

## V oxidation state and coordination number in silicate glasses by XAS

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### ABSTRACT

The local structure of vanadium (V) in synthetic glasses of basaltic composition has been studied by means of high-resolution V *K*-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy to obtain quantitative data on <V-O> distances, V coordination number (CN), and oxidation state. The compositions and experimental conditions were chosen so as to verify the effect of bulk-glass composition (using a diopside-anorthite composition, a sodium disilicate glass, and an iron-titanium-bearing basaltic glass) and V content (from 0.1 to 5 V<sub>2</sub>O<sub>5</sub> wt%) on the structural role of V in these glasses.

The combined analysis of high-resolution XANES spectra and EXAFS data indicate that on average, the Fe-free glasses synthesized in air show vanadium in the V<sup>5+</sup> state, mainly in tetrahedral coordination (less than 20% <sup>51</sup>V<sup>5+</sup>) and with <V-O> distances of 1.697 (± 0.020) Å, in agreement with the values found for tetrahedral V in minerals. In contrast, the Fe-bearing basaltic glasses display a mixture of V<sup>5+</sup> in fourfold and fivefold coordination, 40% <sup>44</sup>V<sup>5+</sup>–60% <sup>51</sup>V<sup>5+</sup> in proportion, and the EXAFS-derived distances and coordination numbers are in agreement with this interpretation. No significant changes in the V local structure were found in the glasses analyzed as a function of V-contents in the 0.1 to 5 V<sub>2</sub>O<sub>5</sub> wt% range. The data obtained suggest that the structural role of vanadium in these melts is rather insensitive to bulk composition, in terms of V and alkali content, but can be strongly affected by the presence of other transition elements, e.g., Fe<sup>3+</sup> competing with V to enter the tetrahedral framework.

### INTRODUCTION

Much of the recent interest on the structural role of transition elements (Fe, Ti, V, Co, Ni, Nb, Ta, W, Zr) in silicate glasses arose because of their importance in controlling melt properties such as density, viscosity, and refraction index (see Mysen 1988). Moreover, their structural role in the melt affects partition coefficients between melt and crystals in natural systems and it is therefore important to understand their behavior during crystallization. The knowledge of the control exerted by melt composition on the local structure of the transition elements is therefore of fundamental importance in relating the atomistic structure of silicate melts to their macroscopic properties. An element that has received much attention in recent years is vanadium, for its capability of existing in three different valence states, V<sup>3+</sup>, V<sup>4+</sup>, and V<sup>5+</sup>, in magmas under terrestrial conditions (Canil 2002; Borisov et al. 1987).

Vanadium content in basaltic rocks is highly variable, ranging from 10 to 600 ppm (Prinz 1967) with an average of 250 ppm. Vanadium displays a wide range of compatibility with common magmatic mineral phases. Important host phases for V include, in approximate order of importance, magnetite, ilmenite, mica, amphibole, and clinopyroxene (Canil 1999; Toplis and Corgne 2002). The most common substitution responsible for the incor-

poration of V in mineral lattices is the replacement of Fe<sup>3+</sup> by V<sup>3+</sup> (see Evans 1972), whereas other substitutions such as Al, Ti, and Mn occur much less frequently. In the trivalent oxidation state V has commonly an octahedral coordination with O atoms and it is similar in its crystal chemical behavior to Fe<sup>3+</sup> and Mn<sup>3+</sup> (Evans 1972). In oxide minerals, when V is in the 4+ and 5+ oxidation states, it is usually bonded to O atoms in square pyramidal and tetrahedral coordination, respectively.

Since vanadium exists in terrestrial magmas as V<sup>3+</sup>, V<sup>4+</sup>, and V<sup>5+</sup> (Borisov et al. 1987; Carmichael and Ghiorso 1990; Hanson et al. 1996; Gaetani and Grove 1997; Canil 2002; Toplis and Corgne 2002), the partitioning of V between coexisting silicate melts and oxide or silicate mineral phases at equilibrium is a sensitive function of O atom fugacity (Canil 2002; Toplis and Corgne 2002, and references therein). Due to the dependence of its partition coefficient on  $f_{O_2}$ , vanadium has recently been used as a potential redox indicator during crystallization in mafic and ultramafic magmas (Canil 1997, 1999).

Although there are numerous studies on partitioning behavior of transition elements in magmas, little information is available on the structural configurations of these elements in silicate melts. Information such as oxidation state and coordination of these transition metal ions in melts as a function of melt composition,  $f_{O_2}$ ,  $P$ , and  $T$  is very important because it can strongly influence the partitioning behavior.

Carmichael and Ghiorso (1990) suggest that V<sup>3+</sup> is the only

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stable species in most magmas, whereas Rammensee et al. (1983) suggested the presence of  $V^{3+}$ , or a mixture of  $V^{3+}$  and  $V^{5+}$ , in basaltic melts at 1600 °C. Hanson et al. (1996) and Gaetani and Grove (1997) predicted the presence of  $V^{3+}$  and  $V^{4+}$  in silicate melts based on their studies of crystal-liquid element partitioning. Keppler (1992) reported  $V^{3+}$  in sixfold coordination in glasses along the diopside-albite join synthesized under reduced  $f_{O_2}$  conditions ( $\approx$  NNO-4).

In view of the lack of structural data and in an attempt to derive possible correlations between the geometrical configuration of the silicate framework and the observed variations in the physical and chemical properties, we present here a study devoted to the determination of the structural environments of vanadium in aluminosilicate glasses by XAS. X-ray absorption spectroscopy remains, as compared to other spectroscopic methods (e.g., NMR, Raman, Mössbauer) the most versatile element-specific technique as it allows study of the local environment of elements even in the presence of others with similar atomic number and at low to very low concentrations, as is the case in natural systems or their synthetic analogues. X-ray absorption spectroscopy can give information on the coordination number of these elements as well as the cation-anion (i.e., O atom) bond length. Information on the oxidation state for elements with several possible valence states such as the transition elements can also be obtained.

The O atom fugacity can vary over many orders of magnitude if the entire spectrum of terrestrial magmas is considered, and within the  $T$ - $\log(f_{O_2})$  ranges of magmas one can expect to find both  $V_2O_3$  and  $V_2O_5$  species. As a starting point we investigated the relationships between composition and structural role of V (oxidation state and coordination number) in silicate glasses under highly oxidizing conditions using samples with different bulk compositions.

## MATERIALS AND METHODS

The Fe-free glasses were produced by rapid quenching from high temperature melts at 1400 °C in Pt crucibles in air. The glasses thus produced were finely ground and re-melted to achieve the best possible homogeneity and were then examined by optical microscopy and SEM to verify the absence of crystals. Fe-bearing synthetic basalt was prepared by fusing reagent grade oxide and carbonate powders in a Pt wire under air for 18 hours at 1400 °C and then rapidly quenching to room temperature. Repeated analyses of randomly selected chips along multiple traverses by wavelength-dispersive electron microprobe have shown the resulting glasses to be homogeneous within the precision of electron microprobe analysis.

Chemical compositions were obtained by means of a Cameca SX50 electron microprobe operating at 15.0 kV and 10.0 nA, with the electron beam defocused to a radius of 20  $\mu$ m and 20 s counting time for the major elements and 60 s for minor elements. The standards used were: albite for Si and Na, anorthite for Al, ilmenite for Fe and Ti, diopside for Ca, olivine for Mg, sanidine for K, and vanadinite for V. Data were corrected according to the Bence and Albee algorithm (1968). Tabulated data are averages of 30 individual analyses (see Table 1).

The standards used for XAS measurements are: vanadinite (from Mibladen, Morocco) and desclozite (from the Otavi Mountains, Namibia) for  $V^{5+}$  in tetrahedral coordination; reagent grade  $V_2O_5$  for  $V^{5+}$  in square pyramidal coordination; cavanisite (from Poona, India) for  $V^{4+}$  in square pyramidal coordination; reagent grade  $V_2O_4$  for  $V^{4+}$  in octahedral coordination; and natural V-bearing magnetite for  $V^{3+}$  in octahedral coordination. The natural standards were separated by hand picking from thumb-sized crystals and choosing the clearest portions to avoid impurities. All standards were checked for purity by optical microscopy, X-ray diffraction, and SEM.

Samples for absorption measurement were prepared by smearing finely ground powder on a Kapton tape. EXAFS and high-resolution XANES spectra were collected at beam-line BM-08 of the ESRF (European Synchrotron Radiation Facility) storage ring (Grenoble, France) operating at 6 GeV and with ring current ranging from 150 to 200 mA. Radiation was monochromatized by means of two channel-cut Si (311) crystals. Spectra were recorded in step-scan mode measuring the incident beam intensity with an ionization chamber and the fluorescence yield with a high purity Ge detector. Scans ranged from 5350 to 6000 eV with energy step ranging from 0.2 to 2.0 eV (in the XANES and EXAFS regions respectively) and 8 s counting time. Experimental resolution of the Si(311) crystal monochromator at the V  $k$ -edge is  $\approx$  0.07 eV.

## Data reduction

Experimental XANES spectra were reduced by background subtraction with a linear function and were then normalized for atomic absorption with the average absorption coefficient of the spectral region from 5540 to 5650 eV. Energy was calibrated against a standard of V metal (5465 eV). The threshold energy was taken as the first maximum of the first derivative of the spectra, whereas peak positions were obtained by calculating the second derivative of the spectra. Pre-edge peak analysis was carried out following the same procedure reported in Farges et al. (1996a, 1996b, 1996c) and Romano et al. (2000). The pre-edge peak was fitted by a sum of pseudo-Voigt functions, and their intensities along with energy positions were compared with those of the standards analyzed here and others from the literature (Wong et al. 1984) to extract information on V oxidation state and coordination number in the glasses studied. Particular care was taken in using the smallest possible number of components in the pre-edge peak-fitting procedure. In particular, the number (and, in some cases, the approximate energy) of the components was constrained to equal the number (and approximate energy) of the minima in the second derivative spectrum of the pre-edge peak.

EXAFS data reduction and analysis was done by means of the GNXAS package (Filipponi and Di Cicco 2000). This program extracts the EXAFS signal [ $\chi(k)$ ] from the raw spectrum without performing Fourier filtering and thus avoids possible bias derived from incorrect background subtraction. The theoretical amplitudes and phase shifts are calculated ab initio according to the muffin-tin approximation. The Hedin-Lundquist complex potential (Hedin and Lundquist 1971) was used for the exchange-correlation potential of the excited state.

## RESULTS

### Composition

The chemical composition of the samples examined is reported in Table 1 in the form of weight percent oxide content. The glasses labeled DIAN were synthesized at high temperature in air to represent a diopside-anorthite composition with three different V contents, 0.1, 1, and 5 wt%  $V_2O_5$ , to determine if the behavior of V in the glass changes as a function of its own

**TABLE 1.** Chemical composition of the glasses studied

Oxide \ Sample	DIAN-0.1	DIAN-1.0	DIAN-5.0	NS2-0.1	NS2-1.0	Fe-bas-0.1	Fe-bas-1.0
SiO <sub>2</sub>	48.80 (0.7)	48.30 (0.4)	46.70 (0.6)	69.40 (0.8)	68.80 (0.4)	52.37 (0.5)	51.85 (0.5)
TiO <sub>2</sub>	—	—	—	—	—	3.81 (0.04)	3.77 (0.04)
Al <sub>2</sub> O <sub>3</sub>	20.50 (0.3)	20.20 (0.2)	19.30 (0.3)	—	—	12.80 (0.2)	12.68 (0.2)
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	—	—	11.54 (0.2)	11.42 (0.2)
Na <sub>2</sub> O	—	—	—	31.50 (0.3)	31.10 (0.3)	4.07 (0.04)	4.03 (0.04)
CaO	22.90 (0.2)	22.60 (0.1)	21.40 (0.1)	—	—	7.73 (0.04)	7.65 (0.05)
MgO	7.46 (0.1)	7.37 (0.07)	7.08 (0.1)	—	—	3.58 (0.04)	3.54 (0.04)
K <sub>2</sub> O	—	—	—	—	—	2.08 (0.03)	2.06 (0.03)
P <sub>2</sub> O <sub>5</sub>	—	—	—	—	—	1.84 (0.02)	1.83 (0.02)
V <sub>2</sub> O <sub>5</sub>	0.10 (0.01)	0.99 (0.04)	5.04 (0.09)	0.10 (0.02)	1.01 (0.04)	0.10 (0.02)	1.0 (0.01)
Total	99.76	99.46	99.52	101.0	100.91	99.92	99.83

concentration. The second composition represents a sodium disilicate glass (labeled NS2) where the high sodium content is useful for investigating the influence of the alkaline elements on the structural role of V in the glass. The third composition is an Fe and Ti-bearing basaltic glass (labeled Fe-bas), with two different V contents (0.1 and 1 wt%  $V_2O_5$ ) for the purpose again of investigating the dependence of the structural configuration of V on the total content of this element in the melt. The latter compositions better simulate the chemical complexity of a natural Fe-basalt and allow us to study the effects that different transition elements present in the melt may have on the structural behavior of V. The interaction of V with other transition elements like Fe and Ti may significantly affect V oxidation state and coordination in natural magmas.

### XANES

V *K*-edge XANES spectra of the V mineral compounds are shown in Figure 1a whereas those of the DIAN and NS2 glasses and Fe-bearing glasses are shown in Figure 1b.

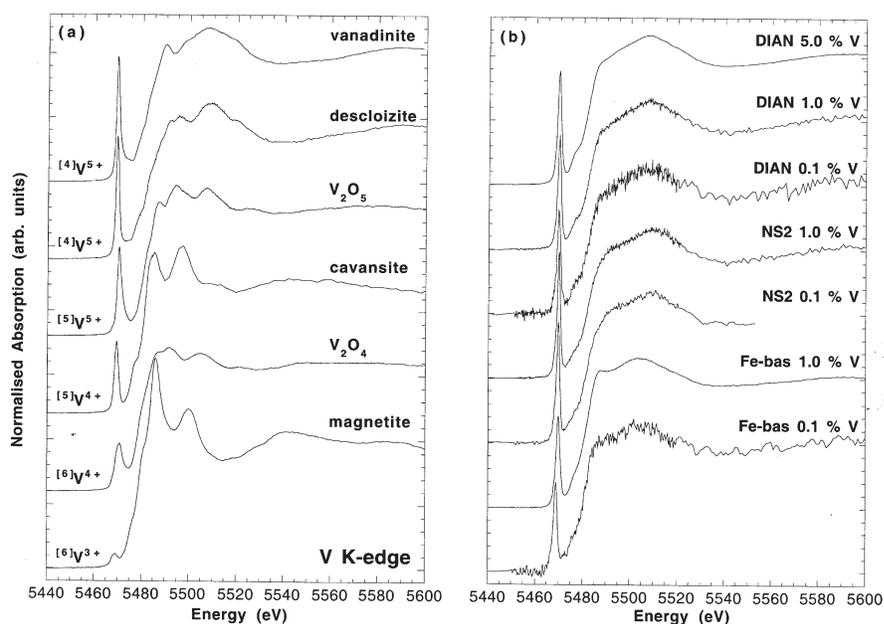
The set of mineral compounds used as standards was chosen to represent a range of oxidation states for V, from  $V^{3+}$  to  $V^{5+}$ , and coordination numbers (CN) from [4] (tetrahedral), to [5] (square pyramidal), to [6] (octahedral). A comparison among the spectra of the standards shows strong variations in energy position and intensity of the peaks both in the pre-edge region (before ca. 5480 eV) and the edge region (after 5480 eV). These are related to the different crystal structures of the compounds and in particular to the oxidation state of the absorber (vanadium), to the coordination polyhedron in which it is located, and to its symmetry. The characteristics of the XANES spectra can be used therefore as a fingerprint method to describe the V environment in a compound. If a detailed study of the pre-edge peak energy region is carried out using high-resolution XANES spectra, comparison with standard materials can provide a quantitative evaluation of the coordination number and oxidation state of V

(Wong et al. 1984).

The pre-edge peak (Fig. 2) is the most useful feature in the XANES spectra to determine both the oxidation state and coordination number of V. This peak represents an *s-d* like transition and is thus dipole-forbidden, but it becomes partially allowed by mixing of the *d*-states of the transition metal with the *p*-states of the surrounding O atoms. This means that the pre-edge peak energy position and intensity depend strongly on the geometry around V and on the mean V oxidation state (Calas and Petiau 1983a, 1983b; Wong et al. 1984; Brown et al. 1995): its intensity will be virtually zero in the case of regular octahedral symmetry ( $O_h$ ) around the absorber, whereas it will reach a maximum in the case of tetrahedral coordination ( $T_d$ ). The absorber oxidation state affects the energy position and intensity of the pre-edge peak since the removal of a valence electron produces a decrease in the screening of core electrons, and an increase of the binding energy of the inner-shell, giving as a result a shift to higher energy of the pre-edge peak with increasing oxidation state of the absorber.

The XANES spectra of the glasses are much less structured than those of the crystalline standards, due to the absence of long-range order. However, structural information on the nearest neighbor environment around vanadium can be obtained. From the comparison between the glass spectra, the DIAN and NS2 glasses are very similar to each other (Fig. 1b), with no significant differences in either the pre-edge or the main absorption edge regions as a function of bulk glass composition or V-content. On the contrary, the Fe-bearing glasses display noticeable changes in peak position and relative intensity, as well as in the height of the pre-edge peak, reflecting a major change in the structural role of V in these glasses.

To extract as much quantitative information as possible from the pre-edge peaks, the high-resolution spectra of this region have been analyzed (Fig. 2) and the peak intensity plotted vs. the energy position (Fig. 3, values reported in Table 2), following the



**FIGURE 1.** Experimental V *K*-edge XANES spectra of (a) model compounds with V in different oxidation states and coordination numbers; (b) glasses. The spectra are normalized to one at the high energy side.

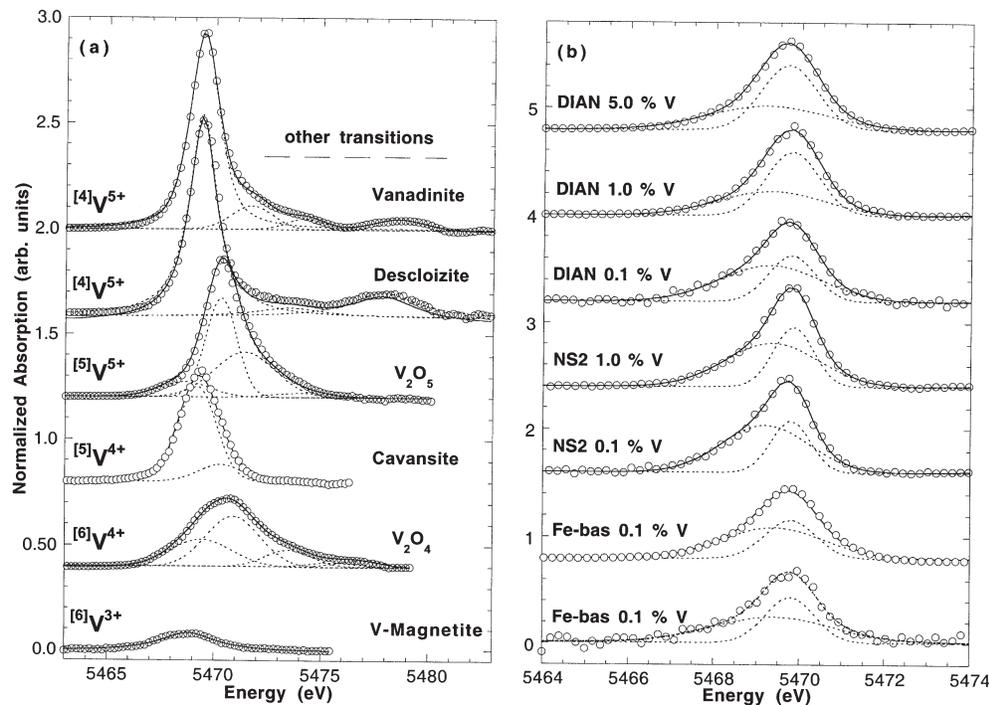
**TABLE 2.** XANES data for the standards and glasses

Sample	Pre-edge peak centroid (eV)	Pre-edge peak position (eV)	Pre-edge peak height*	Fit agreement index (%)	Oxidation state and CN
vanadinite	5469.5	5469.5	0.933	99.80	5 <sup>+</sup> [4] †
descloizite	5469.4	5469.5	0.927	99.90	5 <sup>+</sup> [4] †
V <sub>2</sub> O <sub>5</sub>	5470.8	5470.4	0.656	99.92	5 <sup>+</sup> [5] †
cavansite	5469.4	5469.3	0.501	99.97	4 <sup>+</sup> [5] †
V <sub>2</sub> O <sub>4</sub>	5471.2	5470.8	0.316	99.95	4 <sup>+</sup> [6] †
V-magnetite	5468.8	5468.8	0.081	99.14	3 <sup>+</sup> [6] †
DIAN-0.1	5469.5	5469.7	0.855	99.25	5 <sup>+</sup> [4] ‡
DIAN-1.0	5469.5	5469.8	0.800	99.88	5 <sup>+</sup> [4] ‡
DIAN-5.0	5469.5	5469.7	0.814	99.92	5 <sup>+</sup> [4] ‡
NS2-0.1	5469.4	5469.7	0.855	99.55	5 <sup>+</sup> [4] ‡
NS2-1.0	5469.5	5469.8	0.931	99.90	5 <sup>+</sup> [4] ‡
Fe-bas-0.1	5469.5	5469.8	0.664	97.13	5 <sup>+</sup> [4]+[5] ‡
Fe-bas-1.0	5469.6	5469.8	0.623	98.41	5 <sup>+</sup> [4]+[5] ‡

\* Normalized according to the procedure described in Farges et al. (1996a).

† Literature data.

‡ XANES determination.

**FIGURE 2.** High-resolution spectra of the pre-edge peak of (a) model compounds with V in different oxidation states and coordination numbers; (b) glasses.

procedure described in Farges et al. (1996a) for Ti *K*-edge data. The data obtained for the glasses are compared with those of the standards used in this study. The plot shows that the data from the standards lie in very distinct fields and this allows rigorous discrimination of the oxidation state or the coordination number of V in an unknown sample. Noticeable changes occur in both energy position and intensity of the pre-edge peak as a function of V oxidation state and coordination number. Pre-edge peak data from the Fe-free glasses (DIAN and NS2) closely match corresponding measurements of the model compounds with <sup>4</sup>V<sup>5+</sup> (Fig. 3), indicating that in the Fe-free glasses synthesized in air, V is 5+ and mainly in tetrahedral coordination, although the shift away from the exact position of the standards could be ascribed to contributions from V in coordination numbers other than 4. No significant systematic differences can be noted between glasses with different V-content, so it can be concluded that the structural role of V in the glass is not affected by the V-content in the glass

within 0.1–5.0 V<sub>2</sub>O<sub>5</sub> wt% range as these glasses all plot in the same area within the experimental error. In marked contrast, the pre-edge peak of the Fe-bearing glasses have considerably lower intensities with respect to the Fe-free glasses, about midway between the <sup>4</sup>V<sup>5+</sup> and the <sup>5</sup>V<sup>4+</sup> model compounds.

To establish the contribution from diverse V states to the position and intensity of the pre-edge peaks, weighted sums of the background-subtracted pre-edge peaks of the model compounds were employed to simulate mixing of different V oxidation states and/or coordination numbers. The energy position and intensity of the simulated pre-edge peaks are reported in Figure 3, along with those for the pre-edge peaks of the glasses, as empty symbols (diamonds for mixtures of <sup>4</sup>V<sup>5+</sup> and <sup>5</sup>V<sup>5+</sup> and triangles for mixtures of <sup>4</sup>V<sup>5+</sup> and <sup>5</sup>V<sup>4+</sup>). It can be clearly seen that the trends reported in Figure 3 are markedly non-linear, as previously noted by Farges et al. (1996a), Farges and Brown (1997), and Romano et al. (2000) for the Ti *K*-edge, especially when two

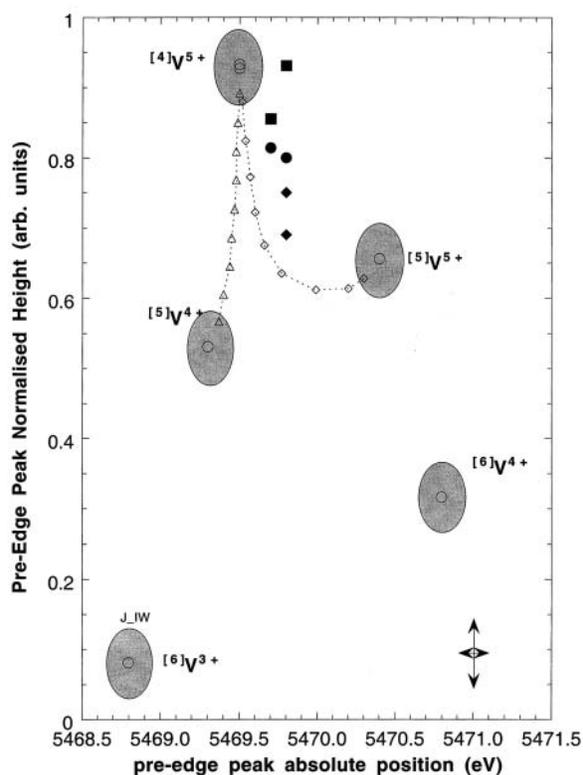


FIGURE 3. Plot of the pre-edge peak normalized intensity vs. energy position. Solid symbols refer to the standards (triangles) and glasses examined (DIAN = circles; NS2 = squares; Fe-bas = diamonds), whereas open symbols refer to modeled combinations of  $[4]V^{5+}$  +  $[5]V^{5+}$  (diamonds) and  $[4]V^{5+}$  +  $[5]V^{4+}$  (triangles) mixtures calculated for 10 mol% step.

V states displaying pre-edge peaks with significantly different height and energy are present in the same sample. The pre-edge peaks of the Fe-bas glasses could thus be explained either as mixtures of  $[4]V^{5+}$  and  $[5]V^{4+}$ , or as mixtures of  $[4]V^{5+}$  and  $[5]V^{5+}$ . Which one of these combinations actually applies to the Fe-bas glasses can be clarified by the EXAFS data, although the correspondence with the mixing curves in Figure 3 suggests that in these glasses V occupies a mixed environment with prevalent  $[5]V^{5+}$  (ca. 40%  $[4]V^{5+}$ –60%  $[5]V^{5+}$ ).

FIGURE 4. Comparison between the experimental, theoretical, and residual Fe *K*-edge EXAFS signals of the V-bearing silicate glasses studied. The EXAFS signals are weighted by  $K^2$ . Symbols are as follows: circles, experimental; solid line, theoretical; dotted line, residual. (a) EXAFS signals. (b) Fourier transforms.

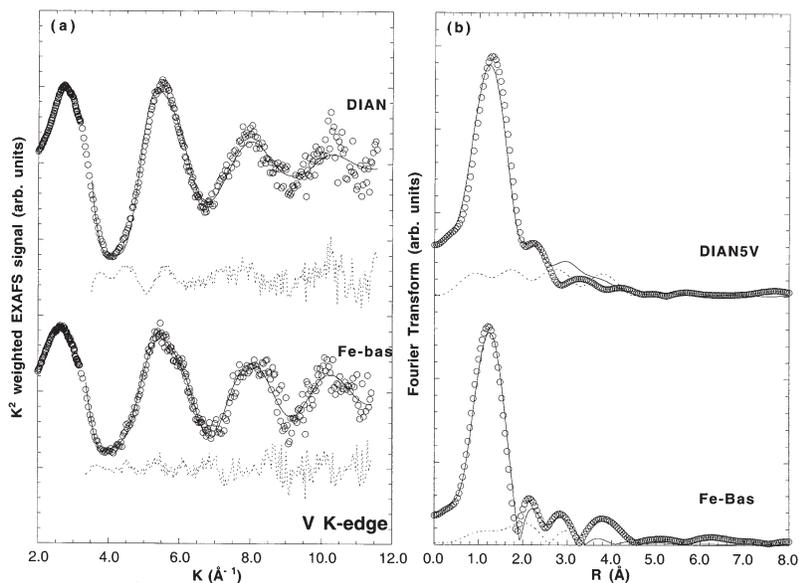


TABLE 3. Essential parameters for the EXAFS refinements

	DIAN-5.0	Fe-Bas-1.0
V-O (Å)	1.697 (20)	1.704 (20)
$\alpha^2$ (Å <sup>-2</sup> )*	0.0097	0.0054
C.N.	4.00 (40)	3.00 (40)
V-O (Å)	–	2.032 (20)
$\alpha^2$ (Å <sup>-2</sup> )	–	0.0123
C.N.	–	1.90 (40)
<V-O> (Å)	1.697	1.831
<C.N.>	4.00 (40)	3.90 (40)
V-Si (Å)	3.400 ()	3.320 ()
$\alpha^2$ (Å <sup>-2</sup> )	0.0199	0.0200
$E_0$ (eV)†	5479.0	5479.9
<i>K</i> range (Å <sup>-1</sup> )	3.5–11.5	3.5–11.5
$S_0^2$	0.85	0.85
<i>R</i> ‡	0.00000560	0.00000357

\* EXAFS Debye-Waller factor.

† Refined value.

‡ Disagreement index (see Filipponi and DiCicco 2000).

## EXAFS

The experimental, theoretical, and residual EXAFS signals of the DIAN-5.0 and Fe-bas-1.0 glasses are shown in Figure 4a, whereas their Fourier transforms are shown in Figure 4b. Despite the relatively low V concentrations, the EXAFS signal is still easily discernible up to approximately 12 Å<sup>-1</sup>, and appreciable differences can be observed in the intensity of the two signals. Although indications of the V environment are revealed by the XANES spectra, both distances and coordination number were left free to vary without constraints during the EXAFS refinement analysis (see Table 3 for the essential parameters of the EXAFS fit).

In the DIAN sample, V was found to be all tetrahedrally coordinated with a V-O distance equal to 1.697 Å (±0.020), which is close to that found in the  $[4]V^{5+}$  crystalline standards (1.701 and 1.713 Å for vanadinite and descloizite, respectively), thus fully confirming the indications obtained from the XANES spectra.

On the contrary, a first attempt to refine a single V-O distance from data collected from the Fe-bas glass was unsatisfactory. A successful fit was only obtained by allowing two different V-O

distances to coexist. The final fit took into account two V-O distances at 1.704 and 2.032 Å, with multiplicities of 3.0 and 1.9, respectively (see Table 3), resulting in a mean <V-O> distance equal to 1.831 Å ( $\pm 0.020$ ) and a mean coordination number of 4.9 ( $\pm 0.4$ ). The mean <V-O> distance is close to that of V<sub>2</sub>O<sub>5</sub> (<V-O> = 1.828 Å for V in square pyramidal coordination). However, the quality of the spectrum, possibly coupled with the high radial disorder, does not allow the detection of any multiple scattering contributions, which could help in discerning the exact geometry of the V-O coordination polyhedron. Moreover, the high radial disorder in the first coordination shell around <sup>51</sup>V<sup>5+</sup> model compounds found in the literature complicates the interpretation of the V-O distances derived from EXAFS in this glass. In particular, although the EXAFS data may be interpreted as due to a fivefold O atom coordination around V with three short equatorial bonds and two long axial bonds (such as in a trigonal bipyramid), the estimated error in the multiplicities ( $\pm 0.4$ ) makes these data also compatible with a mixture of V<sup>5+</sup> in fivefold and fourfold coordination. The latter interpretation is more compatible with the XANES data, indicating that the pre-edge peak of the Fe-bas spectrum can be interpreted as due to a mixture of <sup>41</sup>V<sup>5+</sup> and <sup>51</sup>V<sup>5+</sup>. This interpretation is also in agreement with the observation that EXAFS oscillations in the Fe-bas spectrum have lower intensities than those in the DIAN spectrum. Since the intensity decreases with decreasing coordination number, and since the DIAN sample was found to have tetrahedrally coordinated V<sup>5+</sup>, V in the Fe-bas glass would have, unrealistically, an even lower coordination number. More likely, the lower intensity of the signals can be explained by a more disordered environment around V, due to the coexistence of several coordination geometries and V-O distances in the Fe-bas glass.

## DISCUSSION

Accurate analysis of the pre-edge features in the V *K*-edge high-resolution XANES spectra allowed the assessment of V oxidation state and coordination number in V-bearing silicate glasses down to a V content of 0.1 wt% V<sub>2</sub>O<sub>5</sub>. When V is present simultaneously in different oxidation states and coordination numbers, combined use of XANES and EXAFS analysis can help greatly in discerning the contributions of different V environments to the spectral features.

In the Fe-free silicate glasses (DIAN and NS2) synthesized in air, V was found to be virtually all pentavalent and in tetrahedral coordination, with a V-O distance close to 1.70 Å. No noticeable differences have been found between glasses with different base compositions (CaMgSi<sub>2</sub>O<sub>6</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, and Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>), indicating that the presence of excess sodium in the glass does not cause appreciable variations in the short-range environment around V. Similarly, varying V-contents from 0.1 to 5.0 wt% does not result in any significant changes to the V environment.

The case is different for the Fe-bearing basaltic glasses investigated in this study. In this case, both XANES and EXAFS show changes in the local environment around V. The pre-edge peak has a reproducibly lower intensity and a slightly higher energy than in the Fe-free glasses; these effects can be reproduced when modeling a mixture of two different V states (<sup>41</sup>V<sup>5+</sup> and <sup>51</sup>V<sup>5+</sup>) by summing the pre-edge peaks of the appropriate model compounds. EXAFS data indicate that V is in a more disordered

coordination environment than in the DIAN glasses, possibly due to the presence of two or more coordination geometries. In particular, both the XANES data and the EXAFS-derived V-O distances in the Fe-bas glass are compatible with a mixture of <sup>41</sup>V<sup>5+</sup> and <sup>51</sup>V<sup>5+</sup>.

In view of the constancy of V environment in the Fe-free glasses with such different compositions (DIAN and NS2) and V contents (from 0.1 to 5.0 wt%), it is interesting to find large variations of the structural configuration of V in the Fe-Bas glasses. This change can be tentatively interpreted as due to the entry of other cations (like Fe<sup>3+</sup>, P, Ti, etc.) competing for the tetrahedral sites in the glass network as previously suggested by Romano et al. (2000) for the Al-induced coordination change in Ti-silicate glasses.

These results have interesting implications for the behavior of transition elements during magmatic crystallization and melting processes. Transition elements predominantly occupy octahedral sites in crystal structures, whereas in magmas these same elements can be incorporated in different coordination states (four-, five-, or sixfold coordinated). Thus, it can be suggested that the partitioning behavior of transition elements between crystalline phases and silicate melts is influenced by the octahedral site preference energy (OSPE) of the ion (see Burns 1970; Henderson and Dale 1970).

In our study we determined that the coordination number of V for DIAN and NS2 does not change significantly as a function of melt polymerization, being tetrahedral in all Fe-free glasses. One possible explanation could be that under very oxidizing conditions (in equilibrium with air), V was found to be preferentially in the 5+ valence state. Because V<sup>5+</sup> has a very small ionic radius (0.36 Å for <sup>41</sup>V<sup>5+</sup> according to Shannon and Prewitt 1970), this results in a very low octahedral site preference energy and a preference for small coordination polyhedra like tetrahedral. We can suggest that under very oxidizing conditions, the influence of melt bulk composition (in terms of Si, Al, Ca, and alkali concentration) on the coordination number of V will be small, and as a consequence, the partitioning behavior, if affected by the OSPE energy, will be similar for DIAN and NS2 melts (as the coordination state is identical). On the other hand, addition of other elements like Fe<sup>3+</sup>, P, or Ti may change significantly the coordination environment of V in the melt and, consequently V partitioning behavior. Even if V<sup>3+</sup> does not enter directly into the crystal structure of common rock-forming minerals (Horn et al. 1994; Hill et al. 2000), where V<sup>3+</sup> is predominant, the presence of V<sup>5+</sup> in the liquid can be important in influencing the relative abundance of V<sup>3+</sup> and V<sup>4+</sup>, and should therefore be taken into account.

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