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The effect of Fe spin crossovers on its partitioning behavior and oxidation state in a pyrolitic Earth's lower mantle system

Clemens Prescher[a,∗,1], Falko Langenhorst[b], Leonid S. Dubrovinsky[a], Vitali B. Prakapenka[c], Nobuyoshi Miyajima[a]

[a] *Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany*
[b] *Institute for Geosciences, Mineralogy Dept., University of Jena, 07745 Jena, Germany*
[c] *Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60439, USA*

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ABSTRACT

Geophysical interpretations of the Earth's interior and its dynamics are significantly influenced by phase transitions of the constituting minerals and their chemical compositions. Pressure induced Fe spin crossovers in the main mineral phases of the Earth's lower mantle, Mg–Fe silicate perovskite and ferropericlase, have been suggested to influence Fe partitioning resulting in separate layers with distinct physical properties. However, previous results remain ambiguous regarding the exact effect of Fe spin crossovers and the actual transition pressures. We observe here a continuous decrease of the Fe^{2+}–Mg partition coefficient K_D between silicate perovskite and ferropericlase from 25 GPa to 79 GPa in a pyrolitic Earth's lower mantle system. At about 97 GPa the K_D significantly increases with an accompanied decrease of the $Fe^{3+}/\Sigma Fe$ ratio in perovskite, which therefore leads to an amplified change in the Fe^{2+} K_D. We conclude that the Fe^{2+} high-spin to low-spin crossover in ferropericlase and the Fe^{2+} high-spin to intermediate spin crossover in perovskite at mid-lower mantle pressures (30–80 GPa) exert no control on K_D, but the Fe^{2+} intermediate-spin to low-spin crossover in silicate perovskite at about 100 GPa preferentially partitions Fe into silicate perovskite and reduces its Fe^{3+} content. The change in oxidation state and partitioning behavior of Fe will increase thermal conductivity and probably could induce a thermal boundary layer at this depth.

1. Introduction

The concentration of iron and its oxidation state in minerals of the Earth's lower mantle are fundamental for understanding the structure and dynamics of the Earth's interior. Both factors significantly influence densities, elasticity, and transport properties such as electrical and thermal conductivities of the major minerals constituting the lower mantle. In comparison to the complex structure of the Earth's upper mantle, the lower mantle is considered to be relatively homogeneous. However, recent seismological studies have demonstrated that discontinuities exist in the upper and lower sections of the lower mantle (Kaneshima and Helffrich, 1999; Kawakatsu and Niu, 1994; Van der Hilst, 1999; Williams and Garnero, 1996). These discontinuities have been attributed either to the presence of remnant subducted slabs (Kaneshima and Helffrich, 1999; Kawakatsu and Niu, 1994), melts (3), or electron spin crossovers in Fe-bearing materials (Badro et al., 2003). To assign these discontinuities to a specific origin, precise investigation of phase relations and partitioning behavior between the minerals constituting the Earth's lower mantle is needed.

In a pyrolitic mantle system, major phases constituting the Earth's lower mantle are Mg-silicate perovskite (Mg–Pv), ferropericlase (Fp) and Ca-silicate perovskite (Ca–Pv). In addition, majorite garnet (Irifune, 1994) and post-perovskite (Murakami et al., 2004) are present in the uppermost and lowermost parts of the lower mantle, respectively. Experimental investigations in simplified $MgO–FeO–SiO_2$ systems have shown that Fe preferentially partitions into Fp relative to Mg–Pv, with the partitioning coefficient $K_D = (Fe/Mg)_{Mg-Pv}/(Fe/Mg)_{Fp}$ ranging from 0.1–0.3 (Ito and Takahashi, 1989; Nakajima et al., 2012; Narygina et al., 2011; Sakai et al., 2009; Sinmyo et al., 2008). However, in more complex systems, particularly in the presence of Al, the partitioning coefficient K_D increases considerably to about 0.35–0.9 due to the coupled incorporation of Fe^{3+} and Al^{3+} for Mg^{2+} and

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[∗] Corresponding author.
E-mail address: clemens.prescher@gmail.com (C. Prescher).

[1] Present address: Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60439, USA.

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Si^{4+} in Mg–Pv (Frost and Langenhorst, 2002; Irifune et al., 2010; Kesson et al., 2002; Murakami et al., 2005). Laser heated diamond anvil cell (LHDAC) studies report a K_D of ~0.4–0.5 from 25 to 90 GPa (Kesson et al., 1998; Murakami et al., 2005; Sinmyo and Hirose, 2013) and a subsequent increase to 0.9 at 120 GPa (Sinmyo and Hirose, 2013). However, multi-anvil studies have shown a K_D increasing to almost unity in the top of the lower mantle (30 GPa) with a subsequent drop in K_D at 40 GPa (Irifune et al., 2010) to the values obtained by LHDAC experiments (Kesson et al., 2002; Murakami et al., 2005).

All of the previous investigations on the Fe partitioning behavior in the Earth's lower mantle have reported K_D values for bulk iron content in the constituting minerals, neglecting the oxidation state of iron or used only indirect measures. It is however well known that Fe^{3+} is structurally stabilized in Mg–Pv (Lauterbach et al., 2000; Frost and Langenhorst, 2002). The formation of Fe^{3+} is explained by a disproportionation reaction of the form: $3Fe^{2+} \rightarrow 2Fe^{3+} + Fe^0$ (Frost et al., 2004). This reaction is considered to exert an important control on the partitioning of siderophile elements in the lower mantle. Furthermore, the Fe^{3+} content is a major factor determining the physical properties of Mg–Pv and Fp, such as their elasticities (Glazyrin et al., 2014) and thermal conductivities (Goncharov et al., 2010, 2009). Besides the Fe^{3+} content, electron spin crossovers of Fe in Fp and Mg–Pv have been proposed to significantly alter the K_D in favor of the phase with stable Fe (Badro et al., 2003).

To estimate the effect of spin crossovers on the partitioning behavior and oxidation state of Fe, we have separately determined the Fe^{2+} and Fe^{3+} partitioning coefficients between Mg–Pv and Fp in a pyrolitic lower mantle system at pressure and temperature conditions of the whole Earth's lower mantle.

2. Experimental details

A pyrolitic starting powder was prepared from reagent grade oxides with Fe added as hematite (in wt%, SiO_2: 44.95; TiO_2: 0.71; Al_2O_3: 3.53; FeO: 9.33; MgO: 37.30; CaO: 3.06; Na_2O: 0.57; K_2O: 0.13; Cr_2O_3: 0.43). The oxides were ground together, cold pressed into pellets and then fired in a CO–CO_2 gas mixing furnace at 1000 °C for 1 day at an oxygen fugacity 2 log units below the fayalite magnetite quartz buffer. Quenched samples were re-ground thoroughly. The absence of remnant hematite in the starting powder was confirmed by Mössbauer spectroscopy. The pyrolitic lower mantle assemblage was then synthesized employing a multianvil press with 7/3 octahedral pressure assemblies. A $LaCrO_3$ furnace and a Re capsule were used. The experiment was run for 8 h at 25 GPa and 1650 °C. The recovered sample was crushed and subsequently used as starting material for the diamond anvil cell experiments. A Mössbauer spectrum of the synthesized starting material was recorded at room temperature in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 370 MBq ^{57}Co high specific activity source in a 12-μm-thick Rh matrix. The velocity scale was calibrated relative to a 25-μm-thick natural α-Fe foil. The spectrum was analyzed with the MossA software package (Prescher et al., 2012).

Six separate laser heated diamond anvil experiments between 33 to 130 GPa were conducted. Ne was used as pressure medium and pressure calibrant (Kurnosov et al., 2008). A double-sided YLF laser system with a Pi-shaper was used for heating the samples to temperatures corresponding to respective geotherm temperatures at each pressure. Each sample was heated for at least 30 min to ensure equilibrium. Detailed experimental conditions are given in Table 1. X-ray diffraction maps of every experiment were measured before and after heating to observe if any phase changes or phase transformations occurred. X-ray diffraction spectra were measured using a monochromatic X-ray beam (0.3344 Å) at 13ID-D of the Advanced Photon Source (APS), Argonne National Laboratory (ANL).

Table 1
Experimental conditions of the laser heated diamond anvil cell experiments. Errors in pressure were calculated by estimating the pressure from the Ne equation of state before and after the heating procedure. Temperatures are calculated as mean values from measured temperatures every minute of the 30 min laser heating time. Errors in temperatures are calculated as standard mean deviation.

Sample	Pressure (GPa)	T (K)	D_C (μm)	D_S (μm)
PyAPS-C6	33(1)	1980(80)	250	120
PyAPS-C4	40(2)	2120(150)	250	120
PyAPS-C5	59(2)	2190(90)	250	120
PyAPS-C2	79(2)	2300(140)	120_B	60_L
PyAPS-C1	97(3)	2450(140)	120_B	60_L
PyAPS-C7	130(3)	2500(150)	60_B	30_L

D_C – diamond anvil culet diameter, B – beveled diamond anvil; D_S – sample hole diameter, L – was drilled by laser.

Thin slices of 30–60 nm thickness were prepared from the central laser heated part of the recovered samples and the starting material using the FEI Quanta3D field-emission FIB-SEM. These slices were observed in a PHILIPS CM20 FEG (field emission gun) STEM operating at 200 kV. To reduce electron irradiation damage during operation, TEM thin foils were cooled to nearly liquid nitrogen temperature (ca. 100 K) in a Gatan cooling holder. Compositions were determined using a ThermoNoran Vantage energy-dispersive X-ray (EDX) microanalysis system equipped with a Norvar ultra-thin window and a germanium detector. The EDX spectra were quantified according to the method by van Cappellen and Doukhan (1994), involving an absorption correction on the basis of charge balance between cations and anions and taking into account the $Fe^{3+}/\Sigma Fe$ ratios determined by electron energy loss spectroscopy (EELS). EDX maps were measured for every recovered sample in order to detect possible chemical heterogeneities. The $Fe^{3+}/\Sigma Fe$ ratios were analyzed using a Gatan PEELS 666 (parallel electron energy-loss spectrometer). The determination of the $Fe^{3+}/\Sigma Fe$ ratio was based on the quantification method of Van Aken and Liebscher (2002). This method is based on the white line intensities at the Fe $L_{2,3}$ edge. Fe $L_{2,3}$ ELNES spectra were measured in diffraction mode with an energy dispersion of 0.01 eV per channel. An energy resolution, measured as width of the zero-loss peak at half maximum, of 0.8–0.9 was obtained. Special care was taken to only measure fresh crystalline grains of magnesium silicate perovskite, since Mg–Pv easily amorphizes under the high electron flux needed for Fe–L edge EELS measurements. To check for possible beam induced changes in valence state, six spectra were measured in a time series with integration times of 20 s each. Spectra were then corrected for dark current and channel-to-channel gain variation. The pure single-scattering core-loss signal was extracted by subtracting an inverse power-law background and removing the multiple scattering contribution by the Fourier-ratio technique (Egerton, 1996). The consistency of the $Fe^{3+}/\Sigma Fe$ ratios estimated from EELS was checked performing EELS and Mössbauer spectroscopy measurements on different Mg–Si perovskites. The resulting $Fe^{3+}/\Sigma Fe$ ratios are in agreement within experimental uncertainties.

3. Results and discussion

The EDX maps of the recovered samples show that the samples are chemically homogeneous (Fig. 1) and do not show any evidence of Soret diffusion. We did not observe strong differences of the chemical compositions of Mg–Pv and Fp in the heated areas, on the contrary to previously reported studies on Mg/Fe partitioning in a pyrolitic system (Sinmyo and Hirose, 2013, 2010). This is probably partly because of the flat-top laser heating system