

ORIENTATION DEPENDENCE OF VANADIUM X-RAY ABSORPTION SPECTRA: IMPLICATIONS FOR STUDIES OF V VALENCE AND RESULTANT FUGACITY. M. D. Dyar^{1,2}, M. C. McCanta³, A. Lanzirotti⁴, M. Gunter⁵, C. Steven⁵, L. Breitenfeld², C. Wagoner². ¹Planetary Science Institute, 1700 E. Fort Lowell, Tucson, AZ 85719 (mdyar@psi.edu), ²Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, ³Dept. of Earth and Planetary Sciences, Univ. of Tennessee, Knoxville, TN 37996, ⁴Dept. of Earth Science, Northeastern Illinois Univ., Chicago, IL 60625, ⁵Dept. of Geological Sciences, Univ. of Idaho, Moscow, Idaho 83844.

Introduction: Accurately constraining the oxygen fugacity (f_{O_2}) of planetary materials is important for understanding the evolution of their interiors as well as post-crystallization processes. The V valence [1-5] proxy for f_{O_2} can provide a highly sensitive measure of melt redox in both terrestrial and extraterrestrial minerals and magmas (Figure 1). Vanadium can exist as V^{3+} , V^{4+} , and V^{5+} ; in some highly reduced extraterrestrial systems V^{2+} may potentially be stable. In minerals, both f_{O_2} and crystal chemistry control V valence states.

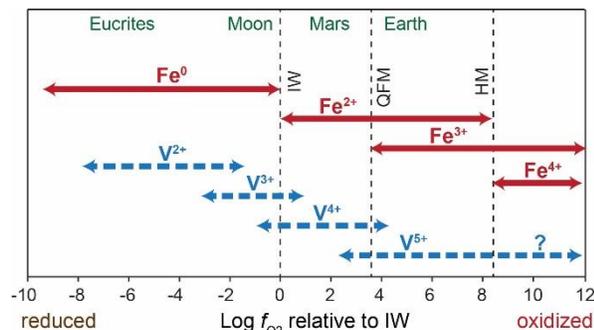


Figure 1. Oxygen fugacity ($\log f_{O_2}$ relative to the IW buffer) of V and Fe buffers relevant to planetary science, adapted from [3]. Ranges for Fe oxidation states are well-constrained, but less is known about V. Change in V valence state at reduced $\log f_{O_2}$ values is far more diagnostic than Fe, which remains divalent down to extremely reducing conditions.

Vanadium K-edge X-ray absorption near-edge structure (XANES) spectroscopy of magmatic glasses has recently been used to develop a precise and accurate oxybarometer [6,7] based on multivariate analysis of the full spectral range without a need to quantify V valence state and then indirectly calculate f_{O_2} . V XANES spectroscopy shows great promise for quantifying f_{O_2} of both magmatic glasses and minerals formed in extremely reduced environments such as are found in numerous places in our solar system, including the Moon and many types of meteorites (cumulate eucrites, lodranites, diogenites, and aubrites). Crystalline phases such as pyroxene are far more common in many of these materials than glasses, and may experience slower diffusion rates more resistant to resetting from subsequent processes, making them better geobarometers. But the extent to which anisotropy of minerals may complicate or confound interpretation of V XANES data and inference of f_{O_2} is unknown. Previous workers have found it difficult to accurately quantify the effects of crystal orientation

on XAS data. This pilot study assesses the potential for using V K-edge XANES data from pyroxene to determine f_{O_2} of crystallization over a wide range by examining orientation effects on measured V XANES data.

Table 1. Samples Studied

Sample	Px	Orientations	$Fe^{3+}/\Sigma Fe$, ref.
DH-231	cpx	OA+45, OA+90, OA, OA-45, OA-90	35 [13/8]
Ba-1-74	opx	AB, OB, ON	10 [13/8]
Ba-2-3	opx	AB, OB, ON	14 [9]
DH-207	cpx	AB, OB, ON	40 [13/8]
DH-220	cpx	ON	29 [13/8]
DH-231	cpx	AB, OB, ON	35 [13/8]
H30-B1	cpx	AB, OB, ON	17 [10]
H312-47	cpx	AB, OB, ON	30 [13/8]
H366-89	cpx	AB, OB, ON	46 [13/8]
97544	opx	OB, ON	7 [13/8]
Sierra de Mage	opx	AB, OB, ON	0 [11,12]

Samples studied: Eleven pyroxene samples were studied, as shown in Table 1. Nine of the samples are from mantle xenoliths, which have a likely f_{O_2} above QFM. Paragenesis is unknown for 87544 and the Sierra de Mage orthopyroxene is very reduced [11,12]. Previous studies of these samples by Mössbauer spectroscopy [9,10], XANES [11], and oxybarometry [12] indicate that they cover a range of Fe^{2+}/Fe^{3+} ratios. Thus it was expected that a range of f_{O_2} would be represented, although additional samples between the eucrite and our highly oxidized samples would be needed. However, the emphasis of this study is on the effect of orientation so this suite provides a useful point of comparison.

Experimental Methods: Single crystals of assorted pyroxenes from terrestrial rocks and meteorites (Table 1) were oriented morphologically and with the aid of EXCALIBUR [13] using a spindle stage equipped polarizing light microscope (Figure 2). The optical orientations of all the samples were either checked morphologically or determined. Goniometer head settings were recorded to allow each crystal to be oriented along optical orientations: for biaxial+ minerals, $AB=\gamma$, $ON=\beta$, and $OB=\alpha$ while for biaxial- samples, $AB=\alpha$, $ON=\beta$, and $OB=\gamma$. The μ XANES data (2 μ m beam size) were acquired at the GSECARS 13-ID-E beamline at the Advanced Photon Source using a special beam geometry. On the beamline, a spindle stage was mounted with the plane of rotation perpendicular to the path of the beam. The structure of the V K absorption edge was scanned

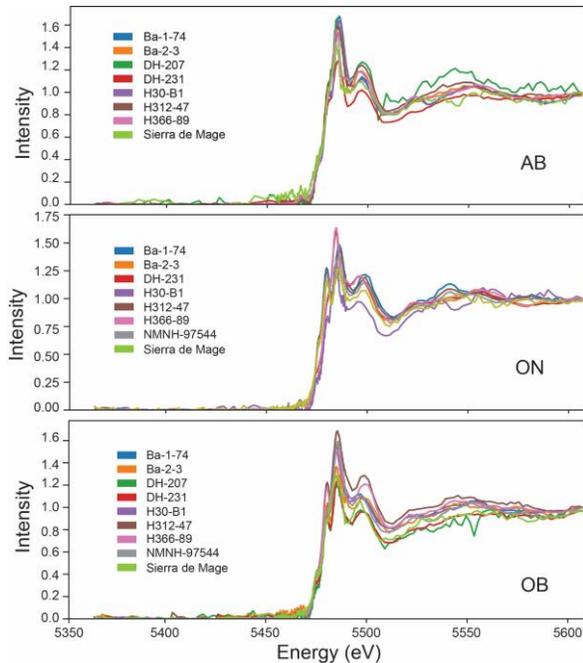


Figure 2. V XANES spectra collected at different orientations relative to the polarized synchrotron beam.

in the near edge region. Incident beam energies from 50 eV below the main absorption edge energy 5360 eV for V) to about 60 eV above the main edge were used (5600 eV). Details of these techniques can be found in [14,15].

Results: Spectra are shown in **Figure 2** grouped by optical orientation; data collected from the same orientation are generally similar and distinct from those of other orientations. These differences are seen in **Figure 3** for an opx (Ba-1-74) and a cpx (H312-47); both peak intensities and positions change with orientation.

All spectra show the peak at 5485 eV that represents the $1s \rightarrow 4p$ transition [16]. Most spectra display a peak ca. 5480 eV that is suppressed in the AB orientation. It is generally attributed to the $1s \rightarrow 4p$ shakedown transition. Its absence in the AB orientation must be related to the pyroxene crystal structure in some unknown fashion. Another feature is visible on the main edge shoulder ca. 5470-5475 eV; it is most intense in the highly reduced Sierra de Mage sample, and may thus be typical of highly reduced samples. The EXAFS features all show a depression in the spectral range around 5490 eV of variable depth, with the OB orientation showing the greatest depth. Further work is needed to understand how f_{O_2} changes modify the intensity and position of these peaks at given crystallographic orientations.

Discussion: It is difficult to link the intensities and energies of these peaks directly to the valence state of V, such assignments may not be necessary if the goal of the work is to obtain a robust estimate of crystallization f_{O_2} . The benefit of multivariate analysis methods used to

assess f_{O_2} in V-bearing glasses [6,7] is that an oxybarometric model can be generated without a need to quantify V valence. Spectral resonances such as the $1s \rightarrow 4p$ whitenline and shakedown transitions, do change intensity and energy as a function of crystal orientation, but may also show additional variations (once polarization is accounted for) that may indicate changes in the site geometry, coordination and valence state of V in pyroxene as a function of f_{O_2} .

Future Work: This pilot study highlights many issues to be studied in future work on oriented samples: suppression of the pre-edge features, assignment of main-edge peaks to valence states, the potential for understanding cation ordering, and extrapolation to f_{O_2} . Coupled equilibration experiments, single crystal refinements, and many more samples/spectra are needed to allow V XANES spectra to be correctly interpreted.

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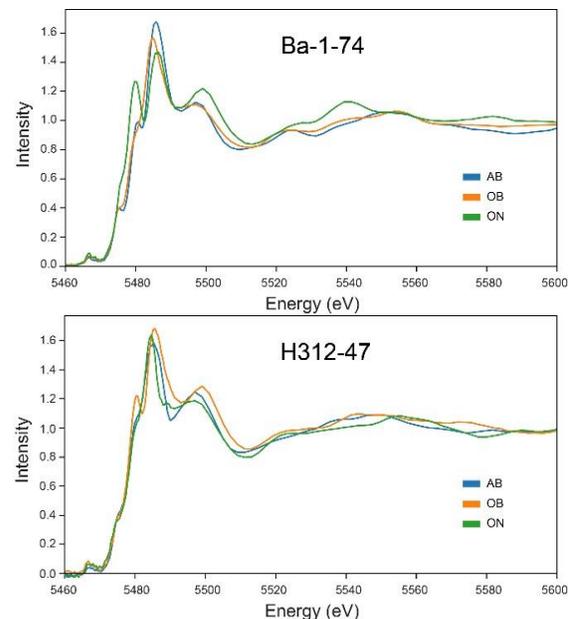


Figure 3. V XANES spectra collected at different orientations relative to the polarized synchrotron beam.