Ferric iron content of ferropericlase as a function of composition, oxygen fugacity, temperature and pressure: Implications for redox conditions during diamond formation in the lower mantle

Kazuhiko Otsuka [a,*], Micaela Longo [b], Catherine A. McCammon [c], Shun-ichiro Karato [a]

[a] Yale University, Department of Geology and Geophysics, 210 Whitney Avenue, New Haven, CT 06511, USA
[b] University of Padua, Department of Geosciences, Via Giotto 1, 35137 Padua, Italy
[c] Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

ARTICLE INFO

ABSTRACT

We investigated the ferric iron (Fe^{3+}) concentration in $(Mg,Fe)O$ ferropericlase using the flank method applied to Mg–Fe interdiffusion couples of ferropericlase. Diffusion couples with $Mg/(Mg+Fe)$ in the range 0.44 to 1 were annealed at temperatures of 1673–1873 K and pressures of 5–24 GPa over a wide range of oxygen fugacities. Oxygen fugacity was controlled by Fe, Ni, Mo, and Re metal capsules and their corresponding oxide phases. Based on our results and available experimental data, we derived an equation for the Fe^{3+} solubility in ferropericlase applicable to depths at the top of the lower mantle: $[Fe^{3+}] = C \, (X_{Fe}^4 \, f_{O2})^m \exp\{-((1-X_{Fe})E^*_{Mg} + X_{Fe}E^*_{Fe} + PV^*)/RT\}$, where $C = 2.6(1) \times 10^{-3}$, $m = 0.114(3)$, $E^*_{Mg} = -35(3)$ [kJ/mol], $E^*_{Fe} = -98(2)$ [kJ/mol], and $V^* = 2.09(3)$ [cm^3/mol]. The value of the oxygen fugacity exponent m implies that Fe^{3+} mostly occupies tetrahedral sites under these conditions, which is consistent with the results of previously reported Mössbauer spectroscopy studies. Based on this relationship, we calculated the redox conditions of ferropericlase inclusions in diamonds believed to have come from the lower mantle. 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, which suggests that ferropericlase inclusions recorded and preserved the conditions at which diamond was precipitated from carbonates or carbonatite melts near the top of the lower mantle.

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1. Introduction

The oxidation state of iron in $(Mg,Fe)O$ ferropericlase, the second most abundant phase in the lower mantle, has an important influence in controlling the chemical and physical behavior of the material. The variation in its oxidation state affects various transport properties such as atomic diffusion (Mackwell et al., 2005), electrical conductivity (Dobson. et al., 1997; Hansen and Cutler, 1966; Wood and Nell, 1991) and rheological properties (Gordon, 1973; Tremper et al., 1974) through its influence of point defect populations. Small amounts of Fe^{3+} (or the oxygen fugacity) can affect phase relations and element partitioning between ferropericlase and coexisting phases, including melting relationships (Frost and McCammon, 2008; Gessmann et al., 1999; Rohrbach and Schmidt, 2011).

Laboratory studies on Fe^{3+} solubility in ferropericlase have been conducted at room pressure (Dobson et al., 1998; Hilbrandt and Martin, 1998; Katsura and Kimura, 1965; O'Neill et al., 2003; Speidel 1967; Srečec et al., 1987; Wiser and Wood, 1991) and at high pressures (Bolfan-Casanova et al., 2002; Frost and Langenhorst,

2002; McCammon et al., 2004a; Otsuka et al., 2010; Sinmyo et al., 2008a, 2008b). It is generally assumed that Fe^{3+} is the most dominant positively charged point defect in ferropericlase (e.g., Hazen and Jeanloz, 1984), although ferropericlase dissolves other trivalent cations such as Al^{3+}, Cr^{3+}, and monovalent cations such as Na^+, K^+, and H^+ (Bolfan-Casanova et al., 2002; Irifune et al., 2010; Wood, 2000). In the case where sufficient monovalent cations are not available to maintain charge neutrality conditions, the substitution of trivalent cations is charge compensated by the creation of cation vacancies. In ferropericlase these are predominantly created by chemical impurities in the extrinsic regime, which dominate over thermally activated Schottky defects in the intrinsic regime (e.g., Van Orman et al., 2009). Therefore, vacancy concentrations can be obtained by measuring impurity concentrations, rather than by calculating the free energy of vacancy formation (e.g., de Koker and Stixrude, 2010).

The concentration of Fe^{3+} in ferropericlase changes by orders of magnitude with variation of thermochemical parameters such as oxygen fugacity, chemical composition, temperature, and pressure (e.g., Otsuka et al., 2010). The precise knowledge of solubility of Fe^{3+} and other cations is critical to constrain the charge neutrality conditions and the behavior of transport properties. Furthermore, an understanding of Fe^{3+} solubility provides

* Corresponding author. Tel.: +1 203 432 5791; fax: +1 203 432 3134.
E-mail address: kazuhiko.otsuka@yale.edu (K. Otsuka).

an experimental basis for inferring the oxygen fugacity and other thermochemical states in the lower mantle from ferropericlase inclusions encapsulated in diamond believed to have been derived from the lower mantle (Brenker et al., 2002; Harte, 2010; Hayman et al., 2005; Hutchison et al., 2001; McCammon et al., 1997, 2004b; Stachel et al., 2000).

Several techniques are available to determine the oxidation state of Fe, including the Mössbauer spectroscopy (e.g., McCammon, 2004), electron energy loss spectroscopy (e.g., van Aken and Liebscher, 2002), X-ray absorption near edge structure spectroscopy (e.g., Cottrell et al., 2009), and techniques using an electron probe (e.g., Höfer et al., 1994). As one of the methods involving an electron microprobe, the flank method has several advantages compared with other techniques. The flank method permits simultaneous determination of the oxidation state of Fe and the major element chemistry on the same analytical point, which minimizes systematic biases that might appear between separate measurements. It has relatively high spatial resolution (on the order of 1 μm), large spatial coverage (up to cm-sized samples), and short acquisition time (on the order of a few tens of minutes). These features make it suitable to determine Fe^{3+} contents in heterogeneous samples such as the diffusion couples explored in this study.

The flank method analyzes the variation of $FeL\alpha$ and $FeL\beta$ X-ray emission spectra caused by different valence states of Fe using a hybrid approach that incorporates both the $L\beta/L\alpha$ intensity ratios and the peak shift (Höfer et al., 1994). The spectrometer positions of the wavelength dispersive system are set to the positions on the flanks of the $FeL\alpha$ and $FeL\beta$ emission lines where Fe^{2+} and Fe^{3+}-bearing samples exhibit the largest difference to each other. Since X-ray emission spectra are sensitive to the crystal structure, it is necessary to construct a calibration curve specific to each mineral species (Höfer and Brey, 2007). So far, the flank method has been successfully applied to sodic amphibole (Enders et al., 2000), garnet (Höfer and Brey, 2007), and ferropericlase (Höfer et al., 2000; Longo et al., 2011).

In this article, we report an investigation of the oxidation state of Fe using the flank method applied to Mg–Fe interdiffusion couples of ferropericlase with a wide range of chemical composition annealed at different pressures, temperatures and oxygen fugacities. Our results enable the derivation of an equation for Fe^{3+} solubility in ferropericlase applicable to depths at the top of the lower mantle, which can be used to infer the conditions at which ferropericlase inclusions in the lower mantle diamonds may have formed.

2. Experiments

2.1. Sample synthesis

The ferropericlase single crystals for high-P,T diffusion experiments were prepared by Mg–Fe interdiffusion between single crystal MgO periclase and mixtures of periclase and Fe_2O_3 hematite powder annealed at 1873 K for 200–300 h at an oxygen fugacity of 1 Pa in a gas-mixing furnace, following previously reported procedures (Otsuka et al., 2010). The observation of synthesized ferropericlase crystals by a field-emission-gun electron probe microanalyzer (JXA-8530 F) confirmed that the chemical composition varied by less than a few % in molar Mg/(Mg+Fe) ratio over the sample size used for high-P,T experiments. No detectable contamination of elements other than Fe, Mg, and O was observed. Subsequently, the ferropericlase samples were polished and drilled into cylindrical shapes with thicknesses from 0.5 to 0.8 mm and diameters of 1.4, 1.2, or 1.0 mm, depending on the capsule size for high-P,T experiments. The periclase single crystals that were used as one half of the diffusion couple were prepared in a cylindrical shape with thicknesses from 0.2 to 0.5 mm. Although ferropericlase is

isotropic with respect to diffusion in cubic symmetry, the diffusion interface was oriented close to the (100) surface.

2.2. Mg–Fe interdiffusion experiments

The high-P,T Mg–Fe interdiffusion experiments were performed using diffusion couples typically composed of two single crystals of periclase and ferropericlase, and, in some experiments, a single crystal of periclase surrounded by mixtures of periclase and hematite at 5–24 GPa and 1673–1873 K for 2.5–27 h (Table 1). The diffusion couples were loaded into an inner Re, Mo, Ni, or Fe metal capsule in order to control redox state of the experimental charges (Rubie et al., 1993). In addition, ReO_2 or MoO_2 oxides were added to the Re or Mo inner capsules, respectively, while no oxides were typically added to Ni or Fe capsules since NiO and FeO are miscible in ferropericlase. The sample charge in the inner capsule was enclosed in the Pt outer capsule, which was sealed by welding to minimize water exchange with the surrounding environment.

The Pt capsules containing the sample charges were set into 18/11, 14/8, or 8/3 octahedral assemblies. Each assembly consists of the following ceramic and metal parts: a semi-sintered Cr_2O_3-doped MgO octahedron or a MgO+spinel injection-molded octahedron (Leinenweber et al., 2006) with an edge length of 18, 14 or 3 mm as a pressure medium, a ZrO_2 thermal insulation sleeve, a graphite or $LaCrO_3$ stepped cylindrical furnace, a MgO or BN sleeve which insulates the sample capsule from the furnace, and Mo electrodes. Temperature was monitored using a $W_5Re–W_{26}Re$ thermocouple with the thermocouple junction placed in direct contact with one end of the sample capsule. The ceramic parts were fired at approximately 1000 K overnight before assembling.

The octahedral assemblies were loaded into a 1000-ton Kawai-type multi-anvil apparatus installed at Yale University. The confining pressure was exerted on the cell assembly by eight tungsten carbide cubes with an edge length of 26 mm and corner truncations of 11, 8, or 3 mm. Sample pressure was calibrated against hydraulic oil pressure using the following phase transformations: quartz–coesite (Bose and Ganguly, 1995) and coesite–stishovite (Zhang et al., 1996) at 1473 K for the 18/11 assembly, coesite–stishovite and forsterite–wadsleyite in Mg_2SiO_4 (Katsura et al., 2004) at 1673 K for the 14/8 assembly, and wadsleyite–ringwoodite in Mg_2SiO_4 (Inoue et al., 2006) and ringwoodite–perovskite+periclase in Mg_2SiO_4 (Fei et al., 2004) at 1873 K for the 8/3 assembly (see supplementary information). We found that the MgO+spinel injection-molded octahedron exhibited slightly better pressure-efficiency than the commonly-used Cr_2O_3-doped MgO octahedron, probably due to the higher inherent strength of the material as well as its lower porosity.

3. Analytical procedures

3.1. Electron probe microanalysis

We carried out flank method and quantitative elemental analysis on the synthesized Mg–Fe interdiffusion couples using a Jeol XA-8200 electron microprobe equipped with five wavelength dispersive spectrometers at Bayerisches Geoinstitut (BGI) following the procedures reported previously (Longo et al., 2011). We also analyzed the interdiffusion couples using a field-emission-gun electron probe micro-analyzer (JXA-8530 F) with a wavelength dispersive system and a scanning electron microscope (XL30 ESEM-FEG) at Yale University. The analytical conditions for the flank method and major element chemistry analysis were an acceleration voltage of 15 kV and a beam current of 80 nA with a focused electron beam at BGI, and 10 kV and 10 nA at Yale. For the flank method, we measured the $FeL\alpha$ and $FeL\beta$ X-ray intensities at the peak flank positions of 706.4 and 716.3 eV using