

OXIDATION STATE OF VANADIUM IN GLASS AND OLIVINE FROM TERRESTRIAL AND MARTIAN BASALTS: IMPLICATIONS FOR OXYGEN FUGACITY ESTIMATES. J.M. Karner¹, (jkarner@unm.edu), S.R. Sutton^{2,3}, J.J. Papike¹, C.K. Shearer¹, and M. Newville³. ¹Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131-1126; ²Department of Geophysical Sciences and ³Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637

INTRODUCTION Several studies have demonstrated the usefulness of Synchrotron micro x-ray absorption near edge structure (XANES), or (SmX) spectroscopy, to determine the oxidation state of elements in planetary materials. Delaney et al. [1] used SmX to investigate the oxidation states Fe, Cr, and V in extraterrestrial samples, and later determined the oxidation state of V in experimental glasses as a function of oxygen fugacity [2]. More recently, Sutton et al. [3] studied the oxidation state of V in meteoritic fassaite and also synthetic pyroxene. This paper reports our first results using SmX spectroscopy to determine the oxidation state of vanadium in olivine and glass from a terrestrial ocean floor (OF) basalt and a martian basaltic shergottite meteorite, Dar Al Gani 476. The goal of this study, and of future studies, is to use V (and Cr, Fe) valence states to determine the oxygen fugacity of basalts from different planetary bodies.

METHODS All SmX analyses were performed with the GeoSoilEnviroCARS (GSECARS) x-ray microprobe at the Advanced Photon Source (APS), Argonne National Laboratory, IL. The microprobe consisted of an APS undulator x-ray source, a silicon monochromator, Kirkpatrick-Baez microfocussing mirrors and a germanium solid state x-ray fluorescence detector. The beam size was approximately 5 μm . XANES spectra were measured over the V K absorption edge (5465 eV) from 5450 eV to 5600 eV. Measurements made below and above the absorption edge provided for normalization of the peaks. The pre-edge peak (near 5470 eV) was distinguished by the energy and normalized intensity at the maximum. Previous studies have shown these parameters to be useful for determining the valence state of V [1-3].

Three sets of standards were used to calibrate the experiment in terms of pre-edge peak intensity versus oxidation state of V, and oxygen fugacity. The first standards are two basaltic glasses by H. Schreiber [4] that provide independent calibration of the valence state of V at high $f\text{O}_2$ conditions. The second standard is a basaltic glass produced at known $f\text{O}_2$ conditions (IW + 1) by Hanson and Jones [e.g., 5]. A third set, by Canil [6], are komatiite compositions produced at known oxygen fugacities.

RESULTS A summary of the XANES data, as well as the standard information is given in Table 1. For

the OF sample, XANES measurements were taken on both glass and olivine; DaG 476 contains no glass, and thus measurements were only taken on olivine.

Figure 1 is a plot of pre-edge peak intensity versus the oxidation state of V for measurements on both glass and olivine. Here we used the Schreiber glasses (oxidation states determined previously by optical spectrometry) as standards, and determined the oxidation states for the unknowns using linear interpolation/extrapolation. The Hanson glass was treated as an oxidation state unknown, while the komatiite glasses are secondary oxidation state standards being tied previously to the Schreiber glasses. The oxidation states determined for V in OF glass cluster between 3.37 and 3.47, with one analysis of 3.25, therefore the glass contains about 75% V^{3+} and 25% V^{4+} . Measurements on OF olivine range from 3.19 to 3.41 for the oxidation state of V. In DaG 476, three analyses on olivine show the oxidation state of V to range from 3.07 to 3.17.

Figure 2 shows pre-edge peak intensity against oxygen fugacity for both glass and olivine measurements. The Canil glasses are used as standards ($\log f\text{O}_2 = -5.5$ and -9.1) and the oxygen fugacities for the unknowns were obtained by linear interpolation/extrapolation. Five of the six measurements on the OF glasses lie between $\log f\text{O}_2$ -8.7 to -9.1 with one at -9.6. Olivine measurements on the OF sample yield oxygen fugacity values from $\log f\text{O}_2$ -8.92 to -9.78. Measurements on DaG 476 olivine show $\log f\text{O}_2$ values of -9.87 to -10.27. Also shown is the pre-edge peak intensity for Hanson's IW + 1 glass (known $\log f\text{O}_2 = -9.55$).

DISCUSSION XANES measurements on OF glass yield an average oxidation state of V of 3.40, i.e., about 60% of the V is 3+, and about 40% is 4+. These determinations imply an average oxygen fugacity of $\log f\text{O}_2 = -9.0$ for the OF basalt. The XANES spectra for OF olivine give slightly more reduced results than the OF glass, implying a slight preference of olivine for V^{3+} over V^{4+} . The averages are different in oxidation state by 0.09, and in $\log f\text{O}_2$ by 0.4. This is consistent with the result for the Canil standards, where the glass gave a V oxidation state of 3.3 and the olivine was 3.16 (see Table 1). Overall, a $\log f\text{O}_2 = -9$, just below the liquidus (1150-1200° C), for an OF basalt is consistent with conditions derived by other techniques. For example, Christie et al. [7]

used Fe redox states to determine an fO_2 of QFM-1 to QFM-2 for mid-ocean ridge basalts.

The data on DaG 476 are few and only from one phase (olivine), but the spectra indicate a V oxidation state of ~3, and a $\log fO_2 \approx -10$ at the liquidus ($\sim 1200^\circ C$) for this martian basalt. These values are slightly more reduced than those for terrestrial OF basalts, and are fairly consistent with fO_2 values of ~QFM-2 given for DaG 476 [8]. In addition, we expect our extrapolation method at low fO_2 to yield results systematically too oxidized, due to the known non-linearity of the intensity vs. oxygen fugacity trend under very reducing conditions. More accurate results are anticipated using more reduced standards.

CONCLUSIONS Our preliminary XANES work illustrates its usefulness in obtaining fO_2 data that is consistent with other analytical approaches. It will be extremely useful in assessing fO_2 in samples where mineralogical indicators are compromised by subsolidus re-equilibration (i.e., FeTi oxides), or in extraterrestrial materials that crystallized at or below the IW buffer, and only contain Fe^{2+} . For these materials, fugacities based on other elements such as V and Cr are needed. In addition, XANES provides insight into the behavior of trace elements whose valence states are susceptible to changing fO_2 . Vanadium is a particularly useful element because of its high degree of multivalency and corresponding applicability over a large range of redox conditions.

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Table 1.

Sample	Peak intensity	$\log fO_2$	V*
Schreiber V^{5+} glass	740	0	4.72
Schreiber V^{3+} glass	65	-9.00	3.17
Canil glass	550	-5.50	4.30
Canil glass	150	-9.10	3.30
Canil olivine	60	-9.10	3.16
Hanson glass IW+1	142	-9.55	3.35
OF-glass average	164	-8.97	3.40
OF-olivine average	125	-9.33	3.31
DaG 476 olivine average	38	-10.1	3.11
Bold = standard			

Figure 1.

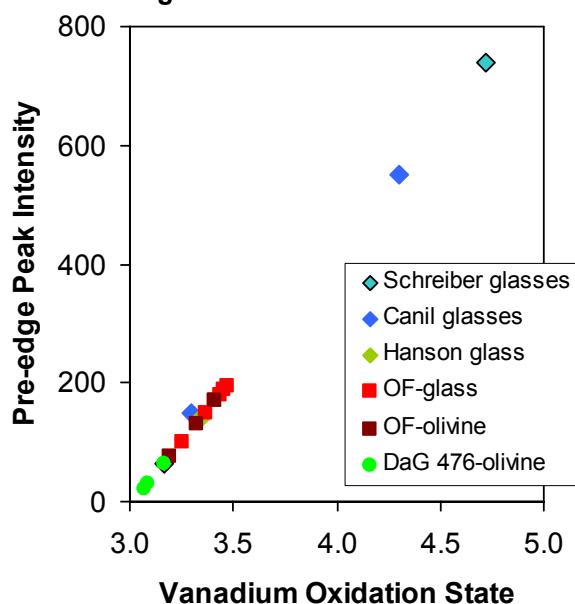


Figure 2.

