

In-situ Determination of Cation Oxidation States in Silicate Melts at Temperatures to 1750 K

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The oxidation state of transition metal cations is a sensitive indicator of the redox conditions under which a melt solidified and is important for understanding the partitioning between a melt and the residual solid. In natural melt compositions, oxidation states at elevated temperatures are poorly known due to the possibility of redox reactions on quenching to a glass. For example, Cr²⁺ oxidises to Cr³⁺ in the presence of Fe³⁺ on cooling ($\text{Cr}^{2+} + \text{Fe}^{3+} = \text{Cr}^{3+} + \text{Fe}^{2+}$). This Cr/Fe redox interaction may explain why all Cr occurs as Cr³⁺ in terrestrial basaltic glasses (which contain Fe³⁺) even though Cr²⁺ occurs in analogous Fe-free systems at typical terrestrial oxygen fugacities. The absence of Fe³⁺ in the more reducing lunar environment enables Cr²⁺ to persist in lunar samples. The importance of Cr²⁺ at elevated temperatures in terrestrial basaltic or komatiitic magmas is that it increases the solubility of Cr in the melt by suppressing chrome-spinel stability.

XANES spectroscopy can be used to determine and quantify oxidation states using the position and intensity of pre-edge features. To record spectra of silicate melts, a high temperature X-ray absorption spectroscopy furnace has been designed and constructed. The water cooled furnace contains radiation shielding surrounding a Pt/Rh heater wound on an alumina tube. The windows are made of aluminised mylar allowing excellent fluorescence transmission but almost no radiative

heat. Samples of glass spheres are suspended in the furnace on loops of Pt or Re wire. The samples remain suspended at temperatures above their melting point due to the high viscosity of the melts. The oxygen fugacity inside the furnace can be defined by a variable CO/CO₂ atmosphere using mass-flow controllers. Spectra were recorded in fluorescence mode at the Australian National Beamline Facility, Photon Factory, Japan.

Cr K-edge XANES spectra have been recorded for a number of compositions. Variations in oxidation state with changes in oxygen fugacity were observed at temperatures up to 1750 K and monitored as a function of time. The time required for equilibration after a change in oxygen fugacity or temperature depended upon the total concentration of redox active species (Fe and Cr) but was typically less than 30 minutes for natural compositions. At high oxygen fugacities and low temperatures a spectrum characteristic of Cr in the spinel structure was observed. This is consistent with the reduced solubility of Cr in a silicate melt under these conditions. The oxygen fugacity at which spinel crystallisation occurs for a given temperature varies with composition and can be reversibly determined.

New results quantifying the effect of temperature on the stability of Cr²⁺ in the presence of Fe³⁺ will be discussed.