

Chromium Oxidation State in Planetary Basalts: Oxygen Fugacity Indicator and Critical Variable for Cr-spinel Stability.

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Introduction: Cr is a ubiquitous and relatively abundant minor element in basaltic, planetary magmas. At the reduced oxidation states (<FMQ) of many planetary basalts Cr is present in melts in both divalent and trivalent forms. The ratio of trivalent to divalent Cr present in the melt has many consequences for the stability and Cr concentration of magmatic phases such as spinel, clinopyroxene, and olivine. However, understanding the Cr valence in quenched melts has historically been plagued with analytical obstacles, and only recently has reliable methodology for quantifying Cr valence in quenched melts been developed. Despite this substantial difficulty, the pioneering works of Hanson and Jones [1] and Berry and O'Neill [2] provided important insights into the oxidation state of Cr in silicate melts. Here we present a series of 1-bar gas mixing experiments performed with a Fe-rich basaltic melt in which we have determined the Cr redox ratio of the melt over a range of fO_2 values by measuring this quantity in olivine with X-ray Absorption Near Edge Spectroscopy (XANES). The measured Cr redox ratio of the olivine phenocrysts can be readily converted to the ratio present in the conjugate melt via the ratio of crystal-liquid partition coefficients for Cr^{3+} and Cr^{2+} [3]. We have applied these results to model Cr spinel stability and Cr redox ratio in a primitive, iron-rich martian basalt.

The Petrologic Importance of Cr-Spinel: Cr-spinel plays many significant roles in modulating the concentrations of important trace elements. Cr spinel has been demonstrated to be a potentially important sink of highly siderophile elements (HSEs) such as Rh, Re and Ir [4, 5]. Cr-Spinel is also an important host for transition metals such as Ni, Co, and V. Additionally, the composition of Cr-spinel is highly sensitive to changing melt chemistry and fO_2 during magmatic differentiation; these relationships render Cr-spinel crystals a sensitive petrologic indicator [5]. Within this work we attempt to lay a framework with which fundamental questions about the link between magmatic Cr-spinels and their conditions of formation can be addressed. In broad terms the data and modeling presented in

this abstract will ultimately help answer outstanding questions such as: 1) How much Cr^{3+} is required to meet the threshold for a melt to attain Cr-Spinel saturation, and what implications does this have for the fO_2 and bulk Cr contents of planetary magmas? 2) How is the Cr redox ratio in the melt (changing as a function of fO_2) manifested in the equilibrium composition of Cr-spinel? 3) What can the composition of early formed Cr-spinel in martian meteorites reveal about the undifferentiated melt composition, redox state, and chemistry of its mantle source?

Experiments: Wire loop experiments were conducted in the one-bar gas mixing laboratory at NASA Johnson Space Center (JSC). The experiments were performed using Re loops to prevent Fe-loss with the exception of experiments run at oxygen fugacity values near the FMQ buffer, which employed Pt-Rh loops. The starting materials consisted of a composition patterned after the whole rock composition of Martian meteorite Yamato 980459 (Y-98). Experiments were performed at temperatures of 1300°C, 1320°C and 1380°C. Experimental fO_2 was controlled with CO-CO₂ mixtures that were calibrated with a zirconia electrochemical oxygen sensor.

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. Cr valence ratios measured with XANES in olivine have been re-calculated to reflect the liquid from which they grew (using the ratio of DCr^{3+}/DCr^{2+} and the mole fractions of Cr^{3+} and Cr^{2+} in the olivine).

Cr Valence in the Experimental Melts: As a first order observation, the calculated $Cr^{2+}/\Sigma Cr$ values for the melt show a distinct trend as a function of the experimental fO_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. Additionally, plots of the average corrected $\ln[\text{Cr}^{3+}/\text{Cr}^{2+}]$ vs. $\ln f\text{O}_2$ yield a linear array. Fitting the 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 $\ln[\text{Cr}^{3+}/\text{Cr}^{2+}]$ and $\ln f\text{O}_2$ is in excellent agreement with the stoichiometry of the homogenous Cr^{2+} - Cr^{3+} oxidation equilibrium [3]. Using the calculated $\text{Cr}^{3+}/\text{Cr}^{2+}$ of the experimental melts it is possible to model the $\text{Cr}^{3+}/\Sigma\text{Cr}$ of the melt as a function of oxygen fugacity. Figure 1 presents a plot of the modeled $\text{Cr}^{3+}/\Sigma\text{Cr}$ values vs. $f\text{O}_2$ for the experimental Y-98 melts.

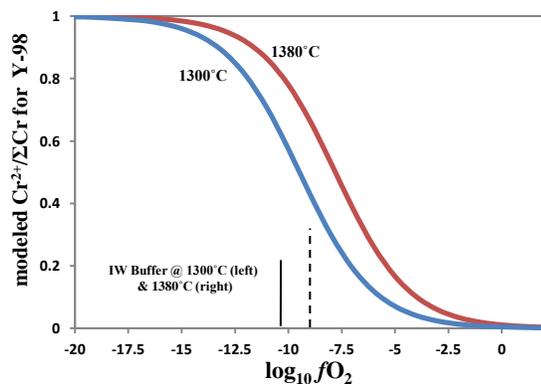


Figure 1. Modeled $\text{Cr}^{3+}/\Sigma\text{Cr}$ for experimental Y-98 liquids at 1300°C and 1380°C; model curves constructed with equilibrium constants derived from XANES based measurements of Cr^{3+} and Cr^{2+} contents of the melts.

How Much Cr^{3+} is Required in the Melt to Attain Cr-Spinel Saturation? Cr-spinel is a stable phase in nearly all of the experimental charges, with the notable exception of experiments conducted at $f\text{O}_2$ values below the IW buffer. Using the XANES measured Cr redox ratios of the melt we have calculated the concentration of Cr^{3+} in the experimental melts. Figure 2 shows the calculated Cr^{3+} contents of the experimental melts as well as model curves for the Cr^{3+} , Cr^{2+} and Fe^{3+} content of the experimental melts. Our measurements indicate that the elemental Cr^{3+} concentration in the liquid must exceed 1450ppm to achieve Cr-spinel saturation. The most reduced experiments (IW-1) contained only 750ppm Cr^{3+} , and therefore did not contain any spinel. As the $f\text{O}_2$ of the experimental charges was increased, the Cr^{3+} content concurrently increased until reaching the level required for spinel saturation. From this point the presence of Cr-Spinel buffers the concentration of Cr^{3+} in the liquid at a constant value (at a fixed Cr-spinel composition).

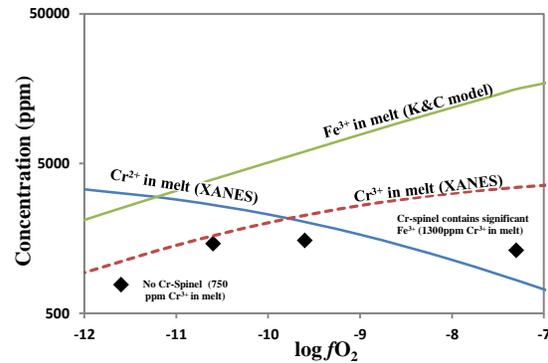


Figure 2. Modeled Cr^{2+} , Cr^{3+} , and Fe^{3+} contents of the Y-98 melts as a function of $f\text{O}_2$. Calculated Cr^{3+} contents of experimental melts are plotted with the black diamonds.

the oxidized experiments appear to have required less Cr^{3+} in the liquid to maintain Cr-spinel saturation. This observation can be readily explained considering the precipitous increase of Fe^{3+} present in both the melt and the spinel. The Cr-spinels in the most oxidized experiments (FMQ) have a much larger magnetite component than do the other spinels. The fact that the spinels from the oxidized experiments have a lower mole fraction of the chromite component, is consistent with the lower abundances of Cr^{3+} required to maintain Cr-spinel saturation in these experiments. This observation suggests that the stability field of Cr-spinel can be greatly expanded (in $f\text{O}_2$ space) when a small quantity (~1-2 wt. %) of ferric iron is present in the liquid. **Conclusions:** Assuming that the effects of pressure on the Cr redox equilibrium are minimal, results from this work suggest that the primitive, Y-98 melt may have contained significant quantities of both trivalent and divalent chromium at temperatures below 1380°C. Results from our modeling also suggest that a substantial quantity of Cr^{3+} is required in the melt to attain Cr-spinel saturation in iron rich martian basalts. One implication that falls out of this observation is that Cr-spinel may not be a liquidus phase but rather a late crystallizing phase in relatively Cr poor liquids, even at moderately oxidizing $f\text{O}_2$ values.

References: [1] Hanson and Jones (1998) Am. Min. [2] Berry and O'Neill (2004), Am. Min. [3] Bell et al. (2014) Am. Min. [4] Righter et al. (2004) GCA [5] Arskin and Nikolaev (1996) Contrib. Mineral. Petrol.

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