

**OXYGEN BAROMETRY OF BASALTIC GLASSES BASED ON VANADIUM VALENCE DETERMINATIONS USING SYNCHROTRON MICROXANES.** S.R. Sutton<sup>1,2</sup> (Sutton@cars.uchicago.edu), J.M. Karner<sup>3</sup>, J.J. Papike<sup>3</sup>, J. S. Delaney<sup>4</sup>, C.K. Shearer<sup>3</sup>, M. Newville<sup>2</sup>, P. Eng<sup>2</sup>, M. Rivers<sup>1,2</sup>, and M. D. Dyar<sup>5</sup> <sup>1</sup>Department of Geophysical Sciences and <sup>2</sup>Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637; <sup>3</sup>Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131-1126; <sup>4</sup>Geology Department, Rutgers University, New Brunswick, NJ 08903; <sup>5</sup>Department of Earth and Environment, Mount Holyoke College, South Hadley, MA.

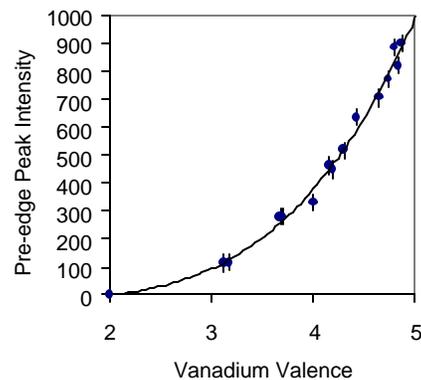
**Introduction:** A promising proxy for oxygen fugacity is the valence of vanadium because it has a large number of valence states in nature (2+, 3+, 4+ and 5+) and is ubiquitous in earth and planetary materials. We describe here a new, non-destructive method for valence determinations of vanadium and oxygen fugacity estimates for basaltic glasses with spatial resolution of a few micrometers using synchrotron x-ray absorption near edge structure (XANES) spectroscopy. Details of this method and applications to martian, lunar and terrestrial glasses are described in [1] and in accompanying abstracts [2,3].

**Experimental: Approach.** The basis of XANES spectroscopy is the mapping of the x-ray absorption edge of the element of interest with high energy resolution. Typically, the XANES spectrum is obtained by measuring the intensity of a characteristic fluorescence line (in this case, V K<sub>α</sub>) as the incident x-ray energy is scanned over the appropriate absorption edge. The valence determination uses a pre-edge peak near 5470 eV interpreted to be due to a dipole-forbidden, 1s-3d electron transition [4]. The intensity (and energy) of this peak increases systematically as valence becomes more oxidized [5]. Intensity values are normalized to the “above edge” intensity, defined to be 1000.

**Apparatus.** Vanadium K XANES spectra were measured using the undulator-based microprobe at Sector 13 (GeoSoilEnviroCARS) at the Advanced Photon Source, Argonne National Laboratory [6]. The overall resolution of the V K XANES spectra was about 1.5 eV. Two different “focusing mirror/detector” setups were used. The first setup consisted of Kirkpatrick-Baez (KB) microfocusing mirrors [7] and a 16-element Ge array energy dispersive x-ray fluorescence detector (Canberra Industries, Inc.) coupled with digital signal processing electronics (XIA, Inc.) (spot size  $\cong$  3  $\mu$ m; energy resolution  $\cong$  150 eV for the V K<sub>α</sub> fluorescence peak). The second setup consisted of large versions (meter long; [8]) of the above mirrors coupled with a wavelength dispersive spectrometer (WDX-600; Oxford Instruments, Inc.) (spot size  $\cong$  40  $\mu$ m; energy resolution = 20 eV at 6 keV, resolves V K<sub>α</sub> from the typically more intense Ti K<sub>β1</sub>).

**Standards.** Four suites of experimental glasses of basaltic or komatiitic composition with ~1% V<sub>2</sub>O<sub>3</sub> dopant were studied for valence and oxygen fugacity standardization purposes: *Schreiber suite* (H. Schreiber, Virginia Military Inst): FAD and FAS composition [9] 1500 °C at log  $f$ O<sub>2</sub> from 0 to -9. V valences (V<sup>5+</sup> to

V<sup>3+</sup>) were previously obtained independently by optical spectrometry. *Hanson suite* (B. Hanson, Corning Glass; J. Jones, NASA-JSC): FAD composition [10], 1310 or 1320 °C at  $f$ O<sub>2</sub> from air to the Cr-CrO buffer. *Canil suite*



**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<sup>2+</sup> based on the expectation of high symmetry for VO<sub>6</sub> groups [5]. The curve, a 3<sup>rd</sup>-order polynomial fit to the data, was the basis of valence determinations for unknowns.

(D. Canil, University of Victoria, Canada): Komatiitic composition [11]; 1225 to 1425 °C at log  $f$ O<sub>2</sub> from -5.5 to -10.7. *Beckett suite* (J. Beckett, Cal. Inst. Tech.): CMAS composition; an isobaric experiment (log  $f$ O<sub>2</sub> = -8), 1274 to 1425 °C.

**Vanadium Valence Systematics:** A plot of vanadium pre-edge peak intensity versus known valence state (Figure 1) for the Schreiber glasses shows a well-defined trend. For the present purposes, we have assumed the intensity of V<sup>2+</sup> is zero, based on the expectation of near perfect octahedral symmetry and, therefore, a very weak 1s-3d transition [5]. Figure 1 shows the huge dynamic range of this approach allowing valence determinations for V<sup>2+</sup> to V<sup>5+</sup>.

Using this calibration curve, the effective valences of the other glasses can be determined. For example, the Canil glasses range from 2.9 to 4.3 with the pure V<sup>4+</sup> composition occurring near log  $f$ O<sub>2</sub> = -7. This result is consistent with Canil’s prediction that V<sup>3+</sup> becomes the dominant species near NNO-3 (log  $f$ O<sub>2</sub> = -9.5 at 1300 °C)[11]. The XANES data indicate a V valence of 3.5 (50/50 mixture of V<sup>3+</sup> and V<sup>4+</sup>) at log  $f$ O<sub>2</sub> ~ -9.5.

**Comparison of XANES and Optical Spectra:** The pre-edge peaks are actually multiplets and a compari-

son with optical spectra can be made using a Z+1 model approach (e.g., [4]). In this model, the XANES spectrum for element Z should match the optical spectrum for element Z+1. These predictions indicate that, for glasses, a very weak pre-edge would be expected for  $V^{2+}$ , three peaks are predicted for both  $V^{3+}$  and  $V^{4+}$ , and an intense singlet might be expected for  $V^{5+}$ . The number and energy separations of the multiplet components in the XANES are in good agreement with these predictions [1].

**Melt Composition Dependence:** The oxygen fugacity dependence of the Schreiber glass intensities shows slight composition dependence with the FAS (low Ca) glasses showing slightly more reduced vanadium than the FAD (high Ca) glasses at the same  $fO_2$  ( $\leq 10\%$  intensity difference). This result is consistent with the notion that increased basicity of the melt leads to increased valence of a redox couple [9]. No attempt has been made at the present time to correct for these small effects.

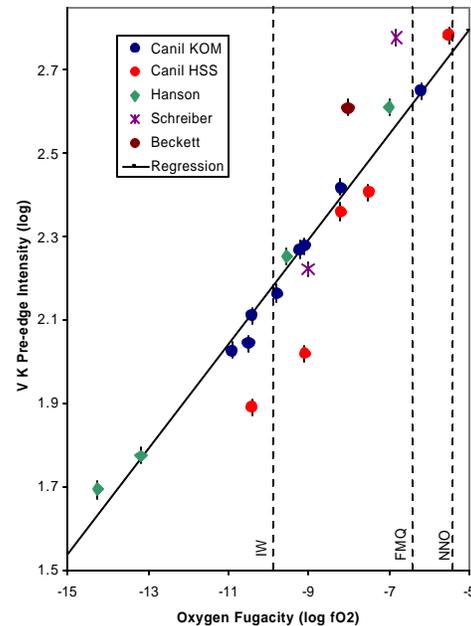
**Temperature Dependence:** The Beckett suite and several of the Hanson samples represent isobaric couples that were used to determine the magnitude of valence variations due to temperature differences. The fractional intensity change per degree,  $d$ , was found to be  $-0.0027 \pm 0.0002$ . Thus, the standard measurements can be corrected to the estimated liquidus temperature of an unknown glass using:

$$I(std, T_{unk}) = I(std, T_{std}) * [1 - d * (T_{unk} - T_{std})]$$

In this way, a calibration curve for peak intensity vs. oxygen fugacity can be produced for each unknown, an example for 1400 °C is shown in Figure 2.

**Vanadium Site Geometry by MicroEXAFS:** Because site geometry can also affect pre-edge peak intensity, we make the implicit assumption that changes in coordination in basaltic glasses occur in the unknowns in an analogous way to those in the standards. To test this assumption, microEXAFS (extended x-ray absorption fine structure) spectra were obtained on five synthetic and natural glass samples covering the range of the observed redox states. The microEXAFS data (first-shell analysis with IFEFFIT; [12]) for both natural and synthetic glasses studied here can be satisfactorily interpreted within a coordination sequence involving octahedral coordination of V for valences between  $V^{3+}$  and  $V^{4+}$  with smaller coordination numbers becoming dominant for oxidized samples between  $V^{4+}$  and  $V^{5+}$ . These results support the suitability of the synthetic glasses as standards in the oxybarometric method described here covering V valences from 2+ to 5+.

**Conclusions:** A new oxybarometer for solar system basaltic glasses based on vanadium K edge microXANES spectra was described. Vanadium is unique among abundant elements in siliceous materials in that it can occur in nature in four valence states:  $V^{2+}$ ,  $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$ . Consequently, the vanadium redox system is an amazingly robust oxybarometer covering at least



**Figure 2:** Pre-edge peak intensity versus oxygen fugacity for standards after temperature correction to 1400 °C. Two Canil komatiite glasses from natural starting material plot below the trend even though two other samples from this suite are consistent with the other standards. The line is a linear regression of the Hanson and Canil data ignoring these two points and dashed lines are shown for the IW, FMQ and NNO oxygen buffers at this temperature. This regression and analogous ones produced for other liquidus temperatures were the basis of the oxygen fugacity estimates for unknowns [2].

eight orders of magnitude in oxygen fugacity. Applications of the method to natural glasses from Mars, Earth and the Moon [2, 3] demonstrate the great potential of this new non-destructive microanalytic technique. Further work is in progress to improve our understanding of the effects of melt composition and temperature.

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