Valence state partitioning of V between pyroxene-melt: Effects of pyroxene and melt composition, and direct determination of V valence states by XANES. Application to Martian basalt QUE 94201 composition

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Abstract—Experiments on a Martian basalt composition show that $D_V$ augite/melt is greater than $D_V$ pigeonite/melt in samples equilibrated under the same $fO_2$ conditions. This increase is due to the increased availability of elements for coupled substitution with the $V^{3+}$ or $V^{4+}$ ions, namely Al and Na. For this bulk composition, both Al and Na are higher in concentration in augite compared with pigeonite; therefore, more V can enter augite than pigeonite. Direct valence state determination by XANES shows that $V^{3+}$ and $V^{4+}$ are the main V species in the melt at $fO_2$ conditions of IW−1 to IW+3.5, whereas pyroxene grains at IW−1, IW, and IW+1 contain mostly $V^{3+}$. This confirms the idea that $V^{3+}$ is more compatible in pyroxene than $V^{4+}$. The XANES data also indicates that a small percentage of $V^{2+}$ may exist in melt and pyroxene at IW−1. The similar valence of V in glass and pyroxene at IW−1 suggests that $V^{2+}$ and $V^{3+}$ may have similar compatibilities in pyroxene.

INTRODUCTION

This paper is the third part of a study on the partitioning of multivalent elements between pyroxene and melt in QUE 94201 composition samples. In the first part (Karner et al. 2007a), we used Cr and V partitioning between pyroxene and melt to estimate the oxygen fugacity ($fO_2$) condition for Martian basalt Queen Alexandra Range (QUE) 94201. This inference was possible because Cr and V are both multivalent elements and thus their partitioning (i.e., $D$-values) between pyroxene and melt is mainly controlled by $fO_2$. Our protocol was to produce synthetic charges of QUE 94201 composition at several different $fO_2$ values, crystallizing only pyroxene. We then used the charges to calibrate $D_{Cr}$ and $D_{V}$ versus $fO_2$ curves for early crystallizing pyroxene pigeonite cores and the bulk starting composition. Martian basalt QUE 94201 represents a liquid composition, so measuring $D_{Cr}$ and $D_{V}$ pigeonite/melt in both the synthetic charges and natural sample was the best way to estimate $fO_2$ at the onset of crystallization. Fitting $D_{Cr}$ and $D_{V}$ pigeonite/melt in the natural sample to the calibrated curves gave an $fO_2$ of ~iron wüstite (IW)+0.6, which we believe is a solid assessment for a number of reasons (see Karner et al. 2007a). During the course of the study, however, we realized that Cr and V partitioning is not only controlled by $fO_2$, but it is also affected by the availability of charge-balancing elements for coupled substitution (e.g., Al and Na) into the pyroxene structure.

The second part of our study built on the first and explored in detail how the availability of Al and Na for coupled substitution affects $D_{Cr}$ between pigeonite/melt and augite/melt in the synthetic QUE 94201 samples (Karner et al. 2007b). For example, we determined that $D_{Cr}$ augite/melt is approximately double that of pigeonite/melt in charges equilibrated at the same $fO_2$. This increase is not due to changing valence, but rather to the increased availability of elements for coupled substitution with the Cr$^{3+}$ ion, namely Al and Na. To complement the Cr partitioning analysis, we also used X-ray absorption near edge structure (XANES) spectroscopy to determine the valence state of Cr within the pyroxene and glass in each charge. The XANES data showed that Cr$^{3+}$ is the dominant valence state in pyroxene at $fO_2$ conditions of IW−1, IW and IW+1, and that Cr$^{3+}$ is much more compatible in pyroxene than Cr$^{2+}$.

This third part of our study continues our work on the partitioning of V between augite/melt and pigeonite/melt for the same QUE 94201 synthetic charges. Our interest in V...
partitioning stems from the fact that V can exist in four potential valence states \((V^{2+}, V^{3+}, V^{4+}, V^{5+})\) in magmas and thus information on the valence state partitioning of V can be used to estimate redox conditions of planetary magmas (Lindstrom 1976). Because of this, several workers have used the partitioning of V between minerals and melt to estimate the \(f_O^2\) condition and setting of terrestrial lavas (e.g., Shervais 1982; Canil 1997, 1999, 2002; Canil and Fedorchouk 2002; Lee et al. 2003, 2005). Other workers examined V partitioning in extraterrestrial lavas in order to gain an understanding of the redox states of planetary bodies such as the Moon, Mars and the asteroid 4 Vesta (Schreiber and Balazs 1982; Hanson and Delano 1992; Herd et al. 2002; Papike et al. 2004; Shearer et al. 2006a). Although the V partitioning studies have been successful in estimating \(f_O^2\) conditions, they provide no direct determination of V valence in the minerals or the melt. That information is now obtainable through XANES spectroscopy, and this information is an excellent compliment to the partitioning data. Our goal then in this paper is to provide a valence interpretation to the partitioning of V between augite/melt and pigeonite/melt in the QUE 94201 composition samples. Our results advance the understanding of how changing \(f_O^2\) influences the V valence state and partitioning into pyroxene, and also explain the effect of the availability of charge balancing elements (such as Al and Na) on \(D_V\). Lastly, we present XANES data on the direct determination of V valence in both minerals and melt and compare these data with the partitioning data.

**SAMPLES AND ANALYTICAL TECHNIQUES**

**Samples**

The samples used in this study were the same pyroxene-bearing glasses of Martian basalt QUE 94201 composition as those used in Karner et al. (2007a, 2007b) but a more detailed description of the samples and experimental techniques is provided here. A synthetic glass of the QUE 94201 (see Table 1) composition was prepared from reagent grade oxide powders in an agate mortar. This mixture was then fused into glass and reground back into a powder. Pressed pellets were then sintered to PtRh-wire loops and subsequently hung within Deltech DT-31-V-OT vertical tube furnaces at the 1 atm laboratory at Johnson Space Center (JSC). Oxygen fugacity was controlled by CO-CO\(_2\) gas mixing and was measured in each experiment with a solid zirconia electrolyte cell. Temperature was measured with a Pt\(_{90}\)Rh\(_{10}\)--Pt\(_{90}\)Rh\(_{10}\) thermocouple calibrated at the melting point of gold.

The charges were first held for 48 h at 1300 °C in the furnace at imposed \(f_O^2\) conditions of iron-wüstite (IW)--1, IW, 1W+1, and 1W+3.5 (i.e., quartz-fayalite-magnetite-QFM). After quenching to room temperature, the charges were then returned to their respective furnaces and cooled from a near liquidus temperature (1170 °C) to ~1100 °C at a rate of 1 °C/h. The PtRh-loops were then quickly removed from the furnace and quenched in air.

After each experiment the charges were mounted in epoxy, sectioned, polished, and examined by electron microbeam techniques. Major and minor element compositions were determined using a JEOL JXA 8200 electron microprobe (EMP) at the University of New Mexico, operating at 15 kV, 20 nA and a 1 µm beam. Wavelength dispersive spectrometer counting times of 20 s were used for major elements and 30 s for minor elements, and all data were reduced using a ZAF correction program. Ferric iron was estimated for each analysis using the method described by Droop (1987), and V concentrations were corrected for interference from the Ti K\(_β\) peak by the procedure detailed by Snetsinger et al. (1968).

**XANES Analysis**

XANES analyses on the polished mounts were performed with the GeoSoilEnviroCARS (GSECARS) X-ray microprobe at the Advanced Photon Source (APS), Argonne National Laboratory, IL (Sutton et al. 2002). An APS (7.0 GeV electrons) Undulator A (critical energy = 23.6 keV) was used on the first harmonic.

The monochromator was a cryogenic silicon (111), double-crystal instrument. For XANES measurements, the monochromator angle and undulator gap were scanned synchronously. The instrumental energy resolution (0.8 eV) was comparable to the natural V K line width (~1.1 eV; Krause and Oliver 1979) so that the overall resolution of the V K XANES spectra was about 1.5 eV. Energy calibration was obtained from XANES spectra of a V metal foil (EXAFS Materials, Danville, CA) where the first peak in the derivative XANES spectrum was defined to be 5465 eV. A feedback system, used to maintain a constant beam intensity on the sample, consisted of an ion chamber situated downstream of the beam defining slits for the microfocusing mirrors (see below). The angle of the second monochromator crystal was adjusted via a piezoelectric motor at ~10 Hz to maintain a constant ion chamber signal.

The microfocusing Kirkpatrick-Baez (KB) system (Eng et al. 1998) consisted of two mirrors (100 mm length), one in the horizontal plane and one in the vertical plane, which collected 300 µm of X-ray beam in both directions and produced a focal spot of 3 µm in both directions (flux density gain of about 10\(^4\)). The mirrors were highly polished single crystal silicon coated with several hundred Å of Rh and were dynamically bent to elliptical shapes using a mechanical bender. This “double-bounce” focusing system provides excellent harmonic rejection capabilities with an overall efficiency at the fundamental monochromator energy of about 60% (Eng et al. 1998). This produced a beam intensity at the V K absorption edge of about \(5 \times 10^{10}\) photons/second on sample.
Table 1. Average augite and coexisting glass compositions in synthetic QUE samples. Also shown is the starting composition used to produce the synthetic samples.

<table>
<thead>
<tr>
<th></th>
<th>Augite</th>
<th>Glass</th>
<th>Augite</th>
<th>Glass</th>
<th>Augite</th>
<th>Glass</th>
<th>Starting melt</th>
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<td>50.7</td>
<td>50.2</td>
<td>47.6</td>
<td>50.7</td>
<td>47.4</td>
<td>47.7</td>
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<td>Al₂O₃</td>
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<td>97.8</td>
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Atoms per formula unit based on 6 oxygens

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<tr>
<td>Dᵥ</td>
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<td>5.3 ± 0.04</td>
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<td>3.1 ± 0.02</td>
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¹Averages are from 3–6 analyses at similar Wo-En-Fs (for pyx) values.
²Electron microprobe analyses have typical errors of 3% for major elements and up to 5% for minor and trace elements.
³Fe³⁺ determinations calculated from pyroxene cations according to Droop (1987).

The detector used was a Vortex-EX silicon drift, solid state X-ray fluorescence detector (SII NanoTechnology USA, Inc.). The active area was 50 mm² with a crystal thickness of 350 µm. Digital signal processing electronics were set to a peaking time of 2 µs which resulted in a detector resolution of ~120 eV at V Kα. Kapton® (Dupont) film was used on the detector to suppress the intense K fluorescence from calcium thereby allowing greater incident beam intensities on sample.

Full XANES spectra were measured in fluorescence mode over the V K absorption edge (5465 eV) from 5400 eV to 5600 eV using 5.0 eV steps from 5400 to 5455 eV, 0.25 eV steps from 5455 to 5495 eV and 2.5 eV steps from 5495 to 5600 eV. For samples with low V K fluorescence yield, a pre-edge focused scan was used with 0.25 eV steps from 5460 to 5475 eV and 5 eV steps from 5550 to 5600 eV. Total acquisition times per energy step were typically 2 seconds for full XANES spectra and 10 seconds for pre-edge focused scans. Normally, three spectra acquired at each analysis point were summed.

Each XANES spectrum consisted of the total counts in a multichannel analyzer region of interest (ROI) versus incident beam energy. This ROI was set to encompass the V Kα (4950 eV) and Ti Kβ (4930 eV) fluorescence peaks, two peaks that are unresolvable with the detector used. Thus, the pre-edge background is significant being due to the substantial Ti concentrations in these samples (Ti > V).

Each XANES spectrum was normalized by subtracting the pre-edge background, normalizing to the counts measured at 5600 eV and multiplying by 1000. This resulted in normalized spectra with zero at the lowest energy and 1000 at 5600 eV. Analysis of the pre-edge region was conducted after subtracting the absorption edge step contribution via an
Fig. 1. XANES V valence calibration curve based on the pre-edge peak intensity versus effective valence for several standards. The solid black circles are fit with a power law curve that is the solid line. The open circles are samples that were removed from this calibration and were not included in the fit curve. See text for discussion.

interactive spline-fitting routine. The “pre-edge peak intensity” was defined to be the maximum intensity in this net pre-edge peak multiplet.

The intensity of the pre-edge peak at ~5470 eV in the normalized XANES spectra was the basis of the valence determination following the procedure of Sutton et al. (2005). The principal valence standards were forsterite-anorthite-diopside (FAD) and forsterite-anorthite-silica (FAS) composition glasses synthesized by H. Schreiber (VMI; Schreiber and Balazs 1982). These glasses have independent determinations of V\textsuperscript{4+} concentration using a titration/optical spectrometry method. V\textsuperscript{3+} concentrations were obtained for oxidized samples by subtraction of the V\textsuperscript{4+} concentration from the nominal total V concentration (0.97%). Similarly, Sutton et al. (2005) estimated V\textsuperscript{3+} concentrations for the reduced samples by subtraction of the V\textsuperscript{4+} concentrations from the nominal total V concentration. An effective valence was determined for each sample by concentration-weighted averaging of the appropriate end-member valences. A valence calibration curve was then produced of pre-edge peak intensity versus effective valence (Sutton et al. 2005, therein Fig. 4).

Subsequently, it was discovered that V loss may have occurred in the reduced samples (those more reduced than pure V\textsuperscript{4+}) thus potentially impacting the reliability of the V\textsuperscript{3+} estimates. In the present work, this valence calibration curve was reproduced, omitting these four reduced samples (110, 111, 112, and 113) and replacing them with XANES results for two alternative V\textsuperscript{3+} standards; V\textsubscript{2}O\textsubscript{3} and MgV\textsubscript{2}O\textsubscript{4} (Righter et al. 2006). These standards are appropriate because V occurs in them in octahedral coordination as expected for the glasses with V\textsuperscript{3+}. This new data set was then fit with a power law curve (Fig. 1). The dark line in Fig. 1 is the fitted function and the dashed line is its extrapolation to V\textsuperscript{2+}. The V\textsuperscript{2+} intercept is ~10 which is within error of the expected value of zero. Also shown are the FAS/FAD reduced samples that were omitted and not included in the fitted function (white circles). The new calibration curve is virtually identical to the original one of Sutton et al. (2005) and the omitted points lie close to this curve. Uncertainties (2\(\sigma\)) in quoted valences for unknowns include random errors of the XANES measurements and uncertainties associated with this calibration curve, the two sources summed in quadrature.

RESULTS AND DISCUSSION

Partitioning of Elements between Pyroxene and Melt

The charges produced at IW−1, IW, and IW+1 consisted of pyroxene plus glass, while the charge produced at QFM contained olivine plus glass. All four charges produced crystals approximately 100 to 400 \(\mu\)m in size, and in each charge the degree of crystallization was less than 10% as determined by optical point counting. Each pyroxene-bearing charge was composed of pyroxene grains with pigeonite cores and augite rims set in a matrix of glass. The compositions of these phases, along with the starting melt composition, is shown in Table 1. Our approach was to first examine the pyroxene grains and glass by EMP elemental X-ray mapping and detailed analysis to understand the crystallization sequence with respect to elemental partitioning.

Figure 2 shows a backscattered electron (BSE) image and corresponding elemental X-ray maps for Ca, Al, Ti, Cr, and V in pyroxene and glass from the IW−1 charge. Here the pyroxene c-axis is approximately normal to the image and therefore the center of the grain consists of a Ca-poor pigeonite core zoning to a Ca-rich augite rim (e.g., note the Ca X-ray map). The Ca X-ray map also shows that the grain is sector zoned. The Al and Ti X-ray maps show that both of these elements increase in concentration from pigeonite core to augite rim, but also that both of these elements are in a higher concentration in the coexisting glass. This behavior is expected for incompatible elements. Chromium and V also increase from pigeonite to augite, but here the maps show that the glass contains lower concentrations of these elements than the pyroxene. The zoning in pyroxene is not what is expected for the compatible elements. The reason for this is that \(D_{Cr}\) and \(D_{V}\) increase from pigeonite to augite.

While the X-ray maps in Fig. 2 show the qualitative concentrations of the elements in the glass and pyroxene, Fig. 3a–c shows the results of a quantitative EMP traverse across the glass and pyroxene (the location of the traverse is shown in the BSE image in Fig. 2). Figure 3a shows (oxide wt%) of the major elements) that Al\textsubscript{2}O\textsubscript{3} is more abundant in the glass than in the pyroxene, while conversely MgO is more than three times more abundant in the pyroxene than the
Fig. 2. Backscattered electron (BSE) image and corresponding elemental X-ray maps of a QUE 94201 composition synthetic pyroxene and coexisting glass in the IW–1 charge. The ε-axis is approximately normal to the image and the field of view is ~275 µm. Warmer colors indicate higher elemental concentration (note intensity bar on the right). The BSE image also denotes a 230 µm EMP traverse that is plotted in Fig. 2.
glass. CaO is most abundant in the augite rim, but the coexisting glass has more CaO than the pigeonite. Note that CaO and Al$_2$O$_3$ are enriched in the augite rim compared with the pigeonite core, while the MgO trend is the opposite. Lastly, note that the starting melt compositions for each oxide are indicated on the y-axis with an asterisk and a dotted line. These starting compositions are shown to illustrate the distribution of elements during crystallization and are used to calculate $D$-values for elements in pigeonite.

Figure 3b shows the minor element oxide compositions for the EMP traverse. Here we see that TiO$_2$ and Na$_2$O are higher in the glass than the pyroxene, while V$_2$O$_3$ and Cr$_2$O$_3$
share the opposite trend. All the elements in Fig. 3b, however, are enriched in the augite rim compared with the pigeonite core. Again, the starting compositions of these oxides are noted on the y-axis. The difference between the starting Na$_2$O abundance and the Na$_2$O in the glass and pyroxene reveal there was Na loss to volatilization in the experiments.

Figure 3c shows the approximate Cr, V, Ti, and Al D-values for both the pigeonite core and the augite rim of the traversed pyroxene grain. D-values for pigeonite were calculated by dividing the measured element of interest in the pigeonite by the measured element of interest in the starting composition, while D-values for augite were determined by dividing the measured element of interest in augite by the measured element of interest in the coexisting glass. Our differing methods to determine D-values are based on our conclusions that the pigeonite cores were in equilibrium with the starting bulk composition, while the augite rims were in equilibrium with the coexisting glass. Our assessment of equilibrium between the pigeonite cores and the starting bulk composition is based on the following: 1) that QUE 94201 has been determined to be a melt (Koizumi 2001), i.e., its minerals crystallized from a melt of the rock’s bulk composition. Our experiments mimic the crystallization of the natural sample, especially reproducing the crystallization sequence (pigeonite zoning to augite) and composition of the pyroxene grains (see Karner et al. 2007a, therein Fig. 1). 2) D-values were measured in the first crystallizing, most Mg-rich pigeonite cores 3) analysis of glasses equilibrated at the experimental $fO_2$ values showed no loss of elements (in which we determine D-values for), to the Pt-wire. Figure 3c shows that for all elements shown, D is higher in augite than pigeonite. The plot also shows that for this bulk composition, Cr and V are compatible in pyroxene ($D > 1$) while Ti and Al are incompatible in pyroxene ($D < 1$).

After mapping and traversing several pyroxene grains, we proceeded to determine quantitative D-values for V in augite to compare to D-values for V pigeonite. Figure 4 shows $D_V$ for both augite/melt and pigeonite/melt versus the $fO_2$ at which the samples were synthesized. $D_V$ pigeonite/melt values were reported in our earlier paper (Karner et al. 2007a), and we simply reproduce them here. $D_V$ augite/melt values were determined by dividing the concentration of V in augite by the concentration of V in the coexisting glass. Error bars (x-axis) for each data point are based on the $fO_2$ calibration of furnaces at the JSC laboratory, while the y-axis error is represented by the size of the symbol and represents the uncertainty associated with the standard deviation of several V measurements in determining D-values. Our data shows $D_V$ augite ranges from about 3 to 6 over an $fO_2$ range of IW+1 to IW−1, and in general these values are in good agreement with those from the literature (see Toplis and Corgne 2002, therein Fig. 9a.) Figure 4 shows that in both pigeonite and augite, $D_V$ decreases with increasing $fO_2$. This decrease in $D_V$ with increasing $fO_2$ is a result of the redox sensitive valence of V. At the $fO_2$ conditions of these experiments, V exists as a mixture between V$^{3+}$ and V$^{4+}$ (Sutton et al. 2005), and the V$^{3+}$/V$^{4+}$ ratio in the melt depends on $fO_2$. Since V$^{3+}$ is more compatible in pyroxene than V$^{4+}$ (e.g., Canil 1999; Papike et al. 2005; Karner et al. 2006a), the decrease in $D_V$ in pyroxene from IW−1 to IW+1 is the result of increasing $fO_2$ and the subsequent increase of V$^{4+}$ relative to V$^{3+}$ in the crystallizing melt.

Figure 4 also shows that $D_V$ augite is greater than $D_V$ pigeonite in samples synthesized at the same $fO_2$. This increase in $D_V$ from pigeonite to augite is obviously not a function of $fO_2$ and the redox-sensitive valence of V, but rather a result of the ease with which elements required for charge balance (i.e., coupled substitution with V$^{3+}$ and V$^{4+}$) can enter the pyroxene structure. Coupled substitution is required to incorporate V$^{3+}$ and V$^{4+}$ into the pyroxene crystal structure because these cations are replacing divalent Mg and Fe in the M1 site (Papike et al. 2005), thus creating an excess charge of +1 or +2. Crystal charge balance must be maintained and can be accomplished by simultaneously substituting 1) an Al cation(s) into the tetrahedral (IV) site for Si, or 2) a Na cation(s) into the M2 site for Ca. Both of these substitutions create a charge deficiency of −1 (or −2), and thus neutralize the crystal charge. Therefore, an increase in $D_V$ from pigeonite to augite can be explained by an increase in the ease with which Al and Na can enter augite (compared with pigeonite) for the required charge-balancing coupled substitution. This explanation is supported by Fig. 2 and 3b., which clearly show that Al and Na increase from pigeonite to augite. For the QUE bulk composition, Al and Na increase from pigeonite to augite because the nucleation of plagioclase is delayed and thus there is a build-up of Al and Na in the evolving melt. Na also increases from pigeonite to augite because the augite structure, with Ca in the M2 site, allows the similar-sized Na atom to more readily substitute into the M2 site. The correlation of Ca with Na has been documented by Papike (1981) for Martian basalt Shergott- where the high-Ca pyroxene trend is also the high-Na pyroxene trend, and has also been noted by Blundy et al. (1995) in experiments. We emphasize, however, that Ca content, and the structure of augite compared with pigeonite, does not sufficiently explain V partitioning into pyroxene. Vanadium partitioning is dependent on both the structure of augite compared with pigeonite, which in turn allows more Na and Al to enter the structure, and also on coupled substitution. For example, previous studies on pyroxene have shown that there is a strong correlation of trace element partitioning with Al and Na contents, but these elements do not necessarily correlate with the Ca content of the pyroxene (Schwandt and McKay 1998; Karner et al. 2006a; Shearer et al. 2006b).

The dependence of $D_V$ pyroxene on Al and Na is further illustrated in Fig. 5. In Fig. 5, arrows indicate the crystallization sequence from pigeonite to augite in the samples equilibrated at IW−1, IW and IW+1. The figure clearly shows that $D_V$ increases (from pigeonite to augite) with increasing Na and
Increasing IVAl concentration in clinopyroxene coupled with increasing $D$-values for several trace elements has also been noted by Hill et al. (2000). The figure also shows that IVAl and Na increase from pigeonite to augite (note arrows), but also that IVAl and Na increase in both pigeonite and augite with increasing $f_{O_2}$. The correlation of increasing Al and Na in pyroxene with $f_{O_2}$ occurs because of the additional Fe$^{3+}$ (and Cr$^{3+}$) that occurs in basaltic melts at higher $f_{O_2}$ conditions. Just as Al and Na provide charge balancing coupled substitution for elements such as V, and Cr$^{3+}$ provide the same for Al and Na. In support of this conclusion, acmite (NaFe$^{3+}$Si$_2$O$_6$) has been shown to be an important pyroxene component at high $O_2$ conditions (Blundy et al. 1995; Karner et al. 2006a, therein Fig. 4).

**Determination of V Valence States by XANES**

In order to supplement the V partitioning data, we examined the same samples by XANES spectroscopy. XANES utilizes X-ray absorption associated with core-electronic transitions (absorption edges) to reveal spectral features that indicate the V valence state in the phase of interest. Our first V XANES work concentrated on determining the valence of V in volcanic and impact glasses from the Earth, Moon, and Mars (Sutton et al. 2005). The method worked well and our calculated $O_2$ conditions for these basalts were consistent with $O_2$ conditions derived by other methods (Karner et al. 2006b). The advantage of measuring V valence in glasses is that the XANES spectra are uncomplicated by orientation effects compared to minerals (see Dyar et al. 2002; McCanta et al. 2004). Such orientation effects result from the synchrotron radiation preferentially sampling the crystal structure in the polarization plane (typically horizontal). Iron valence measurements in pyroxene show that orientation effects are at most $\pm 20\%$ in Fe$^{3+}$/Fe total where this level of uncertainty includes all other uncertainties in the measurements (McCanta et al. 2004). For V in olivine and pyroxene, these orientation effects are similarly subtle (Sutton et al. 2002; Sutton and Newville 2005). Work on Ti valence in pyroxene from carbonaceous chondrites has also produced rigorous results (Simon et al. 2007). Here we report on the valence state of V in the same pigeonite and coexisting glass in which we also measured V concentrations used for calculating $D$-values.

Figure 6 shows the XANES results for the valence state of V in the experimental crystals and in the coexisting glass. The glass data shows a steady increase in V valence from mostly V$^{3+}$ at IW−1 to mostly V$^{4+}$ at IW+3.5, which is consistent with our assessment that V$^{3+}$ and V$^{4+}$ predominate in basaltic melts over this range of $O_2$ values. There is evidence for non-negligible V$^{2+}$ in the glass at IW−1, but this determination is at or very near the calculated uncertainty. The mineral data shows that V is mostly in the 3+ valence state in pyroxene at IW+1, IW, and IW+1. Furthermore, the valence state of V in olivine crystallized at QFM is approximately 70% V$^{3+}$.

If we compare the glass data to the mineral data, we can make several observations about the valence state partitioning of V into minerals. First, the difference in V
Valence state partitioning of V between pyroxene-melt

Valence between olivine (mostly 3+) and coexisting glass (mostly 4+) suggests that V$^{3+}$ is more compatible than V$^{4+}$ in the olivine structure. This observation is consistent with conclusions drawn from partitioning studies (Papike et al. 2005; Shearer et al. 2006a). Second, the data at IW+1 show similar results to the data at IW+3.5. Here we see that the glass is about 80% V$^{3+}$ and 20% V$^{4+}$, but the pyroxene shows only V$^{3+}$, although the error bars for the two phases are in contact. Again, the difference between the glass and pyroxene suggests that V$^{3+}$ is more compatible in pyroxene than V$^{4+}$. This conclusion is also consistent with those derived from partitioning studies (Canil 1999; Toplis and Corgne 2002; Papike et al. 2005). The data at IW shows that all the V in both the glass and pyroxene is V$^{3+}$ (within error), and thus there is no difference in V valence between the two phases. Lastly, the data shows that both the glass and pyroxene at IW−1 may contain a small percentage of V$^{2+}$, and there is essentially no difference in V valence between the glass and pyroxene at this low fO$_2$. These observations suggest that V$^{2+}$ could be equally compatible as V$^{3+}$ in pyroxene.

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