# XANES measurements of Cr valence in olivine and their applications to planetary basalts

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### ABSTRACT

In this work we present a series of experiments that examine the relationship between oxygen fugacity and Cr valence ratio in olivine grown from a basaltic liquid. These experiments are specifically targeted for an olivine-rich martian basalt composition that was modeled after the bulk chemistry of the meteorite Yamato 980459 (i.e., Y-98). The chromium valence ratio in the olivine crystals was measured with X-ray absorption near edge spectroscopy (XANES) at the Advanced Photon Source, Argonne National Laboratory. Results from the XANES measurements indicate that the ratio of divalent to trivalent Cr in the olivine is not only systematically correlated with  $f_{02}$ , but is also reflective of the molar Cr<sup>3+</sup>/Cr<sup>2+</sup> in the silicate liquid from which it grew. In this way, measurements of Cr valence in olivine phenocrysts can yield important information about the oxygen fugacity and molar Cr<sup>3+</sup>/Cr<sup>2+</sup> of its parental liquid in the absence of a quenched melt phase. Although the results from the experiments presented in this work specifically apply to the Y-98 parental melt, the concepts and XANES analytical techniques discussed within the text present a novel, generalized methodology that may be applicable to any olivine-bearing basalt. Furthermore, the XANES-based measurements are made on a micrometer-scale, thus potential changes of the Cr<sup>3+</sup>/Cr<sup>2+</sup> in the melt during crystallization could be examined with a great deal of spatial detail.

Keywords: XANES, Cr valence, redox equilibria, martian basalts

### INTRODUCTION

#### Oxidation state, basaltic magmas, and their mantle sources

Quantifying and understanding the redox evolution of basaltic liquids and their mantle source regions has been a major theme in magmatic petrology for over 30 years (Fudali 1965; Arculus et al. 1981; Ballhaus 1993; Carmichael 1991; Brandon and Draper 1996; Canil 2002; Kelley and Cottrell 2009). Oxygen fugacity is a critical variable that exerts profound influence on basaltic phase equilibria, magmatic differentiation paths, C-O-H-S volatile speciation, metallic core segregation, and even peridotite rheology (Mathez 1984; Wood et al. 1990; Carmichael 1991; Righter 2003; Shearer et al. 2006; Mackwell 2008). In general, calculating the oxidation state of planetary basalts is a vexing problem. Oxygen fugacity calculations for planetary basalts are frequently impeded by: (1) the paucity of glassy material that could be used to infer  $f_{O2}$  from direct measurements of Fe<sup>2+/</sup>  $Fe^{3+}$ ; (2) difficulties associated with redox-sensitive mineral assemblages that are susceptible to subsolidus re-equilibration (e.g. the Fe-Ti oxides); and (3) understanding how calculated  $f_{02}$ values fit into the temporal evolution and petrologic context of the sample. More often than not, the relationship between the  $f_{0_2}$ values calculated for a crystallized basaltic sample and the  $f_{02}$  of its mantle source region is difficult to discern due to post-melting compositional modification during ascent and differentiation.

Despite these difficulties, many studies have produced robust  $f_{0_2}$  estimates for the olivine-phyric Shergottite-Nakhlite-Chassignite (SNC) suite meteorites. These estimates have been made using various different oxybarometers. The  $f_{0_2}$  values calculated for the olivine-phyric martian basalts show a curious degree of dispersion in that the calculated  $f_{0_2}$  values range from IW-0.5 to IW+4.4 (Wadhwa 2001; Herd 2003; and Shearer et al. 2006). Calculated  $f_{0_2}$  values have even been observed to vary by two to three orders of magnitude in a single sample depending on which mineral pairs and compositions were used in the calculations.

In light of these difficulties and uncertainties, there is naturally much impetus to develop more sensitive methods with which to calculate  $f_{02}$  values for not only the olivine-phyric martian meteorites, but also a generalized methodology that is applicable to any crystallized basaltic material. Measurements of the formal valence state of trace Cr that is present in olivine present a potential solution to this problem. Such measurements may yield important insight into the oxidation state of the parental liquid while circumventing problems associated with the lack of glassy material or reset mineral equilibria.

# The utility of chromium as a petrogenetic tracer and a redox indicator

The consequences of variable  $Cr^{3+}/Cr^{2+}$  in basaltic melts have long been recognized as playing a critical role in dictating the

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geochemical behavior and distribution of Cr in mantle-derived basalts (Irvine 1975; Delano 1990; Papike et al. 2005; Karner et al. 2007). Understanding the interplay between Cr valence and  $f_{O_2}$  in primitive basaltic magmas is a prerequisite for developing petrogenetic models of lunar, terrestrial, and planetary basalts, as well as constraining the composition of their mantle sources. The study of Schreiber and Haskin (1976) suggested that measurements of Cr valence in experimentally produced melts would help illuminate the link between Cr geochemistry and its valence ratio in lunar and planetary basalts. However, a comprehensive understanding of Cr redox systematics in silicate liquids has been hindered by the difficulty of interpreting Cr valence measurements. For example, quench-induced modification of the Cr<sup>2+</sup>/Cr<sup>3+</sup> ratio in ferric iron-bearing silicate liquids muddied the understanding of Cr redox equilibria in silicate liquids (Schrieber and Haskin 1976). Recent pioneering efforts of Berry and O'Neill (2004) and Berry et al. (2006) have begun to illuminate the behavior of Cr in Fe-free systems, but the direct measurement of Cr valence in natural Fe-bearing glasses remains a difficult analytical problem because the  $f_{02}$  range over which Cr<sup>2+</sup> is oxidized to Cr<sup>3+</sup> overlaps that of the homogenous ferric-ferrous equilibria for many basaltic liquid compositions.

#### Cr valence in olivine as a proxy for the liquid

Proxy measurements of Cr valence in near-liquidus phases present a natural solution to this problem. Olivine is a prime candidate for three reasons: (1) olivine is the liquidus phase in many basalts of planetary origin; (2) olivine does not show strong preference for one valence state of Cr over another (Hanson and Jones 1998); and (3) olivine from reduced basaltic liquids ( $f_{02} < FMQ$ ) contains vanishingly small quantities of Fe<sup>3+</sup> (Canil and O'Neill 1996), mitigating issues associated with the temperature-dependent electron exchange reaction between Cr<sup>2+</sup> and Fe<sup>3+</sup> that is responsible for affecting the equilibrium Cr<sup>3+</sup>/Cr<sup>2+</sup> in the melt. In this way, olivine crystals can effectively record the Cr<sup>3+</sup>/Cr<sup>2+</sup> of their parental liquids, in much the same way as melt inclusions record the composition of the melt from which a particular crystal grew.

# EXPERIMENTAL TECHNIQUES AND ANALYTICAL METHODS

### **Experimental techniques**

Wire loop experiments were conducted in the 1-bar gas mixing laboratory at NASA Johnson Space Center (JSC). The majority of the experiments were performed using Re loops to prevent Fe-loss. Experiments run at oxygen fugacities near the FMQ buffer employed Pt-Rh loops. The starting materials consisted of two compositions patterned after the whole rock composition of martian meteorite Yamato 980459. Both compositions consisted of a mixture of synthetic oxides. One of these compositions was doped with REE, whereas the other was a REE-free base composition. The REEs were added to the doped composition as 0.6% of their individual oxides, to yield a total abundance of ~4.5 wt% REE-oxide. Scandium and vandium were also added to this mixture as  $Sc_2O_3$  and  $V_2O_3$  at a concentration of 0.1 wt% each. We recognize that the doping levels employed in this study do not realistically approximate the actual Y-98 bulk composition; however, such elevated concentrations of trace elements are required for future XANES measurements of the valence states of other important trace elements. The experiments presented here are part of a larger, ongoing phase equilibrium and partitioning study that focuses on compositions of martian basaltic liquids.

Experiments were performed at temperatures of 1300, 1320, and 1380 °C. The 1300 °C experiments utilized the doped composition (Y-98A series), whereas the

1320 °C (Y-98B797 and B791) and 1380 °C (Y-98B796 and B790) experiments used the un-doped starting mixture. Experimental  $f_{0_2}$  was controlled with CO-CO<sub>2</sub> mixtures that were calibrated with a Y-stabilized zirconia electrochemical oxygen sensor, specifically the SIRO<sub>2</sub> from COF-Australia, housed in a dedicated reference furnace. Experimental runs were conducted at the following relative  $f_{0_2}$  values: IW-1, IW, IW+1, and IW+3.4 (= FMQ) for the 1300 °C series of REE-doped experiments, and IW-1 and IW+3.4 for the un-doped 1320 and 1380 °C experiments. Each experiment was initially held at super-liquidus conditions (1500 °C) for eight hours and subsequently cooled to target dwell temperature at a rate of 1000 °C h<sup>-1</sup>. The liquidus for the Y-98 composition has been determined to be ~1420 °C at 1 bar (Musselwhite et al. 2006). Experiments were held at the target dwell temperature for a minimum of 48 h and terminated by drop-quenching into distilled water.

# Electron microprobe analysis (EPMA) of the experimental glasses and olivine

Electron microprobe (EPMA) analyses were conducted using the JEOL JXA 8200 electron microprobe in the Institute of Meteoritics at the University of New Mexico. Quantitative analyses were collected for Si, P, Al, Fe, Ti, Cr, Ca, Na, K, Mn, and Mg at an accelerating voltage of 15 kV, a beam current of 10 nA, and a 1  $\mu$ m spot size. Standardization was carried out using a combination of CM Taylor electron microprobe mineral standards, specifically orthoclase, albite, diopside, olivine, spessartine, apatite, and chromite, as well as in-house standards for rutile, almandine, and fayalite. All data were reduced with a ZAF matrix correction algorithm within the JEOL software. Care was taken to ensure that chosen spots were a significant distance (typically >100  $\mu$ m) away from any Cr-spinel inclusions in the olivine or glass to mitigate potential enhancement of the apparent Cr content of olivine and glass resulting from Cr secondary fluorescence originating from Cr-spinel crystals.

# X-ray absorption near edge spectroscopy (XANES) data acquisition and reduction

Chromium K-edge XANES data were acquired with the X-ray microprobe of GSECARS beamline 13-ID-E at the Advanced Photon Source (APS), Argonne National Laboratory, Illinois. The X-ray source at APS beamline 13-ID-E was a 72-pole, 33 mm period undulator. Beam focusing was accomplished with dynamically figured Kirkpatrick-Baez focusing mirrors; this configuration vielded a beam focused to a final spot size of ~4 µm2. All spectra were acquired in fluorescence mode utilizing a cryogenically cooled Si(311) monochromater and a silicon-drift solid state detector offset at a 45° angle from the sample. Spectra were collected through the energy range of 5939-6213 eV. The energy step width was set to 0.2 eV in the near edge region (5984-6014 eV) and to 4.0 eV in the far pre-edge and far post-edge regions. Data acquisition consisted of two spectral sweeps per spot analysis. The two resultant spectra were subsequently merged into a single spectrum to maximize signal-to-noise. Multiple olivine crystals were analyzed in each experimental charge. Locations for the analytical spots were purposefully selected to sample both the core and rim of the olivine crystal in an attempt to assess the homogeneity of the Cr valence within individual olivine phenocrysts. A total of four to five olivine spot analyses were obtained for each experimental charge. Two standards were used to define the Cr-valence end-members. The Cr3+ standard was an iron-free glass produced experimentally in the study of Hanson and Jones (1998), and the Cr2+ was a Cr-bearing ureilite olivine that was previously characterized by Goodrich et al. (2013).

The formal oxidation state of Cr has been shown to correlate with the intensity of a shoulder on the main Cr-*K* absorption edge (Berry and O'Neill 2004). Existence of this spectral feature at ~5994 eV has been attributed to a 1s-4s electron transition (Sutton et al. 1993). The 1s-4s electron transition is forbidden for cations in non-centrosymmetric coordination polyhedra, however, with respect to Cr<sup>2+</sup> in octahedral coordination, the Jahn-Teller effect causes symmetry-breaking site distortion making 1s-4s transition permissible (in contrast, the Jahn Teller effect for Cr<sup>3+</sup> in octahedral coordination is negligible). Therefore, the 1s-4s absorption at ~5994 eV is diagnostic of the presence of Cr<sup>2+</sup> in the olivine structure. The intensity of the 1s-4s shoulder at ~5994 eV is directly correlated with the abundance of divalent Cr present in the olivine relative to trivalent Cr (Berry and O'Neill 2004). Data reduction and calculation of Cr<sup>2+</sup>/Cr<sup>3+</sup> values followed the general procedures outlined in the work of Berry and O'Neill (2004). Both of these works conclude that both the area and the intensity of the Spectral feature associated with 1s-4s electron transition are correlated with the Cr<sup>2+</sup> content of the olivine.

Figure 1 is a stack plot of representative Cr spectra, including both standards and some examples from the olivine crystals from the Y-98A experiments. The normalized spectra were first smoothed with a three iteration moving average, and then differentiated to obtain the final processed spectra. The derivatives of the normalized intensity spectra help facilitate the accurate calculation of the intensity of the absorption associated with the 1s-4s transition. In the derivative spectra, the 1s-4s transition is prominently manifested as a single peak roughly centered about 5994.5 eV (Fig. 2). The valence ratios for unknown olivine crystals were obtained using the linear mixing line between the 1s-4s intensity of the Cr<sup>3+</sup> standard (defined as Cr<sup>2+</sup>/ $\Sigma$ Cr = 0) and the equivalent intensity for the Cr<sup>2+</sup> standard (defined as Cr<sup>2+</sup>/ $\Sigma$ Cr = 0).

 $\Sigma$ Cr = 0.95). Intensities of the 1s-4s transition calculated from the derivative spectra as well as their corresponding Cr<sup>2+</sup>/Cr<sup>3+</sup> values are listed in Table 1. Calculations of Cr<sup>2+</sup>/ $\Sigma$ Cr presented in this study were made with the intensity (height) of the 1s-4s peaks in the derivative spectra (Table 1).

For comparison, we have also calculated  $Cr^{2+}/\Sigma Cr$  of the unknown olivine using the area of the 1s-4s peaks from the derivative spectra. Intensities calculated with this data reduction scheme were obtained through the numerical integration of the derivative spectra over an energy interval from 5991.5 to 5995 eV. The area of the peak obtained through the integration (i.e., the integrated intensity) scales



FIGURE 1. We present a few examples of normalized Cr *K*-edge spectra from Y-98A series olivine as well as the spectra from the  $Cr^{3+}$  and  $Cr^{2+}$  standard materials. Note the increasing intensity of the 1s-4s feature as the abundance of  $Cr^{2+}$  is increased relative to  $Cr^{3+}$ .

 TABLE 1.
 XANES data and Cr contents of olivine and melt

oreo (000000000000000000000000000000000000	Y-98A2 Y-98A10 Y-98A14 Y-98A14		1	s-4s absorp	tion peak		į
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0.05 Der	-					1	
0.00	5985 5987	5989	5991	5993	5995	5997	5999

**FIGURE 2.** We present the derivatives of the same spectra that were plotted in Figure 1. The 1-4s absorption features show a clear, systematic change in intensity that scales with the  $Cr^{2+}/Cr^{3+}$  ratio.

Sample ID	$\log_{10} f_{O_2}$	Int. 1s-4s <sup>a</sup>	B-line Cor <sup>b</sup>	Cr <sup>2+</sup> /ΣCr	Phases	Cr olivine <sup>c</sup>	Cr liquid <sup>c</sup>
Cr <sup>3+</sup> H&J Glass	-	0.0176	NA	0.000	NA	NA	NA
Cr <sup>2+</sup> Ureilite	-	0.1754	NA	0.950	NA	NA	NA
Y98-A10	-7.25	0.0668	0.0492	0.267	Lig, Ol, Spinel	1060 (135)	1750 (165)
	(IW+3.4)	0.0724	0.0548	0.297			
		0.0703	0.0527	0.286			
		0.0712	0.0536	0.290			
Y98-A2	-9.59	0.1076	0.0900	0.487	Liq, Ol, Spinel	2086 (120)	2970 (125)
	(IW+1)	0.1121	0.0945	0.512			
		0.1086	0.0910	0.493			
		0.1111	0.0935	0.506			
Y98-A14	-10.59	0.1366	0.1190	0.645	Liq, Ol	2940 (205)	4280 (300)
	(IW)	0.1420	0.1244	0.674			
		0.1392	0.1216	0.659			
Y98-A17	-11.59	0.1538	0.1362	0.738	Liq, Ol	2950 (150)	4310 (205)
	(IW-1)	0.1848	0.1672	0.906			
		0.1522	0.1346	0.729			
		0.1842	0.1666	0.902			
Y98-B797	-11.39	0.1600	0.1424	0.771	Liq, Ol	4000 (190)	5575 (200)
	(IW-1)	0.1510	0.1334	0.723			
		0.1570	0.1394	0.755			
		0.1590	0.1414	0.766			
Y98-B791	-7.06	0.0690	0.0514	0.278	Liq, Ol, Spinel	1340 (250)	2265 (225)
	(IW+3.4)	0.0665	0.0489	0.265			
		0.0670	0.0494	0.268			
		0.0716	0.0540	0.292			
Y98-B796	-10.8	0.1600	0.1424	0.771	Liq, Ol	3400 (190)	5420 (295)
	(IW-1)	0.1700	0.1524	0.825			
		0.1730	0.1554	0.842			
Y98-B790	-6.45	0.0731	0.0555	0.301	Liq, Ol, Spinel	2025 (340)	3270 (290)
	(IW+3.4)	0.0842	0.0666	0.361			
		0.0898	0.0722	0.391			

<sup>a</sup> Data in the column are the raw intensities associated with the 1s-4s electron transition from the derivative spectra.

<sup>b</sup> Background subtracted intensities.

<sup>c</sup> Cr content of the glass and olivine are reported in ppm of elemental Cr; the value following in parentheses is the 1σ uncertainty associated with the EPMA measured Cr contents. NA = not applicable. with  $Cr^{2+/}\Sigma Cr$  of the standards in a manner nearly identical to the relationship between the peak height and  $Cr^{2+/}\Sigma Cr$ . The olivine  $Cr^{2+/}\Sigma Cr$  values obtained using the integrated area reduction scheme are nearly identical to those calculated using the peak height, suggesting that both methods render robust Cr valence data.

Based on replicate measurements, we estimate that the inherent uncertainty associated with the measured  $Cr^{2+}/\Sigma Cr$  values is approximately  $\pm 0.05$  (1 $\sigma$ ). We also recognize that crystallographic orientation can affect the measured intensity of the 1s-4s absorption The orientation effect is about  $\pm 10\%$  of the  $Cr^{2+}$  peak intensity, which corresponds to a maximum valence uncertainty of  $\pm 0.1$  for a sample containing only  $Cr^{2+}$  (Goodrich et al. 2013). These observations indicate that significant orientation effects are only manifested in materials containing high  $Cr^{2+}/\Sigma Cr$ .

#### RESULTS

#### The compositions of the quenched liquid and olivine

All experimental run products consisted of some combination of quenched liquid, olivine, and Cr-enriched spinel. The phase assemblages for each experiment are also listed in Table 1. To assess whether or not the experiments attained equilibrium, we have examined the olivine-liquid Fe-Mg exchange K<sub>d</sub> values. The calculated K<sub>d</sub> values for experimental olivine-liquid pairs range from 0.32 to 0.35, suggesting that the olivine has indeed approached compositional equilibrium with the liquid (Roeder and Emslie 1970; Filiberto and Dasgupta 2011). Inter-experiment variation in the major element composition of the olivine is very low, such that all of the analyzed olivine crystals from the Y-98A experiments fall within compositional range Fo77 to Fo81, and all of the olivine crystals from the Y-98B experiments fall within the compositional range Fo<sub>82</sub> to Fo<sub>86</sub>. The compositions of the olivine and glass from all of the experimental charges are supplied in Electronic Appendix I1. The low variability in the Fe/Mg ratios of the experimental olivine, however, are not unanticipated as the low ferric iron contents of all the experimental melts severely limit any variation in the ratio of activities of FeO and MgO. Calculations using the Kress and Carmichael (1991) equation support this interpretation by indicating that the maximum Fe<sup>3+</sup>/ $\Sigma$ Fe is ~0.12, even for the most oxidized experimental liquids.

The EPMA-determined Cr<sub>2</sub>O<sub>3</sub> content (reported in Table 1 as parts per million elemental Cr) of the quenched Y-98A series liquids ranged from a high of  $6300 \pm 300$  ppm (1 $\sigma$ ) at IW-1, monotonically decreasing to a low of  $2550 \pm 236$  ppm (1 $\sigma$ ) at IW+3.4. A similar trend is observed for the liquids resulting from the Y-98B experiments. In the 1320 °C experiments, the Cr content drops from  $8150 \pm 290$  ppm at IW-1 to  $3310 \pm$ 330 ppm at IW+3.4; in the 1380 °C experiments, Cr content decreases from 7920  $\pm$  430 ppm at IW-1 to 4790  $\pm$  420 ppm at FMQ. We interpret the monotonic decrease in the Cr content of the guenched liquids as an effect of the increasing modal abundance of Cr-spinel in the more oxidized experiments. The early crystallization of Cr-rich spinel depletes the residual liquid of Cr in the more oxidized charges. As expected, the Cr content of the olivine that crystallized from the liquids also decreased from a high of  $4300 \pm 225$  ppm (1 $\sigma$ ) at IW-1 to a low of 1500  $\pm$  200 ppm (1 $\sigma$ ) at FMQ in an analogous, monotonic fashion. The Cr content of the olivine in both sets of Y-98B experiments mirrors the trend observed for the Y98-A series. Cr content of both the liquid and olivine are plotted vs.  $f_{O2}$  in Figure 3a.

## **Total Cr partition coefficients**

The calculated total Cr partition coefficients for olivineliquid pairs range from 0.59 to 0.72. Both the 1300 and 1320 °C experiments show some systematic variation of the  $D_{Cr}$  with  $f_{02}$ . In contrast, the high temperature Y-98B experiments yield a  $D_{Cr}$  that is constant with respect to  $f_{O_2}$ . The bulk  $D_{Cr}$  values are plotted vs.  $f_{02}$  in Figure 3b. The apparent effect of  $f_{02}$  on  $D_{\rm Cr}$  in the lower temperature experiments will be addressed in detail in the discussion section below. Propagated 10 uncertainties for the partition coefficient values are approximately  $\pm 0.09$ . The olivine-liquid partition coefficients calculated in this study are in excellent agreement with the values derived from multiple experimental Cr partitioning studies (Mikouchi et al. 1994; Gaetani and Grove 1997; Hanson and Jones 1998; Mallmann and O'Neill 2009). Results of studies at comparable temperatures (1300-1400 °C) unanimously suggest that the  $D_{\rm Cr}$  value falls between 0.55 and 0.85, a range consistent with the range of values from this study. The reader should bear in mind that the liquids from previous studies span a fairly large compositional range, many of which have stark differences from the liquid compositions encountered in this study.



**FIGURE 3.** (a) Shows how the Cr content of both the melt and its equilibrium olivine decrease as a function of  $f_{o_2}$ . The stabilization of Cr as the liquidus phase in the more oxidized experiments is responsible for this decrease. (b) A plot of the total Cr partition coefficient as a function of  $f_{o_2}$ .

<sup>&</sup>lt;sup>1</sup> Deposit item AM-14-704, Appendices. Deposit items are stored on the MSA web site and available via the *American Mineralogist* Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

### XANES measurements of Cr valence in olivine

The measured  $Cr^{2+}/\Sigma Cr$  values from individual olivine spot analyses display a relatively large range, varying from a low of 0.26 to a high of 0.90. Dispersion, as measured using the  $1\sigma$ standard deviation in the  $Cr^{2+}/\Sigma Cr$  within single experiments is generally low. The standard deviation of the  $Cr^{2+}/\Sigma Cr$  values within a single experimental charge is ~0.03 in the IW, IW+1, and IW+3.4 experiments, and 0.09 in the IW-1 experiment. The measured  $Cr^{2+}/\Sigma Cr$  values for the olivine in the IW-1 Y-98A experiments range from 0.74 to 0.90. Normalized XANES spectra from all experiments have been supplied in Electronic Appendix II<sup>1</sup>.

The dispersions displayed in these analyses are likely a reflection of orientation effects, as orientation effects are most strongly realized in olivine with high  $Cr^{2+}/\Sigma Cr$ . This is consistent with the observation that olivine in the most reduced experiments contains not only the largest quantity of  $Cr^{2+}$ , but also show the largest spread in calculated  $Cr^{2+}/\Sigma Cr$  values. Therefore, the mean of these values represents a more accurate reflection of the actual  $Cr^{2+}/\Sigma Cr$  present in the olivine than any of the individual analyses. The fact that the mean  $Cr^{2+}/\Sigma Cr$  of 0.82 yields a regression slope of 0.24 in a plot of  $\ln[Cr^{3+}/Cr^{2+}]$  vs.  $\ln f_{O_2}$  is strong evidence that the mean value is indeed an accurate measure of  $Cr^{2+}/\Sigma Cr$  for this experiment.

Figure 4 is a plot of the  $Cr^{2+}/\Sigma Cr$  vs.  $\log_{10}f_{O_2}$ ; this plot clearly shows that  $Cr^{2+}$  comprises an increasing proportion of the total Cr content in the olivine as the experimental oxygen fugacity is lowered. As a first-order observation, the calculated  $Cr^{2+}/\Sigma Cr$ values show a distinct trend as a function of the experimental  $f_{O_2}$ values. The trend in the data suggests that the Cr valence ratio in the olivine is indeed sensitive to the oxidation state of the experimental charge and, by extension, the oxidation state of the melt from which the crystals in question nucleated and grew. The quantitative links between the measured Cr valence ratio in the experimental olivine and the valence ratio of its parental melt will be explored in detail in the next section.



**FIGURE 4.** A plot of the XANES determined  $Cr^{2+}/\Sigma Cr$  vs.  $\log_{10} f_{O_2}$  for experimental olivine crystals from all of the experimental charges. We also point out the striking similarity between the values for the Y-98A series and the Y-98B 1320 °C series.

### DISCUSSION

# Relationship of Cr valence ratio in olivine to the Cr valence ratio of the melt

The measured  $Cr^{2+}/\Sigma Cr$  of olivine can be quantitatively related to the  $Cr^{2+}/\Sigma Cr$  of its parental liquid through the olivine-melt partition coefficients for both divalent and trivalent chromium. In other words, the ratio of  $Cr^{3+}$  to  $Cr^{2+}$  in olivine is defined by the ratio of  $Cr^{3+}$  to  $Cr^{2+}$  in its parental liquid, multiplied by a factor equal to the ratio of  $D_{Cr^{3+}}$  to  $D_{Cr^{2+}}$ . This relationship is defined by Equation 1,

$$\left(\frac{XCr^{3+}}{XCr^{2+}}\right)^{\text{olivine}} = \left(\frac{XCr^{3+}}{XCr^{2+}}\right)^{\text{liquid}} \cdot \left(\frac{D_{Cr^{3+}}^{\text{ol·liq}}}{D_{Cr^{2+}}^{\text{ol·liq}}}\right)$$
(1)

where  $XCr^{3+}$  and  $XCr^{2+}$  represent the mole fraction of that cation present in a given phase and  $D_{Cr^{2+}}$  and  $D_{Cr^{3+}}$  represent the olivine liquid Nernst-type partition coefficients for divalent and trivalent Cr, respectively. From a practical standpoint,  $Cr^{3+}/Cr^{2+}$  of any olivine-bearing melt can be inferred from direct measurements of the  $Cr^{3+}/Cr^{2+}$  present in its olivine phenocrysts; however, this relationship is only useful provided that the ratio of Cr partition coefficients for (trivalent to divalent) are known with sufficient accuracy. Fortunately, for many common basaltic compositions, the partition coefficient ratio for  $Cr^{2+}$  and  $Cr^{3+}$  is closely approximated to be a constant with a value of ~1.0. However, this may not be the case for all basaltic melt compositions (Hanson and Jones 1998).

To calculate the individual values for  $D_{Cr^{3+}}$  and  $D_{Cr^{2+}}$ , knowledge of the molar ratio of Cr3+/Cr2+ in both the olivine and the quenched liquid is required. This is not possible for the experiments in this study because of the difficulties associated with quench modification of the  $Cr^{3+}/Cr^{2+}$  in the high  $f_{O_2}$ , iron-rich experimental liquids. A simple analysis of the bulk  $D_{Cr}$  behavior was used to circumvent this obstacle. This test consists of a comparison of the bulk olivine-liquid partition coefficients from experiments performed at different oxygen fugacity values. Upon close examination, the bulk  $D_{Cr}$  values slightly deviate from a constant value as  $f_{O_2}$  is increased. The calculated values become slightly lower, decreasing from 0.70 to 0.59 as  $f_{02}$  is increased from IW-1 to FMQ. This behavior is observed in both the doped 1300 °C and un-doped 1320 °C series experiments. The subtle decrease of the bulk  $D_{Cr}$  values may be interpreted in two different ways:

- (1) One or both of the individual partition coefficients that comprise the bulk  $D_{Cr}$  vary as a function of  $f_{02}$  in a manner that yields a non-constant ratio of D values; or
- (2) The individual partition coefficient values for Cr<sup>3+</sup> and Cr<sup>2+</sup> are fixed with a trivalent to divalent ratio less than one.

Although these possibilities may appear similar on the surface, each has very different implications for the geochemical behavior of Cr in basaltic magmas. The first interpretation suggests that the behavior of Cr<sup>3+</sup> and Cr<sup>2+</sup> oxide components are governed by complex thermodynamic relationships. Such behavior implies that as the relative abundances of trivalent and divalent Cr change in the liquid with either increasing or decreasing  $f_{02}$ , the bonding behavior and speciation of these components in the liquid must be substantially altered. In other words, this interpretation requires that the activities of CrO1.5 and CrO in the liquid are variable with respect to  $f_{0_2}$ ; however the work of Berry and O'Neill (2004) directly contradicts this interpretation. Berry and O'Neill (2004) concluded that the activity coefficient ratio ( $\gamma Cr^{3+}/\gamma Cr^{2+}$ ) is, in fact, invariant with respect to  $f_{02}$  in liquids of constant bulk composition and sufficiently dilute total Cr contents (<1.0 wt%). The total Cr content of the melts in all experimental charges of this study is sufficiently dilute so as to display activity composition relationships that comply with Henry's Law. Furthermore, differences in the major element composition of the liquid in experiments run at differing oxygen fugacity values are minimal and therefore cannot explain the variation in the bulk  $D_{Cr}$  with  $f_{O2}$ .

The second interpretation offers a parsimonious explanation that is consistent with the conclusions of Berry and O'Neill (2004). This interpretation simply requires that the partition coefficient for Cr<sup>3+</sup> be slightly less than that for Cr<sup>2+</sup>. Olivine crystalized from liquids in systems that follow such partitioning behavior must have  $Cr^{2+}/\Sigma Cr$  that is greater than the liquid. The most important consequence is that this interpretation requires bulk  $D_{Cr}$  to be a function of the  $f_{O_2}$  of the liquid. The observed trend in bulk  $D_{Cr}$  vs.  $f_{O_2}$  can (Fig. 3b) be reproduced if the ratio of  $D_{Cr^{3+}}$  to  $D_{Cr^{2+}}$  is ~0.80 (see Eq. 1). In this case, the value of the partition coefficient ratio is a simple manifestation of the fact that divalent Cr is preferred in the olivine structure over trivalent Cr. This interpretation implicitly requires that the crystal chemistry of the olivine dictate the variation of  $D_{Cr}$  with  $f_{O2}$ , rather than non-Henrian behavior where CrO and CrO<sub>1.5</sub> display oxygen fugacity-dependent activity coefficients. It is, however, notable that the  $D_{Cr}$  values for the two Y98B experiments conducted at 1380 °C show little variation as a function of  $f_{0_2}$ . This observation suggests that the ratio of  $D_{Cr^{3+}}$  to  $D_{Cr^{2+}}$  in the higher temperature experiments may be closer to ~1.0, however, considering that only two experiments were conducted at this temperature it is difficult to fully vet this conclusion. We have chosen to use a  $D_{Cr^{3+}}$  to  $D_{Cr^{2+}}$  ratio of 0.80 to calculate the  $Cr^{2+}/\Sigma Cr$  of the experimental liquids. Because the application of the correct  $D_{Cr^{3+}}$ to  $D_{Cr^{2+}}$  ratio is critical to obtaining accurate  $Cr^{2+}/\Sigma Cr$  for the liquid we have also calculated the  $Cr^{2+}/\Sigma Cr$  of the Y98B 1380 °C experiments with  $D_{Cr^{3+}}/D_{Cr^{2+}}$  1.0. We found that calculating the  $Cr^{2+}/\Sigma Cr$  values for Y98B (1380 °C) liquids with a  $D_{Cr^{2+}}$  to  $D_{Cr^{2+}}$ ratio of 1.0 did not substantially change the modeled Cr valence ratios (Figs. 7 and 8) presented later in this work. Therefore, we assert that applying a single correction factor of 0.80 to all of the experiments is the most justifiable treatment of the  $D_{Cr}$  data.

A plot of the corrected  $\ln[Cr^{3+}/Cr^{2+}]$  values vs.  $\ln f_{0_2}$  yields a linear array of points for the Y-98A experiments and both Y-98B series experiments (Fig. 5). For the Y-98A experiments a plot of the average corrected  $\ln[Cr^{3+}/Cr^{2+}]$  vs.  $\ln f_{0_2}$  yields a linear array of points. Fitting the liquid-corrected data via linear regression yields a line with a slope of 0.24 and a correlation coefficient of  $R^2 = 0.97$ . The observed relationship between  $\ln[Cr^{3+}/Cr^{2+}]$  and  $\ln f_{0_2}$  in the Y-98B experiments is consistent with that of the Y-98A experiments, which is somewhat surprising considering the intrinsic errors associated with the measurements, and that

experiments from only two  $f_{O_2}$  values (IW-1 and IW+3.4) are represented. The regressed slopes of  $\ln[Cr^{3+}/Cr^{2+}]$  vs.  $\ln f_{O_2}$  for the un-doped Y-98B experiments are 0.21 and 0.23 for the 1320 and 1380 °C experiments, respectively.

# Crystal chemical aspects controlling Cr partitioning into olivine

The fidelity of olivine as a recorder of Cr valence in the parent liquid hinges on the fact that the compatibility of  $Cr^{2+}$  and  $Cr^{3+}$  are approximately equal in the olivine structure. For example, if the olivine/liquid partition coefficients for divalent and trivalent Cr were different by a factor of five, it would greatly restrict the  $f_{02}$  range over which Cr could have multiple valences in olivine. Therefore, the question of why  $Cr^{3+}$  is so compatible (relative to  $Cr^{2+}$ ) must be reconciled with the crystal chemistry of olivine, and any observed trends in Cr partitioning behavior must be consistent with known crystal chemical constraints. A few qualitative explanations of Cr behavior in olivine are offered in the next paragraph.

Hanson and Jones (1998) suggest that while  $Cr^{2+}$  is the correct charge, its radius is a bit too large to be compatible in the olivine crystal structure; for  $Cr^{3+}$ , the opposite is true: its charge is too large, but its radius is nearly identical to that of  $Mg^{2+}$ . As far as charge balance for  $Cr^{3+}$  in the olivine lattice is concerned, existing data suggest that either  $Al^{3+}$  (in the tetrahedral site) nor Na<sup>+</sup> (in one of the octahedral sites) act as a significant charge couple for  $Cr^{3+}$ unless pressures exceed 3 GPa (Taura et al. 1998). These data suggest that at lower pressures, vacancy-based substitutions must be required for charge balance. Hanson and Jones (1998) and Papike et al. (2005) both suggested that the mechanism by which  $Cr^{3+}$  is accommodated at low pressures may be a vacancy substitution where two  $Cr^{3+}$  substitute for three  $Mg^{2+}$  cations and a vacancy

$$2^{VI}Cr^{3+} + {}^{VI}\Box \leftrightarrow 3^{VI}Mg^{2+}$$
$$2^{VI}Cr^{3+} + {}^{VI}\Box \leftrightarrow 3^{VI}Fe^{2+}$$



**FIGURE 5.** A ln-ln plot of the average molar ratio of divalent to trivalent Cr in the liquid vs.  $f_{02}$ . The plotted Cr<sup>3+</sup>/Cr<sup>2+</sup> values were corrected from the measured olivine values to those of the liquid. The regression slope for the Y-98A experiments is 0.24 with an R<sup>2</sup> = 0.97. This slope is in excellent agreement with the slope of 0.25 that is dictated by the stoichiometry of the homogenous Cr redox equilibrium.

yielding the olivine formula units  $Cr(Mg_{0.5}\Box_{0.5})SiO_4$  and  $Cr(Fe_{0.5}\Box_{0.5})SiO_4$ , respectively. The nature of the substitution mechanism is important because the partitioning behavior for  $Cr^{3+}$  is decoupled from the presence of other charge-balancing cations within the olivine structure. Rather than Cr compatibility scaling with the vacancy density of the olivine, the presence of  $Cr^{3+}$  in olivine partially controls the vacancy density of the olivine.

### Thermodynamics of Cr redox equilibria in the melt

If the  $Cr^{2+}/\Sigma Cr$  measured in olivine does indeed reflect that of the liquid, then it must be consistent with the Cr redox behavior observed for liquids from other studies of Cr redox systematics. The  $Cr^{2+}/\Sigma Cr$  observed in olivine can be defined by the homogenous redox equilibrium between divalent and trivalent Cr in the melt (cast here as the oxide components CrO and CrO<sub>1.5</sub>):

$$CrO^{liq} + \frac{1}{4}O_2^{sys} = CrO_{1.5}^{liq}$$
 (2)

or it can be defined in standard thermodynamic notation as:

$$\ln\left(\frac{X\mathrm{CrO}_{1.5}}{X\mathrm{CrO}}\right)^{\mathrm{liq}} = \frac{1}{4}\ln f_{\mathrm{O_2}} - \ln\left(\frac{\gamma\mathrm{CrO}_{1.5}}{\gamma X\mathrm{CrO}}\right) + \frac{\Delta G^{\circ}\mathrm{rxn}}{-\mathrm{R}T}$$
(3)

The olivine  $Cr^{3+}/Cr^{2+}$  values determined from the XANES measurements can be translated into the  $Cr^{3+}/Cr^{2+}$  of the melt by re-arranging and substituting Equation 1 into the expression above (Eq. 3), using the partition coefficient ratios derived in the Discussion section.

We have calculated the empirical equilibrium constant logK' for the homogenous CrO-CrO<sub>1.5</sub> equilibrium with the olivine derived Cr<sup>2+</sup>/ $\Sigma$ Cr values of the melt, where logK' by definition includes the ln[ $\gamma$ CrO<sub>1.5</sub>/ $\gamma$ CrO] term from Equation 3. The logK' values determined from this study overlap those determined by Berry et al. (2006) and, considering the effects of temperature and composition, the results are in excellent agreement. Figure 6 shows the logK' values from this study plotted vs. log $f_{O_2}$ , as well as a few values from the Berry et al. (2006) data set. It is important to note that logK' values for all of the Y-98A series experiments are constant with respect to  $f_{O_2}$ . This observation corroborates the assumption that melts with dilute Cr contents display Henrian behavior (i.e.,  $f_{O_2}$  invariant  $\gamma CrO/\gamma CrO_{1.5}$ ), as made in Berry and O'Neill (2004) and Berry et al. (2006). The identical logK' values for the REE-doped Y-98A (1300 °C) and un-doped Y-98B (1320 °C) experiments suggest that the presence of the REE do not fundamentally affect the observed Cr redox systematics, at least within the resolution with which Cr<sup>2+</sup>/ $\Sigma$ Cr can be measured.

A comparison of the logK' values from the 1300 °C Y-98A and 1320 °C Y-98B experiments with the logK' values in the 1380 °C experiments clearly indicates that increasing temperature at constant  $f_{0_2}$  (relative to a buffer) depresses logK'. Or in other words, increased temperature translates to an increased Cr<sup>2+</sup>/ΣCr at constant  $f_{O_2}$  in the Y-98 liquids. The effects of temperature on the logK' are caused by the individual effects of temperature on the  $\Delta G^{\circ}$  of the equilibrium in Equation 2 and the effects of temperature on the activity coefficient ratio,  $\gamma CrO_{1.5}/\gamma CrO$ . Unfortunately these two effects cannot be disentangled from one another, as no thermodynamic data exist with which to calculate the  $\Delta G^{\circ}$ of the Cr redox equilibrium as a function of temperature. That said, it is unlikely that temperature affects the  $\Delta G^{\circ}$  and not the  $\gamma$ CrO<sub>1 5</sub>/ $\gamma$ CrO. Partitioning data from Hanson and Jones (1998) support this interpretation by showing that  $D_{Cr^{2+}}$  is a function of temperature; this observation implies that the  $\gamma$ CrO of the melt is indeed a function of temperature.

Small differences between the  $\log K'$  values of the Y-98 experiments and those from the Berry et al. (2006) study (Fig. 6) arise naturally because of differences in melt compositions and



**FIGURE 6.** Display of the logarithm of the apparent equilibrium constants plotted vs.  $\log f_{0_2}$ . The dashed lines represent mean  $\log K'$  values from this study as well as  $\log K'$  values derived from Berry and O'Neill (2006) for comparison. Note that the Berry and O'Neill (2006) data was obtained from Fe-free analog basalts at 1400 °C. The  $f_{0_2}$  invariance of the data affirms the assumption that Cr obeys Henry's law in the Y-98 melt.

temperature. All of the compositions investigated by Berry et al. were restricted to the CMAS system at temperatures of 1400 °C. Most of the difference between the Berry and O'Neill logK' values and those from the 1300 °C Y-98A and 1320 °C Y-98B experiments can be attributed to the differences in temperature. The higher  $\log K'$  values (~2.3) associated with the 1300 °C Y-98A and 1320 °C Y-98B experiments are consistent with the observation that decreasing temperature causes an increase in  $\log K'$ . In contrast, the  $\log K'$  values calculated for the 1380 °C Y-98B experiments are strikingly similar to those reported in the Berry et al. data set. The logK' values from the 1380 °C Y-98B experiments fall between the AnDi+Fo and AnDi+Wo (where AnDi = anorthite-diopside) compositions from Berry et al. (2006). This suggests that at ~1400 °C, the  $\gamma$ CrO<sub>1.5</sub>/ $\gamma$ CrO for the Y-98 composition must lie somewhere between the  $\gamma$ CrO<sub>1</sub>  $_{5}$ /  $\gamma$ CrO values of anorthite-diopside + foresterite (AnDi+Fo) and anorthite-diopside + wollastonite (AnDi+Wo) compositions from Berry et al. (2006).

Using the log K' values calculated for the melts in this study, it is possible to construct a model curve of  $Cr^{2+}/\Sigma Cr$  as a function of  $f_{O_2}$  and the K' values for melts of Y-98 bulk composition:

$$\frac{XCr^{2+}}{\Sigma Cr} = \left[1 + e^{\left(\frac{1}{4}\ln f_{o_2} + \ln K'\right)}\right]^{-1}$$
(4)

Figure 7 contains plots of the modeled Cr<sup>2+</sup>/ΣCr values for Y-98 liquids at 1300 °C. Our modeling indicates that the  $Cr^{2+}/\Sigma Cr$ value for a Y-98 liquid at 1300 °C varies from 0.65 at IW to 0.53 at IW+1.5. Similarly the modeled  $Cr^{2+}/\Sigma Cr$  values for 1380 °C vary from 0.89 at IW to 0.77 at IW+1.5. This modeling places important constraints on the manner in which temperature affects equilibrium Cr<sup>2+</sup>/ΣCr in planetary basalts. Figure 8 illustrates the effects of temperature on the homogenous Cr redox equilibrium with a plot of the modeled Cr redox curves at 1300 and 1380 °C. With increasing temperature there is a prominent displacement of the center of the sigmoidal curve (i.e., the point corresponding to an equal mixture of  $Cr^{2+}$  and  $Cr^{3+}$ ) to higher  $f_{O_2}$  values. To the first order, increasing temperature for the Y-98 bulk composition appears to cause the reduction of  $Cr^{3+}$  to  $Cr^{2+}$  at a constant  $f_{O_2}$ value (defined relative to a buffer). The model curves indicate that an 8.5% reduction in the  $Cr^{2+}/\Sigma Cr$  of the melt is caused by simply increasing the temperature of the system 80 °C.

## CONCLUSIONS AND IMPLICATIONS FOR THE NATURAL Y-98 MELT

The results of this study demonstrate that  $Cr^{2+}/\Sigma Cr$  systematically changes with the oxidation state of its equilibrium melt. Measured  $Cr^{2+}/\Sigma Cr$  can be translated to the  $Cr^{2+}/\Sigma Cr$  of the melt if the ratio of  $D_{Cr^{3+}}$  to  $D_{Cr^{2+}}$  is well known for the system of interest. Ratios of  $D_{Cr^{3+}}$  to  $D_{Cr^{2+}}$  are not canonical, but instead vary with temperature and melt composition. The systematic variation of Cr oxidation state in olivine with  $f_{O_2}$  can be viewed in two lights: (1) as a calibration of Cr valence that is a function of  $f_{O_2}$  and directly applicable to Y-98 melts, or (2) as a general method for estimating  $Cr^{3+}/Cr^{2+}$  of the melt from which the olivine crystal grew. For the latter to be useful, a comprehensive understanding of Cr redox systematics as a function of composition, temperature, and pressure is required. If more data were available, K' could be cast as a function of *P*-*T*-X, potentially making the Cr<sup>2+</sup>/ $\Sigma$ Cr measurements in olivine applicable to any melt composition. In either case, measurements of Cr<sup>2+</sup>/ $\Sigma$ Cr in olivine that was crystallized from primitive mantle derived melts can yield important insights into the equilibrium ratio of Cr<sup>2+</sup>/ $\Sigma$ Cr that was present in these melts. Furthermore, such measurements may



**FIGURE 7.** Shows the Cr<sup>2+</sup>/ $\Sigma$ Cr modeled with the logK' values determined in this study. The points plotted along with the curve are the mean Cr<sup>2+</sup>/ $\Sigma$ Cr values from the Y-98A and Y-98B (1320 °C) experiments from which the apparent equilibrium constants used in the construction of the curve were derived. The dashed lines represent the l $\sigma$  uncertainty associated with the calculated curve (based on the 1 $\sigma$  standard deviation of the calculated logK' values). The arrows and dashed lines in the plot represent the range of  $f_{0_2}$  values that are thought to be representative for many primitive martian magmas.



**FIGURE 8.** The Cr<sup>2+</sup>/ $\Sigma$ Cr modeled with the log*K'* values determined in this study. The points plotted along with the curve are the mean Cr<sup>2+</sup>/ $\Sigma$ Cr values from the Y-98A and Y-98B (1380 °C) experiments from which the apparent equilibrium constants used in the construction of the curve were derived. Notice how the Cr redox curve is displaced to higher  $f_{O_2}$ values as temperature is increased. The solid line represents the location of the IW buffer at 1300 °C and the dashed line represents the location of the buffer at 1380 °C. Simply increasing the temperature at a constant relative  $f_{O_2}$  value imparts an 8.5% increase in the Cr/ $\Sigma$ Cr of the melt.

allow for the calculation of the oxidation state of the magmas and potentially that of their mantle source regions. Specifically, Cr redox measurements from this study have derived valuable estimates of the K' for the homogenous  $CrO_{1.5}$ -CrO equilibrium in a composition representing a primitive, iron-rich martian basalt. Future efforts concentrating on constraining the effects of pressure on the homogenous Cr redox equilibrium may provide more important insight into the  $Cr^{2+}/\Sigma Cr$  redox ratio of the earliest partial mantle melts.

Assuming the effects of pressure on the Cr redox equilibrium are minimal (in the absence of data), results from this work also suggest that the primitive Y-98 melt may have contained significant quantities of both trivalent and divalent chromium at temperatures below 1380 °C. Interestingly, this conclusion places the valence ratio of Cr in martian basalts somewhere in between that of the Moon (highly Cr<sup>2+</sup> enriched) and that of the Earth (highly  $Cr^{3+}$  enriched). The  $Cr^{2+}/\Sigma Cr$  of the melt can also change substantially as a function of temperature without a concomitant change in the  $f_{02}$  of the melt. Given a constant relative  $f_{02}$  value, melts at higher temperatures appear more reduced with respect to their  $Cr^{2+}/\Sigma Cr$  than that of the same melt composition at a lower temperature. This observation importantly suggests that Cr valence ratios in natural magmas must be interpreted in the context of an equilibration temperature. Finally, XANES-based measurements of  $Cr^{2+}/\Sigma Cr$  in olivine can potentially be used as an  $f_{02}$  sensor, provided that the olivine crystallization temperature and K' for the composition of interest are known.

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