

**VANADIUM K XANES OF SYNTHETIC OLIVINE: VALENCE DETERMINATIONS AND CRYSTAL ORIENTATION EFFECTS.** S. R. Sutton<sup>1,2</sup> and M. Newville<sup>2</sup>, <sup>1</sup>Dept. of Geophysical Sciences and <sup>2</sup>CARS, University of Chicago, Chicago, IL. 60637.

**Introduction:** Vanadium can exist in a large number of valence states in nature (2+, 3+, 4+ and 5+) and determinations of V valence is therefore valuable in defining the oxidation states of earth and planetary materials over a large redox range. Synchrotron-based x-ray absorption near edge structure (XANES) spectroscopy is well-suited for measurements of V valence with ~micrometer spatial resolution and ~ppm elemental sensitivity. Applications of microXANES have been demonstrated for basaltic glasses [1-6]. Applications to minerals are feasible but complicated by orientation effects (e.g. [7]; due to polarization of the synchrotron x-ray beam) and some results for spinel have been reported [8]. Here we report initial results for olivine from laboratory crystallization experiments. The goal is to define the valence partitioning between olivine and melt and quantify the magnitude of orientation effects, the latter tested by measuring grains at a variety of orientations in the same charge.

**Experimental:** The valence determination uses the intensity of a vanadium K XANES pre-edge peak near 5470 eV interpreted to be due to a dipole-forbidden,  $1s-3d$  electron transition [9]. The intensity (and energy) of this peak increases systematically as valence becomes more oxidized [9]. Intensity values are normalized to the "above edge" intensity, defined to be 1000.

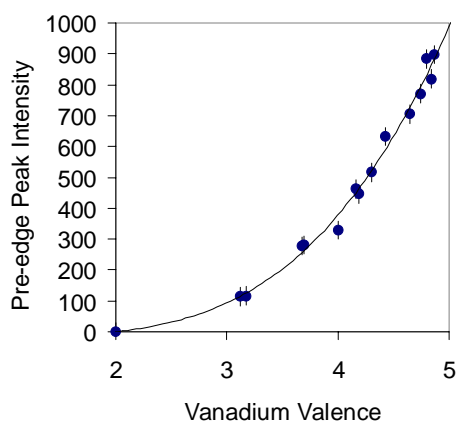
Vanadium K XANES spectra were measured using the undulator-based microprobe at Sector 13

(GeoSoilEnviroCARS) at the Advanced Photon Source, Argonne National Laboratory [10]. The overall resolution of the V K XANES spectra was about 1.5 eV. The microprobe consisted of Kirkpatrick-Baez (KB) microfocusing mirrors [11] and a Vortex energy dispersive x-ray fluorescence detector (Radiant Detector Technologies, LLC) (spot size  $\approx 3 \mu\text{m}$ ; energy resolution  $\approx 150 \text{ eV}$  for the V  $K_{\alpha}$  fluorescence peak).

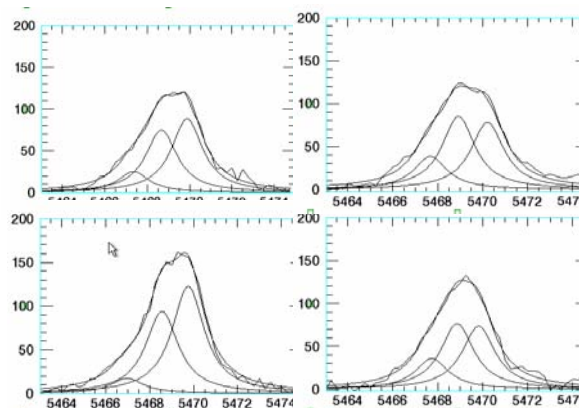
Two suites of experimental glasses of basaltic or komatiitic composition with vanadium dopant were studied *Hanson suite* (B. Hanson, Corning Glass; J. Jones, NASA-JSC): FAD composition [12], 1310 or 1320 °C at  $f\text{O}_2$  from air to the Cr-CrO buffer. Analyzed here were the FAD-CRV samples (doped with both Cr and V) produced at IW, FMQ and  $10^{-9}$ . *Canil suite* (D. Canil, University of Victoria, Canada): Komatiitic composition [13]; 1225 to 1425 °C at log  $f\text{O}_2$  from -5.5 to -10.7. Analyzed here were KOM25 ( $10^{-5.5}$ ; 1425 °C), KOM24 ( $10^{-8.2}$ ; 1350 °C) and KOM27 ( $10^{-9.1}$ ; 1425 °C). For each charge, V K XANES spectra were acquired for multiple olivine crystals (between two and twelve) plus the glass matrix.

Valence calibration (Figure 1) was obtained using synthetic glasses where valences had been previously determined by titration (H. Schreiber, Virginia Military Inst; FAD and FAS composition [14] 1500 °C at log  $f\text{O}_2$  from 0 to -9 (see [1] for details). We define an effective valence  $V^*$  to represent the average valence of a sample as determined from this calibration curve.

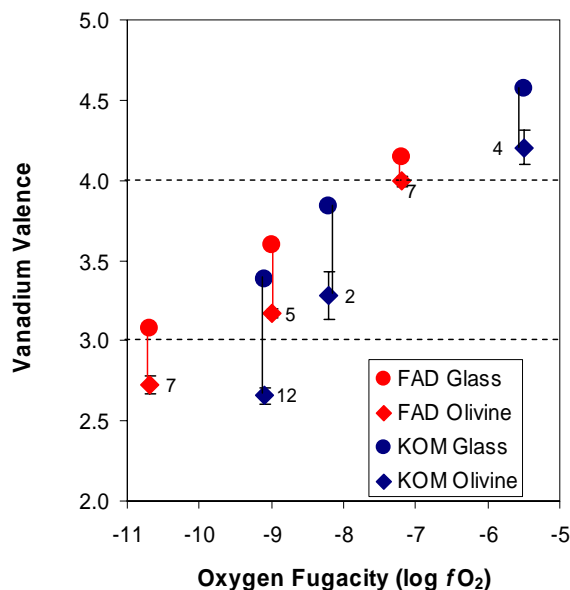
**Results and Discussion:** In general, we found the



**Figure 1:** Pre-edge peak intensity data for Schreiber FAS/FAD glass suite showing the dependence on valence. Valence values were determined independently by Schreiber. An intensity value of zero was assumed for pure  $V^{2+}$  based on the expectation of high symmetry for  $\text{VO}_6$  groups [9]. The curve, a 3<sup>rd</sup>-order polynomial fit to the data, was the basis of valence determinations for unknowns.



**Figure 2:** Pre-edge peaks (V K fluorescence intensity versus incident beam energy in eV) for 4 olivine grains from KOM27. Shown are the raw spectra, 3 fitted Lorentzian peaks and the combined fit. These spectra show the subtle effects of crystal orientation (due to the polarization of the synchrotron radiation) and demonstrate a weak variation in overall intensity, the basis for the valence determination.



**Figure 3:** Plot of vanadium valence for glass (circles) and olivine (diamonds) from the komatiite (KOM) and basaltic (FAD) suites. The tie-lines connect associated olivine-glass pairs. The number of analyzed olivine grains is adjacent to each olivine datum and their valence standard deviation is shown by vertical error bars.

effects of crystal orientation to be subtle. Figure 2 shows the pre-edge spectra for four olivine grains at different orientations. The relative intensities of the component peaks of the multiplet vary from grain to grain leading to subtle changes in overall spectral shape. The overall intensity varies by only about 10% corresponding to a valence variation of only about 2% for this relatively reduced specimen.

Figure 3 shows the valence results for the 6 experimental charges studied (3 KOM and 3 FAD). In each case, one glass spectrum was acquired plus spectra for multiple, randomly oriented olivine grains. The tie-lines in Fig. 3 show the olivine-glass associations and the data cover the log  $fO_2$  range from -5.5 to -10.7. Temperatures of the runs ranged from 1320 to 1425 °C. Previous work has shown a temperature effect on vanadium valence where higher temperatures produce more reduced V [1,12]. This effect can be seen in comparing the KOM and FAD data at log  $fO_2$  of -9 where the KOM sample (1425 °C) is slightly more reduced than the FAD one (1320 °C). No attempt was made to correct for this effect here.

For each olivine-glass association in Fig. 3, we show the number of olivine grains analyzed (number next to olivine data points) and the standard deviation of the olivine grain population (error bar on olivine data points). One can see that there is a well defined trend versus log  $fO_2$  for the glasses (circles in Figure

3), consistent with previous results [1] and both sample suites fall on the same general trend. The relationship between the glass and olivine valences is less uniform. There are two samples at the oxidizing end, systems containing both  $V^{4+}$  and  $V^{5+}$ , at log  $fO_2$  of -5.5 (FAD) and -7.2 (KOM). Although the glass valences differ significantly, the olivine valences are both near 4.0 suggesting that the partition coefficient for  $V^{5+}$  is small compared to that of  $V^{4+}$ . For systems with an average glass valence between  $V^{3+}$  and  $V^{4+}$ , the olivine tends to be close to  $V^{3+}$  indicating a preference for  $V^{3+}$  over  $V^{4+}$ . This is particularly noticeable in the sample at log  $fO_2$  of -8.2 (KOM) where the glass valence is 3.84 ( $V^{4+}$  dominant) and the olivine valence is 3.29 ( $V^{3+}$  dominant), a situation that is also observed in the KOM sample at log  $fO_2$  of -9.0.

The more reduced samples log  $fO_2$  -9.1 and -10.7 are somewhat problematic. Both the glasses and olivines are dominated by  $V^{3+}$  but the olivine valences appear to be significantly more reduced than pure  $V^{3+}$ . The most straightforward interpretation is that these grains contain significant levels of  $V^{2+}$  but another possibility is that the  $V^{3+}$  octahedra are more symmetric than those in the glasses leading to lower pre-edge peak intensities for equivalent valence. If the latter is correct, it indicates that the valence calibration for glasses (Fig. 1) is not exactly accurate for olivine and a mineral-specific calibration will be required for highest accuracy. Extended x-ray absorption fine structure (EXAFS) measurements should help to clarify this issue.

**Conclusions:** Vanadium K microXANES is a promising technique for V valence determinations in olivine and may eventually lead to valence-specific partitioning information. Vanadium in olivine tends to be more reduced than its melt source indicating a preference (greater partition coefficient) for more reduced species. The effects of crystal orientation on V K pre-edge peak intensity (basis of valence determination) due to the polarization of the synchrotron radiation appear to be subtle suggesting that valence determinations on single olivine grains of unknown orientation from a thin section of a natural sample would be appropriate.

**References:** [1] Sutton, S., et al. (2005) GCA, in press ; [2] Karner, J. M. et al. (2005) Am. Min. submitted ; [3] Karner, J.M. et al. (2004) LPSC XXXV, #1269; [4] Sutton, S.R. et al. (2002) LPSC XXXIII, #1907; [5] Karner, J.M. et al., (2003) LPSC XXXI ; [6] Giulii, G. et al. (2004) Am. Mineral. 89, 1640-1646; [7] Dyar, M. D., et al. (2002) Am. Min. 87, 1500-1504; [8] Righter, K. et al. (2005) this conference; [9] Wong, J. et al. (1984) Phys Rev B 30, 5596-5610; [10] Sutton S. R. et al. (2002) RiMG 49, 429-483; [11] Eng P. J. et al. (1998) SPIE Proc. 3449, 145 ; [12] Hanson B. and Jones J. H. (1998) Am. Min. 83, 669-684 ; [13] Canil, D. (1999) GCA 63, 557-572; [14] Schreiber H. (1986) J. Non-Cryst. Solids 84, 129-141.