

DECODING THE REDOX HISTORY RECORDED IN THE OLIVINE MEGACRYSTS OF YAMATO 980459 WITH CHROMIUM K-EDGE XANES. A.S. Bell¹ (asbell@unm.edu), P.V. Burger¹, C.K. Shearer¹, and J.J. Papike¹ ¹Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque New Mexico 87131

Introduction: Olivine can serve as a high fidelity recorder of the Cr valence ratio and the fO_2 of the melt from which it grew [1]. Therefore, high spatial resolution x-ray absorption near edge structure (XANES) measurements of Cr valence in olivine phenocrysts may capture the fO_2 evolution of olivine-phyric, martian basalts. In this way, these measurements can potentially serve as a window into the relationship between the pristine fO_2 of mantle derived magmas and how the Cr valence ratio in olivine may have been altered by processes such as crustal assimilation and degassing. Although Cr valence measurements in olivine are not in and of themselves direct measurements of magmatic fO_2 , the Cr^{2+}/Cr^{total} values can be converted to magmatic fO_2 values, provided that partitioning behavior and Cr redox systematics are calibrated for the olivine-melt system of interest.

The olivine megacrysts of Yamato 980459 are ideal candidates for a detailed Cr valence study because: (1) Y98 is believed to represent a near-primary, partial melt of the martian mantle, therefore olivine in this sample has the greatest potential to preserve the fO_2 of its mantle source; (2) the olivine megacrysts preserve complex and protracted growth histories that that have been suggested to record a late-stage oxidation event [2,3]; and (3) we have developed an extensive database of redox controlled experiments that have been conducted for the purpose of understanding the phase equilibria of Y98 (and potentially other olivine-phyric martian basalts), its olivine-melt Cr partitioning systematics, as well as the effects of temperature and melt composition on the equilibrium Cr valence ratio in coexisting olivine and melt.

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. The beam was focused to final spot size of approximately $5\mu m$ by $5\mu m$ with dynamically configured Kirkpatrick-Baez focusing mirrors.

All spectra were acquired in fluorescence mode utilizing a cryogenically cooled Si (311) monochromator and a silicon-drift solid state detector offset at a 45° angle from the sample. Spectra were acquired in three distinct crystallographic orientations and merged in order to mitigate the effects of crystalline anisotropy on the intensity of the peak associated with the 1s-4s transition [1, 4].

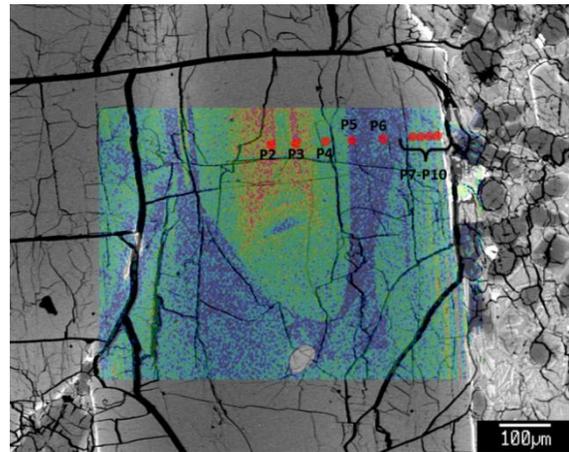


Figure 1 is a composite backscattered electron image and phosphorus WDS x-ray map showing the location of the XANES spot analyses on an olivine megacryst in Y98.

Results: We have obtained Cr *K*-edge spectra for an olivine megacryst as well as for a smaller “ground mass” olivine phenocryst. The analytical transects were specifically targeted to sample a region from Mg-rich core to the ferroan rim. Figure 1 shows the location of the analytical transect in the megacryst, superimposed on a composite backscattered electron

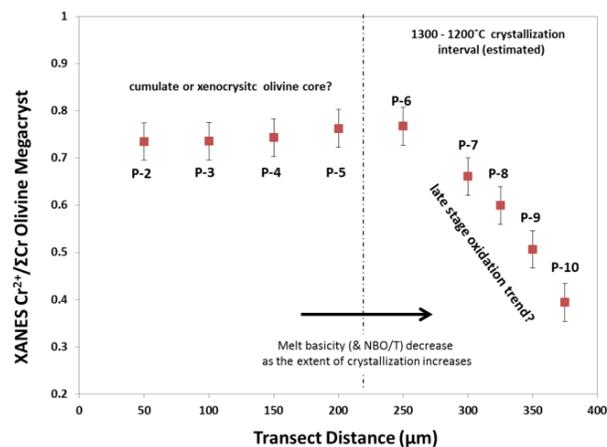


Figure 2 shows the XANES measured Cr valence ratios for the Y98 olivine megacryst depicted in Fig. 1. The distances on the X-axis are arbitrary, and have been included to depict the distance between the analytical spots.

image and phosphorus x-ray map. The P-map has been obtained in order to help place the valence measurements into an “olivine-growth stratigraphy”. The calculated Cr^{2+}/Cr^{total} values obtained for the megacryst are plotted as a function of position in Figure 2. Beginning in the core of the megacryst, the measured Cr^{2+}/Cr^{total} values are effectively constant within the uncertainty of the measurements, for a

distance of approximately 300 μm (corresponding to spots P2-P5). The XANES spectra corresponding to spots P7-P10 show a monotonic decrease in the calculated $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ from 0.77 to 0.39 (Figure 2). Data from a groundmass phenocryst indicate that the measured $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ values are significantly lower than those observed in the megacryst transect, with values ranging from a maximum of 0.48 to a minimum of 0.20.

Interpreting the Cr valence Measurements:

Valence ratios of heterovalent elements in melts are not only controlled by $f\text{O}_2$, but can also be significantly influenced by temperature, melt composition, and pressure. Therefore, in order to correctly interpret to redox evolution recorded by the measured Cr valence values, the effects of all of these variables must be quantified for the Y98 system.

The crystallization depths for Y98 have been estimated to be relatively shallow, corresponding to pressures of less than 300 MPa [5]. Based on these estimates, it is unlikely that magma ascent and decompression plays a significant role in modifying the $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ recorded in conjugate olivine-melt pairs.

The effects of decreasing temperature may have a significant influence on the Cr valence ratio of the melt. For example, decreasing temperature has been shown to increase the equilibrium valence ratio for $\text{V}^{4+}/\text{V}^{5+}$ in silicate melts [6]. In other words, at constant a $f\text{O}_2$ value, decreasing temperature stabilizes the oxidized half of the redox couple. To test the extent to which this may be true for Cr redox ratio, we have performed a series of experiments on the Y98 bulk composition, as well a low liquidus CMAS bulk composition. These experiments indicate that the effects of temperature on the Cr valence ratio of the melt are relatively minor, such that a 100°C decrease in temperature depresses $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ by approximately 5%. Coincidentally, at $f\text{O}_2$ values along the IW buffer curve, the decrease in $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ caused by decreasing temperature is nearly offset by the temperature dependent decrease of the buffer curve-defined $f\text{O}_2$ value. The results of these experiments are depicted in Figure 3; they suggest that the temperature effects on the Cr valence ratios of melt-olivine pairs are of relatively little consequence, at least relative to the effects of changing $f\text{O}_2$.

Variable melt composition may also affect the $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ of the Y98 melt. As the extent of crystallization increases, the composition of the residual liquid becomes enriched in the CaO and Al_2O_3 components, while becoming depleted with respect the MgO. The effect of changing melt composition on the valence ratios of heterovalent elements may be rationalized in terms of melt's optical basicity; numerous studies have demonstrated that melts with higher values of optical basicity preferentially shift redox equilibria so that the cation

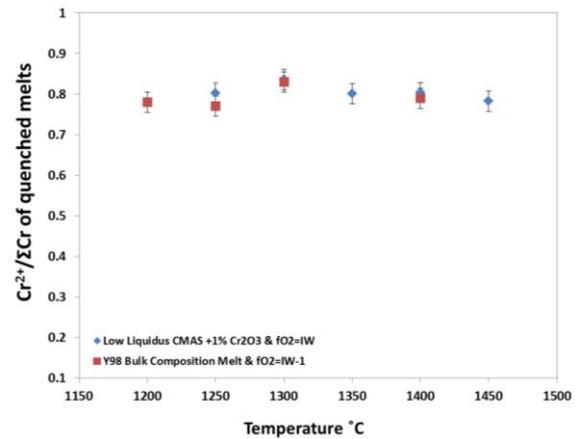


Figure 3 shows the Cr valence ratio determined for both a CMAS melt composition and the quenched melts from one bar Y98 phase equilibrium experiments. The intrinsic temperature effects on the $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ of both melts is relatively minimal. Note that the trend for the Y98 data also included the effects of the changing composition of the melt.

of the higher valence state is preferentially stabilized [3]. Our calculations indicate that the optical basicity of the Y98 melt slightly decreases with increasing crystallization from a value of 0.62 at 1400°C to 0.57 at 1200°C. This suggests that the effect of changing melt composition may in fact cause a small increase in the $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$; this effect is the opposite of the trend observed in the megacryst analytical transect, lending additional credence to the interpretation that the Cr valence ratio reflects a late-stage magmatic oxidation event.

The $f\text{O}_2$ values recorded by Y98 Olivines: Based on the conclusions of the previous section, we interpret the decrease in $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ observed in the megacryst rim to be representative of a late-stage oxidation event. We calculate the $f\text{O}_2$ in the core of the megacryst to be at or slightly below the IW buffer, perhaps as low as $\Delta\text{IW}+0$ (± 0.2). As Y98 represents a primary mantle melt, this value likely represents the best estimate for the $f\text{O}_2$ of the depleted martian mantle.

The decreasing $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ values preserved in the olivine rim suggest that the $f\text{O}_2$ increased from an initial value of ΔIW to a maximum of $\Delta\text{IW}+2$. Recent SIMS work on olivine-hosted melt inclusions and groundmass glass suggests that the residual late stage melt experienced significant hydrogen and carbon loss due to shallow degassing [5]; therefore, the late stage oxidation event recorded in the olivine m degassing of the residual Y98 liquid.

References: [1] Bell et al. (2014) Am.Min. 99, 1404-1412; [2] Shearer et al. (2013) GCA 72, 17-38; [3] Usui et al. (2008) GCA 72, 1711-1730; [4] Berry et al. (2006) Am. Min. 91, 1901-1908; [5] Usui et al (2012) EPSL 357-358, 119-129; [6] Schreiber and Haskin (1976), LPSCVII, 1221-1259

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