IRON OXIDATION STATE IN (Mg,Fe)O: CALIBRATION OF THE FLANK METHOD ON SYNTHETIC SAMPLES AND APPLICATIONS ON NATURAL INCLUSIONS FROM LOWER MANTLE DIAMONDS

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INTRODUCTION

Iron oxidation state is intensively studied in geosciences as well as in materials science because of its effect on the physical and chemical properties of minerals and materials. In minerals, $Fe^{3+}/\Sigma Fe$ is important because it reflects the oxygen fugacity (fO_2) of the environment where the assemblage last equilibrated, and hence it can record the nature of interactions between different regions of the Earth, such as between the mantle and the Earth's surface.

To investigate $Fe^{3+}/\Sigma Fe$ on both single crystals and powders, several experimental techniques are available. Mössbauer spectroscopy is the most commonly used method. Mössbauer measurements can be performed on powders (conventional form) or on single mineral grains using a point source to determine $Fe^{3+}/\Sigma Fe$, however the resolution limit is at about 100-200 μm in size (McCammon *et al.*, 1991; McCammon, 1994), it requires long measuring times (minimum 1-2 days), and corrections due to recoil-free fraction differences and thickness must be considered.

Other methods of determining $Fe^{3+}/\Sigma Fe$ include transmission electron microscopy using Electron Energy Loss Spectroscopy (EELS), offering nanometer-scale spatial resolution (van Aken & Liebscher, 2002; van Aken *et al.*, 1998, 1999), X-ray Absorption Near Edge Structure (XANES) spectroscopy (Berry *et al.*, 2003; Delaney *et al.*, 1998; O'Neill *et al.*, 2006; Wilke *et al.*, 2001) through the use of microXANES (Dyar *et al.*, 2002; Schmid *et al.*, 2003), and X-ray photoelectron spectroscopy (XPS) (Raeburn *et al.*, 1997a, 1997b). Each of these methods have specific challenges related to either destructive (EELS) or difficult sample preparation (XPS), or limited accessibility to synchrotron facilities (XANES). Therefore, it is of great interest to improve and develop in-house techniques which are easily accessible.

New methods of $Fe^{3+}/\Sigma Fe$ determination from the Fe*L*β and Fe*L*α emission spectra using the electron microprobe have been developed (Fisher, 1965; Albee & Chodos, 1970; O'Nions & Smith, 1971; Pavicevic *et al.*, 1972, 1989, 1992; Grasserbauer, 1975a, 1975b; Dodd & Rippe, 1978; Legkova *et al.*, 1982; Fialin *et al.*, 2001). The so-called flank method, correlates a particular *L*β/*L*α ratio as a function of Fe bulk composition (in wt.%), and has been already applied to wüstite, magnetite and hematite (Höfer *et al.*, 1994, 2000), garnet (Höfer, 2002; Höfer & Brey, 2007) and sodic amphiboles (Enders *et al.*, 2000). The flank method offers reasonably high spatial resolution due to the small sampling volume (≤ 1 μm^3, spot beam size), and therefore only a small sample is needed (on the order of the beam size, 1 to 10 μm, significantly smaller compared to Mössbauer spectroscopy). Sample preparation is relatively straightforward and mostly nondestructive. Further advantages include the possibility to perform *in situ* $Fe^{3+}/\Sigma Fe$ measurements simultaneously with major element analysis. The successful calibration for

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garnets (Höfer & Brey, 2007) has enabled a number of recent studies focused on the oxygen fugacity of the mantle (Creighton *et al.*, 2009; Malaspina *et al.*, 2009).

As the flank method shows to be sensitive to the coordination polyhedron for iron, a calibration is required for each mineral structure (Höfer & Brey, 2007). In this study we calibrate the flank method for synthetic (Mg,Fe)O over a wide Fe compositional range for the determination of *in situ* $Fe^{3+}/\Sigma Fe$. We show how the flank method can quantify inhomogeneity in oxidation state, with potential application to processes such as diffusion. We also investigate its sensitivity to the presence of additional phases, as the detection of magnesioferrite exsolution from primary (Mg,Fe)O. Finally, we apply the flank method to a suite of natural (Mg,Fe)O ferropericlase inclusions selected from various provenances worldwide established to be of ultra deep origin. As (Mg, Fe)O ferropericlase is the second most abundant phase of the lower mantle, this new calibration provides a direct tool to investigate deeper portions of the Earth's mantle and to provide new insights on the oxygen fugacity of the less explored deep Earth.

EXPERIMENTAL METHODS

Sample synthesis

The calibration sample suite for ferropericlase consists of synthetic (Mg,Fe)O crystals covering a wide range of composition (x_{Fe} = 2 to 47 at.%) and $Fe^{3+}/\Sigma Fe$ (1 to 15%). To synthesise the samples, Mg and Fe metals were mixed in stoichiometric proportions to give a wide compositional range of Fe in (Mg,Fe)O. All synthetic powders were equilibrated in a gas-mixing furnace under CO/CO_2 at 1300°C and controlled oxygen fugacity (fO_2) in order to obtain various $Fe^{3+}/\Sigma Fe$ ratios (fO_2 ranged from 10^{-7} to 10^{-11}). X-ray powder diffraction and Mössbauer spectroscopy were used to verify the structure of the polycrystalline powders and to determine $Fe^{3+}/\Sigma Fe$. The range of $Fe^{3+}/\Sigma Fe$ obtained was between 1 and 15 at.%.

Single crystals were obtained at high pressure and temperature using a multianvil apparatus. The (Mg,Fe)O polycrystalline powders were loaded into Re capsules of 1.6 mm diameter and 2 mm long, compressed up to 15 GPa and heated to 1800-2000°C for about one hour. Crystals were analyzed using point-source Mössbauer spectroscopy to determine the final $Fe^{3+}/\Sigma Fe$ and then were mounted in epoxy for the electron microprobe measurements.

RESULTS AND DISCUSSION

Calibration of the flank method on synthetic (Mg,Fe)O

The flank method was calibrated for the Jeol XA-8200 electron microprobe in use at Bayerisches Geoinstitut for the synthetic (Mg,Fe)O ferropericlase. Following the same approach used for the garnet calibration (Hofer & Brey, 2007), the behavior of the $L\beta/L\alpha$ ratio was studied for the entire solid solution $(Mg_xFe_{1-x})O$-FeO as a function of bulk ΣFe (wt.%) and Fe^{2+} (wt.%) concentration (Fig. 1 a,b). Flank method measurements ($L\beta/L\alpha$) show a strong correlation as a function of ΣFe (wt.%) within a Fe compositional range of 0.2-50 wt.% (Fig. 1a), proving that the $L\beta/L\alpha$ ratio is strongly sensitive also for ferropericlase and in particular for a low range of Fe content, which makes the flank method suitable to investigate natural (Mg,Fe)O occurring as diamond inclusions (typically covering such a range of ΣFe bulk composition at lower mantle depths).

The calibration curve determined is Fe^{2+} = 46.238 + 8.161 · ln (ΣFe) - 137.01 · ($L\beta/L\alpha$) + 85.57 · $(L\beta/L\alpha)^2$, for a Fe compositional range between 3 and 47 wt.%. A comparison of $Fe^{3+}/\Sigma Fe$ determined by
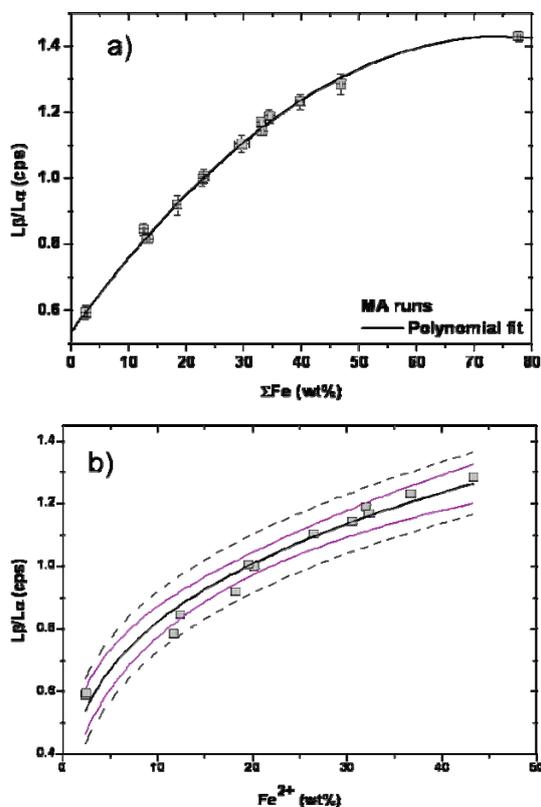
Fig. 1 - a) $L\beta/L\alpha$ variation as a function of ΣFe (wt.%) for synthetic (Mg,Fe)O crystals; b) $L\beta/L\alpha$ variation as a function of Fe^{2+} (wt.%) calculated from Mössbauer data. Dashed grey and solid purple lines indicate the 95% confidence and prediction intervals, respectively, obtained for the polynomial fit.

flank method and values determined earlier by Mössbauer spectroscopy shows that results are generally consistent between the two different methods within the experimental errors (Fig. 2).

Application of the flank method to synthetic (Mg,Fe)O containing exsolved magnesioferrite

To explore applications of the flank method, a set of (Mg,Fe)O single crystals (Jacobsen *et al.*, 2002) synthesized by interdiffusion of Fe and Mg between single-crystal MgO and (Mg,Fe)O pre-reacted powders was studied. For these samples the presence of magnesioferrite had been detected previously by Mössbauer spectroscopy (0.2-11 vol.%) and in this study its presence was confirmed by TEM analysis. Flank method measurements showed that the $L\beta/L\alpha$ ratio is affected by the different chemical compositions (ΣFe and $Fe^{3+}/\Sigma Fe$) of magnesioferrite and (Mg,Fe)O. As a result, the data do not follow the theoretical trend described for pure (Mg,Fe)O (Fig. 3).
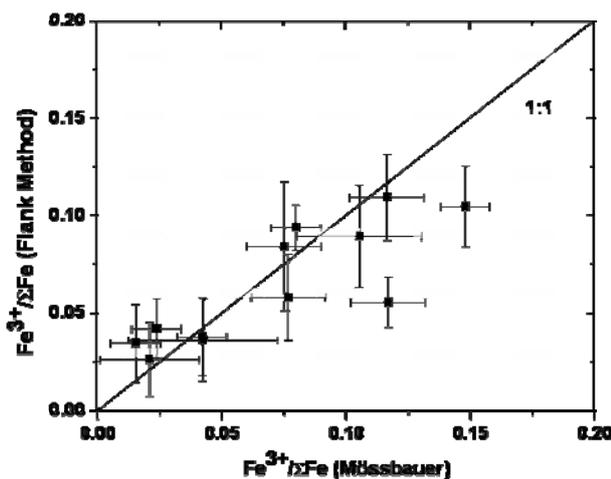

Fig. 2 - $Fe^{3+}/\Sigma Fe$ in synthetic (Mg,Fe)O determined using the flank method according to equation (1) *vs.* $Fe^{3+}/\Sigma Fe$ determined using Mössbauer spectroscopy.
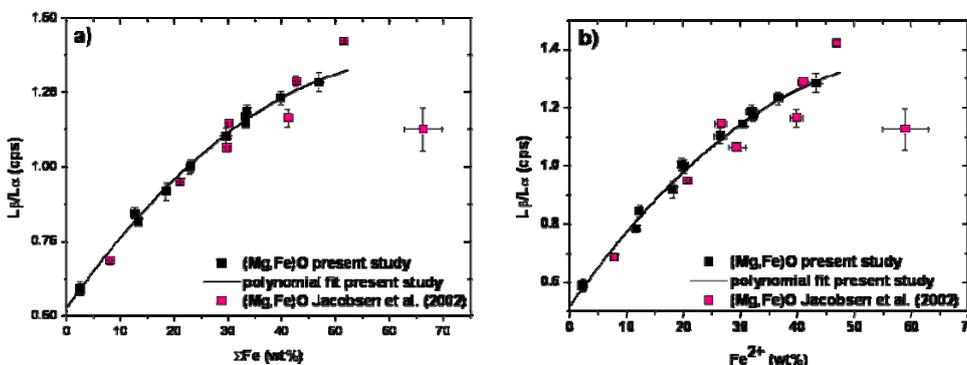
Fig. 3 - Flank method measurements *vs.* ΣFe (%) (a), and Fe^{2+} (%) (b), on (Mg,Fe)O samples from Jacobsen *et al.* (2002) (in red) compared to synthetic (Mg,Fe)O samples from the present study (in black).

Application of the flank method to synthetic (Mg,Fe)O from diffusion studies

Three additional (Mg,Fe)O crystals were measured by electron microprobe in order to test the sensitivity and accuracy of the flank method for small variations of bulk ΣFe (wt.%) as well as to measure Fe^{3+}/ΣFe along diffusion profiles (Fig. 4). Here it is demonstrated how the flank method can be a powerful tool to measure small variations in Fe^{3+} content, with a spatial resolution of only few microns (2-3 µm) and a lower detection limit of ΣFe of 3 wt.%. Moreover, the measurement of Fe^{3+} content on the micron scale (Fig. 4d) enables the study of the variation of oxygen fugacity conditions along diffusion gradients.
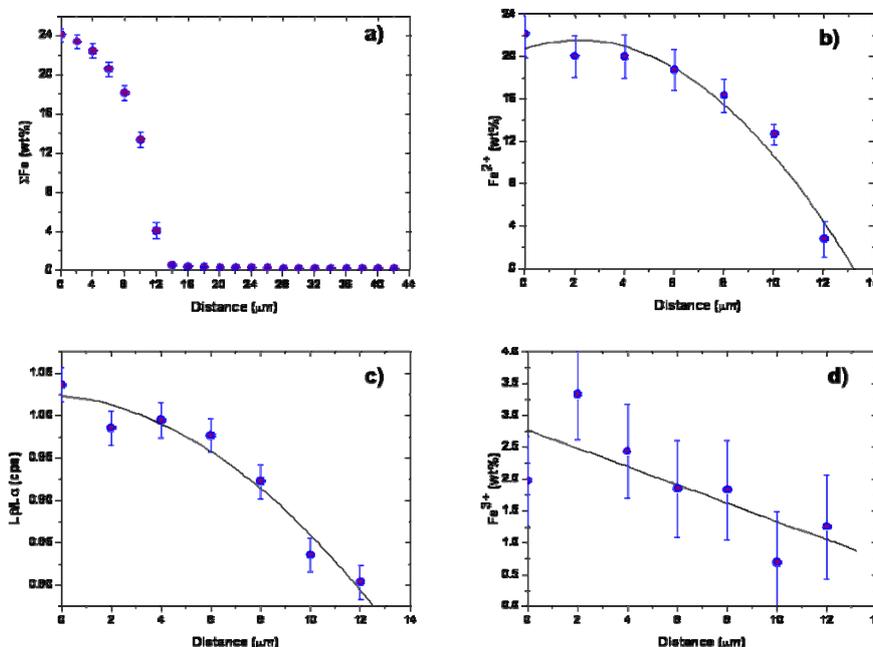

Fig. 4 - Variation of a) ΣFe (wt.%), b) Fe^{2+} (wt.%) c) $L\beta/L\alpha$ (cps) and d) Fe^{3+} (wt.%) *vs.* measurement position, reported as distance in µm along the diffusion profile.

Application of the flank method to synthetic (Mg,Fe)O from diffusion studies

The last application of the flank method was performed on a set of (Mg,Fe)O ferropericlase inclusions from ultra deep diamonds selected worldwide were analyzed by the flank method. The data set consists of eighteen (Mg,Fe)O ferropericlase samples from Juina, Brazil, Machado River, Brazil, and Ororoo, Australia. Inclusions are between 10 and 50 µm in size, therefore they are suitable to perform flank method measurements to determine $Fe^{3+}/\Sigma Fe$.

Results for the (Mg,Fe)O inclusions show good agreement with the theoretical trend described by the synthetic samples, which confirms high phase homogeneity for most of the samples (Fig. 5). Flank method measurements show a large range of $Fe^{3+}/\Sigma Fe$ values for (Mg,Fe)O inclusions (Table 1), which implies a large range of oxygen fugacities based on charge balance calculations.

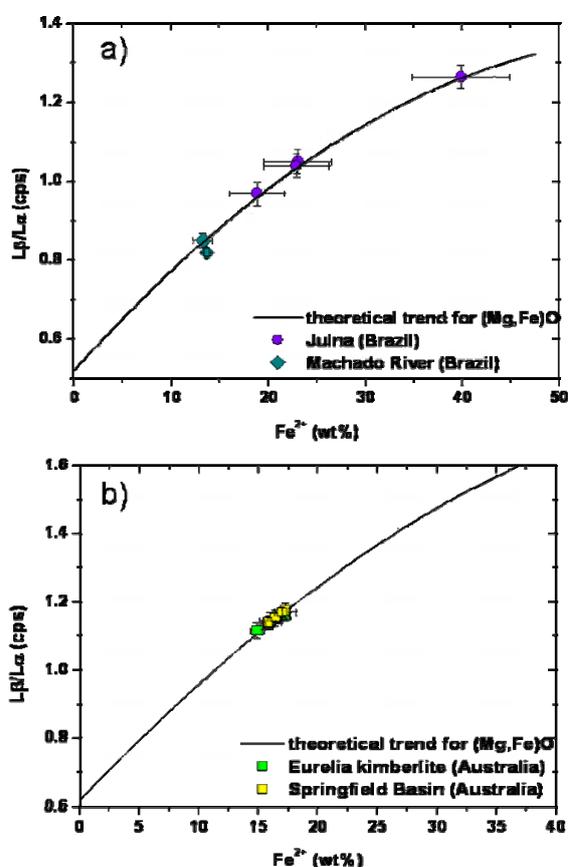Fig. 5 - $L\beta/L\alpha$ ratios *vs.* Fe^{2+} for (Mg,Fe)O. Natural (Mg,Fe)O inclusions from Brazil (a), and from Australia (b), show good agreement with the theoretical line described by synthetic (Mg,Fe)O (black line). Error bars for Fe^{2+} (wt.%) in a) are propagated using equation (8) (see § 3.3); whereas error bars for Fe^{2+} (wt.%) in b) are propagated using equation (9) (see § 3.3.1).

Table 1 - Natural (Mg,Fe)O diamond inclusions: flank method $L\beta/L\alpha$ ratios (counts per second) as a function of the bulk Fe content (wt.%) and the related $Fe^{3+}/\sum Fe$ ratio obtained using the flank method calibration for ferropericlase.

Sample	Fe (wt.%)	$L\beta/L\alpha$	$Fe^{3+}/\sum Fe$
F6-04B	17.3(1)	1.16(2)	0.04
F6-04D	16.9(2)	1.12(2)	0.12
F5-07C	18.3(1)	1.17(3)	0.01
F5-07D	17.4(2)	1.14(3)	0.08
F5-07E	17.6(1)	1.16(1)	0.01
F5-07F	17.7(1)	1.16(2)	0.06
511A	17.1(1)	1.15(2)	0.04
5-11B	17.6(1)	1.17(2)	0.04
5-11C	-	-	-
5-11D	17.4(2)	1.14(1)	0.09
5-11E	17.4(1)	1.17(1)	0.01
5-11F	16.7(1)	1.14(2)	0.05
1-49 I	25.3(2)	1.05(3)	0.08
7-100	21.5(1)	0.97(3)	0.12
1-143	26.2(2)	1.04(3)	0.13
P11	14.3(2)	0.85(2)	0.08
P12	15.3(1)	0.82(1)	0.12

CONCLUSIONS

We can conclude that the flank method was successfully calibrated using the Jeol XA-8200 electron microprobe at Bayerisches Geoinstitut for a set of (Mg,Fe)O samples synthesized at 15 GPa and 1800-2000°C over a Fe compositional range from < 3 to 46.8% *ca.* in weight and $Fe^{3+}/\sum Fe$ from 1 to 15%. $Fe^{3+}/\sum Fe$ determined by the flank method was generally in agreement within experimental error with Mössbauer data. As the flank method offers several advantages, such as reduced measuring times (on the order of few hours) and much higher spatial resolution of 1-10 μm (versus no smaller than 100 μm), it appears to be suitable to determine $Fe^{3+}/\sum Fe$ in natural ferropericlase from diamond inclusions, which are commonly less than 50 μm in size.

For the first time *in situ* $Fe^{3+}/\sum Fe$ was determined for (Mg,Fe)O ferropericlase inclusions from lower mantle diamonds worldwide (Juina area and Machado River, Brazil, Eurelia and Springfield Basin, Australia) of less than 50 μm in size without destroying the samples. The measured $Fe^{3+}/\sum Fe$ ratio of the inclusions varied from to 1 to 13%. Such ratios are similar to results for a suite of much larger inclusions from Kankan, Guinea, and São Luiz, Brazil, that were studied using Mössbauer spectroscopy (McCammon *et al.*, 1997, 2004). The variation of the $Fe^{3+}/\sum Fe$ seems to be correlated to the geographical distribution of the inclusions studied, showing a redox gradient with more reducing conditions at Kankan, Guinea, and São Luiz, Brazil, and more oxidized in the case of Juina and Machado River, Brazil, and

Eurelia, Australia, and ultimately linked to the proto-pacific subduction mechanism. Inclusions recovered from the same host diamond from Eurelia shows a strong redox gradient, which suggests a drastic change in the oxygen fugacity conditions during diamond growth.

Flank method measurements are sensitive to chemical composition, because the presence of extra phases in (Mg,Fe)O can affect the $L\beta/L\alpha$ ratio. The lack of a clear correlation as a function of the amount of magnesioferrite exsolved from (Mg,Fe)O ferropericlase brings to the consideration that the energies associated with the Fe$L\alpha$ and Fe $L\beta$ lines might be affected differently depending on the Fe site distribution (*e.g.*, clustering) and structural and electronic configuration (*e.g.*, spin state).

The $L\beta/L\alpha$ ratio is highly sensitive to iron concentration, suggesting the possibility for the flank method to be applied to diffusion studies. The application of the flank method to ΣFe gradients demonstrated for the first time the possibility to follow the variation of the $Fe^{3+}/\Sigma Fe$ ratio on a micron scale and provided a measure of the lower detection limit of ΣFe for flank method measurements on (Mg,Fe)O ferropericlase (3 wt% of ΣFe).

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