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The Oxidation State of Chromium in Silicate Glasses as a Function of Oxygen Fugacity, Composition, Temperature, and Pressure

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Cr K-edge XANES spectra were used to determine the Cr^{2+}/Cr^{3+} oxidation state ratio of Fe-free silicate glasses in the system $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2 \pm TiO_2$ containing 0.5 wt% Cr_2O_3. Spectra were recorded in fluorescence mode at the Australian Nuclear Beamline Facility; Photon Factory, Japan. The XANES spectra were normalised to the main peak height to account for variations in total Cr concentration, sample alignment, and beam intensity.

The 1s-4s pre-edge transition is symmetry forbidden, but may gain intensity through orbital mixing in low symmetry environments. For the co-ordination freedom available in a glass, the high symmetry octahedral geometry favoured by Cr^{3+} results in this transition being weak or absent, whereas the transition becomes allowed in the Jahn-Teller distorted co-ordination common for Cr^{2+}. The main absorption edge and the edge crest also shift to higher energy with increasing oxidation state. The transition energies characteristic of various Cr oxidation states have been determined previously with reference to a series of standards (Sutton et al., 1993). Features in the absorption edge are most easily identified in a derivative spectrum, with the Cr^{2+} 1s-4s transition appearing as a peak near 5997 eV. Other peaks correspond to the 1s-3d transition and the main absorption edge. The variations in intensity or energy of all these features can be used to determine the Cr^{2+}/Cr^{3+} ratio, however, the narrow, intense 1s-4s derivative peak was found to be the most sensitive indicator of changes in oxidation state.

A series of calibration curves were produced using the height of the 1s-4s derivative peak for a number of compositions containing a known percentage of Cr^{2+}, prepared from a powdered mixture of glasses containing only Cr^{2+} ($-\log fO_2$ = 14) and only Cr^{3+} ($-\log fO_2$ = 2). This procedure allowed the $Cr^{2+}/\Sigma Cr$ content of glasses with similar composition to be determined within 5%. The calibration curves vary with melt composition indicating the sensitivity of the 1s-4s transition intensity to the co-ordination environment. For all compositions, the slope of $\log[Cr^{2+}/Cr^{3+}]$ against $\log fO_2$ is 0.25, within experimental error, as expected for the reaction:

$$CrO_{(melt)} + 0.25\ O_2 = 0.5\ Cr_2O_{3(melt)}.$$

Over 200 Cr XANES spectra have been recorded to allow the effects of oxygen fugacity, composition, temperature, pressure, and concentration to be determined. The importance of each of these variables will be discussed.

Sutton SR, Jones KW, Gordon B, Rivers ML, Bajt S & Smith JV, *Geochim.Cosmochim.Acta*, **57**, 461-468, (1993).