

A XANES determination of the oxidation state of chromium in silicate glasses

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ABSTRACT

Cr *K*-edge X-ray absorption near-edge structure (XANES) spectra were recorded for silicate glasses of various compositions in the system $\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3 + \text{SiO}_2 \pm \text{TiO}_2$, quenched from melts equilibrated as a function of oxygen fugacity (f_{O_2}) at 1400 °C. The spectra vary systematically with f_{O_2} ($\log f_{\text{O}_2} \sim 0$ to -16) indicating changes in the Cr oxidation state. The intensity of a shoulder on the absorption edge (attributed to the $1s \rightarrow 4s$ transition) was quantified using the corresponding peak in the XANES derivative spectrum and used to determine $\text{Cr}^{2+}/\Sigma\text{Cr}$. The resulting $\text{Cr}^{2+}/\Sigma\text{Cr}$ values are in agreement with the theoretical dependence on $\log f_{\text{O}_2}$, suggesting that the $1s \rightarrow 4s$ feature is diagnostic of Cr^{2+} in a silicate glass and $\sigma(\text{Cr}^{2+}/\Sigma\text{Cr}) = \pm 0.015$. The $\text{Cr}^{2+}/\Sigma\text{Cr}$ ratio for a given $\log f_{\text{O}_2}$ changes with the glass composition which may reflect the ability of the melt to accommodate the Jahn-Teller distorted coordination geometry which stabilizes Cr^{2+} . $\text{Cr}^{2+}/\Sigma\text{Cr}$ varies between ~ 0.3 and 0.8 over the $\log f_{\text{O}_2}$ range bounded by the Ni/NiO and Fe/FeO f_{O_2} buffers, suggesting that Cr^{2+} may be important in natural melts even though this oxidation state has never been identified in a terrestrial material. The development of a methodology for determining $\text{Cr}^{2+}/\Sigma\text{Cr}$ from XANES spectra of quenched glasses is an essential precursor to in situ experiments on Fe-bearing silicate melts at high temperature.