

## Experimental investigation of basalt and peridotite oxybarometers: Implications for spinel thermodynamic models and Fe<sup>3+</sup> compatibility during generation of upper mantle melts

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### ABSTRACT

Peridotites dredged from mid-ocean ridges and glassy mid-ocean ridge basalts (MORB) transmit information about the oxygen fugacity ( $f_{O_2}$ ) of Earth's convecting upper mantle to the surface. Equilibrium assemblages of olivine+orthopyroxene+spinel in abyssal peridotites and Fe<sup>3+</sup>/ΣFe ratios in MORB glasses measured by X-ray absorption near-edge structure (XANES) provide independent estimates of MORB source region  $f_{O_2}$ , with the former recording  $f_{O_2}$  approximately 0.8 log units lower than the latter relative to the quartz-fayalite-magnetite (QFM) buffer. To test cross-compatibility of these oxybarometers and examine the compositional effects of changing  $f_{O_2}$  on a peridotite plus melt system over a range of Earth-relevant  $f_{O_2}$ , we performed a series of experiments at 0.1 MPa and  $f_{O_2}$  controlled by CO-CO<sub>2</sub> gas mixes between QFM-1.87 and QFM+2.23 in a system containing basaltic andesite melt saturated in olivine, orthopyroxene, and spinel.

Oxygen fugacities recorded by each method are in agreement with each other and with the  $f_{O_2}$  measured in the furnace. Measurements of  $f_{O_2}$  from the two oxybarometers agree to within 1σ in all experiments. These results demonstrate that the two methods are directly comparable and differences between  $f_{O_2}$  measured in abyssal peridotites and MORB result from geographic sampling bias, petrological processes that change  $f_{O_2}$  in these samples after separation of melts and residues, or abyssal peridotites may not be residues of MORB melting.

As  $f_{O_2}$  increases, spinel Fe<sup>3+</sup> concentrations increase only at the expense of Cr from QFM-1.87 to QFM-0.11. Above QFM, Al is also diluted in spinel as the cation proportion of Fe<sup>3+</sup> increases. None of the three spinel models tested, MELTS (Ghiorso and Sack 1995), SPINMELT (Ariskin and Nikolaev 1996), and MELT\_CHROMITE (Poustovetov and Roeder 2001), describe these compositional effects, and we demonstrate that MELTS predicts residues that are too oxidized by >1 log unit to have equilibrated with the coexisting liquid phase. Spinel generated in this study can be used to improve future thermodynamic models needed to predict compositional changes in spinels caused by partial melting of peridotites in the mantle or by metamorphic reactions as peridotites cool in the lithosphere.

In our experimental series, where the ratio of Fe<sub>2</sub>O<sub>3</sub>/FeO in the melt varies while other melt compositional parameters remain nearly constant, experimental melt fraction remains constant, and Fe<sup>3+</sup> becomes increasingly compatible in spinel as  $f_{O_2}$  increases. Instead of promoting melting, increasing the bulk Fe<sup>3+</sup>/ΣFe ratio in peridotite drives reactions analogous to the fayalite-ferrosilite-magnetite reaction. This may partly explain the absence of correlation between Na<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub> in fractionation-corrected MORB.

**Keywords:** Oxygen fugacity, XANES, spinel peridotite oxybarometry, electron microprobe, experimental petrology, MORB, abyssal peridotite, MELTS