The effect of composition on Cr\(^{2+}\)/Cr\(^{3+}\) 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\(_2\)O\(_3\)-SiO\(_2\) (CMAS) glass compositions quenched from melts equilibrated at various oxygen fugacities (\(f_{\text{O}_2}\)) at 1400 °C. Values of Cr\(^{2+}\)/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\(^{3+}\) in these glasses. For each composition, Cr\(^{2+}\)/ΣCr could be quantified as a function of \(f_{\text{O}_2}\), using a theoretical expression, from as few as three samples (Cr\(^{2+}\)/ΣCr = 0, 0.5, and 1). This allowed log\(K_f\), or the reduction potential of the Cr\(^{3+/2+}\) half-reaction, and hence the relative change in the ratio \(\Delta\Sigma\text{Cr}_{\text{O}_2}/\Delta\Sigma\text{Cr}_{\text{O}_2}\) to be determined for each composition. At constant \(f_{\text{O}_2}\), log[Cr\(^{2+}\)/Cr\(^{3+}\)] was found to decrease linearly with increasing optical basicity. The variation in log\(K_f\) with composition is controlled by \(\gamma_{\text{CrO}_2}\), corresponding to the capacity of the melt to stabilize both the charge and the preferred solvation site of Cr\(^{3+}\). The method was then applied to spectra recorded in situ at 1400 °C for a synthetic mid-ocean ridge basalt (MORB) composition, allowing Cr\(^{2+}\)/ΣCr to be quantified in a Fe-bearing melt for the first time. Cr\(^{2+}\)/ΣCr was found to vary from ~0.45 at the nickel-nickel oxide (NNO) \(f_{\text{O}_2}\) buffer to ~0.90 at iron-wüstite (IW). This indicates that Cr\(^{2+}\) is likely to be the dominant oxidation state in terrestrial basaltic melts.

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

INTRODUCTION

Chromium occurs exclusively as Cr\(^{3+}\) in minerals crystallized at mantle oxygen fugacities (\(f_{\text{O}_2}\)) values (Burns and Burns 1975). If Cr were to occur as both Cr\(^{3+}\) and Cr\(^{2+}\) in mantle melts, the crystal-melt partition coefficients would be expected to exhibit anomalous behavior relative to those of elements that occur in a single valence state; which may account for the early crystallization of chromite from basalts (Li et al. 1995). The presence of Cr\(^{3+}\) at values of terrestrial \(f_{\text{O}_2}\) has been known for some time (Schreiber and Haskin 1976). The importance of Cr\(^{3+}\) in Fe-bearing compositions, however, has been less clear. Although crystal-melt partitioning experiments strongly indicate that Cr\(^{3+}\) does occur in Fe-bearing melts (e.g., Barnes 1986; Hanson and Jones 1998; Pousovetov and Roeder 2000), this oxidation state has never been observed directly in a single valence state; which may account for the early crystallization of chromite from basalts (Li et al. 1995).

The abundance of Fe relative to Cr indicates there will always be sufficient Fe\(^{3+}\), at terrestrial \(f_{\text{O}_2}\) values, to completely react with, and remove, Cr\(^{2+}\) on cooling. Recently a XANES method for quantifying Cr\(^{2+}\)/ΣCr in glasses has been presented (Berry and O’Neill 2004). A shoulder on the main absorption edge systematically changes intensity with \(f_{\text{O}_2}\), and must relate to, and can be used to quantify, the oxidation state of Cr. The intensity of this shoulder was determined for five CaO-MgO-Al\(_2\)O\(_3\)-SiO\(_2\) (CMAS) compositions (plus one containing TiO\(_2\)) equilibrated at ~20 values of log\(f_{\text{O}_2}\) (between −0.68 and −16.13 at 1400 °C) and fit to a thermodynamically derived expression (see section on XANES analysis), allowing Cr\(^{2+}\)/ΣCr to be evaluated for each sample. The good agreement between the data and the fit suggests that it should be possible to determine the dependence of Cr\(^{2+}\)/ΣCr on log\(f_{\text{O}_2}\) from a more limited number of data points. Indeed, samples prepared under conditions where Cr\(^{2+}\)/ΣCr = 0, 0.5, and 1 should be sufficient, making the investigation of a large range of melt compositions feasible.

In the present study, Cr K-edge XANES spectra were recorded for glasses of 27 compositions quenched from melts equilibrated at 1400 °C and log\(f_{\text{O}_2}\) values of −2 (Cr\(^{2+}\)/ΣCr ~ 0), −7, −9 (Cr\(^{2+}\)/ΣCr < 0.5) and 0.5. This indicates that Cr\(^{2+}\) is likely to be the dominant oxidation state in terrestrial basaltic melts.