Oxidation potential in the Earth's lower mantle as recorded by ferropericlase inclusions in diamond

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ARTICLE INFO

ABSTRACT

Ferropericlase (fPer) inclusions from kimberlitic lower-mantle diamonds recovered in the Juina area, Mato Grosso State, Brazil were analyzed with transmission electron microscopy, electron energy-loss spectroscopy and the flank method. The presence of exsolved non-stoichiometric Fe^{3+}-enriched clusters, varying in size from 1–2 nm to 10–15 nm and comprising $\sim$3.64 vol.% of fPer was established. The oxidation conditions necessary for fPer formation within the uppermost lower mantle ($P = 25$ GPa, $T = 1960$ K) vary over a wide range: $\Delta \log f_{O_2}$ (IW) from 1.58 to 7.76 ($\Delta = 6.2$), reaching the fayalite–magnetite–quartz (FMQ) oxygen buffer position. This agrees with the identification of carbonates and free silica among inclusions within lower-mantle Juina diamonds. On the other hand, at the base of the lower mantle $\Delta \log f_{O_2}$ values may lie at and below the iron–wüstite (IW) oxygen buffer. Hence, the variations of $\Delta \log f_{O_2}$ values within the entire sequence of the lower mantle may reach ten logarithmic units, varying from the IW buffer to the FMQ buffer values. The similarity between lower- and upper-mantle redox conditions supports whole mantle convection, as already suggested on the basis of nitrogen and carbon isotopic compositions in lower- and upper-mantle diamonds. The mechanisms responsible for redox differentiation in the lower mantle may include subduction of oxidized crustal material, mechanical separation of metallic phase(s) and silicate–oxide mineral assemblages enriched in ferric iron, as well as transfer of fused silicate–oxide material presumably also enriched in ferric iron through the mantle.

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1. Introduction

Oxygen fugacity is a fundamental thermodynamic parameter in the growth and stability of mineral phases formed in the Earth's mantle. At the top of the upper mantle, the calculated oxygen fugacity is shown to vary between -3 to $+2$ logarithmic units of the fayalite–magnetite–quartz (FMQ) oxygen buffer (Frost and Mc-Cammon, 2008; Stagno et al., 2013). With increasing depth, f_{O_2} decreases relative to oxygen buffers as a result of elevated pressure controlling Fe^{3+}/Fe^{2+} equilibria (Wood et al., 1990). At approximately 8 GPa ($\sim$250 km depth), f_{O_2} should be 5 log units below FMQ, and at the base of the upper mantle ($\sim$14 GPa) f_{O_2} has been suggested to extend to $\sim$0.8 log units below the iron–wüstite (IW)

buffer, assuming the precipitation of Ni in bulk silicate Earth at this depth (Frost and McCammon, 2008).

These calculated data were supported by direct analyses of $Fe^{3+}/\Sigma Fe$ ratios in garnet grains hosted as inclusions within peridotite xenoliths present in South African (Woodland and Koch, 2003; Lazarov et al., 2009; Hanger et al., 2015) and Canadian (McCammon and Kopylova, 2004; Creighton et al., 2010) kimberlites. Similar results were obtained from spinel and garnet peridotites in Siberia, demonstrating the decrease of f_{O_2} with increasing pressure: from $+1$ to -4 $\Delta \log f_{O_2}$ (FMQ) at a depth of 180 km (Goncharov et al., 2012) and from -2.5 to nearly -5.9 $\Delta \log f_{O_2}$ (FMQ) at a depth of 90–220 km (1.2–7.1 GPa pressure) (Yaxley et al., 2012). Local variations in oxygen fugacity within the upper mantle are caused by petrological processes such as partial melting, mantle metasomatism, and the recycling of oxidized material during subduction (Rohrbach and Schmidt, 2011; Berry et al., 2013); controls relating to the local tectonic environment have also been suggested (Foley, 2011).

Table 1
Characteristics of the host diamonds, containing ferropericlase inclusions.

Sample	Pipe	Weight (mg)	Morphology	Color	δ^{13}C. VPDB (‰)	Nitrogen content (ppm)	Nitrogen aggregation (%B)
1-49	Pandrea-1	10	Dodecahedroid	Colorless	-3.27 ± 0.15	36.2	89.2
7-100	Pandrea-7	8	Combination octahedron + dodecahedroid	Brownish	-4.59 ± 0.07	n.d.	n.d.
A-7	Aripuana-1	70	Dodecahedroid	Grayish	-4.91 ± 0.04	12.6	66.9
C-143	Collier-4		Dodecahedroid		-4.47 ± 0.08	n.d.	n.d.

Note: n.d. – not determined.

Estimates of oxygen fugacity for the deep mantle suggest that at depths in excess of 250 km (>8 GPa), the range of f_{O_2} variation is highly constrained due to saturation with (Fe, Ni) metal (Rohrbach and Schmidt, 2011). In this case f_{O_2} is restricted to values from around the IW equilibrium (where the metal would be Ni-rich) to about 1.5 log units below IW (where the metal would be close to pure iron). The same range of f_{O_2} variation (between IW and IW-1.5) was inferred for the entire lower mantle, suggesting the bulk oxygen content of the lower mantle to be similar to that of the upper mantle (Frost and McCammon, 2008).

Direct measurements of lower-mantle redox conditions, which provide crucial constraints on the true oxidation state of the lower mantle, are scarce. To date, less than 20 grains of ferropericlase (fPer), former bridgmanite (Bridg, the new mineral name for MgSi-perovskite, recently approved by the IMA as specimen IMA-2014-017; Tschauner et al., 2014) and tetragonal almandine–pyrope phase (TAPP) from São Luiz (Brazil) and Kankan (Guinea) placer deposits have been analyzed, by means of Mössbauer spectroscopy, to determine their $Fe^{3+}/\Sigma Fe$ ratios (McCammon et al., 1997, 2004b). The results demonstrated the small amount of Fe^{3+} in fPer ($Fe^{3+}/\Sigma Fe = 0.1$–6.0%), in contrast to high amounts of Fe^{3+} in former bridgmanite (9–75%) and particularly in TAPP (66–74%). These differences are characteristic even for coexisting phases, such as associations in samples #BZ238 (3% in fPer and 74% in TAPP) and #BZ251 (0% in fPer and 20% in former bridgmanite), and have been considered to reflect differences in the crystal structures. For example, large amounts of Fe^{3+} in former bridgmanite and TAPP were considered to be the result of the presence of Al in their compositions, which stabilizes Fe^{3+} in the perovskite structure, independent of oxygen fugacity (McCammon, 1997; McCammon et al., 2004a). Based on these results, supported by experimental data, the overall picture of redox conditions in the lower mantle was suggested to be generally reduced for the bulk mantle, but possibly with more oxidized regions associated with subduction (McCammon et al., 2004b).

Otsuka et al. (2013) calculated the redox conditions of previously studied (McCammon et al., 1997, 2004b) lower-mantle fPer inclusions in diamond. The calculated $\Delta \log f_{O_2}$ (IW) values vary from 4.3–3.3 for Kankan, Guinea to 3.2–2.6 for São Luiz. As stated by Otsuka et al. (2013), the estimated oxygen fugacities "are close to the upper stability limit of diamond in mantle peridotite at the top of the lower mantle at adiabatic or slightly superadiabatic temperatures". The range from 2.6 to 4.3 log units above the IW buffer ($\Delta = 1.7$ log units) is slightly more oxidized than predicted by Rohrbach and Schmidt (2011), but narrowly constrained as they suggested.

Alternative calculations performed recently by Ryabchikov and Kaminsky (2013, 2014), based on the calculated Ni/Fe partition coefficient, estimated the variation of $\log f_{O_2}$ values in the lower mantle (at pressures from 30 to 70 GPa) to be over a much wider range from -1 and -1.5 log units below the IW buffer to $+3$ and $+5$ log units (and even higher, in the presence of carbonates) above the IW buffer ($\Delta \geq 7$ log units). Evidence for such large variations of f_{O_2} is the presence, among inclusions in lower-mantle diamonds, of native iron and iron carbides (Kaminsky and Wirth, 2011) on the reduced side, and magnesite and other car-

bonate minerals (Kaminsky et al., 2009b, 2013) on the oxidized side.

For the evaluation of true oxygen fugacity conditions in the lower mantle, natural mineral associations are of great value, but they are very rare. Here we report a study of the internal structure and oxygen fugacity conditions of several ferropericlase inclusions from lower-mantle diamonds, recovered from the Chapadão and other kimberlites in the Juina area, Mato Grosso State, Brazil (Kaminsky et al., 2009a, 2010), and present our findings and their significance.

2. Samples

2.1. Host diamonds

The Juina area in Brazil is known for numerous finds of lower-mantle inclusions in diamond grains from within the São Luiz and other placer deposits (Harte et al., 1999; Kaminsky et al., 2001; Pearson et al., 2014). In 2006–2007, the kimberlitic sources of these diamonds were discovered, and diamonds from these kimberlitic pipes (forming the Chapadão, or Pandrea cluster) were studied (Kaminsky et al., 2009a). Among the inclusions in the diamonds, ferropericlase is most abundant. Its origin in the lower mantle is confirmed by the association of this mineral with other lower-mantle mineral phases, such as former bridgmanite (samples ##BZ251, 16b, 103a and 108d).

For this study, we investigated four samples: two samples from the Chapadão kimberlites, one from the Aripuana-1 pipe, located approximately 20 km southwest of the Chapadão cluster, and one from the Collier-4 pipe, located approximately 17 km northwest of the Chapadão kimberlites. Information concerning the studied diamonds is summarized in Table 1.

According to these data, the diamonds are typical lower-mantle samples with 'juvenile' carbon isotopic characteristics, low nitrogen content and a high level of nitrogen aggregation.

2.2. Compositions of ferropericlase inclusions

The compositions of fPer inclusions, used for the Fe/(Fe+Mg) ratio calculations, were studied by means of a JEOL XA-8200 electron microprobe, housed at the Bayerisches Geoinstitut, Bayreuth, Germany; the operating conditions were 15 kV accelerating voltage and 80 nA beam current. The analyses are in general agreement with microprobe results performed earlier for these grains, utilizing a Cameca SX-100 electron microprobe at GEMOC, Macquarie University, Australia (Kaminsky et al., 2009a). Both instruments were used in wavelength-dispersive mode. For the calculations presented here, we utilized the analyses performed at Bayreuth (i.e., total Fe concentrations as presented below in Table 2).

3. Methods

The internal structure of the ferropericlase grains was studied with the use of various transmission electron microscopy techniques, and the oxygen fugacity conditions of the formation of these grains were determined utilizing the flank method.