

Cr K-EDGE XANES ANISOTROPY & OLIVINE ORIENTATION: DEVELOPING A TECHNIQUE FOR THE ASSESSMENT OF THE OXIDATION STATE OF MAGMATISM ON THE ANGRITE PARENT

BODY A.S. Bell¹ (asbell@unm.edu), P.V. Burger¹, C.K. Shearer¹,¹Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque New Mexico 87131

Introduction: Cation valence ratio measurements made using synchrotron based XANES techniques are a potentially powerful tool for understanding the redox histories of igneous meteorites. For example, Bell et al. [1] used synchrotron based Cr K-edge XANES measurements to unravel the magmatic redox history as recorded by the olivine megacrysts of Yamato 980459. This study revealed that the technique could be used to reveal changes in the Cr valence ratio and magmatic fO_2 that occurred throughout the growth history of the megacrysts. Despite this early success, there are still issues that hamper the full utilization technique to extract quantitative redox information from crystalline materials. The primary obstacle associated the technique is related to understanding how the crystallographic orientation affects the apparent oxidation state cation of interest. Numerous studies clearly demonstrate that the intensities and overall shape of the XANES spectra depend upon the crystallographic orientation of the phenocryst with respect the polarization vector of the synchrotron x-ray beam. Changes in the spectra arising from orientation-related anisotropy are often a significant source of uncertainty in the calculated cation valence ratios [2,3]. In order to mitigate these issues, the effects of crystallographic orientation must be accounted for in the processing and conversion of XANES spectra into quantitative cation valence information.

This abstract presents a preliminary Cr XANES dataset that obtained for experimentally grown olivine crystals; XANES spectra from were obtained for olivines with known crystallographic orientations. These data have been used to calibrate a model that predicts the variation of XANES absorption intensity as a function of a crystal's orientation. This calibration will aid in the processing and interpretation of Cr K-edge XANES spectra from olivine phenocrysts from a suite of angrites. This necessary groundwork lays a solid foundation for the expansion for the measurement and interpretation of Cr valence ratios in similar investigations of olivine phenocrysts in both chondritic and achondritic meteorites.

Olivine Growth Experiments: The olivine crystals used in this study were experimentally grown from An-Di-Fo melts doped with 0.50 wt. % Cr_2O_3 . The olivine growth experiments were performed in the gas mixing laboratory at the University of New Mexico (UNM). All of the atmospheric pressure experiments were conducted in a vertical Deltech tube furnace equipped with $MoSi_2$ heating elements and a programmable, microprocessor-based Eurotherm[®]

controller. The oxygen fugacity values of the experiments were imposed with CO-CO₂ mixtures. The experiments were performed by heating the starting material above the liquidus at 1400°C and subsequently cooled to a final sub-liquidus temperature of 1300°C. The competed experiments produced quenched glasses that contained approximately 15% forsterite (Figure 1).

XANES Spectra Acquisition & Determining Olivine Orientations: 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-

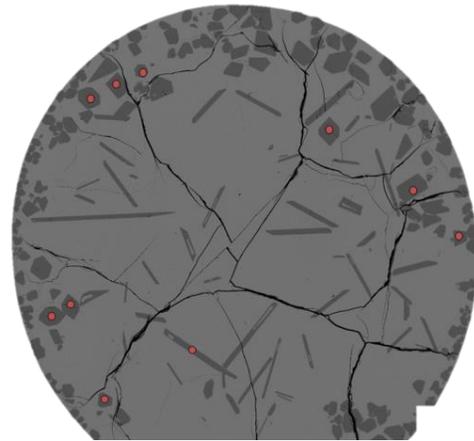


Figure 1 shows a backscattered electron image of one of the experimental charges used in this study. The light gray phase is quenched CMAS glass and darker gray phase are small euhedral olivine crystals. Red spots on the olivine crystals indicate that these olivines were targeted for XANES and subsequent orientation analysis. The width of the experimental charge shown above shown is approximately 3.5mm.

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 Olivines slated for XANES analysis were carefully selected based. This was done to ensure that a wide range of potential crystallographic orientations would be sampled as a part of this study. Preliminary identification of olivine orientations has been accomplished by visual inspection and with measurements of the angles between crystal face (made with the angle measurement tool in the NIH ImageJ software. These preliminary orientation

estimates will also be augmented with a detailed electron backscatter diffraction study (EBSD) of the target olivines. The orientations obtained as a part of the EBSD study will ultimately be incorporated into a predictive model of the anisotropy in the Cr-K edge XANES spectra.

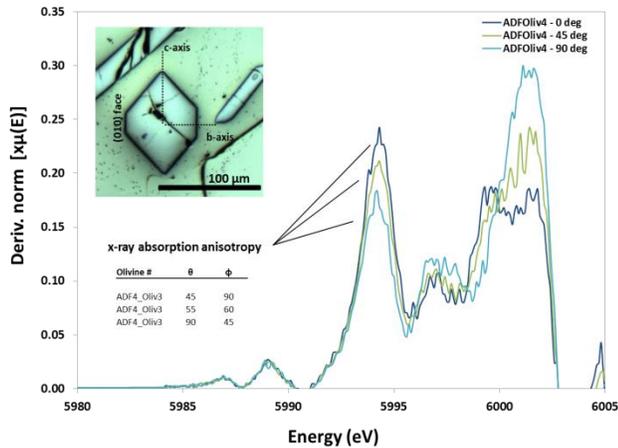


Figure 2 shows the variation in the XANES signal as a function of crystallographic orientation. The reflected light image in the upper right-hand corner of the graph shows the olivine from which these spectra were obtained. The olivine was rotated at $\sim 45^\circ$ intervals relative to the polarization vector of the beam. The intensity of the 1s-4s absorption features clearly changes with the olivine's orientation.

Discussion: Our data clearly show that the intensity of the 1s-4s absorption features varies systematically as a function of the olivine's crystallographic orientation. The spectra shown in Figure 2 illustrate the orientation induced variability in the XANES signal.

The variation of the 1s-4s absorption intensity has several important consequences. The most important of these is that the $\text{Cr}^{2+}/\Sigma\text{Cr}$ ratios calculated from the XANES spectra are a function of olivine's orientation. For example, if the spectra in for the olivine shown in Figure 2 were converted into apparent $\text{Cr}^{2+}/\Sigma\text{Cr}$ ratios, they would vary from a low of 0.80 to a high of 0.99 (where the actual $\text{Cr}^{2+}/\Sigma\text{Cr}$ of the olivine shown is 0.93).

In order to account for and correct these effects we have we have constructed a model "x-ray absorption indicatrix". This model describes how the intensity of the 1s-4s absorption varies as a function of the olivine orientation relative to the polarization vector of the x-ray beam. This model uses the olivine's orientation in and the observed intensity of the 1s-4s absorption for that orientation and corrects this value the isotropic absorption cross section value (e.g. the "true" absorption value that would be obtained for a powder of randomly oriented crystals). Preliminary testing of our model suggests that absorption indicatrix model indicates that the orientation correction can reduce uncertainty in a measured $\text{Cr}^{2+}/\Sigma\text{Cr}$ value by a factor

of three from an uncorrected value of ± 0.15 to ± 0.04 for orientation corrected spectra.

Conclusions and Future Directions: The preliminary results from this study have several important conclusions. The first conclusion is that developing an orientation based correction can significantly reduce the analytical uncertainty arising from crystallographic orientation effects. Provided that the orientation of the olivine of interest is known that application of this correction can reduce the analytical uncertainty to less than 5%; this reduction in uncertainty renders the Cr in olivine method especially sensitive to small changes in Cr valence that were difficult to resolve without the orientation correction.

The increased precision in the measurements of the Cr valence ratios in olivine also has been highly beneficial in the interpretation and translation of Cr measurements obtained on martian olivines. The lower valence ratio uncertainties brought about by this calibration have substantially improved the accuracy of the calculated $f\text{O}_2$ values for the Y98 magma system.

Finally, we note that this study is the foundation of what will be longer term investigation the $f\text{O}_2$ as recorded by Cr valence state in olivine from a suite of angrites. This larger study will allow us test models for primordial melting of chondritic material to produce the angrite parent melts. The results of several experimental studies indicate that the partial melting of CR and CV chondrites provided that the $f\text{O}_2$ of the system is oxidized enough to prevent the formation of metallic Fe (or Fe-Ni alloys). However, upon detailed inspection the angrites themselves have given mixed signals with respect to their oxidation state, therefore the oxidation state of angrite magmatism and its relationship to their mode of petrogenesis remains an unresolved issue. With additional work, the development of the Cr in olivine redox sensor and this new orientation calibration we will determine to redox conditions of angrite magmatism and ultimately test the competing petrogenetic models for their formation.

References: [1] Bell et al. (2014) *Am. Min.* 99, 1404-1412. [2] Dyar et al. (2002) *Canadian Mineralogist*, 40, 1375-1393 [3] Evans et al. (2014) *Am. Min.* 99, 443-457.

Acknowledgements

We gratefully acknowledge the beamline award, as well as assistance of GSECARS beamline staff. GeoSoilEnviroCARS is supported by the National Science Foundation-Earth Sciences (EAR-1128799) and Department Geosciences (DE-FG02-94ER14466). Use of the Advanced Photon Source was supported by U.S. Department of Energy. Office of Science. Office of Basic Energy Science under Contract No. DE-AC02-06CH11357.