The effect of composition on Cr²⁺/Cr³⁺ 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-Al₂O₃-SiO₂ (CMAS) glass compositions equilibrated from melts at 1400 °C with various oxygen fugacities (fO₂) (Berry et al. 2003). Values of Cr²⁺/ΣCr were determined from the intensity of a shoulder on the main absorption edge, attributed to the 1s → 3s transition, which is characteristic of Cr²⁺ in these glasses. For each composition, Cr²⁺/ΣCr could be quantified as a function of fO₂ using a theoretical expression, from as few as three samples (Cr²⁺/ΣCr ≈ 0, 0.5, and 1). This allowed logKfO₂, or the reduction potential of the Cr³⁺/²⁺ half-reaction, and hence the relative change in redox potential, to be determined for each composition. At constant fO₂, log[Cr²⁺/Cr³⁺] was found to be nearly linear with increasing optical basicity. The variation in logKfO₂ with composition is controlled by the composition of the melt, where the abundance of Fe relative to Cr indicates the redox state of Cr in the melt. The method was then applied to spectra recorded in situ at 1400 °C for a synthetic mid-ocean ridge basalt (MORB) composition, allowing Cr²⁺/ΣCr to be determined in a Fe-bearing melt for the first time. Cr²⁺/ΣCr was found to vary from ~0.45 at the nickel-nickel oxide (NNO) fO₂ buffer to ~0.90 at iron-wüstite (IW). This indicates that Cr²⁺ 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 Cr³⁺ in minerals crystallized at mantle oxygen fugacities (fO₂) values (Burns and Burns 1975). If Cr were to occur as both Cr³⁺ and Cr²⁺ 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 Cr²⁺ at values of terrestrial fO₂ (between –2 and –7) has been known for some time (Schreiber and Haskin 1976). The importance of Cr²⁺ in Fe-bearing compositions, however, has been less clear. Although crystal-melt partitioning experiments strongly indicate that Cr³⁺ does occur in Fe-bearing melts (e.g., Burns 1986; Hanson and Jones 1998; Poustovetov and Roeder 2000), this oxidation state has never been observed directly in a terrestrial material. Indeed, it has been argued that Cr²⁺ does not occur in basaltic glasses and melts due to the difference in redox potentials of Cr³⁺ and Fe³⁺, which suggests that only Fe³⁺ and Cr³⁺ should coexist at values of terrestrial fO₂ (Schreiber and Haskin 1976; Schreiber et al. 1987). Recently, it has been shown by in situ X-ray absorption near-edge structure (XANES) spectroscopy of a synthetic mid-ocean ridge basalt (MORB) composition, as a function of variable fO₂ (terrestrial values) at 1200–1400 °C, that Cr²⁺ is a significant oxidation state in the melt (Berry et al. 2003). Cr²⁺ is, however, retained on quenching to a glass due to an electron exchange reaction with Fe³⁺ (Cr²⁺ + Fe³⁺ → Cr³⁺ + Fe²⁺), suggesting that this reaction, or the difference in redox potentials, is temperature dependent. The abundance of Fe relative to Cr indicates there will always be sufficient Fe³⁺, at terrestrial fO₂, values, to completely react with, and remove, Cr²⁺ on cooling.

Recently a XANES method for quantifying Cr²⁺/ΣCr in glasses has been presented (Berry and O’Neill 2004). A shoulder on the main absorption edge systematically changes intensity with fO₂, 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-Al₂O₃-SiO₂ (CMAS) compositions (plus one containing TiO₂) equilibrated at ~20 values of logfO₂ (between –0.68 and –16.13 at 1400 °C) and fit to a thermodynamically derived expression (see section on XANES analysis), allowing Cr²⁺/ΣCr to be evaluated for each sample. The agreement between the data and the fit suggests that it should be possible to determine the dependence of Cr²⁺/ΣCr on logfO₂ from a more limited number of data points. Indeed, samples prepared under conditions where Cr²⁺/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 logfO₂ values of ~2 (Cr²⁺/ΣCr ~ 0), –7, –9 (Cr²⁺/ΣCr

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~ 0.5), and −16.1 (Cr²⁺/ΣCr ~ 1). All the compositions are Fe-free to enable samples to be studied as quenched glasses that preserve the high-temperature Cr oxidation state ratio. This study should provide insight into the compositional parameters that stabilize Cr²⁺ and/or Cr³⁺ and allow Cr²⁺/ΣCr for natural compositions to be predicted. This was tested using available 1400 °C in situ data for an Fe-bearing MORB melt.

**EXPERIMENTAL METHODS**

Glasses were prepared with 27 different compositions from reagent grade SiO₂, Al₂O₃, MgO, and CaCO₃, to which 0.5 wt% Cr₂O₃ was added. The glasses comprise compositional series previously described and referred to as AD6, CMAS7, CAS/MAS, Longhi6, and Osborn6 (O’Neill and Eggins 2002; O’Neill and Mavrogenes 2002; O’Neill and Berry 2006). The compositions were suspended on loops of either Pt or Re in a gas-mixing vertical tube furnace at 1400 °C and equilibrated with mixtures of O₂/CO₂ (logf O₂ = −16.13 and a Cr₂O₃ solubility of ~0.5 wt% in the melt (O’Neill and Berry 2006). After at least 24 h (72 h for those in equilibrium with Cr₂C₂) all samples were quenched in water to produce glasses, mounted in epoxy, and polished. For the samples equilibrated at logf O₂ = −16.13, any Cr₂C₂ associated with the glass was identified readily by optical microscopy and marked with Pb tape. Further experimental details are given in Berry and O’Neill (2004). The averages of the logf O₂ = −2, −7, and −9 samples for the 27 compositions determined by energy-dispersive electron microprobe analysis, are given in Table 1. An Fe-bearing MORB composition (in wt%: SiO₂ = 51.8, Al₂O₃ = 16.0, CaO = 12.3, FeO = 10.0, MgO = 8.2, TiO₂ = 1.3, Cr₂O₃ = 0.5) was studied at 1400 °C using a furnace designed for in situ XANES spectroscopy of silicate melts (Berry et al. 2003).

Cr K-edge XANES spectra were recorded in fluorescence mode at the Australian National Beamline Facility, Beamline 2B (bending magnet) at the 2.5 GeV Photon Factory (KEK, Tsukuba, Japan). The excitation energy was selected using a Si(111) channel cut crystal monochromator, resulting in a spectral energy resolution (when coupled with the CrKα core-hole width) of 2 eV. Fluorescence was recorded using a Canberra GL0110S 10 element Ge array detector. The energy was calibrated by defining the first derivative peak of Cr in stainless steel foil to be 5989.2 eV. Spectra were recorded from 5985–6025 eV with a step size of 0.25 eV. For further details see Berry and O’Neill (2004).

**TABLE 1.** Average glass compositions expressed as wt% with respect to the fugacity of CO₂, excluding −0.5 wt% Cr₂O₃; the structural parameter NBO/T and the optical basicity; the 1s → 4s derivative peak areas (A₁s/4s) and corresponding Cr²⁺/ΣCr for four values of logf O₂ parameters obtained from the fit to Equation 6 (α₃, α₅, and logk); and activity coefficients (γCr) (see text for definition)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>NBO/T</th>
<th>Basicity</th>
<th>logf O₂ = −2</th>
<th>( \frac{\Sigma}{\alpha} ) Cr²⁺</th>
<th>( \frac{\Sigma}{\alpha} ) Cr³⁺</th>
<th>( \frac{\Sigma}{\alpha} ) Cr³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>50.6(6)</td>
<td>15.1(3)</td>
<td>10.3(2)</td>
<td>24.0(7)</td>
<td>0.941</td>
<td>0.605</td>
<td>0.024*</td>
<td>0.038</td>
<td>0.2075</td>
<td>0.475</td>
</tr>
<tr>
<td>AD+Osborn1</td>
<td>47.1(2)</td>
<td>14.6(1)</td>
<td>13.4(1)</td>
<td>23.6(1)</td>
<td>1.117</td>
<td>0.612</td>
<td>0.013</td>
<td>0.035</td>
<td>0.284</td>
<td>0.673</td>
</tr>
<tr>
<td>AD+Osborn2</td>
<td>48.4(1)</td>
<td>14.6(1)</td>
<td>13.4(1)</td>
<td>23.6(1)</td>
<td>1.117</td>
<td>0.612</td>
<td>0.013</td>
<td>0.035</td>
<td>0.284</td>
<td>0.673</td>
</tr>
<tr>
<td>AD+Osborn3</td>
<td>52.3(1)</td>
<td>14.6(1)</td>
<td>13.4(1)</td>
<td>23.6(1)</td>
<td>1.117</td>
<td>0.612</td>
<td>0.013</td>
<td>0.035</td>
<td>0.284</td>
<td>0.673</td>
</tr>
<tr>
<td>AD+Osborn4</td>
<td>57.0(9)</td>
<td>14.2(1)</td>
<td>20.1(5)</td>
<td>8.7(1)</td>
<td>0.838</td>
<td>0.564</td>
<td>0.011</td>
<td>0.070</td>
<td>0.244</td>
<td>0.567</td>
</tr>
<tr>
<td>AD+Osborn5</td>
<td>63.4(2)</td>
<td>14.2(1)</td>
<td>4.7(1)</td>
<td>38.3(1)</td>
<td>1.474</td>
<td>0.632</td>
<td>0.020*</td>
<td>0.027</td>
<td>0.103</td>
<td>0.390</td>
</tr>
<tr>
<td>AD+Osborn6</td>
<td>64.6(3)</td>
<td>15.3(1)</td>
<td>10.4(2)</td>
<td>24.7(1)</td>
<td>0.941</td>
<td>0.605</td>
<td>0.024*</td>
<td>0.038</td>
<td>0.2075</td>
<td>0.475</td>
</tr>
<tr>
<td>AD+Osborn7</td>
<td>59.3(9)</td>
<td>12.6(6)</td>
<td>2.2(2)</td>
<td>25.9(2)</td>
<td>0.635</td>
<td>0.585</td>
<td>0.012</td>
<td>0.049</td>
<td>0.194</td>
<td>0.471</td>
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<tr>
<td>AD+Osborn8</td>
<td>61.9(8)</td>
<td>6.1(2)</td>
<td>13.5(4)</td>
<td>18.5(1)</td>
<td>1.057</td>
<td>0.581</td>
<td>0.017</td>
<td>0.083</td>
<td>0.219</td>
<td>0.582</td>
</tr>
<tr>
<td>AD+Osborn9</td>
<td>63.5(1)</td>
<td>14.6(1)</td>
<td>13.4(1)</td>
<td>23.6(1)</td>
<td>1.117</td>
<td>0.612</td>
<td>0.013</td>
<td>0.035</td>
<td>0.284</td>
<td>0.673</td>
</tr>
</tbody>
</table>

**Notes:** Uncertainties are one standard deviation; (logf O₂) = ±0.03; (logA₁s) = ±0.005; (Cr²⁺/ΣCr) = ±0.03; (\( \alpha_{Cr} \)) = ±0.03 (±0.04), (\( \alpha_{Cr} \)) = ±0.06 (±0.09). (logk) = ±0.04 (±0.06). (log(\( \alpha_{Cr} \))) = ±0.04 (±0.06); values in parentheses are uncertainties resulting from fits to only three data points. For compositions 1–5, the values in italics are those determined in Berry and O’Neill (2004).

* Samples containing Cr⁶⁺.
† Samples containing a Cr³⁺ crystalline phase (typically spinel); values omitted for spinel-rich samples.
‡ Samples containing Cr²⁺ and/or Cr³⁺.
¥ fix at 0.029.

**XANES ANALYSIS**

A shoulder on the K absorption edge of Cr in CMAS glasses increases in intensity with decreasing fO₂. This shoulder is attributed to the symmetry forbidden 1s → 4s transition of Cr²⁺ (Sutton et al. 1993), although the exact assignment is irrelevant for this work. The 1s → 4s transition is not observed for Cr⁶⁺ due to the strong preference for high-symmetry octahedral coordination (readily accommodated by the coordination freedom available in a melt), but is allowed for Cr²⁺ that occurs in a Jahn-Teller distorted environment (so as to remove the Cr ² electronic degeneracy); the shoulder is thus diagnostic of Cr²⁺. The intensity of the 1s → 4s transition is most easily quantified from the derivative spectrum in which the shoulder appears as a peak. The area of this peak (from 5991.3–5996.3 eV), denoted as A₁s/4s, is linearly

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- ‡ Samples containing Cr²⁺ and/or Cr³⁺.
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correlated with Cr²⁺/ΣCr resulting in the expression,
\[ \text{Cr}^{2+}/\Sigma\text{Cr} = a_0 + a_1\text{A}_{\text{incl}} \]  
(1)

where \(a_0\) and \(a_1\) are constants that depend on the melt composition. \(\text{Cr}^{2+}/\Sigma\text{Cr}\) is related to \(f_{\text{O}_2}\) by the reaction:
\[ \text{Cr}^{2+} + \frac{1}{4}\text{O}_2 = \text{Cr}^{3+} \]  
(2)

From the equilibrium constant, \(K\), for this reaction we obtain:
\[ \log K = \log \frac{X^{\text{melt}}}{Y^{\text{melt}}} + \frac{1}{4}\log f_{\text{O}_2} \]  
(3)

where \(X\) is the mole fraction and \(\gamma\) the activity coefficient. For low \(\Sigma\text{Cr}\), in this study, it may be assumed that \(Y^{\text{melt}}_\text{Cr}^{2+}\) and \(Y^{\text{melt}}_\text{Cr}^{3+}\) are constant for a given composition (Henry’s Law), and that \(\text{Cr}^{2+}-\text{Cr}^{3+}\) interactions are insignificant. It is then convenient to define a modified equilibrium constant, \(K'\), for the reaction referenced to a standard state of \(\text{Cr}^{2+}\) and \(\text{Cr}^{3+}\) at infinite dilution, such that:
\[ \log K' = \log K - \log \frac{\gamma^{\text{melt}}_\text{Cr}^{2+}}{\gamma^{\text{melt}}_\text{Cr}^{3+}} \]  
(4)

Rearrangement of Equation 3 then gives (Berry and O’Neill 2004),

\[ \frac{\text{Cr}^{2+}}{\Sigma\text{Cr}} = \frac{1}{1 + 10^{[\log f_{\text{O}_2} + \log K']}} \]  
(5)

This function has a sigmoidal form when \(\text{Cr}^{2+}/\Sigma\text{Cr}\) is plotted against \(\log f_{\text{O}_2}\); i.e., at low values of \(f_{\text{O}_2}\), \(\text{Cr}^{2+}/\Sigma\text{Cr}\) is constant and equal to 1, at high values of \(f_{\text{O}_2}\), \(\text{Cr}^{2+}/\Sigma\text{Cr}\) is constant and equal to 0, with the two extremes being connected by a transitional region where both \(\text{Cr}^{2+}\) and \(\text{Cr}^{3+}\) coexist. The \(\log f_{\text{O}_2}\) range over which the oxidation of \(\text{Cr}^{2+}\) to \(\text{Cr}^{3+}\) occurs, or the “slope” of the sigmoidal curve, is controlled by the number of electrons involved in the reaction (one in this case) and is described by the 1/4 coefficient in Equation 5. The position of the curve relative to the \(\log f_{\text{O}_2}\) axis is given by the \(\log K'\) term. \(-\log K'\) is defined as the electrochemical reduction potential \((E'_{0})\) of a metal in a melt (Schreiber 1987). Combining Equations 1 and 5 gives
\[ A_{\text{incl}} = \frac{1}{a_1} \left[ 1 + 10^{[\log f_{\text{O}_2} + \log K'] - a_0} \right]\]  
(6)

Using this equation it is possible to determine \(K'\), \(a_0\), and \(a_1\) (and hence \(\text{Cr}^{2+}/\Sigma\text{Cr}\)) from a series of XANES spectra prepared over a range of \(\log f_{\text{O}_2}\). In our previous work (Berry and O’Neill 2004), \(A_{\text{incl}}\) values were determined for five compositions at \(\sim 20\) values of \(\log f_{\text{O}_2}\). The resulting fits to Equation 6 were excellent and verified the assumptions used in deriving this equation, including both Henry’s Law behavior and the linear relationship between \(\text{Cr}^{2+}/\Sigma\text{Cr}\) and \(A_{\text{incl}}\). The relative stability of \(\text{Cr}^{3+}\) in a particular melt composition is given by the \(\log K'\) value, which displayed substantial variability: i.e., \(\text{Cr}^{2+}/\Sigma\text{Cr}\) varied between \(\sim 0.3\) and 0.7 at NNO-2 for the compositions studied. This indicates a significant compositional effect on either \(\gamma^{\text{melt}}_\text{Cr}^{2+}\) or \(\gamma^{\text{melt}}_\text{Cr}^{3+}\).

The small errors in \(\log f_{\text{O}_2}\) and \(A_{\text{incl}}\), and the resulting good agreement between the data and fit [resulting in \(\sigma(\text{Cr}^{2+}/\Sigma\text{Cr}) = 0.015\)], indicate that the sigmoidal curve, and hence \(K'\), may be defined from samples prepared under conditions where \(\text{Cr}^{2+}/\Sigma\text{Cr} = 0.5, 0, 1\); and the values of \(A_{\text{incl}}\) at \(\text{Cr}^{2+}/\Sigma\text{Cr} = 0\) and 1 effectively define \(a_0\) and \(a_1\), whereas that at 0.5 will constrain \(\log K'\). An extra point in the region where \(\text{Cr}^{2+}/\Sigma\text{Cr}\) is changing rapidly will improve the accuracy of the method.

**RESULTS**

The samples are typically optically transparent and homogeneous, and vary in color from blue (reduced) to green (oxidized). Some samples, most commonly those equilibrated at \(\log f_{\text{O}_2} = -7\), contain crystals of a \(\text{Cr}^{3+}\) phase (usually spinel). Glasses equilibrated at \(\log f_{\text{O}_2} = -2\) and \(-16.1\) lost variable amounts of \(\text{Cr}\) which will not affect the results since we are in the Henry’s Law region and \(\text{SiO}_2\) up to 2 wt%; see O’Neill and Berry 2006) respectively, by volatility.

Chromium K-edge XANES spectra for several glasses are shown in Figure 1. For all spectra a constant baseline was subtracted followed by normalization to the edge crest (maximum intensity). Although it is more common to normalize spectra to fluorescence above the edge, crest normalization is part of an established procedure for quantifying \(\text{Cr}^{3+}/\Sigma\text{Cr}\) in which the predicted relationship between \(\text{Cr}^{2+}/\Sigma\text{Cr}\) and \(f_{\text{O}_2}\) is obtained within extremely precise experimental error (Berry and O’Neill 2004). Figure 1a shows spectra for six compositions equilibrated at

![Figure 1](image-url)
log$_{f_{O_2}}$ = –9. The 1s → 4s transition of Cr$^{4+}$ appears as a shoulder on the absorption edge (Fig. 1a) and a peak in the derivative spectrum (Fig. 1b). The area of this peak, $A_{1s4s}$, (determined between the dashed lines) is linearly correlated with Cr$^{2+}/Σ$Cr. Although $A_{1s4s}$ varies for a given value of Cr$^{2+}/Σ$Cr with composition, to first order, the spectra in Figures 1a and 1b suggest significant differences in Cr$^{2+}/Σ$Cr, at constant $f_{O_2}$, for each glass.

Samples were prepared at four values of log$_{f_{O_2}}$ (–2, –7, –9, and –16.1) and a typical set of spectra for one composition is given in Figure 1c. For increasing $f_{O_2}$, the spectra exhibit a decrease in 1s → 4s transition intensity and an increase in edge energy, as expected for an increase in Cr$^{4+}$ relative to Cr$^{2+}$. The corresponding derivative spectra are shown in Figure 1d, and the areas of the 1s → 4s peaks at all values of log$_{f_{O_2}}$, for all compositions, are given in Table 1. The uncertainty in $A_{1s4s}$ was estimated previously (Berry and O’Neill 2004), for spectra recorded and processed in an identical fashion, as ±0.005 and that in log$_{f_{O_2}}$, as ±0.03 (all errors reported in this paper are quoted as one standard deviation). The presence of Cr$^{4+}$ or Cr-rich spinel in some samples was readily identified by characteristic spectral features; a 1s → 3d pre-edge peak for Cr$^{4+}$, and a shoulder and crest shift for Cr-spinel (Berry and O’Neill 2004). These glasses are indicated in Table 1. The presence of spinel should have no effect on the Cr$^{2+}/Σ$Cr ratio of the melt since the equilibrium between the melt and oxygen buffer (Eq. 2) is independent of this phase. The decrease in the Cr content of the melt resulting from spinel crystallization also has no effect because of Henry’s Law. The presence of a spinel contribution to the XANES spectrum, however, will result in an $A_{1s4s}$ value inconsistent with Cr$^{2+}/Σ$Cr of the melt. For spinel containing samples prepared at log$_{f_{O_2}}$ = –2 (Cr$^{2+}/Σ$Cr ~ 0) the $A_{1s4s}$ values are given in Table 1 since the effect on Cr$^{2+}/Σ$Cr is likely to be small. Spinel is rare at this $f_{O_2}$, presumably because crystallization is suppressed by the volatile loss of Cr from the melt. The $A_{1s4s}$ values are omitted for spinel contaminated samples prepared at log$_{f_{O_2}}$ = –7. The Cr$^{4+}$ contribution is weak in all cases and is not expected to affect $A_{1s4s}$ significantly (Berry and O’Neill 2004). The spectra of two samples equilibrated at log$_{f_{O_2}}$ = –16.1 also indicate a contribution from Cr$_2$O$_3$ (19 and 22).

The $A_{1s4s}$ values were fit to Equation 6. In most cases, the fit is excellent and an example is shown in Figure 2a (solid symbols). The equation is only unable to fit the data adequately when one of the points is for a sample containing Cr-spinel (Fig. 2a; open symbols); if that point is excluded, then the fits are consistent with those of the other data sets. The fit parameters have large uncertainties (e.g., log$_{f_{O_2}}$, $\alpha_1$, and log$K’$, together with the resulting values of Cr$^{2+}/Σ$Cr determined using Equation 1, are given in Table 1. The relationship between Cr$^{2+}/Σ$Cr and log$_{f_{O_2}}$, defined by the value of log$K’$ (Eq. 5) is shown in Figure 2b for several compositions. The uncertainty in Cr$^{2+}/Σ$Cr was estimated as ±0.03 by scaling the value of ±0.015 determined in Berry and O’Neill (2004) for the reduced number of data. If this uncertainty is propagated through Equation 5, the expected error in log$K’$ is ±0.04 for fits to four data points and ±0.06 for fits to three points.

Cr K-edge XANES spectra for a synthetic MORB recorded in situ at 1400 °C and log$_{f_{O_2}}$ values of –6, –7, –8, –9, and –10 have been reported previously (see Fig. 3b of Berry et al. 2003). The spectra were treated in an identical manner as for the glasses described here. The derivative peak areas for each value of log$_{f_{O_2}}$ are given in Table 2 and were fit to Equation 6. The resulting parameters have large uncertainties (e.g., log$K’$ = 1.59 ± 0.12). This is due to the absence of data at very high and low $f_{O_2}$ values.

**Figure 1.** (a) Cr K-edge XANES spectra for compositions (in order of increasing edge energy) 10, 19, 17, 14, 12, and 24, quenched from 1400 °C and log$_{f_{O_2}}$ = –9, and (b) the corresponding derivative spectra. The feature attributed to the 1s → 4s transition of Cr$^{4+}$ is indicated. The integral range used to determine the area of the 1s → 4s peaks in the derivative spectra ($A_{1s4s}$) is shown by the dashed lines. (c) Cr K-edge XANES spectra for composition 18 equilibrated at the values of log$_{f_{O_2}}$ indicated, and (d) the derivative spectra.
The effect of melt composition on stabilizing one oxidation state of Cr is well known (e.g., Morris and Haskin 1974; Kilinc et al. 1983; Dickenson and Hess 1986; Schreiber et al. 1994; Jayasuriya et al. 2004). In general terms, more basic compositions (less polymerization) stabilize higher oxidation states (Schreiber et al. 1994). This is attributed to the increase in the average negative charge of variables. The average difference in log $f_{O_2}$ as suggested by Berry and O’Neill (2004), to reduce the number of variables. The average difference in log $f_{O_2}$ is also given in Table 1. The four-point method also yields satisfactory results. If $a_0$ is set to 0.029 and evaluating as in Table 1, then log $K$ is 1.559 ± 0.028. Although $a_0$ for this composition may be slightly different from the average value, we suggest that a realistic uncertainty in log $K$ is ±0.05, similar to those determined for the Fe-free glasses. The resulting Cr$^{2+}$/ΣCr values and fit are plotted in Figure 2c.

The activity coefficients $\gamma_{CrO}^*$ calculated relative to composition AD (i.e., $\gamma_{CrO}^* = \gamma_{CrO}^0/\gamma_{CrO}^{1.5}$), have been determined at 1400 °C for the melt compositions used in this study (O’Neill and Berry 2006). From Equation 4, we define $\log \gamma_{CrO}^* = \log \gamma_{CrO}^0 − \log K + C$, where $C = \log K$, and then $\log \gamma_{CrO}^* = \log \gamma_{CrO}^0 − \log K$. The calculated activity coefficients $\log \gamma_{CrO}^*$ are given in Table 1. These relative coefficients can be quantitatively used to address the effect of melt composition on reaction 2.

**DISCUSSION**

Equation 6 provides excellent fits to the $A_{\text{obs}}$ values obtained for the four log $f_{O_2}$ conditions at which each composition was equilibrated. The equation, which is based on the $f_{O_2}$ dependence of Cr$^{2+}$/ΣCr in a melt, reassuringly cannot fit the data when one of the points is “contaminated” by a contribution from Cr in spinel or Cr$_2$O$_3$ (Fig. 2a). This suggests that the method is relatively robust. The fit parameters (log $K$, $a_0$, and $a_1$) are given in Table 1, together with those reported in Berry and O’Neill (2004) for compositions 1–5 obtained from fits to up to 16 points (italics in Table 1). Cr$^{2+}$/ΣCr values calculated for each glass using Equation 1 are also given in Table 1. The four-point fits result in larger log $K$ values, but the difference is approximately constant and relatively small (0.045 ± 0.015). Thus, although there may be a small error in the accuracy of the log $K$ values determined in this way, we do not expect significant errors in the relative precision. The data were also fit by fixing $a_0 = 0.029$ and evaluating $a_1$ as $(1 − a_0)/A_{\text{obs};\text{fit}}$ (from Eq. 1 assuming Cr$^{2+}$/ΣCr = 1 at log $f_{O_2}$ = −16), as suggested by Berry and O’Neill (2004), to reduce the number of variables. The average difference in log $K$ is only 0.02 (less than the average uncertainty) suggesting that this approximation method also yields satisfactory results.

Figure 2b shows how Cr$^{2+}$/ΣCr varies with log $f_{O_2}$ for several compositions. Clearly, at a constant log $f_{O_2}$ there is significant variability in Cr$^{2+}$/ΣCr arising from the different compositions of each glass, e.g., at log $f_{O_2}$ = −7, Cr$^{2+}$/ΣCr ranges from 0.23 to 0.70. The effect of melt composition on stabilizing one oxidation state relative to another for various elements, in particular Fe$^{2+}$/Fe$^{3+}$, is well known (e.g., Morris and Haskin 1974; Kilinc et al. 1983; Dickenson and Hess 1986; Schreiber et al. 1994; Jayasuriya et al. 2004). In general terms, more basic compositions (less polymerized due to the presence of network modifiers such as Ca, Mg, Na, and K) stabilize higher oxidation states (Schreiber et al. 1994). This is attributed to the increase in the average negative charge.
on each oxygen arising from largely ionic bonding between O and network modifiers (Ca, Mg, etc.) and more covalent bonding between O and network formers (e.g., Si, Al). The ionically bonded O atoms are better able to donate an electron pair (Lewis base), or electron density, and hence stabilize a highly charged cation. When electron donation to a cation exceeds that which can be accommodated, the cation either oxidizes to increase its charge (by reaction with the \( f_{\text{O}_2} \) buffer) or decreases its coordination number to reduce the number of electron donors (Baucke and Duffy 1991). The general concept has been described and quantified as optical basicity, in which the amount of negative charge received by a probe ion (such as \( \text{Ti}^{4+} \) or \( \text{Pb}^{2+} \)) in a glass composition is determined by optical absorption spectroscopy (Baucke and Duffy 1991). Studies of a large number of glasses have enabled optical basicity values for component oxides to be defined (Duffy 1993), allowing theoretical basicity values to be calculated for each composition (given in Table 1). The optical basicity description is successful for silicate slags and strong correlations with redox ratios have been found for alkali silicate glasses (Baucke and Duffy 1991; Duffy 1993). The correlation between \( \log[\text{Cr}^{3+}/\text{Cr}^{2+}] \) at \( \log_{f_{\text{O}_2}} = -9 \) determined in this work and the optical basicity of the compositions is shown in Figure 3. The points for those compositions for which the fits (and hence evaluation of \( \text{Cr}^{3+}/\Sigma \text{Cr} \)) were compromised by the presence of \( \text{Cr}_2\text{O}_3 \) deviate from the trend and were omitted.

Figure 3 indicates that an increase in the basicity of the melt stabilizes the higher oxidation state (\( \text{Cr}^{3+} \)). Such linear relationships have been reported for several elements (Duffy 1993). There is a similarly strong correlation between \( \log K' \) and optical basicity (expected from the relationship between \( \log K' \) and \( \Sigma \text{Cr}^{2+}/\Sigma \text{Cr} \); Eq. 5). The data suggests that the optical basicity model provides a first order explanation for the stabilization of \( \text{Cr}^{3+} \) relative to \( \text{Cr}^{2+} \), at constant temperature and \( f_{\text{O}_2} \), in melts. Other parameterizations of the melt, including NBO/T and \( \Phi \) [related to \( [\text{O}^2–] \) and proportional to \( (\text{Al}+\text{Si})/\text{O}; \text{Lauer and } \Phi ] \), do not correlate as strongly with \( \log[\text{Cr}^{3+}/\text{Cr}^{2+}] \). The basicity trend is also consistent with the relative stabilities of \( \text{Cr}^{3+} \) and \( \text{Cr}^{2+} \) reported previously for two compositions (Schreiber and Haskin 1976). Furthermore, a \( K' \) value of 1.6 was quoted by Schreiber (1987) for a forsterite-anorthite-silica composition at 1500 °C. For the calculated optical basicity of this glass (0.585) we would predict a \( K' \) of 1.8 at 1400 °C. The two values are in good agreement noting the difference in temperature (an increase in temperature produces an increase in \( \text{Cr}^{3+}/\Sigma \text{Cr} \) and a corresponding decrease in \( K' \) ; Schreiber and Haskin 1976).

The melt structure, which is defined by the melt composition (at constant temperature and pressure) and hence linked to the basicity through the degree of polymerization, also influences redox equilibria due to its ability to provide the preferred solvation sites of each oxidation state. \( \text{Cr}^{3+} \) strongly favors regular octahedral coordination, whereas \( \text{Cr}^{2+} \) typically occurs in a tetragonally distorted octahedral or square planar geometry (e.g., Belsky et al. 1984; Miletich et al. 1999), although there is evidence to suggest that it may be tetrahedrally coordinated in CMAS melts (O’Neill and Berry 2006). This distorted or low-symmetry environment allows the \( 1s \rightarrow 4s \) transition characteristic of \( \text{Cr}^{2+} \) in a glass to gain intensity. The intensity of the transition when

\[
\log[\text{Cr}^{3+}/\text{Cr}^{2+}] = 1
\]

[i.e., at \( A_{\text{alk}_\text{com}2+} \)] was investigated as a function of the concentration of the component oxides. The correlation between \( A_{\text{alk}_\text{com}2+} \) and \( X_{\text{CaO}} \) is shown in Figure 4a. There is no correlation with \( \text{MgO} \) or \( \text{Al}_2\text{O}_3 \) and only a vague positive trend with \( \text{SiO}_2 \) (which probably mirrors the effect of changing \( \text{CaO} \)). The correlation in Figure 4a indicates that at low \( X_{\text{CaO}} \) contents the \( \text{Cr}^{3+} \) site is more highly distorted than at high \( X_{\text{CaO}} \). Given that a distorted site favors \( \text{Cr}^{3+} \) relative to \( \text{Cr}^{2+} \), we would expect large values of \( A_{\text{alk}_\text{com}2+} \) to be associated with compositions that stabilize \( \text{Cr}^{3+} \). This should be reflected by a strong correlation between \( A_{\text{alk}_\text{com}2+} \) and \( Y_{\text{SiO}_2} \) values of which have been determined by O’Neill and Berry (2006). However, no correlation exists, indicating that the \( \text{Cr}^{3+} \) site distortion is a property of the quenched glass rather than the melt. Thus, although quenching preserves the high-temperature oxidation state ratio (in the absence of other redox variable species), it does not maintain the melt coordination environment. Such changes in melt structure with temperature are not unexpected. The internal consistency of the quantification method indicates that the quench rates and thus glass-transition temperatures for our samples must be sufficiently uniform that the same \( \text{Cr}^{3+} \) average site occurs in each glass of a given composition. If the site were to vary between samples, then \( A_{\text{alk}_\text{com}2+} \) would comprise contributions from differences in the site, in addition to variations in \( \text{Cr}^{3+}/\Sigma \text{Cr} \), resulting in scatter from the relatively smooth dependence of \( A_{\text{alk}_\text{com}2+} \) on \( f_{\text{O}_2} \) observed here and in Berry and O’Neill (2004).

The correlation between \( \log \left( X_{\text{CaO}} + f_{\text{O}_2} \right) \) and \( X_{\text{CaO}} \) is shown in Figure 4b. There is a general trend indicating stabilization of \( \text{Cr}^{3+} \) with increasing \( X_{\text{CaO}} \). This finding is consistent with \( \text{CaO} \)-rich melts containing abundant octahedral sites and the strong preference of \( \text{Cr}^{3+} \) for octahedral coordination; \( \text{Si}, \text{Al}, \) and \( \text{Mg} \) may all be tetrahedrally coordinated. The “bulge,” or deviation from the linear trend with \( X_{\text{CaO}} \), corresponds to those compositions rich in \( \text{Mg} \), with the magnitude of this deviation being linearly correlated (\( r = 0.91 \)) with \( X_{\text{SiO}_2} \). This figure, therefore, suggests that two processes are contributing to the stabilization of \( \text{Cr}^{3+} \) in the melt: the availability of a suitable solvation site (related to the \( X_{\text{CaO}} \)), and the optical basicity, which for a given \( X_{\text{CaO}} \),
The $A_{\text{1s}4s}$ value calculated for MORB is plotted in Figure 4a and is inconsistent with the trend found for the Fe-free compositions. This is not unexpected as $A_{\text{1s}4s}$ quantifies the transition intensity, which will vary with changes in $\text{Cr}^{3+}$ coordination between the melt and glass. Thus values for spectra recorded at room temperature and 1400 °C will not be comparable. However, the log $\gamma$ and log[$\text{Cr}^{2+}/\text{Cr}^{3+}$] values determined for MORB are consistent with trends defined by the Fe-free glasses, such as the optical basicity (Fig. 3). This observation suggests that $\text{Cr}^{2+}/\Sigma\text{Cr}$ for Fe-bearing compositions can be predicted from the composition of the melt. Due to experimental limitations none of the compositions studied contain Na$_2$O, K$_2$O, or H$_2$O, all of which will affect the melt structure and basicity. In particular, Na$_2$O and K$_2$O are more “basic” than CaO and may have a strong destabilizing effect on $\text{Cr}^{2+}$, although the relative abundance of these elements suggests that their contribution may be limited.

The XANES method for quantifying $\text{Cr}^{2+}/\Sigma\text{Cr}$ described here has allowed the compositional dependence of $\text{Cr}^{2+}/\Sigma\text{Cr}$ in Fe-free glasses to be determined. The results are in good agreement with the optical basicity description of how melts stabilize oxidation states. The apparent success of this method for quenched glasses has prompted its application to the in situ study of melts, which has allowed $\text{Cr}^{2+}/\Sigma\text{Cr}$ in an Fe-bearing melt to be quantified for the first time. $\text{Cr}^{2+}$ is an important and possibly dominant oxidation state in basaltic volcanism at terrestrial $f_{\text{O}_2}$ values.

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