

A quantitative model for interpreting $\text{Fe}^{3+}/\Sigma\text{Fe}$ heterogeneity in basalts

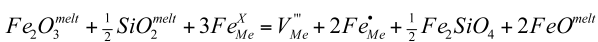
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The application of X-ray absorption near edge structure (XANES) spectroscopy to determine the oxidation state of Fe in submarine glasses and olivine-hosted melt inclusions has provided important new insights into $\text{Fe}^{3+}/\Sigma\text{Fe}$ heterogeneity in the Earth's upper mantle [1,2]. Interpreting this variability requires a thorough understanding of the behavior of Fe^{3+} during the generation and transport of partial melt in the mantle. Quantifying this behavior involves consideration of both point defect equilibria in the solid and the temperature, pressure, and composition dependence of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the melt. Modeling Fe^{3+} as a trace element using partition coefficients and equations for partial melting does not accurately capture its behavior.

At equilibrium, the distribution of Fe^{3+} and Fe^{2+} between olivine and silicate melt is described by the reaction:



where, in Kröger-Vink notation, and and are Fe^{2+} and Fe^{3+} , respectively, occupying octahedral lattice sites. This reaction constrains the mass balance of O^{2-} between olivine and melt. The equilibrium concentration of in olivine is given by the model of Dohmen and Chakraborty [3], while Fe^{3+} in the melt is described by Equation 6 of Kress and Carmichael [4]. Spinel lherzolite partial melting is modelled following Kinzler [5].

Results from these calculations indicate that for the most incompatible case (i.e. all Fe^{3+} resides in olivine), the concentration of Fe^{3+} in the melt initially increases, and then decreases between 1 and 20% partial melting. This behavior reflects changes to the bulk Fe concentration of the melt as well as the mass balance of O^{2-} between solid and melt. The f_{O_2} recorded by $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the melt steadily decreases with increasing extent of melting, but this effect is damped once Fe^{3+} residing in pyroxene and spinel is considered. At low melt-to-rock ratios, interaction between percolating melt and olivine in dunite channels can affect $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the melt.

- [1] Kelly & Cottrell (2009), *Science* **325**, 605-607 [2] Cottrell & Kelly (2011), *Earth Planet Sci Lett* **305**, 270-282 [3] Dohmen & Chakraborty (2007), *Phys Chem Min* **34**, 409-430. [4] Kress & Carmichael (1991), *Contrib Mineral Petrol* **108**, 82-92. [5] Kinzler (1997), *J Geophys Res* **102**, 853-874