

Iron oxidation state in (Mg,Fe)O: calibration of the flank method (EMPA) as a new technique for diamond inclusion studies

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Introduction

The lower mantle consists predominantly of (Mg,Fe)(Si,Al)O₃ perovskite and (Mg,Fe)O ferropericlasite. Studying these phases is therefore critical to determining redox conditions and their consequences for mantle properties and dynamics. Studies have shown that the Fe³⁺ concentration in (Mg,Fe)(Si,Al)O₃ perovskite is essentially insensitive to oxygen fugacity; hence our attention is turned to (Mg,Fe)O. Our goal is to calibrate the “flank method” by electron microprobe using synthetic (Mg,Fe)O, and then apply the method to determine *in situ* Fe³⁺/ΣFe in ferropericlasite inclusions from lower mantle diamonds. Up until now a calibration of the flank method has been reported only for garnets (Höfer and Brey, 2007).

Sample synthesis and experimental methods

The calibration sample suite consists of synthetic (Mg,Fe)O crystals covering a wide range of composition ($x_{\text{Fe}} = 2$ to 70 at.%) and Fe³⁺/ΣFe (1 to 14%). To synthesize the samples, Mg and Fe metals were mixed in stoichiometric proportions to give a compositional range of 2-60 at% Fe in (Mg,Fe)O. Metals were first dissolved in HNO₃, and then the mixture was heated to 50°C to allow HNO₃ to slowly evaporate. Subsequently NO₃ was added to obtain oxide precipitates. Excess HNO₃ and NO₃ were then removed by drying the obtained gels using a Bunsen burner (1200-1500°C). All synthetic powders were then equilibrated in a gas-mixing furnace under CO/CO₂ at 1300°C and controlled oxygen fugacity in order to obtain a wide range of Fe³⁺/ΣFe. Oxygen fugacities were varied over the range 10⁻⁷ to 10⁻¹¹ and were monitored during the experiments using an oxygen fugacity sensor. X-ray powder diffraction and Mössbauer spectroscopy were used to verify the structure of the polycrystalline powders and to determine Fe³⁺/ΣFe. The range of Fe³⁺/ΣFe obtained was between 1 and 15 at%.

In order to obtain the high quality surfaces needed for electron microprobe measurements, the polycrystalline samples were transformed to quasi single crystals 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. Samples were compressed 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 Fe³⁺/ΣFe and then were mounted in epoxy for study using the electron microprobe. Quantitative plus qualitative analysis were performed at 15kV and 80nA according to the procedure developed for garnets by Höfer and Brey (2007). Measurements were performed using a beam size of 1μm. Each Lβ and Lα position was counted for 300 s at each selected point. Spectrometer drifts which may occur during the measurements were monitored by analyzing one of the synthetic (Mg,Fe)O samples at the start and finish of each session. The reproducibility of flank method measurements was also investigated by monitoring Lβ/Lα ratios over several microprobe sessions. Data comparison shows that Lβ/Lα ratios collected on different days are slightly different, but fall within experimental error (Fig.1).

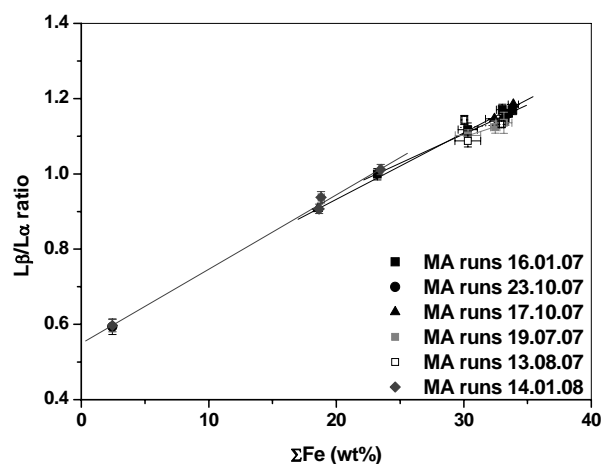


Fig. 1 – Reproducibility of flank method measurements on different days (date indicated) for the same set of (Fe,Mg)O crystals. No significant change in slope is apparent for different electron microprobe measuring days.

Results and discussion

We observe a positive correlation between ΣFe and Lβ/Lα in accordance with the work on garnets by Höfer and Brey (2007) (Fig.2), and also a positive correlation of Lβ/Lα ratios with Fe²⁺ (Fig.3). However

in contrast with the garnet results, the two correlations for (Mg,Fe)O are distinctly nonlinear. This likely arises from the nonlinear variation of weight fraction across the ferropericlase solid solution compared to garnet, where the smaller variation in the latter gives a near linear trend (Fig.4).

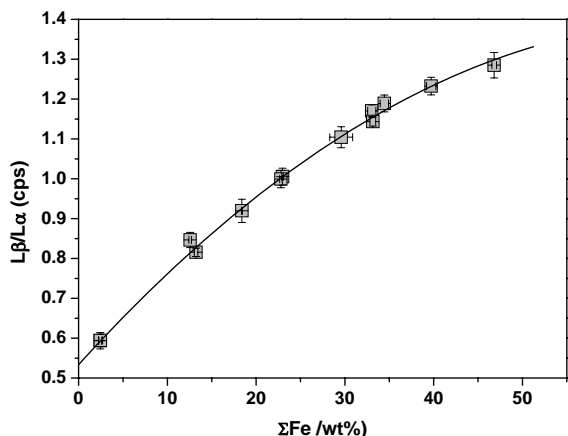


Fig. 2 – $L\beta/L\alpha$ variation as a function of ΣFe (wt%) for (Mg,Fe)O crystals.

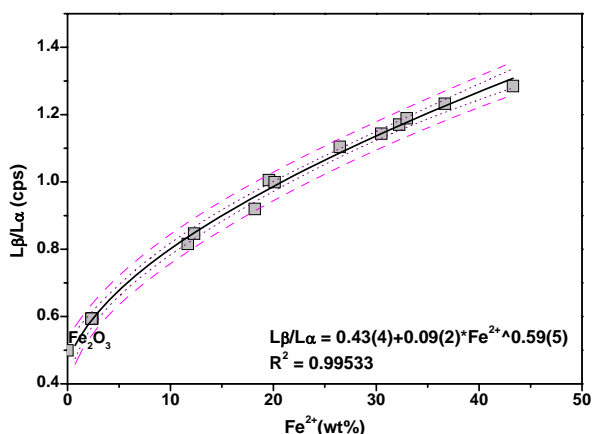


Fig. 3 – $L\beta/L\alpha$ variation as a function of Fe^{2+} (wt%) for (Mg,Fe)O crystals calculated from Mössbauer data. Dashed and dotted lines indicate the 95% confidence and prediction intervals, respectively.

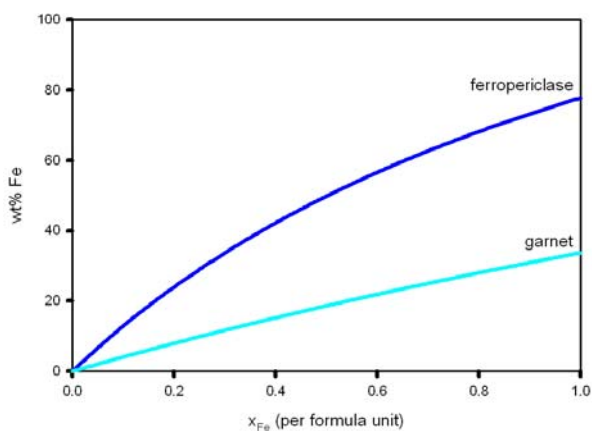


Fig. 4 – Variation of wt% Fe as a function of Fe molar fraction for ferropericlase and garnet (pyrope-almandine) solid solutions.

Following the approach of Höfer and Brey (2007), we applied a least-squares regression model to fit the three variables ΣFe , $L\beta/L\alpha$ and Fe^{2+} , and looked for the simplest equation that was able to fit the data. Thus, for (Mg,Fe)O with x_{Fe} between 2 and 36.6 wt% we report the following calibration:

$$\begin{aligned} \text{Fe}^{2+} = & 46.238 + 8.161 * \ln(\Sigma\text{Fe}) - 137.01 * (L\beta/L\alpha) + \\ & + 85.57 * (L\beta/L\alpha)^2 \\ R^2 = & 0.9967 \end{aligned} \quad (1)$$

where Fe^{2+} and ΣFe are in wt%. A comparison between $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined using flank method data and equation (1) vs. $\text{Fe}^{3+}/\Sigma\text{Fe}$ calculated using Mössbauer spectroscopy shows good agreement within experimental error (Fig. 5).

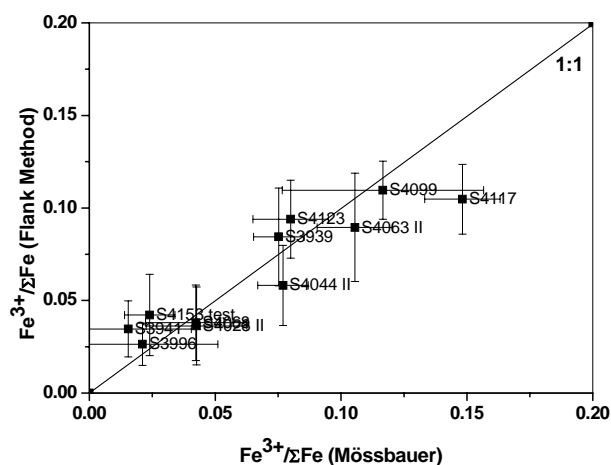


Fig. 5 – $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined using the flank method according to equation (1) vs. $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined using Mössbauer spectroscopy. The calibration was made from 11 of the synthetic (Mg,Fe)O crystals from this study.

Flank method measurements show an agreement within 1σ which is comparable to the accuracy obtained from Mössbauer spectroscopy, but with the additional advantage of a spatial resolution on the order of 10 μm (compared to no smaller than 100 μm for Mössbauer spectroscopy). The flank method therefore appears to be a promising technique for determining $\text{Fe}^{3+}/\Sigma\text{Fe}$ in ferropericlase samples with low to moderate Fe concentrations.

Nearly all of the synthetic (Mg,Fe)O crystals appeared to be homogeneous as shown by the random variation of $L\beta/L\alpha$ vs. wt% Fe within the experimental error of the measurements. However sample S4149 showed a large variation in wt% FeO in measurements taken over different parts of the sample that was strongly correlated with $L\beta/L\alpha$ (Fig. 6), likely indicating that the sample was inhomogeneous. We therefore omitted sample S4149 from the calibration fitting procedure. However the results raise the possibility of quantifying inhomogeneity as a variation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ with position in the sample, with potential application to studying dynamic processes in ferropericlase such as diffusion.

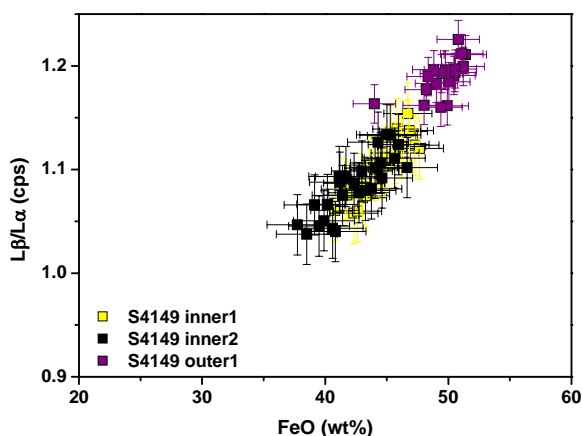


Fig. 6 – $L\beta/L\alpha$ variation as a function of wt% FeO for sample S4149. The positive correlation observed from the inner to the outer part of the crystal indicates inhomogeneity and perhaps the effect of diffusion processes occurring during synthesis.

Application to synthetic crystals containing exsolved magnesioferrite and to diamond inclusions

We measured a second set of synthetic (Mg,Fe)O single crystals that had been synthesized by interdiffusion of Fe and Mg between single-crystal MgO and (Mg,Fe)O prereacted powders (Jacobsen et al., 2002). Mössbauer spectroscopy was used in this previous study to determine $Fe^{3+}/\Sigma Fe$, and had detected the presence of $Fe(Mg,Fe)_2O_4$ (0.2-11 vol.%) which was also confirmed by TEM analysis. Our preliminary flank method data show a deviation of $L\beta/L\alpha$ from the calibration trend line (Fig. 7a), which likely results from the ferrite contribution. Thus we have a possibility to quantify the effect of $Fe(Mg,Fe)_2O_4$ on $L\beta/L\alpha$.

We also measured a suite of four ferropericlasite inclusions in lower mantle diamonds from Juina, Brazil kindly supplied by F. Kaminsky. Preliminary results from the flank method show that $L\beta/L\alpha$ ratios are consistent with the trend line with ΣFe from synthetic (Mg,Fe)O crystals (Fig. 7b), suggesting a minimal contribution from magnesioferrite, and further analysis is underway to determine $Fe^{3+}/\Sigma Fe$ for the inclusions.

Conclusions and outlook

We used the approach of Höfer and Brey (2007) to calibrate the determination of $Fe^{3+}/\Sigma Fe$ using the flank method for (Mg,Fe)O with 2 to 37 wt% Fe. Results from measurements on inhomogeneous samples raise the possibility to quantify the variation of $Fe^{3+}/\Sigma Fe$ with position in samples subject to dynamic processes such as diffusion. Preliminary results on samples containing an exsolved magnesioferrite phase indicate the possibility to quantify the effect of ferrite on $L\beta/L\alpha$, with potential application to ferropericlasite diamond inclusions where a ferrite phase may be present. Future work will focus on determination of $Fe^{3+}/\Sigma Fe$ in these natural samples, which will provide clues to redox conditions at the time of their formation.

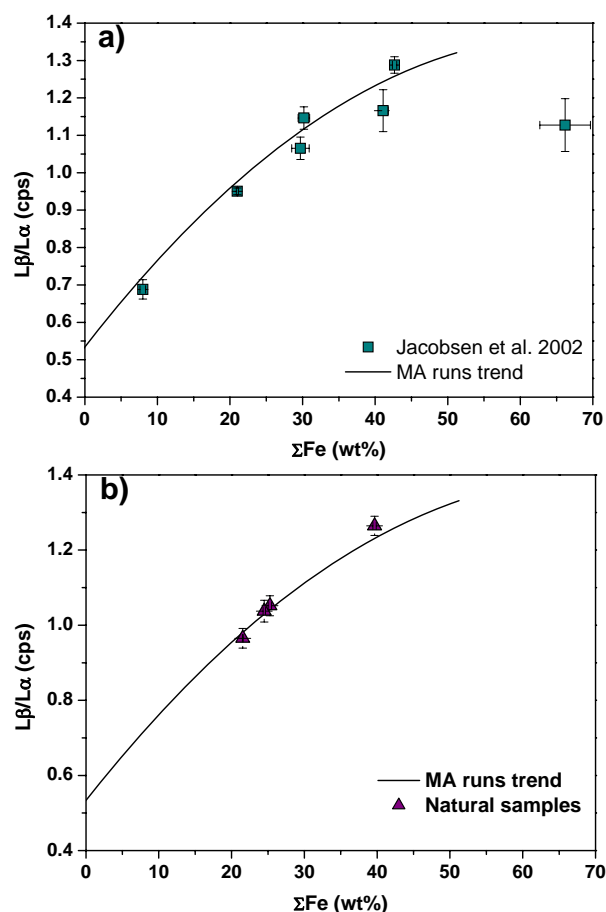


Fig. 7 – $L\beta/L\alpha$ variation as a function of ΣFe (wt%) for synthetic single crystals from Jacobsen et al. (2002) (a) and a suite of ferropericlasite inclusions from lower mantle diamonds from Juina, Brazil (b).

Acknowledgments

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