XANES study of the oxidation state of Cr in lower mantle phases: Periclase and magnesium silicate perovskite

Sigrid Griet Eeckhout, Nathalie Bolfan-Casanova, Catherine Mccammon, Stephan Klemme, Elodie Amiguet

To cite this version:
Sigrid Griet Eeckhout, Nathalie Bolfan-Casanova, Catherine Mccammon, Stephan Klemme, Elodie Amiguet. XANES study of the oxidation state of Cr in lower mantle phases: Periclase and magnesium silicate perovskite. American Mineralogist, Mineralogical Society of America, 2007, 92 (5-6), pp.966-972. 10.2138/am.2007.2318. hal-00328944
XANES study of the oxidation state of Cr in lower mantle phases: Periclase and magnesium silicate perovskite

SIGRID GRIET EECKHOUT,1,* NATHALIE BOLFAN-CASANOVA,2 CATHERINE MCCAMMON,3 STEPHAN KLEMME,4 AND ELODIE AMIGUET2

1European Synchrotron Radiation Facility, 6 rue J. Horowitz, BP220, F-38043 Grenoble, France
2University of Clermont-Ferrand, 5 rue Kessler, F-63038 Clermont-Ferrand, France
3Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany
4CSEC and School of GeoSciences, University of Edinburgh, West Mains Road, Edinburgh EH9 3JW, U.K.

ABSTRACT

Cr K-edge X-ray absorption near-edge structure (XANES) spectra were recorded on Cr:MgO periclase and Cr:(Mg,Fe)O ferropericlase synthesized at different pressures (4 and 12 GPa) and temperatures (1200 to 1400 °C) at reducing oxygen fugacity conditions (~iron-wüstite buffer IW to IW – 2), and on Cr:MgSiO3 perovskite with 0.5 wt% Cr2O3. 57Fe Mössbauer spectra were collected on the Fe-containing samples. The aim of the study was to determine the Cr oxidation state in phases found in the Earth’s lower mantle, and to examine the possible relationship with the Fe oxidation state in the same materials. To calculate the amount of Cr2+, the intensity of the shoulder at the low-energy side of the edge crest was quantified using the area of the corresponding peak in the derivative XANES spectra (Berry and O’Neill 2004). In Cr:(Mg,Fe)O the relative Cr2+ content reached at most 12.5% but results from Mössbauer spectroscopy combined with chemical composition data suggest that some Cr2+ oxidized during cooling through the reaction Cr2+ + Fe3+ → Cr3+ + Fe2+. In iron-free Cr:MgO, the Cr2+ content is much higher and reaches ~40%. In Cr:MgSiO3 perovskite with 0.006 Cr pfu (similar to estimated lower mantle abundance), chromium is mainly divalent.

Keywords: XANES, Cr oxidation state, ferropericlase, periclase, Cr:MgSiO3 perovskite

INTRODUCTION

Previous trace-element studies report that minor amounts of Cr are present in the Earth’s mantle in an oxidized form (~0.3 wt% Cr2O3 is believed to be present in the primitive mantle, from O’Neill and Palme 1998). Chromium is mostly found as Cr3+ and Cr6+ in Earth materials, and the only natural occurrence of Cr2+ was observed in lunar basalts (Sutton et al. 1993). However, Berry et al. (2003) have recently shown that in the presence of iron and at high temperatures, Cr2+ is not quenchable because of electron charge transfer with Fe3+ upon cooling. Changes in the oxidation state of transition elements have been predicted to be induced by high pressure (Li et al. 1995) but have not been verified experimentally, even though such changes would be critical for their partitioning behavior during differentiation processes. Also, the valence state of transition elements in ferropericlase is important because these elements play a role in properties such as electrical conductivity (Dobson and Brodholt 2000), ionic diffusion (Mackwell et al. 2005), H solubility (Bolfan-Casanova et al. 2003), thermal conductivity through radiative heat transfer (Goncharov et al. 2006), and lower mantle oxygen fugacity (McCammon et al. 2004).

To better understand the factors controlling the incorporation of chromium in mantle materials, we investigated the crystal chemistry of Cr in synthetic high-pressure Cr:MgO periclase, Cr:(Mg,Fe)O ferropericlase, and Cr:MgSiO3 perovskite using X-ray absorption near-edge structure (XANES). We focused on pre-edge features, which strongly depend on the valence state and coordination number of transition elements (Calas and Petiau 1983; Farges et al. 2001; Giuli et al. 2003, 2004; Sutton et al. 2005; Westre et al. 1997; Wilke et al. 2001). Additional 57Fe Mössbauer spectra were performed on the Fe-containing samples to examine the relationship between the oxidation state of Cr and Fe.

EXPERIMENTAL METHODS

Two starting materials were used for the high-pressure synthesis of Cr-bearing periclase: one containing iron, of nominal composition Mg82.5Fe16.0Ni1.0Cr0.5O100, and another one without iron, Mg86.5Cr3.5O100, both prepared from mixing oxides MgO, NiO, Fe2O3, and Cr2O3. Metal Fe and Cr. Iron was incorporated in the form of Fe2O3, and Fe in the molar ratio of 1:2.5 to provide excess metallic Fe for maintaining low oxygen fugacity. Cr was added in the form of Cr2O3 and Cr in the molar ratio 2:1. Divalent chromium should be stable at oxygen fugacities below the iron-wüstite buffer (Papke et al. 2005). The high-pressure samples were synthesized in a 1000 ton multi-anvil press at the Laboratoire Magmas et Volcans, Clermont-Ferrand, France. MgO octahedral pressure cells of 25 and 14 mm edge length were used for experiments at 4 and 12 GPa, respectively. Different configurations were adopted depending on the composition of the samples. Metallic iron capsules were used inside a LaCrO3 furnace (β3 slightly below the iron-wüstite buffer, since both phases were still present after the experiment), and graphite capsules in a Re furnace. Both configurations are expected to exert reducing conditions on the samples (Table 1), but the graphite capsule does not contaminate the sample. After the experiment, the iron capsule almost disappeared.

* E-mail: eckhout@esrf.fr
because of the reaction to form ferropericlase. Heating durations ranged from 60 to 330 minutes. For the XANES measurements, a portion of the sample was ground and the metal fraction was removed as much as possible using a magnet. After XANES measurements, Mössbauer spectra were recorded from the remaining phase.

The use of XANES spectroscopy to determine the redox state (Fe^2+/Fe) was calibrated using chromium ferrite (FeCrO3) as a standard. The experimental conditions were 6 GeV electron energy and 200–185 mA electron current. The excitation energy was selected using a fixed-exit Si(220) double-crystal monochromator. For all spectra, a reference foil (metallic Cr or Fe) was used to monitor the intensity calibration and the remainder of the beam was detected by a Si(311) detector. The samples were mounted on a glass cover slip, and their orientation was determined using a goniometer. The background was subtracted from each spectrum, and the data were then normalized to the edge jump. The Fe^2+ and Fe^3+ contributions were modeled using the commercially available fitting program NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany). Mössbauer spectra are similar to those already reported in the literature for perovskite, and were fitted using Voigt lineshapes to two quadruple doublets corresponding to the Fe^2+ and Fe^3+ contributions.

**TABLE 1.** Area of the absorption edge shoulder (a.u.) and Cr^2+ concentration (%) for the Cr reference, CrMgSiO3 perovskite, and CrMgO periclase samples, calculated as Cr^2+(at%) = Cr^2+/(Cr^2+ + Cr^3+) × 100

<table>
<thead>
<tr>
<th>Area (a.u.)</th>
<th>Fit agreement index (%)</th>
<th>Cr^2+ (%)</th>
<th>Fe^3+ (%)</th>
<th>Composition of run products</th>
<th>Capsule</th>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>Furnace</th>
</tr>
</thead>
<tbody>
<tr>
<td>chrome</td>
<td>0.000</td>
<td>99.4</td>
<td>0.00</td>
<td>Cr^2+ = 0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ferropericlase 400</td>
<td>0.007</td>
<td>98.6</td>
<td>1.59</td>
<td>(2) Mg_{98.4}Fe_{1.6}Ni_{0.0}Cr_{0.0}O_{24} + Fe_{0.0}Ni_{0.0}Cr_{0.0}O_{24}</td>
<td>Fe</td>
<td>12</td>
<td>1200</td>
<td>LaCrO3</td>
</tr>
<tr>
<td>ferropericlase 403</td>
<td>0.009</td>
<td>99.4</td>
<td>0.27</td>
<td>(5) Mg_{99.4}Fe_{0.6}Ni_{0.0}Cr_{0.0}O_{24} + Fe_{0.0}Ni_{0.0}Cr_{0.0}O_{24}</td>
<td>Fe</td>
<td>4</td>
<td>1200</td>
<td>LaCrO3</td>
</tr>
<tr>
<td>ferropericlase 401</td>
<td>0.052</td>
<td>97.6</td>
<td>12.0</td>
<td>(2) Mg_{97.6}Fe_{12.0}Ni_{0.0}Cr_{0.0}O_{24} + not analyzed</td>
<td>Fe</td>
<td>12</td>
<td>1400</td>
<td>LaCrO3</td>
</tr>
<tr>
<td>periclase 410</td>
<td>0.143</td>
<td>99.7</td>
<td>34.38</td>
<td>Mg_{99.7}Cr_{0.3}O_{24} + Cr metal</td>
<td>C</td>
<td>10</td>
<td>1200</td>
<td>Re</td>
</tr>
<tr>
<td>periclase 404</td>
<td>0.171</td>
<td>99.8</td>
<td>41.11</td>
<td>Mg_{99.8}Cr_{0.2}O_{24} + Cr metal</td>
<td>C</td>
<td>12</td>
<td>1300</td>
<td>Re</td>
</tr>
<tr>
<td>perovskite 291</td>
<td>0.291</td>
<td>99.5</td>
<td>69.95</td>
<td>Mg_{99.5}Cr_{0.5}O_{24} + Cr metal</td>
<td>C</td>
<td>25</td>
<td>1650</td>
<td>LaCrO3</td>
</tr>
<tr>
<td>enstatite</td>
<td>0.416</td>
<td>99.4</td>
<td>100.00</td>
<td>Mg_{99.4}Cr_{0.6}SiO_{3}</td>
<td>Glass ampoule</td>
<td>1 atm</td>
<td>1350</td>
<td>Glass ampoule</td>
</tr>
</tbody>
</table>

Note: Estimated values of Fe^2+/Fe determined by Mössbauer spectroscopy are also included, as well as information on the synthesis procedure.

**RESULTS AND DISCUSSION**

The use of XANES spectroscopy to determine the redox state and coordination number of transition metal cations generally relies on the analysis of the pre-edge features observed at the
low energy side of the edge (Fig. 1). These features are related to dipole and quadruple transitions from the metal 1s core state to metal 3d with some contribution from 4p depending on the local symmetry. Their intensity and energy therefore depend on the valence state and site symmetry of the metal cation (Calas and Petiau 1983; Farges et al. 2001; Giuli et al. 2003, 2004; Sutton et al. 2005; Westre et al. 1997; Wilke et al. 2001).

The experimental results of the XANES Cr K-edge of ferropericlase (sample 400) are compared with spectra of crocoite (IVCr6+), chromite (VICr3+), and Cr-bearing enstatite (VICr2+) (Figs. 1a and 1b, Table 2).

In the case of IVCr6+, a prominent pre-edge peak is observed at 5992.4 eV (Table 2) caused by a bound-state 1s → 3d transition, which is allowed for the non-centrosymmetric tetrahedral site (Peterson et al. 1997). The high intensity has been attributed to oxygen 4p mixing into the metal 3d orbitals providing some electric dipole allowed 1s → 4p character to the transition. Furthermore, this electric dipole coupled mechanism is much stronger than the electric quadruple coupled mechanism, so that even a small amount of 4p mixing into the 3d orbitals can have a significant effect on the intensity of the pre-edge peak (Westre et al. 1997). The strong pre-edge peak at 5992.4 eV is followed by a smaller one at 5999.7 eV. The XANES features of crocoite are labeled in Table 2.

In a centrosymmetric octahedral site the 1s → 3d transition is electric dipole forbidden by parity consideration. However, small pre-edge features are experimentally observed due to electric quadruple coupling. In chromite (Fig. 1a and Table 2), this pre-edge peak occurs at 5990.6 eV and is followed by a very weak shoulder around 5993.4 eV. The absorption edge lies at 6009.2 eV and shows a shoulder at the low-energy side (Table 2). In Cr-bearing enstatite (Fig. 1a and Table 2), two distinct pre-edge features occur at 5990.5 and 5993.0 eV that are due to 1s → 3d electronic transitions. Burns (1993) related the separation by ~3 eV of the pre-edge features to the 2–3 eV octahedral crystal field splitting between the t_{2g} and e_{g} levels. However, Glatzel et al. (2004) revealed using resonant inelastic X-ray scattering that this separation is due to strong electron-electron (multiplet) interactions. The prominent shoulder at 6009.2 eV, which precedes the absorption edge at 6005.2 eV, further characterizes the XANES spectrum of Cr-bearing enstatite. This feature is absent in chromite (VICr3+) and appears as a shoulder in the studied Cr:MgO periclase samples (Figs. 1a and 2).

**FIGURE 1.** (a) Chromium K-edge XANES spectra of crocoite (dashed line), chromite (dashed-dotted line), Cr-bearing enstatite (dotted line), and ferropericlase sample 400 (full line). (b) Fits of the background subtracted pre-edge peaks of chromite, Cr-bearing enstatite, and ferropericlase sample 400. (c) Fit of the area of the derivative of the shoulder on the Cr²⁺ absorption edge of ferropericlase sample 400 (see arrow).

**TABLE 2.** XANES features of Cr-bearing enstatite, chromite, crocoite, and ferropericlase sample 400

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-edge Feature 1</th>
<th>Pre-edge Feature 2</th>
<th>Edge Feature 1</th>
<th>Edge Feature 2</th>
<th>Edge Feature 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>enstatite</td>
<td>5990.5</td>
<td>5993.0</td>
<td>6000.1 (sh)</td>
<td>6005.2</td>
<td>6009.7</td>
</tr>
<tr>
<td>chromite</td>
<td>5990.6</td>
<td>*</td>
<td>6003.5 (sh)</td>
<td>6009.2</td>
<td>6022.3</td>
</tr>
<tr>
<td>crocoite</td>
<td>5992.4</td>
<td>5999.7</td>
<td>6009.7 (sh)</td>
<td>6016.4</td>
<td>6021.0</td>
</tr>
<tr>
<td>ferropericlase 400</td>
<td>5990.9</td>
<td>5992.6</td>
<td>6000.2 (sh)</td>
<td>6008.7</td>
<td>6018.7</td>
</tr>
<tr>
<td>perovskite</td>
<td>5990.5</td>
<td>5992.3</td>
<td>6001.3 (sh)</td>
<td>6009.1</td>
<td>6014.7</td>
</tr>
</tbody>
</table>

* A very weak shoulder around 5993.4 eV is observed (sh, shoulder).
al. (1993) attributed this shoulder in lunar olivine to the $1s \rightarrow 4s$ electronic transition and used it to confirm the presence of Cr.$^{2+}$. The interpretation was picked up again by Berry et al. (2003) and Berry and O’Neill (2004). However, s orbitals are spherically symmetric and branching of $a_{1g}$ into $a_{1g}$ will only be allowed for very low symmetry. Furthermore, the high intensity of this peak as observed in Cr.$^{2+}$-bearing enstatite makes this interpretation rather implausible. In pyroxene, Cr.$^{3+}$ occupies the octahedrally distorted M2 site (Papike et al. 2005). The degenerate $e_g$ orbitals $d_{x^2-y^2}$ and $d_z^2$ are directed toward the octahedral oxygen ligands, so that uneven electron distributions in the high-spin d$^4$ configuration (Cr.$^{2+}$) lead to strong electron-ligand interactions. Such $\pi$-bonding will result in strong peaks between the pre-edge and edge (de Groot F.M.F. and Glatzel P., personal communication). Since Jahn-Teller effect criteria predict Cr.$^{3+}$ at more distorted octahedral sites, the presence of this feature around 6000.1 eV, together with the absence of a very strong pre-edge peak which is characteristic of tetrahedrally coordinated Cr, can be used to identify the presence of Cr.$^{2+}$.

The experimental Cr K-edge XANES spectra for the studied Cr:MgO and Cr:(Mg,Fe)O samples are depicted in Figure 2, where the spectra of Cr:MgSiO$_3$ perovskite, Cr.$^{2+}$-bearing enstatite and chromite are also shown. Visual inspection of this figure reveals subtle differences in the relative intensity of the lower-energy shoulder for the Cr:MgO samples. As outlined above, this absorption edge shoulder is diagnostic for Cr.$^{3+}$; hence we used the area of the corresponding peak in the derivative XANES spectra to quantify the amount of Cr.$^{3+}$ (Berry and O’Neill 2004). The presence of this feature in periclase and Cr:MgSiO$_3$ perovskite would demonstrate the presence of Cr.$^{2+}$ (Berry and O’Neill 2004). The presence of this feature in periclase and Cr:$^{2+}$bearing enstatite makes this interpretation rather implausible. In pyroxene, Cr.$^{3+}$ occupies the octahedrally distorted M2 site (Papike et al. 2005). The degenerate $e_g$ orbitals $d_{x^2-y^2}$ and $d_z^2$ are directed toward the octahedral oxygen ligands, so that uneven electron distributions in the high-spin d$^4$ configuration (Cr.$^{2+}$) lead to strong electron-ligand interactions. Such $\pi$-bonding will result in strong peaks between the pre-edge and edge (de Groot F.M.F. and Glatzel P., personal communication). Since Jahn-Teller effect criteria predict Cr.$^{3+}$ at more distorted octahedral sites, the presence of this feature around 6000.1 eV, together with the absence of a very strong pre-edge peak which is characteristic of tetrahedrally coordinated Cr, can be used to identify the presence of Cr.$^{2+}$.

The experimental Cr K-edge XANES spectra for the studied Cr:MgO and Cr:(Mg,Fe)O samples are depicted in Figure 2, where the spectra of Cr:MgSiO$_3$ perovskite, Cr.$^{2+}$-bearing enstatite and chromite are also shown. Visual inspection of this figure reveals subtle differences in the relative intensity of the lower-energy shoulder for the Cr:MgO samples. As outlined above, this absorption edge shoulder is diagnostic for Cr.$^{3+}$; hence we used the area of the corresponding peak in the derivative XANES spectra to quantify the amount of Cr.$^{3+}$ (Berry and O’Neill 2004). The presence of this feature in periclase and Cr:MgSiO$_3$ perovskite would demonstrate the presence of Cr at the octahedral site. The results are shown in Figure 3 and labeled in Table 1. Note that an unambiguous interpretation of the edge features (Table 2) which are related to the medium-range order around the Cr cations would require ab initio electronic structure calculations (Gaudry et al. 2005) which are beyond the scope of the present study.

Mössbauer measurements (Fig. 4, Table 3) on ferropericlase synthesized in this study show that Fe$^{3+}$/ΣFe is essentially at the detection limit (2%) for samples 400 and 401, and slightly higher for sample 403, where in the latter spectrum Fe$^{3+}$ absorption can be seen as a shoulder near 0.5 mm/s (Fig. 4). These results likely represent minimum values for Fe$^{3+}$/ΣFe, since Berry et al. (2003) have shown that during quenching from high temperature Cr$^{2+}$ transforms to Cr$^{3+}$ in Fe-containing melt systems according to the reaction

$$\text{Cr}^{2+} + \text{Fe}^{3+} \rightarrow \text{Cr}^{3+} + \text{Fe}^{2+}$$

and it is likely that a similar reaction will occur in ferropericlase during cooling from high temperature. Numerous studies have shown that Fe$^{3+}$ is incorporated into (Mg,Fe)O primarily through substitution on the octahedral site, where charge is balanced by the creation of cation vacancies (e.g., Valet et al. 1975; Hilbrandt and Martin 1998). Since both Fe$^{3+}$ and Fe$^{2+}$ occupy the same site in the crystal structure and Cr is expected to follow the same behavior due to size and crystal field considerations (e.g., Burns 1993), reaction 1 could easily occur as a function of temperature.

Our results show that Fe-free Cr:MgO samples contain significantly more Cr$^{3+}$ compared to Fe-containing samples, even under similar conditions of pressure, temperature and most probably oxygen fugacity (Table 2). Although starting materials for the Fe-free samples contained a higher fraction of trivalent cations (the Cr$^{3+}$/Cr$^{2+}$ ratio was 4:1) and metal in the run products was more difficult to detect than in the Fe-containing samples, we did find a small amount of metal in sample 410, and infer that the oxygen fugacity of the Fe-free Cr:MgO samples was probably not significantly oxidizing.

The most likely reason for this difference in relative Cr$^{3+}$ content between the Fe-free Cr:MgO samples and those containing Fe is the loss of Cr$^{2+}$ during cooling according to reaction 1. The additional Fe$^{3+}$ that was present at high temperature in ferropericlase is equal to the amount of Cr$^{2+}$ that was lost, and if the original relative Cr$^{2+}$ content [defined as Cr$^{2+}/(\text{Cr}^{2+} + \text{Cr}^{3+})$]
at high temperature in the ferropericlase samples is assumed to have been the same as in the Fe-free samples (~40%; Table 1), we calculate high-temperature Fe3+/ΣFe ratios for samples 400, 401, and 403 of 3%, 2%, and 7%, respectively. These values are all within the range expected for fO2 conditions near the iron-wüstite buffer based on experiments on Cr-free (Mg,Fe)O (McCammon 1993; McCammon et al. 1998), so a change in the relative Cr2+ content during quenching for these samples seems likely.

In ferropericlase when the synthesis temperature is increased from 1200 to 1400 °C at 12 GPa, the relative Cr2+ content increases from 1.6 to 12.5% for the same bulk Cr concentration (Table 1). This behavior may be due to the temperature effect in stabilizing Cr2+, similar to observations in the system MgO-SiO2-Cr-O under terrestrial oxygen fugacity conditions where temperature plays an important role in the stability of Cr2+ in olivine (Li et al. 1995). Another possibility, however, is that there was not sufficient Fe3+ present in sample 401 at high temperature to oxidize all Cr2+ to Cr3+ during cooling, since the Fe3+/ΣFe ratio measured for that sample is essentially at the detection limit.

Compared to Cr:MgO, Cr:MgSiO3 perovskite with 0.006 Cr pfu has a much higher relative Cr2+ content, ~70%, even though this sample was synthesized under relatively oxidizing conditions (from MgSiO3 and Cr2O3 with trace amounts of water, in Pt capsule and LaCrO3 furnace). This is surprising because one would have expected Cr3+ to be stable in the octahedral site of the perovskite structure and/or to substitute for Si by coupling with H according to Si4+ = Cr3+ + H+. However, no OH was detected by micro-infrared spectroscopy in the perovskite crystals, which are >100 μm in diameter, even though the technique is capable to detect H contents at the level of 1 ppm wt H2O (see Bolfan-Casanova et al. 2000 for details about the infrared measurements). This result is consistent with previous experiments, which also indicate that Cr3+ is not stable in perovskite (Andrault 2003). In these experiments, 25 mol% of XAlO3 component was mixed with MgSiO3 to study the coupled substitution of Al3+ and other X3+ cations (such as Y, Sc, Ga, Cr, and Fe) for Mg2+ and Si4+. The only cation with which Al did not couple was Cr, suggesting that Cr was not trivalent in these experiments. The amount of Cr in the perovskite analyzed in this study is too low to allow determination of the site occupancy directly from electron microprobe analysis. However, the shape of the Cr edge for perovskite is very different from that of Cr in enstatite where Cr2+ is hosted in octahedral coordination. This underlines the fact that Cr in perovskite is not substituting for silicon but for magnesium. It is even likely that under the more reducing conditions prevailing in the lower mantle, the valence state of Cr in magnesium silicate perovskite is mainly divalent. In this case, the substitution of Cr for Mg does not need to create any other defect in the structure. Compared to periclase, it is possible that more Cr2+ (with respect to Cr3+) was incorporated into magnesium silicate perovskite as the result of the higher temperatures needed to synthesize perovskite.

The oxygen fugacity of the Earth’s lower mantle is believed to be quite reducing, with the Fe3+ concentration being controlled by the crystal chemistry of aluminous (Mg,Fe)(Si,Al)O3 – perovskite

### Table 3. Hyperfine parameters derived from room temperature Mössbauer spectra of Cr:(Mg,Fe)O ferropericlase

<table>
<thead>
<tr>
<th>Ferropericlase sample no.</th>
<th>Fe2+ CS (mm/s)</th>
<th>Fe3+ CS (mm/s)</th>
<th>Cr-rich metal CS (mm/s)</th>
<th>H (mm/s)</th>
<th>A (%)</th>
<th>Cr-rich metal Fe3+/ΣFe at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>1.05(5)</td>
<td>0.40(3)</td>
<td>0.47(5)</td>
<td>33.5(5)</td>
<td>33(2)</td>
<td>–0.13</td>
</tr>
<tr>
<td>401</td>
<td>1.05(5)</td>
<td>0.43(5)</td>
<td>0.11(5)</td>
<td>33.5(5)</td>
<td>11(3)</td>
<td>–0.15</td>
</tr>
<tr>
<td>403</td>
<td>1.04(5)</td>
<td>0.37(2)</td>
<td>0.16(5)</td>
<td>32.6(4)</td>
<td>6(2)</td>
<td>–0.13(5)</td>
</tr>
</tbody>
</table>

Notes: CS = center shift relative to α-Fe; QS = quadrupole splitting; H = hyperfine magnetic field; A = relative area.

* Weighted mean square average of Fe3+ values in ferropericlase.

---

**Figure 4.** 57Fe Mössbauer spectra at room temperature for Cr:(Mg,Fe)O ferropericlase synthesized at low oxygen fugacity conditions: (a) sample 400, (b) sample 401, and (c) sample 403. Absorption due to Fe3+, Fe-rich metal, and Fe-Ni metal is shaded black, striped, and dotted, respectively, while unshaded peaks correspond to Fe2+ in ferropericlase.
partly preserved during cooling if there were not suf-
ficient FeO). The calculation of cation vacancies according to 
reaction 1 during cooling of the diamonds, because the loss 
ences therein). The calculation of cation vacancies according to 
which increases with increasing oxygen fugacity as a function 
of total iron concentration (McCammon et al. 2004 and refer-
ences therein). The calculation of cation vacancies according to 
Equation 2 is not changed if electron exchange occurs according 
to reaction 1 during cooling of the diamonds, because the lack of 
Fe exchange during cooling is balanced by the addition of an equal 
amount of Cr.

An independent measure of oxygen fugacity conditions during 
diamond formation could be obtained by a determina-
tion of the relative Cr\(^{2+}\) content of ferropericlase inclusions. For 
example, the chromium content of lower mantle ferropericlase 
(McCammon et al. 2004) can be used to qualitatively evaluate oxygen fugacity conditions during diamond formation. 

\[
\Delta V = \frac{1}{2} (\text{Fe}^{3+} + \text{Al} + \text{Cr}^{3+} + \text{Na})
\]

where \(\Delta V\) is the number of vacancies on the octahedral cation site, which increases with increasing oxygen fugacity as a function of the number of cations. (Stachel et al. 2000), which combined with Mössbauer determinations of Fe\(^{2+}/\text{Fe}\) show that the cation abundance of Cr is comparable to the abundance of Fe\(^{3+}\). This means that in the case of low oxygen fugacity, since Cr\(^{3+}\) and Fe\(^{3+}\) would be favored at high temperature, Cr\(^{2+}\) could be partly preserved during cooling if there were not sufficient Fe\(^{3+}\) available for reaction 1 to occur. On the other hand if oxygen fugacity were high, the stability of both Cr\(^{3+}\) and Fe\(^{3+}\) at high temperature would mean that no Cr\(^{2+}\) would be expected after cooling. The opportunity to distinguish between reducing and oxidizing conditions during diamond formation using the relative Cr\(^{2+}\) content of ferropericlase inclusions would be best for lower mantle ferropericlase inclusions with Cr contents at the higher end of the range of observed values (e.g., >0.5 wt% Cr\(_2\text{O}_3\)) and iron contents at the lower end of the observed range (e.g., <20 wt% FeO).

ACKNOWLEDGMENTS

We wish to thank the staff of beamline ID26 (ESRF, Grenoble, France) for assistance during the XANES measurements and Leverhulme Trust for financial support with the enstatite synthesis. We appreciate the helpful reviews by Simona Quartieri and by an anonymous colleague.

REFERENCES CITED

Andrault, D. (2003) Cationic substitution in MgSiO\(_3\) perovskite. Physics of the 

state of chromium in silicate glasses. American Mineralogist, 89, 790–798.
furnace design for XANES spectroscopy of silicate melts under controlled oxygen fugacities and temperatures to 1773 K. Journal of Synchrotron Radia-
tion, 10, 332–336.
between mantle phases in the system MgO-SiO\(_2\)-H\(_2\)O up to 24 GPa: Implica-
tions for the distribution of water in the Earths mantle. Earth and Planetary 
Science Letters, 182, 209–221.

state of chromium in silicate glasses. American Mineralogist, 89, 790–798.
furnace design for XANES spectroscopy of silicate melts under controlled oxygen fugacities and temperatures to 1773 K. Journal of Synchrotron Radia-
tion, 10, 332–336.
between mantle phases in the system MgO-SiO\(_2\)-H\(_2\)O up to 24 GPa: Implica-
tions for the distribution of water in the Earths mantle. Earth and Planetary 
Science Letters, 182, 209–221.

state of chromium in silicate glasses. American Mineralogist, 89, 790–798.
furnace design for XANES spectroscopy of silicate melts under controlled oxygen fugacities and temperatures to 1773 K. Journal of Synchrotron Radia-
tion, 10, 332–336.
between mantle phases in the system MgO-SiO\(_2\)-H\(_2\)O up to 24 GPa: Implica-
tions for the distribution of water in the Earths mantle. Earth and Planetary 
Science Letters, 182, 209–221.

state of chromium in silicate glasses. American Mineralogist, 89, 790–798.
furnace design for XANES spectroscopy of silicate melts under controlled oxygen fugacities and temperatures to 1773 K. Journal of Synchrotron Radia-
tion, 10, 332–336.
between mantle phases in the system MgO-SiO\(_2\)-H\(_2\)O up to 24 GPa: Implica-
tions for the distribution of water in the Earths mantle. Earth and Planetary 
Science Letters, 182, 209–221.

REFERENCES CITED

Andrault, D. (2003) Cationic substitution in MgSiO\(_3\) perovskite. Physics of the 

state of chromium in silicate glasses. American Mineralogist, 89, 790–798.
furnace design for XANES spectroscopy of silicate melts under controlled oxygen fugacities and temperatures to 1773 K. Journal of Synchrotron Radia-
tion, 10, 332–336.
between mantle phases in the system MgO-SiO\(_2\)-H\(_2\)O up to 24 GPa: Implica-
tions for the distribution of water in the Earths mantle. Earth and Planetary 
Science Letters, 182, 209–221.

REFERENCES CITED

Andrault, D. (2003) Cationic substitution in MgSiO\(_3\) perovskite. Physics of the 

state of chromium in silicate glasses. American Mineralogist, 89, 790–798.
furnace design for XANES spectroscopy of silicate melts under controlled oxygen fugacities and temperatures to 1773 K. Journal of Synchrotron Radia-
tion, 10, 332–336.
between mantle phases in the system MgO-SiO\(_2\)-H\(_2\)O up to 24 GPa: Implica-
tions for the distribution of water in the Earths mantle. Earth and Planetary 
Science Letters, 182, 209–221.

REFERENCES CITED

Andrault, D. (2003) Cationic substitution in MgSiO\(_3\) perovskite. Physics of the 

state of chromium in silicate glasses. American Mineralogist, 89, 790–798.


