

## The effect of composition on Cr<sup>2+</sup>/Cr<sup>3+</sup> in silicate melts

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### ABSTRACT

Chromium *K*-edge X-ray absorption near-edge structure (XANES) spectra were recorded at room temperature for 27 CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) glass compositions quenched from melts equilibrated at various oxygen fugacities ( $f_{O_2}$ ) at 1400 °C. Values of Cr<sup>2+</sup>/ΣCr were determined from the intensity of a shoulder on the main absorption edge, attributed to the 1s → 4s transition, which is characteristic of Cr<sup>2+</sup> in these glasses. For each composition, Cr<sup>2+</sup>/ΣCr could be quantified as a function of  $f_{O_2}$ , using a theoretical expression, from as few as three samples (Cr<sup>2+</sup>/ΣCr ≈ 0, 0.5, and 1). This allowed log*K'*, or the reduction potential of the Cr<sup>3+/2+</sup> half-reaction, and hence the relative change in the ratio  $\gamma_{Cr^{3+}O_{1.5}}^{melt} / \gamma_{Cr^{2+}O}^{melt}$ , to be determined for each composition. At constant  $f_{O_2}$ , log[Cr<sup>2+</sup>/Cr<sup>3+</sup>] was found to decrease linearly with increasing optical basicity. The variation in log*K'* with composition is controlled by  $\gamma_{Cr^{2+}O_{1.5}}^{melt}$ , corresponding to the capacity of the melt to stabilize both the charge and the preferred solvation site of Cr<sup>3+</sup>. The method was then applied to spectra recorded in situ at 1400 °C for a synthetic mid-ocean ridge basalt (MORB) composition, allowing Cr<sup>2+</sup>/ΣCr to be quantified in a Fe-bearing melt for the first time. Cr<sup>2+</sup>/ΣCr was found to vary from ~0.45 at the nickel-nickel oxide (NNO)  $f_{O_2}$  buffer to ~0.90 at iron-wüstite (IW). This indicates that Cr<sup>2+</sup> is likely to be the dominant oxidation state in terrestrial basaltic melts.

**Keywords:** XANES spectroscopy, chromium oxidation states, silicate melts, MORB