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LETTER

Mössbauer spectra of $^{57}Fe_{0.05}Mg_{0.95}SiO_3$ perovskite at 80 and 298 K

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Abstract

We report Mössbauer spectra obtained at 298 and 80 K of $^{57}Fe_{0.05}Mg_{0.95}SiO_3$ perovskite synthesized at 25 GPa and 1650 °C with excess Fe and SiO_2 using a multianvil press. The spectrum obtained at 298 K can be unambiguously fitted to one Fe^{2+} doublet, one Fe^{3+} doublet, and a sextet corresponding to Fe metal. The Fe^{2+} doublet has a center shift of 1.12 ± 0.01 mm/s relative to Fe, a quadrupole splitting of 1.58 ± 0.01 mm/s, and a line width of 0.45 ± 0.05 mm/s. The data show conclusively that Fe^{2+} occupies a single site in the perovskite structure and strongly suggest substitution on the eight- to 12-coordinated site based on correlations between center shift and bond length. Because this sample was synthesized at the minimum f_{O_2} stability limit, the measured Fe^{3+}/Fe_{tot} of ~0.05 is the minimum for this Fe-Mg composition. The spectrum obtained at 80 K shows broadening of the Fe^{2+} absorption envelope. Although these data can be fitted satisfactorily to two Fe^{2+} doublets, more work is required to determine the nature of the Fe^{2+} environment.

Introduction

The perovskite phase $(Fe,Mg)SiO_3$ is currently believed to constitute the bulk of the lower mantle, and therefore the nature of Fe in the structure is extremely important for characterizing mantle properties. Single-crystal structure refinements of $MgSiO_3$ with the perovskite structure have unambiguously shown that Si^{4+} occupies the octahedral sites, whereas the eight- to 12-coordinated sites are filled by Mg^{2+} (e.g., Horiuchi et al., 1987). The site occupied by Fe in the perovskite structure is not so clear, however. Extended X-ray absorption fine structure (EXAFS) measurements by Jackson et al. (1987) and Mössbauer data of Jeanloz et al. (1991) imply that Fe^{2+} occupies the octahedral site, whereas Parise et al. (1990) and Kudoh et al. (1990) concluded that Fe^{2+} occupies the eight- to 12-coordinated site on the basis of X-ray diffraction and EXAFS data. The amount and location of Fe^{3+} in $(Fe,Mg)SiO_3$ perovskite are problematical because of the small amounts involved but are important for characterizing properties such as electrical conductivity because of their likely role in the conduction mechanism.

Mössbauer spectroscopy is sensitive to the local environment of the Fe nuclei and would seem an ideal method for studying the nature and location of Fe in the perovskite structure. Unfortunately, measurements of Mössbauer spectra of $(Fe,Mg)SiO_3$ perovskite have so far resulted in extremely broad line widths (Jeanloz et al., 1991; Fei et al., 1992), preventing unambiguous fitting and interpretation of the spectra.

In this study we used the following procedures to obtain a well characterized sample: (1) synthesizing under carefully controlled *P,T* conditions using a multianvil press, (2) buffering the sample using Fe and SiO_2 to control the chemical activities of all species, and (3) crushing the sample at liquid N_2 temperature to prevent amorphization. The presence of excess Fe and SiO_2 buffers the perovskite at its low f_{O_2} stability limit by the reaction 2 $FeSiO_3$ (pv) = 2 Fe (metal) + 2 SiO_2 (st) + O_2, thereby achieving a minimum Fe^{3+} content (O'Neill et al., 1992).

Experimental procedure

The sample of perovskite used in this study was prepared using the following method. Starting material with the stoichiometry $Fe_{0.05}Mg_{0.95}SiO_3$ was prepared from a mixture of SiO_2, MgO (both >99.9% pure and dried at 1200 °C), and $^{57}Fe_2O_3$ (92% enrichment) by firing at 1300 °C for 14 h with CO/CO_2 in the ratio 1:1. The sample was cooled slowly to 900 °C and then quenched rapidly to room temperature by removal from the furnace. X-ray diffraction showed the sample to consist solely of clinoenstatite, and Mössbauer spectroscopy failed to detect the presence of Fe^{3+}. The clinoenstatite was mixed with 5 wt% Fe metal (isotopically normal) and 5 wt% SiO_2 (quartz), and then transformed to perovskite (+ Fe + stishovite) at 25 GPa and 1650 °C for 20 min in an Fe capsule using the 1200-ton multianvil press at the Bayerisches Geoinstitut.

Following the high-pressure experiment, we removed the sample from the capsule and, before crushing, ex-

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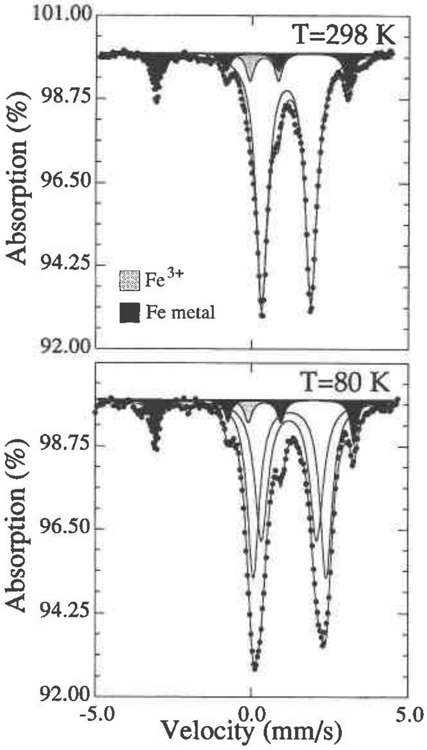

Fig. 1. Mössbauer spectra of $^{57}Fe_{0.05}Mg_{0.95}SiO_3$ perovskite at 298 and 80 K. The spectra were fitted to Lorentzian lines according to models described in the text. Note that peaks corresponding to Fe metal and Fe^{3+} overlap at approximately 0.84 mm/s.

amined each end of the sample pellet using an X-ray microdiffractometer in reflection mode. Only perovskite, stishovite, and metallic Fe were observed to be present. To avoid back transformation or amorphization during the grinding process, we crushed the sample in a hydraulic press using a pellet press 13 mm in diameter where both the sample and pellet press had been precooled to 77 K using liquid N_2. Approximately 2.1 mg of crushed sample was recovered, which was mounted on a plastic foil for powder X-ray diffraction analysis and Mössbauer spectroscopy. The Mössbauer thickness of the sample corresponded to an unenriched concentration of 6 mg of Fe/cm^2.

X-ray powder diffraction data were obtained using monochromated Co$K\alpha_1$ radiation in transmission mode. Data were obtained from 28 to 140° 2θ and revealed the presence of perovskite, Fe metal, and stishovite. No other phases were found. We used the lines corresponding to stishovite as an internal calibration standard (Baur and Khan, 1971) and determined the following refined cell parameters for perovskite: $a = 4.7847(3)$ Å, $b = 4.9304(4)$ Å, and $c = 6.9017(6)$ Å. Microprobe analysis gave a composition of $Fe_{0.056(6)}Mg_{0.958(17)}Si_{0.993(6)}O_3$ (average of seven analyses). From the backscattered electron image, we noted the presence of a small impurity, apparently with olivine stoichiometry and Fe/(Fe + Mg) approximately 0.1. This impurity was not detected in the X-ray diffraction analyses, however, and was detected only in negligible amounts (if at all) in the Mössbauer spectra (see below).

Transmission Mössbauer spectra were recorded on a Mössbauer spectrometer using constant acceleration with a source nominally containing 50-mCi ^{57}Co in a 6-μm Rh matrix. The velocity scale was calibrated with respect to 25-μm Fe foil using the positions certified for National Bureau of Standards standard reference material no. 1541; we obtained line widths for Fe of 0.28 mm/s at 298 K. Spectra were recorded with the absorber at 80 K (source at 298 K) using a cold-finger cryostat capable of controlling to within ±0.5 K. Room-temperature spectra were recorded both before and after cooling to 80 K to verify that no irreversible change in the sample occurred during cooling, and they showed no change in parameters within experimental error. X-ray diffraction patterns recorded both before and after the Mössbauer experiments also showed no detectable change. The spectra were fitted to Lorentzian line shapes with a computer program incorporating nonlinear function minimization and error analysis routines in the Minuit package provided by CERN (available from Program Library, CERN—CN Division, CH-1211 Geneva 23, Switzerland). Errors were estimated from the reproducibility of hyperfine parameters using different fitting models and starting points, as well as from systematic errors present in the experiment.

EXPERIMENTAL RESULTS

The Mössbauer spectra of $^{57}Fe_{0.05}Mg_{0.95}SiO_3$ recorded at 298 and 80 K are illustrated in Figure 1. Calculated curves were fitted as described below. It is significant to note that both spectra exhibit narrow lines compared with all spectra reported previously for iron perovskite (Jeanloz et al., 1991; Fei et al., 1992).

The presence of Fe metal provided both an internal calibration standard and a sensitive measure of how well the tails of the main absorption peaks were modeled by the fits. A magnetic sextet was fitted to both spectra with all widths constrained to be equal and areas constrained to 3:2:1:1:2:3, appropriate to a randomly oriented powder. Several trials were conducted with these constraints removed, which produced similar results. The Fe hyperfine parameters determined from the present spectra are in excellent agreement with published values at 298 and 80 K (Preston et al., 1962), and give equal fractional areas within experimental error at both temperatures (Table 1).

Fe^{3+} is clearly present in both spectra. Neglect of Fe^{3+} absorption produced extremely poor fits to the tails of the low-velocity component, and effects such as texture or crystalline anisotropy do not account for the discrepancy. Fe^{3+}/Fe_{tot} in the perovskite phase is constrained to approximately 0.05, on the basis of the area difference between the high- and low-velocity components. We added a quadrupole doublet (components constrained to equal widths and areas) corresponding to Fe^{3+} and fitted the

Table 1. Mössbauer parameters of $^{57}Fe_{0.05}Mg_{0.95}SiO_3$ perovskite

Site	Parameter	T = 298 K	T = 80 K
Fe^0	field (T)	33.0(5)	34.1(5)
	shift (mm/s)	0.00(1)	0.11(1)
	FWHM (mm/s)	0.27(5)	0.27(5)
	% area	20	18
Fe^{2+} (i)	ΔE_Q (mm/s)	1.58(1)	1.77(5)
	shift (mm/s)	1.12(1)	1.22(3)
	FWHM (mm/s)	0.45(5)	0.50(5)
	% area	73	36
Fe^{2+} (ii)	ΔE_Q (mm/s)	—	2.33(5)
	shift (mm/s)	—	1.24(3)
	FWHM (mm/s)	—	0.46(5)
	% area	—	42
Fe^{3+}	ΔE_Q (mm/s)	0.98	1.08
	shift (mm/s)	0.44	0.42
	FWHM (mm/s)	0.35	0.31
	% area	6	4
Fe^{3+}/Fe_{tot} for perovskite		0.08	0.05

Note: All center shifts are relative to Fe metal.

remaining main Fe^{2+} absorption to a similarly constrained quadrupole doublet. It was clear during fitting that one component of the Fe^{3+} doublet must lie close to 0.84 mm/s to account for the large shoulder on the main absorption peak. Repeated trials indicated the other component must lie below 0 mm/s in order to fit the other shoulder of the same peak.

The 298-K Mössbauer spectrum is well fitted to two quadrupole doublets and one magnetic sextet (see Fig. 1), and the hyperfine parameters for this model are given in Table 1. The line width of the doublet corresponding to Fe^{2+} (0.45 mm/s) is larger than typical values for iron silicates but is within the range possible for local variations in chemistry or geometry. There is a slight misfit of the Mössbauer spectrum near 1 mm/s (see Fig. 1), which might be attributed to the impurity phase (see above), but the presence of this phase has no significant effect on the interpretation of the perovskite Mössbauer spectra.

The 80-K spectrum was poorly fitted to the above model. The line width of the doublet corresponding to Fe^{2+} is extremely large (0.63 mm/s), but the greatest problem is a large discrepancy at the high-velocity shoulder of the main absorption doublet (as seen by the mismatch in areas of corresponding components of the Fe spectrum). The discrepancy is effectively removed by the addition of a second Fe^{2+} doublet with a similar center shift but substantially larger quadrupole splitting. The hyperfine parameters of the second doublet are effectively constrained by a noticeable asymmetry on the inside edges of the main absorption peaks (see Fig. 1), which rules out the possibility of similar quadrupole splitting but different center shifts for the Fe^{2+} doublets. The addition of four extra degrees of freedom lowers the reduced χ^2 from 4.29 to 1.57 (significant at greater than 99.9%, according to a statistical F test). There is no statistical justification for the addition of further Fe^{2+} doublets. The excellent fit obtained to the shoulders of the main absorption peaks would argue in favor of two distinct Fe^{2+} doublets, as opposed to one broadened doublet with a different line shape. The hyperfine parameters resulting from the fit of the 80-K spectrum to three doublets plus one magnetic sextet are listed in Table 1. The line widths of all doublets do not change substantially with temperature, and all area ratios remain consistent between 298 and 80 K.

DISCUSSION

Fe^{2+} in (Mg,Fe)SiO_3 perovskite

The Mössbauer spectrum of (Fe,Mg)SiO_3 perovskite at 298 K demonstrates that Fe^{2+} is located almost exclusively on one site. The octahedral and eight- to 12-coordinated sites in the perovskite structure are quite different, and we can use the values of the Mössbauer hyperfine parameters to identify which site Fe^{2+} occupies.

The center shift can be considered a measure of the isomer shift (e.g., Bancroft, 1973), which is related to the site geometry, chemistry, and electronic configuration of the Fe atom. The isomer shift reflects the s electron density at the nucleus, which is in turn affected by the valence electron density. A reduction in Fe^{2+}-O bond length reduces the shielding of s electrons by valence electrons and therefore decreases the isomer shift. Increasing site distortion also decreases the isomer shift (Bancroft et al., 1968). Although it is difficult to calculate the isomer shift a priori for a given crystallographic site, empirical correlations allow reasonably unambiguous interpretation of isomer shift values (e.g., Bancroft et al., 1968; Burns and Solberg, 1990). The isomer shift of the perovskite Fe^{2+} doublet falls in the range expected for $^{[6]}Fe^{2+}$, but this range is based on minerals with mean Fe^{2+}-O distances all greater than 2.00 Å. The octahedral site in perovskite is substantially smaller than this (see Table 2) and would require a reduction in isomer shift, probably below 1 mm/s. X-ray diffraction data are not consistent with a substantial increase in octahedral site size as a function of increasing Fe content (Kudoh et al., 1990; Parise et al., 1990), and so we therefore rule out the possibility of $^{[6]}Fe^{2+}$ in perovskite. The length and variance of bond lengths in the highly distorted M2 site in ferrosilite are similar to those in the perovskite eight- to 12-coordinated site, and isomer shifts are similar (Table 2). Also, relatively small isomer shifts have been observed for the highly coordinated but probably distorted channel sites for Fe^{2+} in cordierite (Goldman et al., 1977) and osumilite (Goldman and Rossman, 1978). We conclude, therefore, that Fe^{2+} occupies the eight- to 12-coordinated site in perovskite.

The quadrupole splitting can be regarded as a sum of terms related to contributions from the valence electrons and the rest of the crystal lattice (Ingalls, 1964). When distortion from cubic symmetry is small, the valence term dominates, and increasing distortion produces greater quadrupole splitting, eventually reaching a maximum value. If site distortion is large, however, the lattice term (which is of opposite sign) contributes significantly to the

TABLE 2. Comparison of cation site size with Mössbauer isomer shift at 298 K

Site	Cation	Bond length (Å)	Bond length distortion*	Center shift**
		$(Fe,Mg)SiO_3$ perovskite		
6	Si^{4+}	1.78–1.81†	0.02†	—
8–12	Mg^{2+}, Fe^{2+}	1.99–3.11†	26.4†	1.12
		$FeSiO_3$ ferrosilite		
$^{[6]}$M1	Fe^{2+}	2.08–2.19‡	0.4‡	1.18§
$^{[6]}$M2	Fe^{2+}	1.99–2.60‡	10.2‡	1.13§

* Calculated using the relation $1/n\ \Sigma[(r_i - r)/r]^2 \times 10^3$ (Sasaki et al., 1983).

** Millimeters per second, relative to Fe.

† Parise et al. (1990); Kudoh et al. (1990).

‡ Sueno et al. (1976).

§ Dowty and Lindsley (1973).

quadrupole splitting, causing a decrease of quadrupole splitting from the maximum value with increasing site distortion. The low quadrupole splitting of Fe^{2+} in perovskite is therefore consistent with occupation of the eight- to 12-coordinated site.

The 80-K Mössbauer data were fitted to two Fe^{2+} doublets, although this is likely to be a nonunique solution. Possible interpretations include (1) next nearest neighbor interactions that produce temperature-dependent effects on the Mössbauer hyperfine parameters, (2) a phase transition, and (3) a change in positional order-disorder of Fe atoms with temperature. No conclusion can be made from the present data, but variable-temperature Mössbauer measurements are underway to obtain further information on this problem.

Fe^{3+} in $(Mg,Fe)SiO_3$ perovskite

The relative absorption area of the Mössbauer spectrum provides a measure of site proportion if several simplifying assumptions are made (Bancroft, 1969). In our spectra the relative area of Fe^{3+} is constrained by the difference in areas between the two main absorption doublets, giving Fe^{3+}/Fe_{tot} of approximately 0.05 for the perovskite phase. Since the sample was synthesized at the low f_{O_2} stability limit of perovskite, this represents the minimum Fe^{3+} content for perovskite with this Mg/Fe ratio. Iron perovskites synthesized at higher f_{O_2} conditions will contain larger amounts of Fe^{3+}. Since properties such as electrical conductivity are likely to be sensitive to Fe^{3+} concentration, it is important to quantify this concentration. We have shown in this study that Mössbauer spectroscopy is a suitable technique for this determination.

It is difficult to assign the location of Fe^{3+} in the perovskite structure using the Mössbauer data because of the overlap of absorption peaks. Although we successfully fitted one Fe^{3+} doublet to our data, the possibility that Fe^{3+} resides on more than one site cannot be ruled out. For example, the substitution $^{[6]}Fe^{3+} + {}^{[8-12]}Fe^{3+} + {}^{[8-12]}Mg^{2+} + {}^{[6]}Si^{4+}$ would lead to Fe^{3+} on both sites in perovskite, which is probably also consistent with our data. In addition, there is a possibility that defects associated with Fe^{3+} occur, either as Fe^{2+} vacancies or interstitial Fe^{3+}, or both.

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