



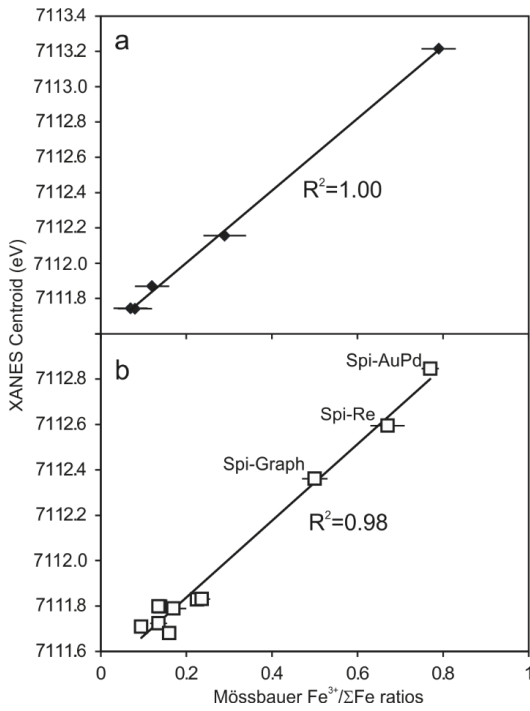
	Experiment title: Determination of the ferric iron (Fe³⁺) behaviour during MORB petrogenesis	Experiment number: ES-173
Beamline: ID21	Date of experiment: from: 24.07.2014 to: 28.07.2014	Date of report: 06.04.2017
Shifts: 12	Local contact(s): Camille Rivard	<i>Received at ESRF:</i>
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Report: The oxidation state of Fe in primitive melts has been proposed to be directly related to the oxygen fugacity of their asthenospheric mantle source region¹⁻². For this reason, the quantification of Fe³⁺/ΣFe ratios in primitive basalts is one of the few plausible gauges for the oxygen fugacity of the asthenospheric mantle³⁻⁵. Recently measured Fe³⁺/ΣFe ratios determined for mid ocean ridge basalts (MORB) show a very narrow range in values, with standard deviations of only a few percent. Most likely as a result of different analytical techniques, the proposed global average Fe³⁺/ΣFe ratios vary somewhat between studies, e.g. 0.12±0.02^[6] and 0.16±0.01^[7], imply that mantle melting occurs over a relatively small range of *f*O₂. In this study, the effects of temperature and *f*O₂ on the Fe³⁺/ΣFe ratio of peridotite melts and on mineral-melt Fe³⁺ partition coefficient have been determined experimentally using the results of partial melting experiments on a MORB mantle source composition “MPY-90”⁸.

Experimental and analytical methods: The experiments were performed in a ½ inch piston-cylinder apparatus at 1.5 GPa, 1310-1450°C, which are suitable conditions for MORB genesis⁹⁻¹⁰. Oxygen fugacity was varied from FMQ-3 to FMQ+6 (FMQ = Fayalite-Magnetite-Quartz oxygen buffer). A set of 8 well-characterized natural spinels from different settings¹¹ that covered a wide range of Fe³⁺ contents (between 0.1 and 0.35 Fe³⁺/ΣFe) were selected as standards for XANES-measurements. To extend this Fe³⁺/ΣFe range, we synthesized 3 spinels at 1.5 GPa and 1400°C at different *f*O₂ conditions using a piston cylinder apparatus. In addition, five silicate glass standards were also synthesized using a 1-atm gas mixing furnace at distinct *f*O₂ conditions between FMQ-2 and air.

Fe³⁺/ΣFe ratios of melts and spinels were measured using Fe K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy analyses¹² at ID21, ESRF. We recorded the XANES spectra using full-field absorption radiographies set-up with a large X-ray beam^{12,13}. This setup allows the acquisition of stacks of more than 200 images at each energy step of the XANES spectrum range. Each pixel contains a full high resolution XANES measurement. We chose this setup in order to improve the determination of Fe²⁺/Fe³⁺ measurement in spinels by increasing the number of XANES spectra collected over a large field of view, in comparison to classical focused beam setup. A monochromatic X-ray beam was obtained using a fixed exit double-crystal monochromator (0.62 eV resolution at 7.2 keV). The monochromatic energy was calibrated against the first inflection point of a Fe foil (4 μm thick) spectrum at 7110.78 eV. The field of view covered by the CCD camera (CMOS PCO.edge) and selected for the acquisition was 0.8 mm² with a pixel size of 0.3x0.3 μm². Before and after each acquisition, a reference image was recorded (using the same experimental parameters), with the sample moved out of the X-ray beam.

Results and conclusions: In order to determine precise *f*O₂ values and test the consistency of our measurements, we compare our XANES data with different thermodynamic models. The results are applied to understanding the behaviour of ferric iron during partial melting of the mantle and to explaining the constant Fe³⁺/ΣFe ratio observed for MORB.



Our results show that this method allows Fe³⁺ measurements of spinels of our experimental charges but is not suitable for quantifying Fe³⁺/ΣFe of glasses (Fig. 1). Fe³⁺/ΣFe ratios of glasses were therefore estimated using thermodynamic models and further constrained by Mössbauer spectroscopy measurements on an additional set of partial melting experiments.

Figure 1. Pre-edge centroids from XANES measurements as a function of Fe³⁺/ΣFe obtained using Mössbauer spectroscopy for (a) glass standards, and (b) spinel standards. R² is the correlation coefficient.

Our experiments indicate that the Fe₂O₃ mineral-melt partition coefficient for spinel ($D_{Fe_2O_3}^{spinel-melt}$) decreases at low fO_2 conditions but remains relatively constant from FMQ-1.5 to higher fO_2 (~ 5-6; Fig. 2a). We have compared our data to results from a batch-melting model using pMELTS¹⁴ (Fig. 2). From this comparison an estimate can be made of the approximate bulk Fe³⁺/ΣFe in the different experimental starting materials.

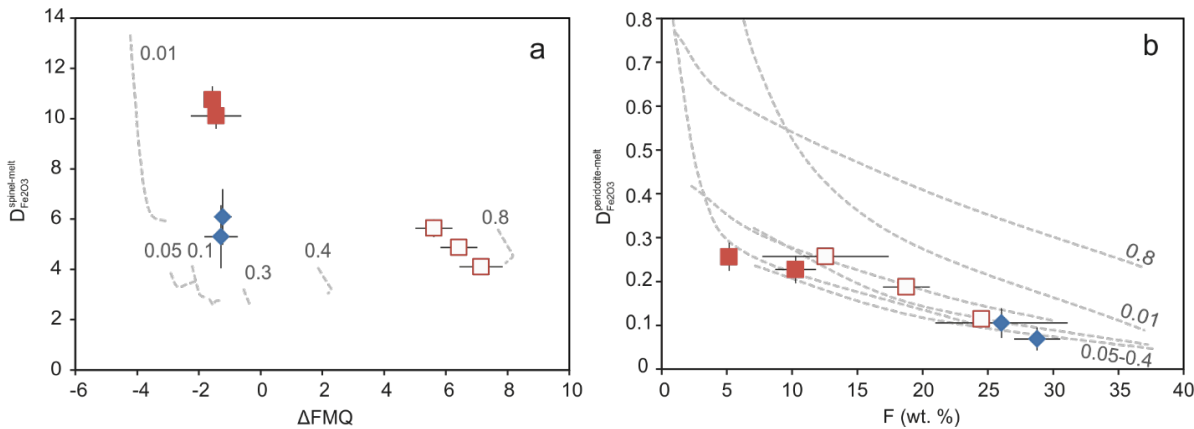


Figure 2. Experimentally determined mineral/melt partition coefficients for Fe₂O₃ compared with values determined using pMELTS calculations (dotted curves) for partial melting of MPY-90 at 1.5GPa. Bulk Fe³⁺/ΣFe ratios for model calculations range from 0.01 to 0.8 (numbers next to the curves). (a) $D_{Fe_2O_3}^{spinel-melt}$ as a function of fO_2 (ΔFMQ). (b) The bulk $D_{Fe_2O_3}^{peridotite-melt}$ as a function of partial melting degree (F [wt.%]).

Overall, there appears to be a correlation between oxygen fugacity (i.e. Fe₂O₃ content of an experimental glass) and the degree of partial melting of peridotite (Fig. 2). This is explained by the presence of water in the more oxidized experiments revealed by Fourier-Transform Infrared (FTIR) measurements. At a given fO_2 , the Fe³⁺/ΣFe ratio in melts remains quite constant with partial melting degree. This is explained by a slight decrease of the bulk partition coefficient of Fe₂O₃ ($D_{Fe_2O_3}^{peridotite-melt}$) as the degree of partial melting increases. The Fe³⁺/ΣFe ratios of resulting melts are thus restricted to a relatively narrow range over large degrees of melting, as observed for global MORB glass analyses. This observation is also confirmed by pMELTS calculations employing different bulk Fe³⁺/ΣFe ratios. We conclude that the Fe³⁺ content in MORB can be accounted for by a bulk $D_{Fe_2O_3}^{peridotite-melt}$ ranging from 0.3 to 0.1 through partial melting and a mantle source containing 0.1-0.5 wt. % Fe₂O₃.

Results of this study were presented at the Goldschmidt Conference 2015 (Sorbadere et al.¹⁵). **A manuscript resulting from this work were submitted to Geochimica et Cosmochimica Acta in 03/2017, i.e.:**

Sorbadere, F., Laurenz, V., Frost, D.J., Wenz, M., Rosenthal, A., McCammon, C., Rivard, C. (submitted). [The behaviour of ferric iron during partial melting of peridotite](#). *Submitted to Geochimica et Cosmochimica Acta in 03/2017*.

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