Oxidation State of Vanadium in Glass and Olivine from Terrestrial and Martian Basalts: Implications for Oxygen Fugacity Estimates

J.M. Karner,[1] S.R. Sutton,[2,3] J.J. Papike,[1] C.K. Shearer,[1] M. Newville[3]

[1]Institute of Meteoritics, Department of Earth and Planetary Sciences,
University of New Mexico, Albuquerque, NM, U.S.A.
[2]Department of Geophysical Sciences and
[3]Consortium for Advanced Radiation Sources (CARS), The University of Chicago, Chicago, IL, U.S.A.

Introduction

Several studies have demonstrated the usefulness of synchrotron micro x-ray absorption near-edge structure (μ-XANES or SmX) spectroscopy in determining the oxidation state of elements in planetary materials. Delaney et al. [1] used SmX to investigate the oxidation states of Fe, Cr, and V in extraterrestrial samples, and they 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 in synthetic pyroxene. This report discusses our first results using SmX spectroscopy to determine the oxidation state of V 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 and future studies is to use V (and Cr, Fe) valence states to determine the oxygen fugacity of basalts from different planetary bodies.

Methods and Materials

All SmX analyses were performed with the GeoSoilEnviroCARS (GSECARS) x-ray microprobe at the APS. The microprobe consisted of an 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 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 the oxidation state of V and oxygen fugacity. The first standards are two basaltic glasses by Schreiber [4] that provide independent calibration of the valence state of V at high fO_2 conditions. The second standard is a basaltic glass produced at known fO_2 conditions (IW + 1) by Hanson and Jones [Ref. 5, for example]. 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. Since DaG 476 contains no glass, measurements were taken only on olivine.

TABLE 1. Summary of XANES data and standard information.[a]

Sample	Peak intensity	fO_2 log	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 olivine average	38	-10.1	3.11
[a]Numbers in bold are standards.			

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 we determined the oxidation states for the unknowns by 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 showing 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.
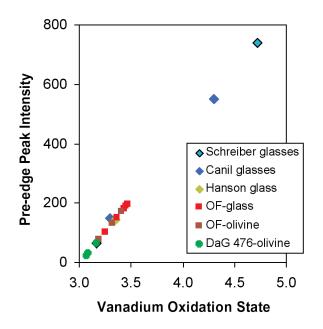
FIG. 1. Plot of pre-edge peak intensity versus the oxidation state of vanadium for measurements on glass and olivine

FIG. 2. Plot of pre-edge peak intensity versus oxygen fugacity for measurements on glass and olivine

Figure 2 shows pre-edge peak intensity against oxygen fugacity for both glass and olivine measurements. The Canil glasses are used as standards ($\log f O_2 = –5.5$ 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 $\log f O_2$ $–8.7$ to $–9.1$, with one lies at $–9.6$. Olivine measurements on the OF sample yield oxygen fugacity values from log $–8.92$ to $–9.78$. Measurements on DaG 476 olivine show $\log f O_2$ values of $–9.87$ to $–10.27$. Also shown is the pre-edge peak intensity for Hanson's IW + 1 (iron-wüstite oxygen buffer) glass (known $\log f O_2 = –9.55$).

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% of it is 4+). These determinations imply an average oxygen fugacity of log $–9.0$ for the OF basalt. The XANES spectra for OF olivine give slightly more reduced results than those for the OF glass, implying a slight preference of olivine for V^{3+} over V^{4+}. The averages in oxidation state are different by 0.09, and the averages in log $f O_2$ are different 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 gave one of 3.16 (see Table 1). Overall, a log $f O_2$ of $–9$, which is 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 $f O_2$ of QFM-1 to QFM-2 for mid-ocean ridge basalts.
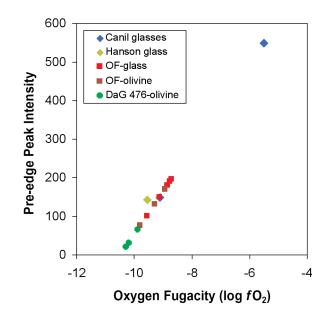
The data on DaG 476 are few and from only one phase (olivine), but the spectra indicate a V oxidation state of ~3 and a log $f O_2$ of about $–10$ at the liquidus (~1200°C) for this martian basalt. These values are slightly more reduced than those for terrestrial OF basalts and are fairly consistent with $f O_2$ values of ~QFM-2 given for DaG 476 [8]. In addition, we expect our extrapolation method at low $f O_2$ to yield results that are systematically too oxidized because of the known nonlinearity of the intensity-versus-oxygen-fugacity trend under very reducing conditions. More accurate results are anticipated from using more reduced standards.

Our preliminary XANES work illustrates its usefulness for obtaining $f O_2$ data that are consistent with other analytical approaches. It will be extremely useful in assessing $f O_2$ 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 $f O_2$. Vanadium is a particularly useful element because of its high degree of multivalency and corresponding applicability over a large range of redox conditions.

Acknowledgments

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