LETTER

Oxygen fugacity and valence state of chromium in ferropericlase: Can Cr$^{2+}$ be a redox indicator for the deep mantle?

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The valence state of chromium in ferropericlase inclusions within diamonds was expected to serve as a redox indicator applicable to the deep earth environment with an extremely reduced condition. In this study, Cr K-edge X-ray absorption near-edge structure (XANES) spectra and $^{57}$Fe Mössbauer spectra were obtained for ferropericlase samples synthesized under controlled oxygen fugacity conditions of $-7$, $-9$, and $-11$ in log $f_{O_2}$. All the ferropericlase samples were shown to have almost identical Fe$^{3+}$/Fe$^{2+}$ ratios; this observation is consistent with a phase diagram of ferropericlase reported previously. All the ferropericlase samples contained Cr$^{2+}$, and the Cr$^{2+}$/ΣCr ratio was almost constant among the samples, within the experimental precision of XANES spectroscopic measurements. Divalent chromium ions are stabilized in ferropericlase by the crystallographic constraint, even under an oxidized condition. The present study proposes that there is room for reconsidering the presence of Cr$^{2+}$ in ferropericlase inclusions in diamonds as evidence of the extremely reduced condition of the lower mantle.

Keywords: Ferropericlase, Chromium, Valence, Oxygen fugacity, Mantle

INTRODUCTION

The redox environment of the deep earth is a very important factor constraining the dynamics of the deep earth (McCammom, 2005 and references therein). One approach to gaining redox information of the earth’s mantle is to investigate the valence state of transition metal ions involved in mineral inclusions in natural diamonds. Natural diamonds serve as chemically and physically stable capsules, transporting deep earth materials ranging from a depth of 150 km in the upper mantle to within the lower mantle. The most abundant transition metal in the earth is iron. Divalent iron is dominant in the upper mantle, and trivalent ion is dominant in the lower mantle, where the redox condition is much more reduced; this is known as the paradox of mantle redox (McCammom, 2005). The paradox suggests that the valence state of iron in the mantle is controlled by the crystallographic structure of the host minerals and not by their redox condition.

In contrast to iron, chromium is a transition element with a redox state that changes in an extremely reduced environment (Hanson and Jones, 1998). Chromium ions have three valence states: +2, +3, and +6. Chromium is thought to occur primarily as Cr$^{3+}$ under terrestrial redox conditions and primarily as Cr$^{2+}$ under extremely reduced conditions such as the lunar environment (Sutton et al., 1993). The lower mantle is expected to be under an extremely low oxygen fugacity ($f_{O_2}$) condition, two orders of magnitude lower than the quartz-magnetite-fayalite (QMF) buffer (McCammom, 2005). Under such a low $f_{O_2}$ condition, it is expected that mineral inclusions derived from the lower mantle contain divalent chromium ions. Indeed, Odake et al. (2008) detected Cr$^{2+}$ in ferropericlase inclusions in natural diamonds derived from the lower mantle, and suggested that the valence state of chromium in the inclusions within diamonds could be a promising indicator of the redox conditions in the lower mantle.
However, no experimental results have been reported on the relationship between redox conditions and chromium valence states in ferropericlase. In this study, we synthesized ferropericlase specimens under controlled $f_{O_2}$ conditions and examined the relations of the valence states of transition metals and $f_{O_2}$ using X-ray absorption near-edge structure (XANES) and Mössbauer spectroscopy.

**EXPERIMENTAL METHODS**

**Sample synthesis**

A starting material was prepared by mixing chemical reagents: 75.2 wt% of MgO, 22.7 wt% of Fe$_2$O$_3$, 1.4 wt% of NiO, and 0.7 wt% of Cr$_2$O$_3$. This chemical composition is almost equivalent to that of a natural ferropericlase inclusion (GU4A1 in Odake et al., 2008). The original ferropericlase inclusion contained 0.19 wt% of MnO, but we eliminated MnO from the starting material to simplify the system. Moreover, as the Mn ions in the present experimental condition are permanently divalent because $f_{O_2}$ at the MnO-Mn$_3$O$_4$ buffer is much higher (Huebner, 1971), the redox reaction of Mn would not have affected the experimental results. A 100 mg pellet was made and placed into a Pt-cup and heated at 1300 °C within an atmosphere-controlled furnace for 48 h. The justification for choosing this temperature condition is that the phase diagram of the MgO-FeO-Fe$_2$O$_3$ system has previously only been established at this temperature condition (Speidel, 1967). The oxygen fugacity (log $f_{O_2}$) was controlled at −7, −9, −11, using a mixed gas of H$_2$ and CO$_2$. The relationship between oxygen fugacity and gas composition was calibrated using a zirconia cell (Miyamoto and Mikouchi, 1996). Mixing ratios of CO$_2$ and H$_2$ were 95:5, 74:26, and 33:67 for −7, −9 and −11 in log $f_{O_2}$, respectively. At 1300 °C, the QMF buffer and the iron-wüstite (IW) buffer correspond to −7.36 and −10.73 in log $f_{O_2}$, respectively.

**X-ray powder diffraction analysis**

Powder X-ray diffraction (XRD) patterns of the synthesized samples were obtained using an X-ray diffractometer (Miniflex; Rigaku Corp.) with Cu-Kα radiation (30 kV, 15 mA), a 1.25° divergence-slit, a 1.25° soller slit, and a 0.3 mm receiver slit. The intensities of the XRD patterns were measured after monochromatization, using a pyrolytic graphite monochromator. The samples were mounted on a silicon non-reflection specimen holder, and the XRD patterns were collected in a step scanning mode over a 2θ range of 25–85° in increments of 0.02°.

**57Fe Mössbauer spectroscopy**

$^{57}$Fe Mössbauer spectra were measured with an Austin Science S-600 spectrometer using a 1.11 GBq $^{57}$Co/Rh source at room temperature. The Doppler velocity was set to a maximum of $\pm$ 10.0 mm·s$^{-1}$. Mössbauer data were collected from each sample for either two or three days. Isomer shifts were expressed with respect to the centroid of the spectrum of metallic iron foil. Mössbauer spectra were fitted using a least-squares method. The curve fitting was performed with a personal computer, assuming that the spectra were composed of peaks with Lorentzian line shapes. Half widths and intensities within each quadrupole doublet were constrained to be equal.

**XANES analysis**

Chromium K-edge XANES spectra were measured in fluorescence mode at room temperature using a BL-9A beamline at the Photon Factory, High Energy Accelerator Research Organization (KEK), Japan. The current of the X-ray storage ring was approximately 450 mA, and the beam energy was 2.5 GeV. The BL-9A is a beamline designed for X-ray absorption spectroscopy. Monochromatic excitation energy was obtained using a Si (111) double-crystal monochromator. The samples were fixed to a sample holder by adhesive tape and positioned at an angle of 45° with respect to the incident beam. The fluorescence X-ray generated from a sample was measured using a 19-element pure-Ge solid-state detector (Nomura, 1998). The intensity of the incident beam ($I_0$) was monitored in an ion chamber filled with N$_2$. The data were collected with energy steps of 1 eV in the range 5950–5973 eV, 0.25 eV in the range 5973–6050 eV, and 1 eV in the range 6050–6080 eV. It took approximately 15 min to complete one scan, and two or three scans were accumulated for one sample.

**RESULTS AND DISCUSSION**

**Synthetic products**

Figure 1 shows the XRD patterns of the three synthesized samples. The patterns obtained indicate that the main component of the samples was ferropericlase, and that minor amounts of magnesioferrite were contained in the run products. No native iron was found in the XRD patterns.

**$^{57}$Fe-Mössbauer spectra**

Figure 2 shows the $^{57}$Fe-Mössbauer spectra of samples

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#1, #2, and #3, synthesized under conditions of ΔQMF \[= \log f_{O2} \text{-QMF}, \] where \( f_{O2} \text{-QMF} \) denotes the \( f_{O2} \) conditions at the QMF buffer\] of 0.36, \(-1.64, \) and \(-3.64, \) respectively. The ΔQMF value (\( \sim -3.64 \)) of the most reduced condition in the present study is slightly lower than that of the IW buffer (ΔQMF \( \sim -3.37 \)) at 1300 ºC. All samples exhibit similar spectral patterns, revealing an intense asymmetric doublet with its center at \( \sim 1 \) mm/s, and weak sextet peaks with their center at \( \sim 0.5 \) mm/s. The \(^{57}\)Fe–Mössbauer spectra obtained were analyzed by deconvolution into the following four components: two \( \text{Fe}^{2+} \) doublets centered at \( \sim 1 \) mm/s with different splits, an \( \text{Fe}^{3+} \) singlet centered at \( \sim 0 \) mm/s, and a sextet centered at \( \sim 0.5 \) mm/s. The doublet peaks and singlet peak are assignable to ferropericlase (McCammon et al., 1998), and the sextet peaks are assigned to a trace amount of magnesiowollastonite. No native iron was detected from the \(^{57}\)Fe–Mössbauer spectra, and this result is consistent with the results of the XRD measurements. The obtained Mössbauer parameters are listed in Table 1.

The phase diagram of the MgO–FeO–FeO\(_2\) system at 1300 ºC (Speidel, 1967) indicates that ferropericlase is the unique stable phase under the experimental conditions in the present study. However, our samples contained a minor amount of magnesiowollastonite, even in synthesized samples. This discrepancy is attributable to the effect of \( \text{Cr}^{3+} \) in our samples, as \( \text{Cr}^{3+} \) is strongly compatible to spinel minerals and tends to expand its thermodynamic sta-

Figure 1. X-ray diffraction patterns of run products synthesized at oxygen fugacities of \(-11, -9, \) and \(-7 \) in \( \log f_{O2} \). The ticks show the diffractions of ferropericlase and magnesiowollastonite from the literature (Hazen, 1976; Antao et al., 2005).

Figure 2. \(^{57}\)Fe Mössbauer spectra of the synthetic samples synthesized under three different oxygen fugacity conditions. The two doublet curves are the deconvoluted components of \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) in ferropericlase, respectively. The weak sextet curve is assigned to magnesiowollastonite. (a) \( \log f_{O2} = -7 \), (b) \( \log f_{O2} = -9 \) (c) \( \log f_{O2} = -11 \).
The area ratio of the singlet peak to the sum of all peaks derived from ferropericlase corresponds to the molar ratio of Fe$^{3+}$/ΣFe. The Fe$^{3+}$/ΣFe ratios are 0.06, 0.05, and 0.07 for samples #1, #2, and #3, respectively. The precision in determining the Fe$^{3+}$/ΣFe ratio using Mössbauer spectroscopy is approximately as much as 5%. The obtained Fe$^{3+}$/ΣFe values of the three run products synthesized under the different $f_{O_2}$ conditions are similar to each other within the experimental errors. The results indicate that the Fe$^{3+}$/ΣFe ratios are almost the same, regardless of the synthesized $f_{O_2}$ conditions, and ferric exists even under the $f_{O_2}$ conditions near the IW buffer. These results are consistent with that of Speidel (1967) in the MgO–FeO–Fe$_2$O$_3$ system; the Fe$^{3+}$/ΣFe ratio decreases from ~ 0.1 to ~ 0.01 as it is reduced from near the QMF buffer to near the IW buffer for ferropericlase with ~ 75 wt% MgO.

**Cr-K edge XANES spectra**

Figure 3 shows the Cr–K edge XANES spectra of the synthesized samples. These spectra have very similar patterns to each other. The obtained spectra reveal an edge crest at around 6004 eV, a shoulder component at 5996 eV, and pre-edge absorption in the region from 5983 eV to 5990 eV. The Cr$^{2+}$/ΣCr ratio in ferropericlase can be estimated from the following three parameters independently: a relative area of shoulder component, a centroid of pre-edge, and a position of absorption edge.

A shoulder component at 5990–6000 eV can be assigned to Cr$^{2+}$ in ferropericlase, and its relative intensity to the main peak varies with $f_{O_2}$ (Eeckhout et al., 2007; Odake et al. 2008). Therefore, the spectral shape, which includes the shoulder part, was expected to be a potential indicator of the redox state in the lower mantle. The samples of the present study show an almost identical shoulder shape (see Fig. 3), whereas the synthesized redox state varied significantly. It is noteworthy that the shoulder feature assigned to Cr$^{2+}$ was observed even under an $f_{O_2}$ condition near the QMF buffer, under which most of Cr is thought to exist as a trivalent (Papike et al., 2005). As reported in Odake et al. (2008), Cr$^{3+}$/ΣCr was estimated from the obtained shoulder area in the derivative spectra using the calibration by Eeckhout et al. (2007). The obtained ratios are listed in Table 2, and they are similar to each other within uncertainty.

Many studies have determined the valence of metallic ions, including Cr, by evaluating the edge position in

<table>
<thead>
<tr>
<th>$f_{O_2}$</th>
<th>Cr$^{3+}$/ΣFe</th>
</tr>
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<tbody>
<tr>
<td>$-11$</td>
<td>0.066 ± 0.001</td>
</tr>
<tr>
<td>$-9$</td>
<td>0.051 ± 0.001</td>
</tr>
<tr>
<td>$-7$</td>
<td>0.062 ± 0.001</td>
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</tbody>
</table>

### Table 1. Mössbauer parameters obtained from synthesized samples

<table>
<thead>
<tr>
<th>$f_{O_2}$</th>
<th>Fe$^{3+}$ inner</th>
<th>Fe$^{2+}$ outer</th>
<th>Fe$^{3+}$</th>
<th>Magnetic</th>
<th>Fe$^{3+}$/ΣFe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-11$</td>
<td>Area (%)</td>
<td>23.18 ± 1.24</td>
<td>52.37 ± 0.87</td>
<td>5.35 ± 0.13</td>
<td>0.066 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>I.S. (mm/s)</td>
<td>1.052 ± 0.001</td>
<td>1.048 ± 0.001</td>
<td>0.055 ± 0.011</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Q.S. (mm/s)</td>
<td>0.452 ± 0.018</td>
<td>0.697 ± 0.024</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$-9$</td>
<td></td>
<td>32.88 ± 1.31</td>
<td>51.50 ± 1.04</td>
<td>4.52 ± 0.16</td>
<td>0.051 ± 0.001</td>
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<tr>
<td></td>
<td></td>
<td>1.049 ± 0.002</td>
<td>1.045 ± 0.002</td>
<td>0.076 ± 0.014</td>
<td>0.020 ± 0.019</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.051 ± 0.004</td>
<td>1.046 ± 0.001</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$-7$</td>
<td></td>
<td>7.89 ± 1.35</td>
<td>56.73 ± 0.87</td>
<td>4.29 ± 0.14</td>
<td>0.062 ± 0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.408 ± 0.027</td>
<td>0.626 ± 0.026</td>
<td>0.002 ± 0.024</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. Cr–K edge XANES spectra of the ferropericlase samples.
the XANES spectra. The positions of the main crest are also similar to each other within the experimental precision as listed in Table 2 (figures not shown), which also suggests that the Cr\(^{2+}/2\)Cr ratios are constant, irrespective of the oxygen fugacity within the experiments. However, the edge energy is not necessarily a reliable measure of determining valence of Cr (Farges, 2009). Farges (2009) suggested the validity of the pre-edge region for valence determination. The calibration between the pre-edge centroid position and Cr\(^{2+}/3^+\) ratio in periclase has not been established, and an absolute ratio cannot be obtained from the pre-edge shape. However, a relative comparison of the Cr\(^{2+}\) contents can be made. Table 2 lists the centroids of the pre-edge for the synthesized samples, and the three centroid values match each other. The centroids were estimated as a centroid weighted average of the pre-edge peak position as reported by Eeckhout et al. (2008).

The trivalent Cr ion should be dominant at an oxygen fugacity of \(-7\) in \(\log f_{O_2}\) (e.g., Papike et al., 2006). However, the present study clarified that the Cr\(^{2+}/3^+\) ratio in ferropericlase is constant in oxygen fugacities ranging from \(-11\) to \(-7\) in \(\log f_{O_2}\). The results indicate that the Cr\(^{2+}/3^+\) ratio in ferropericlase is not sensitive to \(f_{O_2}\) and may therefore be controlled by another factor. Iron ions in synthetic ferropericlase are dominated by Fe\(^{2+}\) (McCannon et al. 1998; McCammon, 2005). Moreover, the ionic radii of Fe\(^{2+}\) (0.78 Å) and Cr\(^{3+}\) (0.80 Å) are similar to each other (Shannon, 1976). The common divalent nature and close ionic radii induce the affinity of Cr\(^{2+}\) in the crystal structure of ferropericlase.

Similar phenomena were reported in the Yb\(^{3+}\) ion trapped in calcium carbonate and calcium fluoride. Yoshiida et al. (2005) reported that a notable amount of Yb\(^{3+}\) ions was incorporated in the crystals of calcite, aragonite, and calcium fluoride, which were synthesized in an atmospheric condition where divalent Yb cannot be stable. The ionic radius of Yb\(^{3+}\) is close to that of Ca\(^{2+}\), and it is expected that Yb\(^{3+}\) can substitute the calcium site of calcite with a higher stability (affinity) than Yb\(^{3+}\), without significant mismatches in the ionic radius and the ionic valence (Tsuno et al., 2003).

According to the present results, it could be suggested that the valence state of the Cr ion in ferropericlase is not sensitive to the redox state in the crystal growth. The finding of divalent chromium in ferropericlase inclusions derived from the lower mantle is very important for mineral science. However, it is difficult to decipher the geochemical implication relating to the redox environment of deep earth from divalent chromium.

CONCLUDING REMARKS

Oda et al. (2008) suggested that the valence state of chromium in ferropericlase inclusions in diamonds can be an indicator for the redox condition of the lower mantle. The present study clarified that Cr\(^{2+}\) is stable in ferropericlase samples, including those synthesized under an oxidized condition where Cr\(^{3+}\) is dominant. It is therefore considered that there is room for reconsidering the importance of the presence of Cr\(^{2+}\) in ferropericlase inclusions in diamonds.

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