VALENCE STATE PARTITIONING OF VANADIUM BETWEEN PYROXENE-MELT: EFFECTS OF PYROXENE AND MELT COMPOSITION AND DIRECT DETERMINATION OF V VALENCE BY XANES.

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INTRODUCTION: This paper continues the study of the partitioning of multivalent elements between pyroxene-melt in synthetic charges of martian basalt QUE 94201 composition (see [1,2]). Here we concentrate on the partitioning of V between augite/melt and pigeonite/melt. Previous studies have used the partitioning of V between minerals and melt to estimate the fO_2 condition and setting of terrestrial and extraterrestrial lavas, e.g., [3-7]. Although the V partitioning studies have been successful in estimating fO_2, they provide no direct determination of V valence in the minerals or the melt. That information is now obtainable through XANES spectroscopy, and here we report XANES data on the same pyroxene grains that we measured the partitioning data.

SAMPLES AND ANALYTICAL TECHNIQUES: The samples used in this study were the same pyroxene-bearing glasses as those used in [1,2]. The starting material for the charges was a synthetic glass of QUE 94201 bulk composition spiked with ~0.1 wt.% V_2O_3. Pressed pellets of the composition were first held for 48 hours at 1300 ºC in the 1 atm gas-mixing furnaces at JSC at imposed fO_2 conditions of IW-1, IW, IW+1, and QFM. After quenching to room temperature, the charges were then returned to their respective furnaces and cooled from a near liquidus temperature (1170 ºC) down to ~1100 ºC at a rate of 1 ºC/hr, and then quenched again.

Charges were first analyzed by electron microprobe (EMP) at 15 kV, 20 nA, with a 1 µm beam. XANES analyses were performed with the X-ray microprobe at the Advanced Photon Source, Argonne National Lab, IL. XANES spectra were measured in fluorescence mode over the V K absorption edge (5465 eV) from 5400 eV to 5600 eV. The intensity of the pre-edge peak at ~5470 eV in the normalized spectra was the basis of V valence determination following the procedure of [8].

RESULTS AND DISCUSSION

Partitioning of V between pyroxene-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 100-400 µm in size, with the degree of crystallization less than 10%. Each pyroxene-bearing charge was composed of pyroxene grains with pigeonite cores and augite rims in a matrix of glass.

Figure 1 shows D_V for both augite/melt and pigeonite/melt vs. the fO_2 at which the samples were synthesized. D_V pigeonite/melt values were reported in [1] and we 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. Figure 1 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+} [8], 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+} [9], 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 1 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 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) 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 [9]. Crystal charge balance 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. 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 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 [10] for martian basalt Shergotty, where the high-Ca pyroxene trend is also the high-Na trend.

The dependence of D_V pyroxene on Al and Na is further illustrated in Figure 2, where arrows indicate the crystallization sequence from pigeonite to augite in the samples at IW-1, IW and IW+1. The plot shows D_V increases (from pigeonite to augite) with increasing Na+^{IV}Al. The plot also shows that Na+^{IV}Al

increases in both pigeonite and augite with increasing fO_2. The correlation of increasing Al and Na in pyroxene with fO_2 occurs because of the additional Fe^{3+} (and Cr^{3+}) that occurs in basaltic melts at higher fO_2. At high fO_2, Fe^{3+} and Cr^{3+} provide charge balancing coupled-substitution for Al and Na. In support of this conclusion, acmite ($NaFe^{3+}Si_2O_6$), has been shown to be an important pyroxene component at high fO_2 (see [11]).

Determination of V valence states by XANES 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. Here we report on the valence state of V in the same pigeonite and co-existing glass in which we also measured V concentrations used for calculating D-values.

Figure 3 shows the XANES results for V valence in both the crystals and the co-existing 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 fO_2 range. There is evidence for non-negligible V^{2+} in the glass at IW-1, but this determination is near the calculated uncertainty. The mineral data shows that V is mostly 3+ pyroxene at IW-1, IW, and IW+1, while the valence of V in olivine at QFM is approximately 70% V^{3+}.

Comparing the glass and mineral data we can make several observations about the valence state partitioning of V into minerals. First, the difference in V valence between olivine (mostly 3+) and co-existing glass (mostly 4+) suggests V^{3+} is more compatible than V^{4+} in the olivine structure. This observation is consistent with those from partitioning studies [9,7]. Secondly, the data at IW+1 shows 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 and crystal chemistry [9]. Thirdly, the data at IW shows that all the V in both the glass and pyroxene is V^{3+} (within error), and there is no difference in V valence between the two phases. A final observation is that both the glass and pyroxene at IW-1 may contain a small percentage of V^{2+}. Given that there is no difference in V valence between glass and pyroxene, we infer that V^{2+} could be as compatible as V^{3+} in pyroxene. We cannot corroborate this inference with other experimental data, but crystal chemical considerations support this conclusion. We predict, based on charge and ionic radii [10] that V^{2+} and V^{3+} behave similarly to Fe^{2+} and Fe^{3+} in pyroxene. Divalent Fe and V prefer the M2

site, while trivalent Fe and V prefer the M1 site. Therefore, even though the two cations (Fe^{2+}-Fe^{3+} and V^{2+}-V^{3+}) differ in size and charge, their D-values may be similar.

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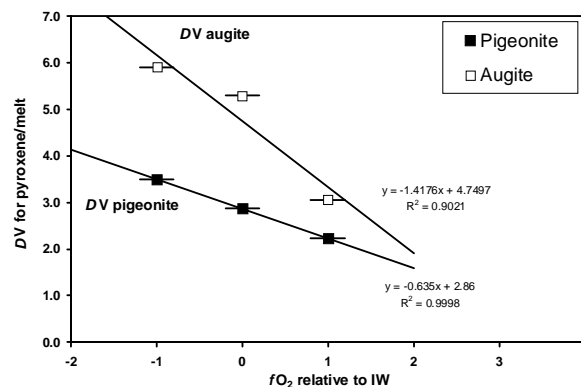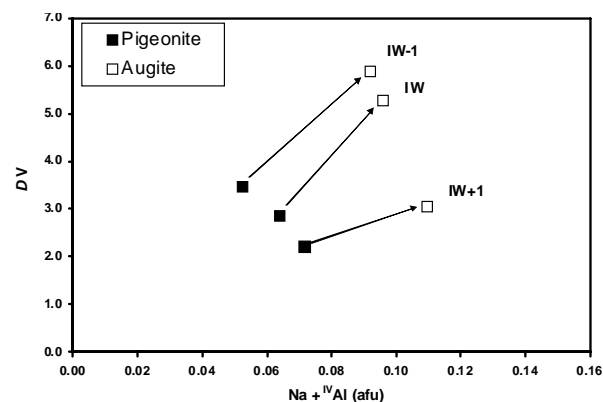
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Figure 2.

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