Tetrahedral occupancy of ferric iron in (Mg,Fe)O: Implications for point defects in the Earth's lower mantle

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We investigated the concentration and site occupation of ferric iron (Fe3+) in (Mg,Fe)O to understand the influence of point defects on transport properties such as atomic diffusion, electrical conductivity and viscosity. We conducted Mössbauer spectroscopy of (Mg0.8Fe0.2)O single crystals synthesized at temperatures from 1673 to 2273 K and pressures from 5 to 15 GPa with Re–ReO2 and Mo–MoO2 oxygen fugacity buffers. The isomer shift of the Mössbauer spectra suggests that Fe3+ occupies mostly the tetrahedral site at reduced conditions and both the octahedral and tetrahedral sites at oxidized conditions. We formulate a thermodynamic model of point defect dissolution in (Mg,Fe)O which suggests that unassociated tetrahedral Fe3+ is more stable than unassociated octahedral Fe3+ at high-pressure and low oxygen fugacity due to the effect of configurational entropy. The pressure dependence of Fe3+ concentration indicates a change in the dominant site occupancy of Fe3+: (1) Fe3+ in the tetrahedral site, (2) Fe3+ in the octahedral site, and (3) defect clusters of Fe3+ and cation vacancy, in the order of increasing oxygen fugacity and decreasing pressure. This is in reasonable agreement with previously reported experiments on Fe3+ concentration, Mg–Fe interdiffusivity and electrical conductivity. We consider it plausible that (Mg,Fe)O accommodates Fe3+ in the tetrahedral site down to the lower mantle. Based on our results and available experimental data, we discuss the solubility competition between Fe3+ and protons (H+), and its implications for transport properties in the lower mantle.

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1. Introduction

The knowledge of transport properties such as atomic diffusion, viscosity and electrical conductivity in lower mantle phases is critical for understanding the dynamics of the lower mantle and interpreting geophysical observations such as electrical conductivity (e.g., Kelbert et al., 2009) or seismic wave attenuation (e.g., Lawrence and Wysession, 2006). The ferropericlase–magnesiowüstite solid solution (Mg,Fe)O, is considered to be the second most abundant phase in the lower mantle, comprising ~20% in the pyrolite model (e.g., Hirose, 2002). (Mg,Fe)O has noticeably higher atomic diffusivity (Holzapfel et al., 2003; Van Orman et al., 2009; Yamazaki and Irifune, 2003), lower viscosity (Poirier et al., 1986; Yamazaki and Karato, 2001), and higher electrical conductivity (Dobson et al., 1997; Ohta et al., 2003; Wood and Nell, 1991; Xu and McCammon, 2002) than magnesium silicate perovskite, the most abundant phase in the lower mantle. Therefore, these transport properties of the lower mantle are likely controlled largely by those of (Mg,Fe)O. Transport properties are highly sensitive to the presence of point defects. Consequently, it is important to characterize the concentration and site occupation of point defects under a wide range of experimental conditions in order to understand the mechanisms that control transport processes and to enable the projection of lower mantle properties through extrapolation of laboratory measurements.

Various investigations have been conducted on point defects in (Mg,Fe)O (e.g., Hirsch and Shankland, 1991). (Mg,Fe)O crystallizes in the B1 (rock salt) structure where the cations occupy a face-centered cubic sublattice. At atmospheric pressure, trivalent iron (ferric iron or Fe3+) is the most abundant positively charged point defect in (Mg,Fe)O, which is charge balanced by negatively charged cation vacancies (e.g., Hazen and Jeanloz, 1984). Based on neutron scattering, Mössbauer and X-ray emission spectroscopy, it has been recognized that Fe3+ occupies not only octahedrally coordinated cation sites but also tetrahedrally coordinated interstitial sites, which are normally vacant in the ideal structure (e.g., Hazen and Jeanloz, 1984; Hilbrandt and Martin, 1998; Jacobsen et al., 2002; Waychunas, 1983). Tetrahedral Fe3+ is observed in (Mg,Fe)O with sufficiently high ratio of Fe3+/(Fe2+ + Fe3+) at oxidized conditions near the phase boundary with magnesioferrite...
(MgFeO₂), which is likely different from the more reduced conditions inferred for the lower mantle (e.g., Frost and McCammon, 2008). Thus, previous studies on transport properties commonly assumed that Fe³⁺ resides only in the octahedral site of (Mg,Fe)O in the lower mantle (e.g., Yamazaki and Irifune, 2003). No detailed studies, however, have been conducted considering the site occupation of Fe³⁺ at reduced conditions and high pressures.

The Fe³⁺/ΣFe ratio at ambient pressure varies with temperature, oxygen fugacity, and Mg/Fe ratio (e.g., Hilbrandt and Martin, 1998; Katsura and Kimura, 1965; Speidel, 1967). The influence of pressure was explored by McCammon et al. (1998), who concluded that Fe³⁺ solubility in (Mg,Fe)O decreases with pressure based on Mössbauer spectroscopy analysis of their multi-anvil and diamond anvil cell experiments. Follow-up experiments using Mössbauer spectroscopy or electron energy-loss near-edge structure (ELNES) spectroscopy reported Fe³⁺/ΣFe ratios of 1–19% in (Mg,Fe)O with Mg numbers (Mg# = Mg/[Mg + Fe] × 100 in an atomic ratio) of 80–93 at 1473–2123 K and 25–26 GPa under oxidized conditions imposed by Re-ReO₂ (Bolfan-Casanova et al., 2002; Frost and Langenhorst, 2002; McCammon et al., 2004). Bolfan-Casanova et al. (2002) also suggested that the dominant positively charged defects may change from Fe³⁺ to protons (H⁺) at high-pressure since H⁺ solubility increases with pressure under water-saturated conditions. The behavior of transport properties may thus change with pressure from mechanisms sensitive to Fe³⁺ content (or oxygen fugacity) to those sensitive to H⁺ content (or water fugacity). Therefore, it is important to explore conditions of the solubility crossover between Fe³⁺ and H⁺ as a guide to understand the nature of such a threshold of material behavior. The previous high-pressure experiments were, however, conducted under a limited range conditions, mostly at high oxygen fugacity or a single temperature. It is not yet clear whether or not such a solubility crossover occurs in the lower mantle.

In this study, therefore, we investigate the equilibrium concentration and site occupation of Fe³⁺ in (Mg,Fe)O based on Mössbauer spectroscopy analysis. We extend experiments to a wider range of temperature and oxygen fugacity relevant to the lower mantle and present a thermodynamic model to examine the influence of thermochemical states based on our new experimental results combined with those of early studies. Finally we discuss implications of these results for transport properties in the lower mantle.

2. Experimental methods

2.1. Starting material

The starting materials for the high-pressure experiments were synthetic (Mg,Fe)O single crystals. The (Mg,Fe)O crystals were prepared by interdiffusion between a MgO single crystal with a thickness of 0.5 mm and reagent grade oxides of periclase (MgO) and hematite (Fe₂O₃) powder in the appropriate ratio for Mg#80. The nominal impurity content of the MgO single crystal was 40 ppm Ca, 15 ppm Al, 50 ppm Fe, 10 ppm Cr, 5 ppm B, and 10 ppm C according to the supplier (SPI supply). The MgO single crystal plate embedded in oxides was annealed in a vertical tube furnace operated at 1873 K for 200 h in total under an oxygen fugacity of 1 Pa (1.5 log–bar units below the phase boundary between magnetite and wüstite). Each of the Re and Mo capsules was loaded into an AuPd or Pt outer tube capsule of 0.2 mm wall thickness. The outer tube capsule was welded to minimize the water input from the surrounding environment. Thus, two different oxygen fugacity environments were imposed on two different samples in a single high-pressure experiment.

2.2. Generation of high-pressure and high-temperature

High-pressure annealing experiments were performed with a 1000-ton Kawai-type multi-anvil apparatus installed at Yale University with the conventional 18–11 or 14–8 assembly. The confining pressure was exerted on the cell assembly by eight tungsten carbide cubes with an edge length of 26 mm and a corner truncation of either 11 or 8 mm. The pressure media consist of a semi-sintered Cr₂O₃-doped MgO octahedron with an edge length of 18 or 14 mm, a graphite or LaCrO₃ stepped cylindrical furnace, and a ZrO₂ sleeve enveloping the furnace as a thermal insulation. Temperature was monitored with a W₅Re–W₁₆Re thermocouple with a thermocouple junction placed in direct contact with one end of the sample capsule. The sample charge was electrically insulated from the furnace by an MgO sleeve. The uncertainty of temperature and pressure was estimated as ±80 K and ±0.5 GPa, respectively, based on previous experiments (Nishihara et al., 2006).

The oxygen fugacity in the samples was controlled by two different metal-oxide buffers: Re-ReO₂ for an oxidized condition and Mo–MoO₂ for a reduced condition as schematically shown in Fig. 1. The synthetic Mg₀.₈Fe₀.₂O single crystals with an approximate edge length of 0.8 mm with thickness of 0.5 mm were placed in the inner Re and Mo capsules, where corresponding oxides (either Re₂O₃ or MoO₂ powder, respectively) were added together with Mg₀.₈Fe₀.₂O powder. The Mg₀.₈Fe₀.₂O powder was prepared from a mixture of MgO and Fe₂O₃ which was annealed for 14 h at 1473 K at an oxygen fugacity of 10⁻⁵ Pa (1 log–bar unit below the phase boundary between magnetite and wüstite). Each of the Re and Mo capsules was loaded into an AuPd or Pt outer tube capsule of 0.2 mm wall thickness. The outer tube capsule was welded to minimize the water input from the surrounding environment. Thus, two different oxygen fugacity environments were imposed on two different samples in a single high-pressure experiment.

2.3. Mössbauer spectroscopy

Mössbauer spectra of ⁵⁷Fe in Mg₀.₈Fe₀.₂O were recorded at room temperature and pressure in transmission geometry at Bayerisches
Table 1
Conditions of high-pressure annealing experiments and results.

<table>
<thead>
<tr>
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<td></td>
<td></td>
<td>Oxide</td>
<td>Mg#</td>
</tr>
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<td>K731</td>
<td>5</td>
<td>1673</td>
<td>120</td>
<td>AuPd</td>
<td>Solid</td>
<td>0.810 (7)</td>
</tr>
<tr>
<td>K733</td>
<td>5</td>
<td>1873</td>
<td>60</td>
<td>AuPd</td>
<td>Solid/melt</td>
<td>0.829 (6)</td>
</tr>
<tr>
<td>K735</td>
<td>5</td>
<td>2073</td>
<td>30</td>
<td>Pt</td>
<td>Melt</td>
<td>0.828 (5)</td>
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<tr>
<td>K742</td>
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<td>2273</td>
<td>10</td>
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<td>Melt</td>
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<td>1673</td>
<td>180</td>
<td>AuPd</td>
<td>Solid</td>
<td>0.826 (7)</td>
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<tr>
<td>K740</td>
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<td>1873</td>
<td>60</td>
<td>AuPd</td>
<td>Solid/melt</td>
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<td>10</td>
<td>Pt</td>
<td>Melt</td>
<td>0.830 (6)</td>
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</table>

() Standard deviation of the last digit.

n.i. Not identified.

Fig. 2. Backscattered electron images of run products: (Mg,Fe)O single crystals annealed at 15 GPa, 1873 K with Re and solid ReO2 (K740, A, B) and 15 GPa, 2173 K with Re and molten ReO2 (K749, C, D). (B) and (C) are expansion of the rectangular areas in (A) and (C), respectively.

Geoinstitut. Synthetic Mg0.8Fe0.2O single crystals were mounted in epoxy resin and polished down to a thickness of approximately 80 μm to optimize the absorber thickness, following Rancourt et al. (1993). A 57Co radioactive source in a Rh matrix was used as a source of single-line γ-rays. The energy of the γ-rays were Doppler shifted with velocities ranging from +5 to −5 mm/s by moving the source relative to the sample in constant acceleration mode. The velocity scale of the spectrometer was calibrated relative to α-Fe foil. Ta foil with a 500 μm hole covered the sample to select the area to be measured. The γ-rays transmitted through the sample were measured using a detector coupled to a 512-channel multichannel analyser and the signal was folded to give a flat background.

3. Experimental results

3.1. High-pressure run products

The high-pressure annealing experiments of Mg0.8Fe0.2O were conducted at 5 and 15 GPa at 1673–2273 K for 10–180 min (Table 1). Chemical equilibria in terms of Fe3+ concentration should be achieved during the run durations if we assume that vacancy diffusion is the rate limiting process for Fe3+ diffusion. The vacancy mobility of (Mg,Fe)O can be approximately estimated as...
$6 \times 10^{-13} \text{ m}^2/\text{s}$ at temperature of 1400 K and atmospheric pressure based on the Mg–Fe interdiffusion coefficient measured by Mackwell et al. (2005) and the Fe$^{3+}$ concentration measured by O’Neill et al. (2003). Activation energy of vacancy mobility was estimated as 220 kJ/mol (Sempolinski and Kingery, 1980). The activation volume of vacancy mobility is not well quantified, but is likely in the range from 1 to $2 \times 10^{-6} \text{ m}^3/\text{mol}$. (see more detailed discussion on the vacancy mobility and concentration in Section

Fig. 4. Mössbauer spectra of (Mg$_{0.8}$Fe$_{0.2}$)O annealed at 1673–2273 K, 5 and 15 GPa with Mo–MoO$_2$ and Re–ReO$_2$. Experimental data is shown by dots, theoretical spectra by solid lines and the residual (experimental minus theoretical) is shown on the top. The absorption corresponding to Fe$^{3+}$ is shaded black.
Fig. 4. (Continued).

Thus, the diffusion length scale of vacancy mobility during the experiments is more than the half of the thickness of the sample size (0.25 mm).

Synthetic Mg$_{0.8}$Fe$_{0.2}$O single crystals recovered from annealing experiments were examined by scanning electron microscope. The presence of the oxygen fugacity buffer, either Re–ReO$_2$ or Mo–MoO$_2$, was confirmed for each sample (except ReO$_2$ of K735), indicating that oxygen fugacity was controlled by the metal and oxide buffers. The buffering oxide phases were round shaped crystals at temperatures below 1873 K, while they were quenched melt with dendritic textures at temperatures above 1873 K for MoO$_2$ and 2073 K for ReO$_2$ (Table 1, Fig. 2). The solid buffering oxides do not interconnect with each other, while molten buffering oxides wet the grain boundaries of (Mg,Fe)O (Fig. 2). Chemical compositions of single crystals were within an Mg$#$ range from 80 to 84 (Table 1). During high-temperature experiments, the Mg$#$ increased slightly towards the rim of the crystal due to the Fe loss into the melt (Fig. 3). The Mössbauer spectra were collected around the center of Mg$_{0.8}$Fe$_{0.2}$O single crystals.

3.2. Mössbauer spectra

Each Mössbauer spectrum shows a dominant quadrupole doublet superimposed with a minor peak on the low-velocity shoulder of the major peak (Fig. 4). They are similar to the spectra reported in previous studies, where the major absorption peak corresponds to Fe$^{2+}$ and the minor peak to Fe$^{3+}$ (e.g., McCammon et al., 1998). No magnetic phases such as magnesioferrite were observed in any of the Mössbauer spectra. The hyperfine parameters were determined by fitting Mössbauer spectra using the commercially available computer software NORMOS. We found that the most stable fitting was obtained using one Voigt doublet (Rancourt and Ping, 1991) for the major peak and one Lorentzian singlet for the minor peak (Table 2). The distinct quadrupole splitting peaks observed for Fe$^{2+}$ absorption are well fitted by the Voigt doublet, which describes the total lineshape in terms of a Gaussian distribution sum of individual peaks with Lorentz lineshape. For the minor peak where two separate peaks could not be resolved only a Lorentzian singlet was used. More complicated fitting models such as a Voigt doublet were
Table 2

Hyperfine parameters derived from Mössbauer spectra.

<table>
<thead>
<tr>
<th>Run name</th>
<th>Temperature</th>
<th>Fe(^{2+})</th>
<th>Fe(^{3+})</th>
<th>Chi(^2)</th>
<th>Fe(^{3+})/(\sum)Fe</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>[K]</td>
<td>WID [mm/s]</td>
<td>ISO [mm/s]</td>
<td>QUA [mm/s]</td>
<td>STQ [mm/s]</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo–Mo(_2)O at 5 GPa(^a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K731-BY4820B</td>
<td>1673</td>
<td>0.32 (2)</td>
<td>0.926 (3)</td>
<td>0.605 (3)</td>
<td>0.096 (9)</td>
</tr>
<tr>
<td>K733-BY4817B</td>
<td>1873</td>
<td>0.32 (1)</td>
<td>0.926 (1)</td>
<td>0.621 (2)</td>
<td>0.110 (5)</td>
</tr>
<tr>
<td>K735-BY4847B</td>
<td>2073</td>
<td>0.35 (2)</td>
<td>0.929 (1)</td>
<td>0.629 (2)</td>
<td>0.112 (5)</td>
</tr>
<tr>
<td>K742-BY4836B</td>
<td>2273</td>
<td>0.38 (1)</td>
<td>0.928 (2)</td>
<td>0.631 (2)</td>
<td>0.127 (6)</td>
</tr>
<tr>
<td>Re–ReO(_2) at 5 GPa(^b)</td>
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<td>K731-BY4821B</td>
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<td>0.44 (1)</td>
<td>0.930 (2)</td>
<td>0.590 (2)</td>
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<td>Mo–Mo(_2)O at 15 GPa(^a)</td>
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<td>0.31 (1)</td>
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<td>0.656 (4)</td>
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<td>0.654 (2)</td>
<td>0.148 (4)</td>
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<td>Re–ReO(_2) at 15 GPa(^b)</td>
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<tr>
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<td>0.930 (2)</td>
<td>0.591 (2)</td>
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WID: full Lorenzian line width at half maximum, ISO: isomer shift, QSD: quadrupole splitting, STQ: Gaussian standard deviation for quadrupole splitting distribution.

\(^a\) Linewidth of Fe\(^{3+}\) is constrained to be the same as the value for Fe\(^{2+}\).

\(^b\) Linewidth of Fe\(^{3+}\) is not constrained to be the same as the value for Fe\(^{2+}\).

attempted for the minor peak, but the residual after fitting was not significantly improved based on the chi-squared fitting test. The Lorentzian linewidths were fitted as variable parameters. The Fe\(^{3+}\) linewidth was assumed to have the same value as the one for Fe\(^{2+}\) in the case of low Fe\(^{3+}\) concentration. The Fe\(^{3+}\)/\(\sum\)Fe ratio was calculated based on the relative absorption areas for Fe\(^{2+}\) and Fe\(^{3+}\).

We estimated the uncertainty based on the statistics of the fitting process and the uncertainty of the fitting model itself. We particularly focus on the isomer shift within the set of determined hyperfine parameters since it is sensitive to valence state and the crystallographic position of iron (e.g., McCammon, 2004). The isomer shift relative to \(\alpha\)-Fe determined for the Fe\(^{2+}\) doublet varies no more than 0.01 mm/s over all spectra and agrees well with the typical value of 0.933 mm/s for Fe\(^{2+}\) in the octahedral site (Waychunas, 1983). In contrast, the isomer shift of the Fe\(^{3+}\) singlet varies systematically with the experimental conditions (Fig. 5). The isomer shift and concentration of Fe\(^{3+}\) absorption are constrained by the asymmetry of the main doublet of Fe\(^{2+}\), and are therefore relatively independent of the fitting model. The Fe\(^{3+}\) isomer shifts are about 0.05 mm/s under reduced conditions buffered by Mo–Mo\(_2\)O except K731-BY4820B (5 GPa and 1673 K), whereas they are higher under oxidized conditions buffered by Re–ReO\(_2\): around 0.13 mm/s at 5 GPa and 0.1–0.07 mm/s at 15 GPa. The pressure dependence of the isomer shift under oxidized conditions has not been discussed previously, but can be observed in Fig. 2 of McCammon et al. (1998). The observed values of the isomer shift indicate a variation of Fe\(^{3+}\) site occupancy since it decreases with atomic distance to the first nearest neighbor: 0.24 mm/s for octahedral occupancy and 0.07 mm/s for tetrahedral occupancy (Waychunas, 1983). Thus,
the low values of the isomer shift obtained under reduced conditions suggest tetrahedral occupancy of Fe$^{3+}$, while the high values under oxidized conditions suggest both tetrahedral and octahedral occupancies. The high isomer shift coincides with a broader linewidth up to around 1 mm/s. There are two possible explanations for the apparent broadening of the linewidth: large variability in the nuclear energy levels of Fe$^{3+}$ due to the multiple site occupancies of Fe$^{3+}$, or large variations in quadrupole splitting.

Fig. 6 shows the relation between the Fe$^{3+}$/∑Fe ratio and the experimental conditions. Fe$^{3+}$/∑Fe increases with oxygen fugacity, and it decreases with pressure at low temperatures when the buffering oxide, either MoO$_2$ or ReO$_2$, is solid, while it remains almost constant at high temperatures when buffering oxide is quenched melt. Fe$^{3+}$/∑Fe at 5 GPa and 2073 K with the Re–ReO$_2$ buffer is lower than the trend extrapolated from low temperatures, which indicates the melting of the ReO$_2$ phase or a deficit of the buffering oxide, either MoO$_2$ or ReO$_2$, is solid, while it remains as a solid at low temperatures.

For Fe$^{3+}$ formation in the tetrahedral site. In the following discussion, we assume that (1) minor species (Fe$^{3+}$, Fe$^{2+}$, V$^{4+}$) are completely disordered in the structure and their activities are proportional to their composition (Henry’s Law), and (2) concentrations of major species (Fe$^{3+}$, Fe$^{2+}$, O$_2^-$) do not change significantly. The law of mass action corresponding to reactions (5) and (6) gives

$$[\text{Fe}^{3+}]_t^2/[\text{Fe}^{2+}]_t = \exp \left[ \frac{-E_{\text{F}1} + PV_{\text{F}1}}{RT} \right] \tag{7}$$

$$[\text{V}^{4+}]_O^2/[\text{Fe}^{2+}]_t = \exp \left[ \frac{-E_{\text{F}2} + PV_{\text{F}2}}{RT} \right] \tag{8}$$

respectively, where $P$ is pressure, $T$ is temperature, $R$ is the gas constant, $E_{\text{F}1}$ and $E_{\text{F}2}$ are the activation energies of reactions (i.e., enthalpy of the reaction at ambient pressure) (5) and (6), and $V_{\text{F}1}$ and $V_{\text{F}2}$ are the volume change for the solid parts of the reactions (5) and (6). Henry’s Law implies that the various point defects do not interact with each other, which is valid for solid solutions with sufficiently small defect concentrations. Substitution of the conservation equations for charge neutrality (Eq. (4)) into the mass action equations (Eqs. (7) and (8)) gives the equilibrium concentration of Fe$^{3+}$:

$$[\text{Fe}^{3+}]_t \propto f_{\text{O}2}^{1/6} \exp \left[ \frac{-E_{\text{F}1} + PV_{\text{F}1}}{3RT} \right] \tag{9}$$

for the octahedral Fe$^{3+}$ dominant regime, and

$$[\text{Fe}^{3+}]_t \propto f_{\text{O}2}^{1/10} \exp \left[ \frac{-E_{\text{F}2} + PV_{\text{F}2}}{5RT} \right] \tag{10}$$

for the tetrahedral Fe$^{3+}$ dominant regime. In either case, the concentration of vacancies is proportional to that of Fe$^{3+}$.

The Mössbauer spectra show that the Fe$^{3+}$ concentration and site occupation are influenced by temperature, pressure, and oxygen fugacity. Here, we present a simple thermodynamic model of Fe$^{3+}$ dissolution in (Mg,Fe)O to interpret the experimental data, especially at low defect concentration. We start by formulating the stoichiometric relations of point defects in (Mg,Fe)O. A general structural formula for (Mg,Fe)O solid solution can be described as

$$V^{VI}[\text{Mg}^{2+}, \text{Fe}^{3+}, \text{Fe}^{2+}][V, \text{Fe}^{3+}][V, \text{Fe}^{2+}][O] \tag{1}$$

where the superscripts $VI$ and $IV$ denote the octahedral and tetrahedral cation sites, respectively, and $V$ indicates a vacancy. Since we ignore other minor point defects such as O vacancies, Mg$^{2+}$ and Fe$^{2+}$ in the tetrahedral site, and trivalent cations such as Al$^{3+}$ and Cr$^{3+}$. The conservation of stoichiometry of the lattice sites gives the following two equations where we use the Kröger–Vink notation:

$$[\text{Mg}^{2+}]_t + [\text{Fe}^{3+}]_t + 1/2[\text{Fe}^{2+}]_t = 1 \tag{2}$$

for the octahedral site, and

$$[V^{VI}]_t + [\text{Fe}^{2+}]_t = 1 \tag{3}$$

for the tetrahedral site, where the brackets denote the concentration in atomic fraction. The electrical neutrality condition is expressed as:

$$[\text{Fe}^{3+}]_t + 6[\text{Fe}^{2+}]_t = 2[\text{V}^{IV}]_t \tag{4}$$

Note that the tetrahedral site has a multiplicity of two per formula unit. This may be simplified if one of the positive defects is dominant: $[\text{Fe}^{3+}]_t = 2[\text{V}^{IV}]_t$ for the regime where octahedral Fe$^{3+}$ dominates or $3[\text{Fe}^{2+}]_t = [\text{V}^{IV}]_t$ for the regime where tetrahedral Fe$^{3+}$ dominates.

We now consider a chemical system consisting of (Mg,Fe)O and O$_2$ to describe the (Mg,Fe)O phase subjected to a change in the Fe$^{3+}$/∑Fe ratio through the interchange of an O atom with an external O$_2$ phase. The equilibrium between two phases is described by the following two relations:

$$2\text{Fe}^{2+} + 2\text{V}^{IV} + 1/2\text{O}_2 = 2\text{Fe}^{3+} + 2\text{Fe}^{3+} + 2\text{V}^{IV} + 1/2\text{O}_2 \tag{5}$$

for the formation of Fe$^{3+}$ in the octahedral site and

$$2\text{Fe}^{3+} + 1/2\text{O}_2 = 3\text{V}^{IV} + 2\text{Fe}^{2+} + 1/2\text{O}_2 \tag{6}$$

are estimated from the molar volume of (Mg,Fe)O, assuming that the presence of point defects does not change the size of the lattice site.

4.2. Pressure and temperature dependence of Fe$^{3+}$ concentration

Fig. 7 plots the Fe$^{3+}$ solubility in (Mg$_{0.8}$Fe$_{0.2}$)O obtained in this study as well as from previous studies (Bolfan-Casanova et al., 2002, 2006; Frost and Langenhorst, 2002; McCammon et al., 1998, 2004; McCammon, 1994) for oxygen fugacity buffered by metal and solid oxide buffers (A) and by metal and molten oxide buffers (B). In order to compare results from various studies with different compositions, Mg# is normalized to 80 assuming a homologous temperature scaling for the activation energy of Fe$^{3+}$ formation. The pressure dependence of Fe$^{3+}$ concentration under a solid buffer (Fig. 7A) suggests the presence of three different regimes depending on pressure and oxygen fugacity buffer: (1) low oxygen fugacity (Mo and solid MoO$_2$), (2) low pressure (<15 GPa) and high oxygen fugacity (Re and solid ReO$_2$), and (3) high-pressure (>15 GPa) and high oxygen fugacity (Re and solid ReO$_2$). We fitted each regime separately using Eq. (11) to provide a first order approximation of the dependence of Fe$^{3+}$ concentration on thermodynamic parameters (Table 4). In the first regime, fitting of our experimental results at reduced conditions (Mo and solid MoO$_2$) gives $V^*_C$ of 1.2(8) $\times 10^{-6} m^3/mol$, which agrees well with the model prediction for tetrahedral Fe$^{3+}$ under the Mo–MoO$_2$ buffer ($V^*_C = 1.23 \times 10^{-6} m^3/mol$, from Eq. (14)). The extrapolation of the fitting result to room pressure and 1473 K yields slightly lower Fe$^{3+}$ concentrations than those found by McCammon (1994). In the second regime, fitting of our experimental results at oxidized conditions (Re and solid ReO$_2$) gives a slightly smaller value of $V^*_C$ (0.73 $\times 10^{-6} m^3/mol$). Extrapolation of this result to higher pressure and low temperature yields higher Fe$^{3+}$ concentrations than the values determined by McCammon et al. (1998) and inferred from Bolfan-Casanova et al. (2002, 2006), indicating that the pressure dependence of Fe$^{3+}$ concentration increases with pressure.

In the third regime, experimental data at high-pressure and oxidized conditions (Bolfan-Casanova et al., 2002, 2006; Frost and Langenhorst, 2002; McCammon et al., 1998, 2004) are insufficient to allow a confident regression of the activation volume. Thus, we assume $V^*_C$ to be 2.16 $\times 10^{-6} m^3/mol$, which is derived from the thermodynamic model for octahedral Fe$^{3+}$ under the Re–ReO$_2$ buffer (Eq. (13)). These observations on the change of the pressure dependence of Fe$^{3+}$ concentration agree qualitatively with the results of previous experiments performed at 1473 K and 5–25 GPa with Mg# 87 and 93 (Bolfan-Casanova et al., 2002, 2006). As shown in Fig. 7(B), in the cases where the buffering oxide is molten, $V^*_C$ is smaller than for the case of solid buffering material. This is attributable to the increase of molar volume of MoO$_2$ or ReO$_2$ during melting that affects the pressure dependence of oxygen fugacity for a given buffer.

Table 3
Summary of activation volumes.

<table>
<thead>
<tr>
<th>Oxygen fugacity buffer</th>
<th>$A_C$</th>
<th>$E^*_C$ [kJ/mol]</th>
<th>$V^*_C$ [$10^{-6} m^3/mol$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo–MoO$_2$ (solid)</td>
<td>0.021(1)</td>
<td>19 (7)</td>
<td>1.2 (8)</td>
</tr>
<tr>
<td>Re–ReO$_2$ (solid)</td>
<td>0.077(8)</td>
<td>6 (2)</td>
<td>0.7 (3)</td>
</tr>
<tr>
<td>Mo–MoO$_2$ (melt)</td>
<td>0.6(1)</td>
<td>85 (3)</td>
<td>0.1 (5)</td>
</tr>
<tr>
<td>Re–ReO$_2$ (melt)</td>
<td>0.007 (1)</td>
<td>–26 (4)</td>
<td>0.1 (7)</td>
</tr>
<tr>
<td>Previous studiesa</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re–ReO$_2$ (solid)</td>
<td>0.061(2)</td>
<td>–16.1 (6)</td>
<td>2.16b</td>
</tr>
</tbody>
</table>

b Estimated from the model prediction for Fe$^{3+}$ in the octahedral site under the Re–ReO$_2$ buffer.

Fig. 7. Fe$^{3+}$ concentration in (Mg$_{0.8}$Fe$_{0.2}$)O as a function of annealing pressure. Color indicates the oxygen fugacity buffer. Mo–MoO$_2$ in red and Re–ReO$_2$ in blue. Solid lines are fitting results for solid buffering oxide (A) and for molten buffering oxide (B). Data are from this study, BC62; Bolfan-Casanova et al. (2006, 2002); MC04: McCammon et al. (2004); FL02: Frost and Langenhorst (2002); MC98: McCammon et al. (1998); MC94: McCammon (1994).
We infer that the observed three regimes of the pressure dependence of \( \text{Fe}^{3+} \) concentration indicates a change of the dominant site occupation of \( \text{Fe}^{3+} \): (1) unassociated \( \text{Fe}^{3+} \) in the tetrahedral site, (2) unassociated \( \text{Fe}^{3+} \) in the octahedral, and (3) defect clusters of \( \text{Fe}^{3+} \) and cation vacancies, in the order of increasing oxygen fugacity and decreasing pressure. This inference is consistent with the observed isomer shift trend showing tetrahedral \( \text{Fe}^{3+} \) under reduced conditions and both tetrahedral and octahedral \( \text{Fe}^{3+} \) under oxidized conditions. The observed tetrahedral \( \text{Fe}^{3+} \) under reduced conditions can be interpreted as unassociated defects based on the pressure dependence of \( \text{Fe}^{3+} \) concentration. The proposed thermodynamic model supports the change from tetrahedral \( \text{Fe}^{3+} \) to octahedral \( \text{Fe}^{3+} \) with increasing oxygen fugacity or decreasing pressures. The mixed occupancy of \( \text{Fe}^{3+} \) observed in Mössbauer spectra under oxidized conditions suggests the presence of tightly bound defect clusters of \( \text{Fe}^{3+} \) both at octahedral and tetrahedral sites and cation vacancies (e.g., Gourdin and Kinsgery, 1979; Hazen and Jeanloz, 1984; Hilbrandt and Martin, 1998; Jacobsen et al., 2002), which is consistent with the fact that point defects interact with each other at high \( \text{Fe}^{3+} \) concentrations.

The change of the dominant site occupancy of \( \text{Fe}^{3+} \) with pressure is in reasonable agreement with the complicated dependence of \( \text{Fe}^{3+} \) concentration on oxygen fugacity observed by Speidel (1967). They performed a thermogravimetric study over a broad range of oxygen fugacity from the stability field of metallic Fe to magnetite. We re-analyzed their data in high Mg# (89 and 75) and found that the oxygen fugacity dependence of \( \text{Fe}^{3+} \) concentration systematically changes with oxygen fugacity: a weak dependence of oxygen fugacity at reduced conditions (fugacity exponent \( n \approx 1/10 \)), a gradual increase in oxygen fugacity dependence at intermediate conditions \( n = 1/4 \), and a weak dependence at oxidized conditions \( n < 1/10 \). The change of fugacity exponent at low to intermediate fugacity agrees well with model predictions for the unassociated point defects: the fugacity exponent increases with oxygen fugacity from \( n = 1/10 \) for tetrahedral \( \text{Fe}^{3+} \) (Eq. (10)) to \( n = 1/6 \) for octahedral \( \text{Fe}^{3+} \) (Eq. (9)).

Independent evidence for the change of \( \text{Fe}^{3+} \) site occupation comes from measurements of transport properties: electrical conductivity and Mg–Fe interdiffusivity. Firstly, electrical charge transfer in \( \text{Mg}^{2+}\text{Fe}^{3+}O \) at low temperature (<1000 K) occurs by electron hopping between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) and by ionic diffusion at high temperature (>1000 K) (Dobson et al., 1997). Thus, a linear correlation between electrical conductivity and \( \text{Fe}^{3+} \) content is expected in the case of \( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \). Measurements of electrical conductivity of \( \text{Mg}^{2+}\text{Fe}^{3+}O \) with a Mg# range from 99 to 80 at 1073–1273 K show that the power dependence of conductivity with oxygen fugacity ranges from 1/10 to 1/3 depending on Mg# and temperature (Iyengar and Alcock, 1970). Based on the thermodynamic consideration, a weak dependence \( n = 1/8–1/10 \) observed at low Fe content (Mg# < 95) indicates the presence of \( \text{Fe}^{2+} \) in the tetrahedral site, whereas a strong dependence \( n = 1/6–1/4 \) at high Fe content (Mg# > 95) indicates \( \text{Fe}^{3+} \) in the octahedral site or a composite of simple defect associates such as \( \text{Fe}^{3+} \)-vacancy dimer or trimer (e.g., Gourdin and Kinsgery, 1979). Secondly, Mg–Fe interdiffusion in \( \text{Mg}^{2+}\text{Fe}^{3+}O \) can be interpreted in terms of vacancy mechanisms (e.g., Mackwell et al., 2005), where the pressure dependence of Mg–Fe interdiffusion \( (V_D) \) includes the pressure dependence of vacancy concentration \( (V_C) \) as well as vacancy mobility \( (V_m) \). \( V_D \) was determined by two recent studies as \( 1.8(10) \times 10^{-6} \text{m}^2/\text{mol} \) under the \( \text{Re}–\text{ReO}_2 \) buffer at 1573–1973 K and 7–35 GPa (Yamazaki and Irifune, 2003), and \( 3.3(1) \times 10^{-6} \text{m}^2/\text{mol} \) under the Ni–NiO buffer at 1673–1873 K and 8–23 GPa (Holzapfel et al., 2003). Based on our observations of pressure dependence of \( \text{Fe}^{3+} \) concentration, this discrepancy is likely due to the oxygen fugacity dependence of \( V_C \): low \( V_C \) at high oxygen fugacity (\( \text{Re}–\text{ReO}_2 \)) to complex defect clusters and high \( V_C \) at intermediate oxygen fugacity (Ni–NiO) due to \( \text{Fe}^{3+} \) in the octahedral site.

### 4.3. Implications for the lower mantle

On the basis of experimental results and the thermodynamic considerations described above, we conclude that tetrahedral \( \text{Fe}^{3+} \) is stabilized relative to octahedral \( \text{Fe}^{3+} \) at high-pressure and low oxygen fugacity due to the influence of the configurational entropy. The oxygen fugacity in the lower mantle is estimated as \( 1.4 \log_{10} \) bar units below \( \text{Fe}–\text{Fe}^{3+}_3 \) (Frost and McCammon, 2008) due to the presence of metallic Fe (Frost et al., 2004), which is even lower than the experimental conditions. We thus consider it plausible that \( (\text{Mg}_2\text{Fe})O \) accommodates \( \text{Fe}^{3+} \) in the tetrahedral site down to the lower mantle. Fig. 8 illustrates our estimates of \( \text{Fe}^{3+} \) concentration under the oxygen fugacity of the lower mantle compared with the \( \text{H}^+ \) solubility determined under water-saturated conditions by Bolfan-Casanova et al. (2002); Murakami et al. (2002). We calculated the \( \text{Fe}^{3+} \) concentration in the lower mantle by extrapolating our results under reduced conditions assuming a Mg# of 80 and the fugacity exponent of 1/10 (Eq. (10)). \( \text{Fe}^{3+} \) concentration was estimated as \( 650 \text{ppm} \) \( (\text{Fe}^{3+})/\text{O}) \) at 1873 K and 25 GPa at the top of the lower mantle. As shown in Fig. 8, two recent studies yield markedly different results on \( \text{H}^+ \) (or \( \text{H}_2\text{O} \)) solubility in \( (\text{Mg},\text{Fe})O \) (see Hirschmann, 2006 for a review). Bolfan-Casanova et al. (2002) obtained the solubility of \( \text{H}^+ \) in \( (\text{Mg}_{0.93}\text{Fe}_{0.07})O \) as \( \sim 100 \text{ppm} \text{H}/\text{O} \) at 1473 K and 25 GPa, while Murakami et al. (2002) determined the \( \text{H}^+ \) solubility in \( (\text{Mg}_{0.92}\text{Fe}_{0.08})O \) as \( \sim 10,000 \text{ppm} \text{H}/\text{O} \) at 1923 K and 25.5 GPa. Thus, the exact conditions of the solubility crossover between \( \text{Fe}^{3+} \) and \( \text{H}^+ \) are poorly constrained due to the large discrepancy in \( \text{H}^+ \) solubility. The spin crossover transition of Fe at high-pressure (starting around 40 GPa, Tsuchiya et al., 2006; Lin et al., 2007) potentially changes the behavior of point defects by decreasing the effective ionic radius of iron.

Recently, Demouchy et al. (2007) obtained a factor of four enhancement of Mg–Fe interdiffusivity in \( (\text{Mg},\text{Fe})O \) under water-saturated conditions at 300 MPa and 1273–1423 K, as compared with experiments under anhydrous conditions by Mackwell et al. (2005). They attributed the enhanced diffusivity to the increased defect concentration by the dissolution of water. However, over the most of the Mg# range that they studied, cation vacancies charge balanced by \( \text{Fe}^{3+} \) are significantly more abundant than those charge balanced by \( \text{H}^+ \). It is thus not yet clear how \( \text{H}^+ \) enhances...
interdiffusion under the Fe$^{3+}$-dominant regime. More importantly, extrapolation of their results to lower mantle conditions may substantially underestimate the influence of water in the lower mantle where H$^+$ concentration may dominate over Fe$^{3+}$ solubility. Further high-pressure studies are needed to determine the relative contributions of oxygen fugacity (Fe$^{3+}$ content) and water fugacity (H$^+$ content) on transport properties in the lower mantle.

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References


