ⁵⁷Fe²⁺ in garnets by Amthauer et al. (1976) (and outside the range for any other coordination or valence state). Fe²⁺(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 Fe²⁺(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 Fe²⁺(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}SiO₃ garnet synthesized at the same P - T conditions in a Mo capsule). Fe²⁺ is strongly partitioned into the dodecahedral site compared with Mg, suggesting that the exchange (Mg,Fe²⁺) + Si \leftrightarrow 2Al on the octahedral sites might be inhibited with increasing Fe²⁺/Mg ratio in garnets at high pressure. Because of the uncertainty in hyperfine parameters, it is not possible to assign the site for Fe³⁺. We suggest occupation of the octahedral sites, however, on the basis that Fe³⁺ occupies the octahedral site in common grosspyrite garnets and in Fe₃Al₂Si₃O₁₂-Fe₃⁺Fe₃²⁺Si₃O₁₂ garnets at high pressure (Woodland and

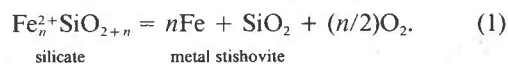
O'Neill, in preparation). We observed the highest minimum Fe³⁺/Fe_{tot} ratio in (Mg,Fe)SiO₃ garnet compared with all other phases and note that even higher Fe³⁺ contents were found in samples synthesized at unbuffered f_{O_2} conditions (O'Neill et al., 1993).

(Mg,Fe)SiO₃ clinopyroxene

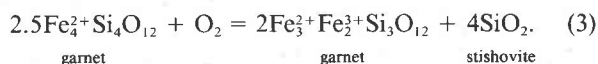
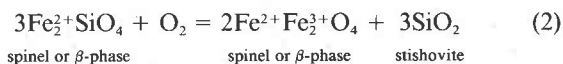
We equilibrated Fe_{0.1}Mg_{0.9}SiO₃ clinopyroxene at conditions similar to other experiments to provide a comparison with upper mantle phases. We obtained a typical pyroxene spectrum and fitted two Fe²⁺ doublets, corresponding to octahedrally coordinated M1[Fe²⁺(i)] and M2[Fe²⁺(ii)] sites. In sharp contrast to the three transition zone phases, we found no Fe³⁺ within the limits of detection. This is consistent with the constraint of f_{O_2} during our experiments to minimum Fe³⁺, since the extensive solubility of Fe³⁺ in clinopyroxene (e.g., Huckenholz et al., 1966) implies a significant Fe³⁺ content at conditions of higher f_{O_2} . Intracrystalline Fe²⁺/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/Fe²⁺ ratios.

DISCUSSION

The low f_{O_2} stability limit of a ferromagnesian silicate (Mg,Fe²⁺)_nSiO_(2+n) in the simplified mantle system MgO-SiO₂-Fe-O is given by



The amount of Fe³⁺ in the silicate is controlled by reactions such as



The combination of Equation 1 with Equation 2 or Equation 3 shows that the minimum amount of Fe³⁺ 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 SiO₂.

The minimum Fe³⁺ contents of transition zone phases (Table 2) are large compared with the small amounts of Fe³⁺ that the dominant upper mantle phases, olivine and orthopyroxene, can accommodate (e.g., Nakamura and Schmalzried, 1983). The concentration of Fe³⁺ in the modally minor phases of clinopyroxene and spinel results in a relatively high f_{O_2} of the upper mantle (near QFM): if Fe³⁺/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 Fe³⁺/Fe_{tot}) with the upper mantle (Fe³⁺/Fe_{tot} \sim 0.02), then we cal-

culate 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 Fe³⁺ that are comparable with, or greater than, the bulk Fe³⁺ content of the upper mantle. The inevitable presence of Fe³⁺ 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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