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Coordination of Ti^{4+} in silicate glasses: A high-resolution XANES spectroscopy study at the Ti *K* edge

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ABSTRACT

The coordination environment of Ti in eight Ti-bearing glasses of the $Na_2Si_4O_9$-$Na_2Ti_4O_9$ join (NTS) and in six ATY2 glasses ($A_2O{\cdot}TiO_2{\cdot}2YO_2$, with A = Na, K, or Rb and Y = Si or Ge) was determined using high-resolution, X-ray absorption near-edge structure (XANES) spectroscopy at the Ti *K* edge in ambient conditions.

Fivefold-coordinated Ti ($^{[5]}Ti$) is the dominant Ti species ($\geq 50 \pm 10\%$ of the total Ti) in all the glasses studied. Sixfold-coordinated Ti was detected mostly in sodic glasses (NTS, NTS2, NTG2), and it increases with TiO_2 content (as high as 40 ± 10% of the total of Ti in the most TiO_2-rich NTS glasses) and in the order Si < Ge. Fourfold-coordinated Ti was detected only in nonsodic ATY2 glasses, and its content increases in the order Na < K < Rb and Ge < Si. Fivefold-coordinated Ti^{4+} is probably present as square pyramidal, titanyl-bearing moieties, or $(^{[5]}Ti{=}O)O_4$.

A synthesis of Ti^{4+} coordination for oxide glasses derived using direct methods (X-ray absorption and neutron scattering) can be used, for instance, to help in the interpretation of Raman scattering spectra collected for Ti-bearing glasses and to estimate NBO/T ratios better for titanosilicate glasses and melts.

INTRODUCTION

The coordination chemistry of Ti^{4+} in silicate glasses and melts has recently received particular attention because of unusual variations in some of the physical properties of these systems, such as density, shear viscosity, and heat capacity (Richet and Bottinga 1985; Mysen 1988; Hess 1991; Dingwell 1992a, 1992b; Lange and Navrotsky 1993; Bouhifd 1995). However, because of the existence of several coordinations around Ti^{4+} in oxide compounds ($^{[4]}Ti$, $^{[5]}Ti$, and $^{[6]}Ti$), the coordination of Ti^{4+} in titanosilicate glasses and melts may also vary extensively. However, the coordination chemistry of Ti^{4+} in oxide glasses is still not well understood. This is due to a lack of accurate direct structural information, despite the many Raman scattering, X-ray absorption, X-ray scattering, X-ray photoemission, and neutron scattering studies that have been published (see Farges et al. 1996a, and references therein).

Among these techniques, X-ray absorption fine-structure (XAFS) methods [which include X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS) spectroscopies] are direct structural probes that are element specific. Therefore, they are the tools of choice for the direct determination of the coordination environment of Ti^{4+} in amorphous materials. Unfortunately, most of the past XAFS studies on the coordination of Ti in glasses were based on a nonrepresentative set of Ti-bearing model compounds (few, if any, model compounds contained $^{[4]}Ti$ and $^{[5]}Ti$). Also, the possible existence of $^{[5]}Ti$ and various mixtures of Ti coordination (and how these mixtures affect preedge features) has long been ignored or considered only briefly. Finally, many preedge spectra have been collected under low-resolution conditions, which resulted in less accurate structural information. Therefore, several previous interpretations of XAFS spectra must be revisited using more comprehensive preedge information.

In an attempt to alleviate these limitations, a large selection of Ti-bearing model compounds has recently been studied by XANES spectroscopy, thanks to the collection of a large set of high-resolution XANES data and the ab-initio calculation of XANES spectra (Farges et al. 1996a). By using this new method for XANES interpretation, these authors were able to demonstrate the importance of square pyramidal $^{[5]}Ti^{4+}$ species in several Ti-bearing silicate glasses and melts, synthetic and natural (Farges 1996; Farges et al. 1996b; Farges and Brown 1997). However, no systematic high-resolution preedge study of the coordination environment of Ti has yet been conducted for oxide glasses of similar composition or structure (such as along a specific join, etc.).

In this paper, high-resolution XANES spectroscopy is used to characterize the local structure around Ti^{4+} in two sets of Ti-bearing silicate glasses. One set consists of eight glasses within the $Na_2Si_4O_9$-$Na_2Ti_4O_9$ join (NTS), and the second set contains six glasses of composition $A_2O{\cdot}TiO_2{\cdot}2YO_2$ (ATY2), where A = Na, K, or Rb and Y = Si or Ge. In the first set of glasses, the calculated num-

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Table 1. Nominal and measured compositions of the 14 glasses studied (mol%)

	Nominal			Measured*		
	SiO_2	TiO_2	M_2O**	SiO_2	TiO_2	M_2O**
		NTS glasses (M = Na)				
20.60	20	60	20			
40.40	40	40	20			
60.20	60	20	20			
64.16	64	16	20			
68.12	68	12	20			
72.08	72	8	20			
76.04	76	4	20			
78.02	78	2	20			
		ATY2 glasses (M = Na, K, or Rb)				
NTS2	50	25	25	49.9	24.9	25.2
NTG2	50	25	25	50.0	25.2	24.4
KTS2	50	25	25	50.3	24.9	24.7
KTG2	50	25	25	50.3	25.1	24.5
RTS2	50	25	25	50.1	24.9	24.7
RTG2	50	25	25	50.1	25.1	24.5

* Averaged electron microprobe analysis (4–6 points; 15 kV, 15 nA). Maximum standard deviation for each analysis ≈ 1.5 mol%. Measured compositions were not available for NTS glasses.

** M = alkali present in the glass (Na, K, or Rb).

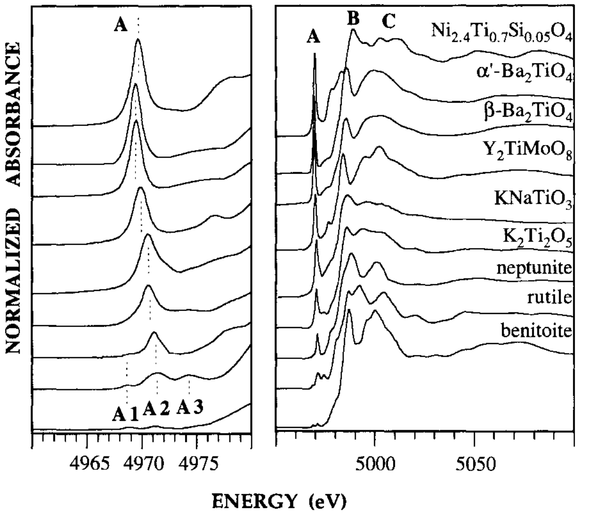

Figure 1. (**right**) Normalized Ti *K*-edge XANES spectra for selected Ti-bearing model compounds containing [4]Ti, [5]Ti, and [6]Ti. (**left**) Detail of the normalized preedge feature.

ber of nonbridging O atoms per tetrahedron, NBO/T, is constant at 0.5 (but this calculation assumes the presence of [4]Ti, which is shown below to be inconsistent with the present XANES information). This set of glasses allows the study of the influence of TiO_2 content on Ti coordination. In the second set of glasses, the effect of replacement of network formers and modifiers is investigated (Na vs. K vs. Rb, and Si vs. Ge). These two sets of glasses were chosen because they show analogies and differences in Ti^{4+} coordination chemistry. The present XANES data suggest the presence of major amounts of [5]Ti in all glasses. However, [6]Ti is important only at high TiO_2 contents (NTS series), and [4]Ti is detected when larger alkalis (K and Rb) are present (ATY2 series).

Experimental details

NTS glasses were prepared originally by D. Neuville and B.O. Mysen at the Carnegie Institution of Washington (D.C.) for a Raman scattering study. The NTS glass-synthesis information is similar to that detailed in Mysen and Neuville (1995). The glass compositions vary in their molar proportions of SiO_2 and TiO_2; the molar Na_2O content is constant at 20% (Table 1). Electron microprobe analyses for these glasses have been determined (Neuville and Richet, in preparation). ATY2 glasses were similarly prepared by P. Richet (NTS2 and KTS2: original samples in Richet and Bottinga 1985) or the author (all other ATY2 glasses) at the Departement des Géomatériaux (CNRS and IPGP, Paris). Electron microprobe analyses (Table 1) are within 1.5 mol% of nominal compositions.

High-resolution Ti *K*-edge XANES spectra for the model compounds and glasses were collected under the same conditions (transmission mode, using an Si(311) double-crystal monochromator and 0.1 eV steps; energy resolution ≈ 1.2 eV at 5 keV) at the EXAFS4 beamstation of LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique), Orsay, France. The DCI storage ring was operating at 1.8 GeV and 100–300 mA positron current. More detailed information on data collection and reduction procedures can be found in Farges et al. (1996a, 1996b).

Results

Figure 1 shows selected Ti *K*-edge XANES spectra collected for oxide-type model compounds in which Ti^{4+} is located in fourfold-, fivefold-, or sixfold-coordination sites. XANES spectra for other model compounds, ab-initio XANES calculations, and crystal-structure information for these materials are detailed by Farges et al. (1996a, 1996b). Refined values for model-compound preedge data are listed in Table 2. Figure 2 shows the variation of preedge spectra when several Ti coordinations are present in a sample and demonstrates the sensitivity of the method. Figures 3 and 4 show the Ti *K*-edge XANES spectra collected for the eight NTS and the six ATY2 glasses, respectively. Refined preedge parameters for these 14 glasses are listed in Table 3 and represented in Figure 5 together with preedge data for model compounds and mixtures of Ti coordination.

Preedge features for model compounds

At the Ti *K* edge, a rather intense preedge feature (feature A in Fig. 1) is located ~18 eV below the main-edge crest (features B and C). These features are commonly attributed to electronic transitions from 1s energy levels of Ti to the Ti 3d or O 2p molecular orbitals. The height and position of the preedge feature are direct functions of the degree of p-d mixing, oxidation state, and experimental resolution of the XAFS spectrometer used [Farges et al. (1996a, 1996b) outlined the dependence in detail].

TABLE 2. Preedge parameters for selected Ti-bearing model compounds

		Preedge parameters			
	Ti coordination	Position (eV)	Normalized height	FWHM (eV)	Area
$Ni_{2.6}Ti_{0.7}O_4$	4	4969.7(1)	0.94(5)	0.8(1)	1.2(1)
$Ni_{2.4}Ti_{0.7}Si_{0.05}O_4$	4	4969.6	0.90	0.8	1.2
β-Ba_2TiO_4	4	4969.4	1.00	0.8	1.2
α-Ba_2TiO_4	4	4969.5	1.00	0.8	1.2
$CsAlTiO_4$	4	4969.7	~0.9*	~0.8*	~1*
Rb_2TiO_3	4	4969.6	1.00	0.8	1.2
$K_6Ti_2O_7$	4	4969.7	0.93	0.9	1.3
Y_2TiMoO_8	4	4969.9	0.74**	0.9	1.0
Na_4TiO_4	4	4969.6	0.70**	0.9	0.9
$KNaTiO_3$	5	4970.6	0.73	0.8	0.8
$Ba_2TiOSi_2O_7$	5	4970.6	0.65	0.8	0.8
$Ba_2TiOGe_2O_7$	5	4970.6	0.65	0.8	0.8
$Sr_2TiOSi_2O_7$	5	4970.5	0.70	0.8	0.8
$Rb_2Ti_4O_9$	5	4970.5	0.47**	1.1	0.8
$K_2Ti_2O_5$	5	4970.6	0.51**	1.1	0.8
r-TiO_2 (rutile)	6	4971.6	0.22	1.3	0.4
a-TiO_2 (anatase)	6	4971.4	0.17	1.3	0.3
$CaTiO_3$ (perovskite)	6	4971.4	0.11	1.4	0.2
$BaTiSi_3O_9$ (benitoite)	6	4971.2	0.04	1.4	0.1
$KNa_2LiFe_2Ti_2Si_8O_{24}$ (neptunite)	6	4971.1	0.32	1.3	0.6
$FeTiO_3$ (ilmenite)	6	4971.7	0.22	1.4	0.5
$CaTiSiO_5$ (titanite)	6	4971.4	0.18	1.3	0.4

* Rough estimate because of the Cs L_{III}-edge interference.

** Highly hygroscopic compound. Some $^{[6]}$Ti (due to hydroxylation by air moisture during sample preparation or due to undissolved TiO_2) may have been present in the sample studied. The preedge height could therefore be slightly underestimated.

With the use of preedge data for Ti^{4+}-bearing model compounds (absolute preedge energy position and normalized preedge height; Table 2), three well-separated domains can be identified for $^{[4]}$Ti, $^{[5]}$Ti, and $^{[6]}$Ti (Fig. 5). The preedge feature is highest for $^{[4]}$Ti-bearing model compounds (e.g., as high as 100% of the edge jump) and is shifted toward lower energies by 1–2 eV in comparison with the other Ti coordinations (Fig. 2, left) (energy reproducibility in the preedge position for this data set is <0.1 eV). In contrast, two to three preedge features were observed for $^{[6]}$Ti-bearing oxide model compounds. The most intense preedge feature for $^{[6]}$Ti-bearing model compounds (feature A2 in Fig. 1, following Waychunas 1987) is shifted toward higher energies (e.g., the most intense preedge feature for rutile, r-$^{[6]}TiO_2$, is shifted by +2.1 ± 0.1 eV in comparison with that for β-$Ba_2{}^{[4]}TiO_4$; Table 2; Fig. 2, left). Preedge energies and heights for $^{[5]}$Ti-bearing model compounds are within the values measured for the other two Ti coordinations (Figs. 2 and 5; Table 2).

The use of both preedge parameters (absolute position and normalized height) is necessary for deriving reliable coordination information about Ti in oxide compounds, especially when mixtures of Ti^{4+} coordination occur. To illustrate this, we examined the preedge region for a sample containing 100% $^{[5]}$Ti and that for a sample containing a 50:50 mechanical mixture of $^{[4]}$Ti and $^{[6]}$Ti (Fig. 2, left) (note that both samples show the same average Ti coordination). If only one preedge parameter is used, the information is imprecise or even misleading. For instance, the preedge position for the mixture would suggest the presence of $^{[4]}$Ti, whereas its preedge height is more consistent with the presence of $^{[5]}$Ti. In turn, a clear distinction between both samples is possible when using both preedge parameters (Fig. 2, left). Indeed, the preedge for the mixture is shifted by ~1.0 ± 0.1 eV in comparison with the sample containing only $^{[5]}$Ti (see also Table 3). Also, the preedge feature for the mixture is broader than that for $^{[5]}$Ti (FWHM ≈ 1.2 and 0.8 ± 0.1 eV, respectively).

Similarly, a complete set of preedge parameters for a variety of mixtures of Ti coordinations was measured and presented in Farges et al. (1996a, 1996b). On the basis of this data set, the average detection level for each Ti coordination is ~10 at% (Fig. 2, right). A summary of this information is shown in Figure 5. It is noteworthy that all these trends and assignments have been verified on a theoretical basis, using the ab-initio, one-electron multiple-scattering theory (FEFF7 code) (see Farges et al. 1996a, 1996b).

Preedge features for Ti-bearing glasses

The Ti *K*-edge preedge information for the 14 glasses studied is close to that for $^{[5]}$Ti (0.5 ± 0.05 and 4970.5 ± 0.1 eV), suggesting that this coordination is important in all these glasses. In detail, the preedge position for the NTS glasses does not vary significantly (4970.4–4970.6 ± 0.1 eV). In contrast, the normalized preedge height is lower for the most TiO_2-rich glasses of that join (0.3–0.4 ± 0.05) and broader (FWHM ≈ 1.2 ± 0.1 eV) than that for glasses with the lowest TiO_2 content (e.g., sample 78.02). This suggests that the local structure around Ti^{4+} is more complex in the former glasses. For the ATY2 glasses, in contrast, preedge position varies greatly

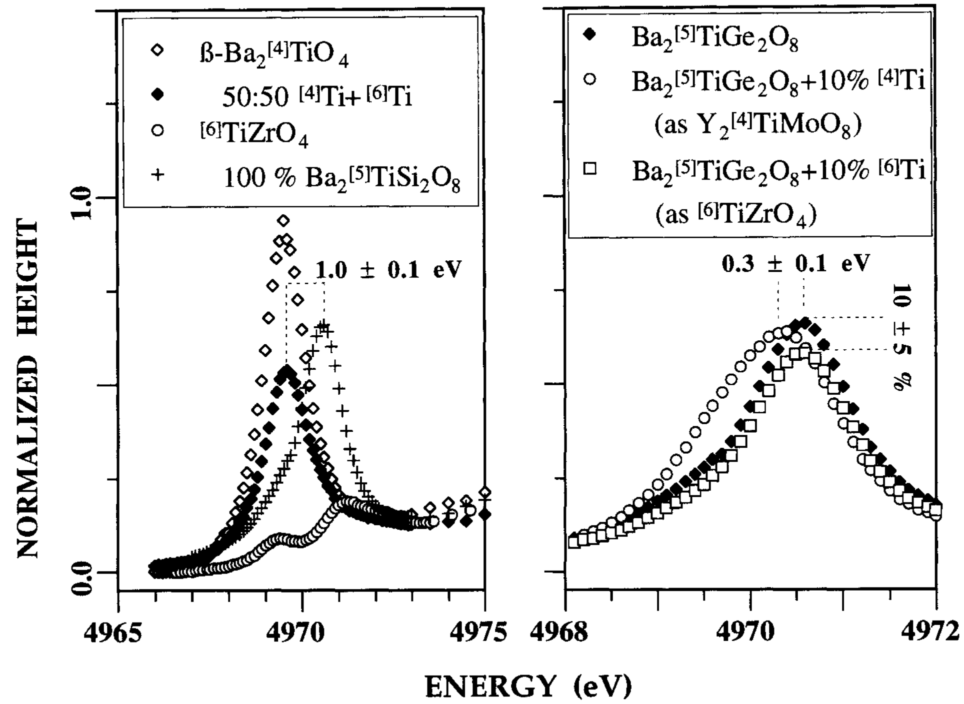

Figure 2. Examples of advantages and limitations of the preedge analysis presented in this study. (**left**) Normalized preedge features for 100% $^{[4]}$Ti (as β-Ba_2TiO_4), $^{[5]}$Ti (as $Ba_2TiSi_2O_8$), and $^{[6]}$Ti (as $TiZrO_4$), in comparison with a preedge feature collected for a 50:50 mixture of $^{[4]}$Ti and $^{[6]}$Ti. Note the large difference (particularly in preedge position) between the preedge feature for the mixture and that for pure $^{[5]}$Ti (both have the same average Ti coordination). Consideration of only the preedge height parameter is not sufficient to distinguish between the two models, and consideration of only the preedge position can be misleading (suggesting the presence of only $^{[4]}$Ti in the mixture of $^{[4]}$Ti and $^{[6]}$Ti). (**right**) Effect of the presence of 10 at% Ti as $^{[4]}$Ti or $^{[6]}$Ti in a preedge feature for $^{[5]}$Ti (as $Ba_2TiGe_2O_8$). Note the significant broadening of the feature and its shift toward lower energies (by 0.3 ± 0.1 eV) when both $^{[4]}$Ti and $^{[5]}$Ti are present. In contrast, the presence of 10 at% $^{[6]}$Ti together with $^{[5]}$Ti decreases the preedge height by ~10 ± 5%. However, a change in preedge height can also be attributed to a change in centrosymmetry around $^{[5]}$Ti, which makes the detection of minor amounts of $^{[6]}$Ti in a mixture more difficult than the detection of $^{[4]}$Ti. All these variations were confirmed using ab-initio multiple-scattering calculations to ensure that the solutions of these fits are unique.

(4969.9–4970.5 ± 0.1 eV), as does normalized height (0.42–0.60 ± 0.05).

DISCUSSION

Coordination of Ti in Ti-bearing glasses of the $Na_2Si_4O_9$-$Na_2Ti_4O_9$ join (NTS)

On the basis of Table 3, the preedge parameters for the TiO_2-rich NTS glasses (e.g., sample 20.60) belong to the very left side of the domain for a mixture of $^{[5]}$Ti and $^{[6]}$Ti coordinations, as shown in Figure 5. This suggests that $^{[5]}$Ti and $^{[6]}$Ti are the dominant Ti coordinations in these glasses. Fourfold-coordinated Ti is at the limit of detection (<10 at%), otherwise the preedge feature would be shifted toward lower energies (<4970.5 ± 0.1 eV). In contrast, the most Ti-poor glasses (e.g., sample 78.02) have preedge features typical of large amounts of $^{[5]}$Ti (similar to those for crystalline $K_2Ti_2O_5$; Tables 2 and 3). This type of preedge feature cannot be due to an ~50:50 mixture of $^{[4]}$Ti and $^{[6]}$Ti because the preedge position would be much lower (near ~4969.7 ± 0.1 eV; Table 3; Fig. 2). In the Ti-poor glasses, $^{[4]}$Ti is not significant and $^{[6]}$Ti (~15 at%) is near the detection limit (±10 at%). Between the most Ti-rich and the most Ti-poor glasses studied (e.g., samples 20.60 and 78.02), preedge parameters vary directly with TiO_2 content.

Average values for the preedge positions and normalized heights for $^{[4]}$Ti, $^{[5]}$Ti, and $^{[6]}$Ti (4969.7 and 0.9, 4970.5 and 0.6, and 4971.4 eV and 0.2, respectively; Table 3) can be used to estimate the relative amounts of these three Ti coordinations in the eight NTS glasses studied (Table 3). The preedge feature for the most dilute glasses (sample 78.02) can be modeled using an 85:15 (±10) mixture of $^{[5]}$Ti and $^{[6]}$Ti ($^{[4]}$Ti is insignificant, but it can be present at minor or trace levels). In contrast, the preedge feature for the most Ti-rich glass (sample 20.60) is typical for a 50:40 (±10) mixture of $^{[5]}$Ti and $^{[6]}$Ti coordinations, respectively, with $^{[4]}$Ti still below the limit of detection (≤10 at%). The presence of a large mixture of Ti coordination in the most Ti-rich NTS glasses can be viewed from the Ti *K*-edge crest surface (Fig. 3). In the previous studies (Farges et al. 1996a, 1996b), we noticed from ab-initio XANES calculations that the normalized

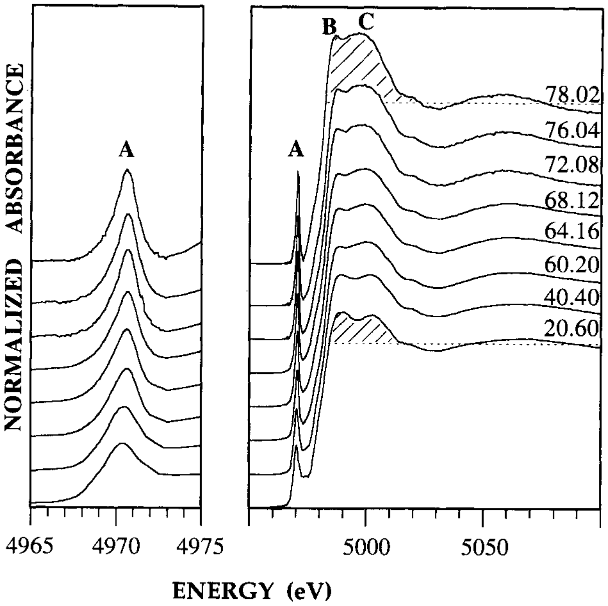

Figure 3. (**right**) Ti K-edge XANES spectra for the eight Ti-bearing glasses of the $Na_2Si_4O_9$-$Na_2Ti_4O_9$ join. (**left**) Detail of the normalized preedge feature.

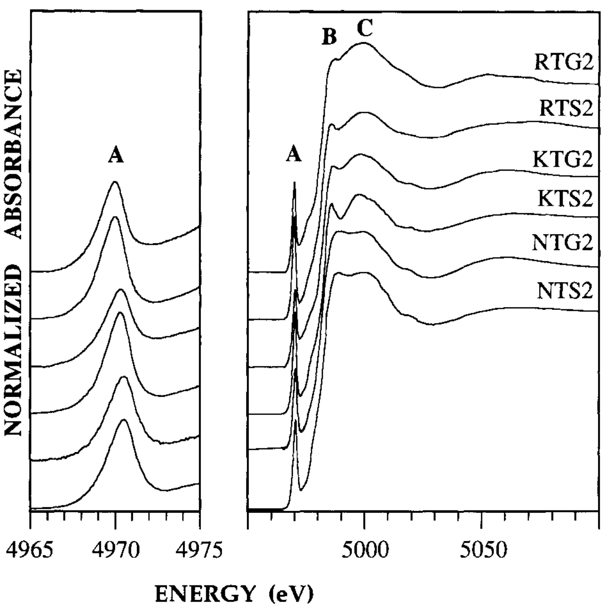

Figure 4. (**right**) Ti K-edge XANES spectra for the six ATY2 glasses (A = Na, K, or Rb and Y = Si or Ge). (**left**) Detail of the normalized preedge feature.

edge crest surface (dashed area in Fig. 3) is an indication of the degree of ordering in the local structure around many elements, including Ti^{4+}. Indeed, sample 20.60 shows a lower edge crest surface than sample 78.02. This suggests that the former has a more disordered local structure around Ti^{4+} (because of the presence of several Ti sites), whereas Ti probably has a more defined local structure in the latter glass (where $^{[5]}$Ti predominates). This observation is therefore consistent with the preedge parameters.

On the basis of these models, the calculated average Ti coordination in NTS glasses decreases from ~5.4 to 5.1 (±0.1) with decreasing TiO_2 content. The absolute molar concentrations for the various Ti coordinations can be calculated for each NTS glass (Fig. 6). The decrease in the concentration of $^{[6]}$Ti with decreasing TiO_2 content is more pronounced than with $^{[5]}$Ti, suggesting that $^{[6]}$Ti may predominate at high TiO_2 contents. Also, the absolute amount of $^{[5]}$Ti is the highest at 20–30 mol% TiO_2.

Coordination of Ti in ATY2 glasses

On the basis of Table 3, the preedge parameters for the ATY2 glasses belong to the lower side of the domain for $^{[5]}$Ti (NTS2 and NTG2 glasses) or that corresponding to a mixture of $^{[4]}$Ti and $^{[5]}$Ti coordinations (other ATY2 glasses), as shown in Figure 5. For the latter glasses (K- and Rb-bearing ATY2 glasses), the models of coordination mixture suggest the presence of ~85–60% $^{[5]}$Ti and 15–40% $^{[4]}$Ti (Table 3). The preedge parameters for the RTS2 and RTG2 glasses can also be interpreted to suggest an ~80:20 mixture of $^{[4]}$Ti and $^{[6]}$Ti or an ~60:20:20 mixture of $^{[4]}$Ti, $^{[5]}$Ti, and $^{[6]}$Ti. The two last models are consistent with large amounts of $^{[4]}$Ti. By analogy with NTS2, KTS2, and KTG2 glasses (with similar main edge crests; Fig. 4), RTS2 and RTG2 glasses would also be expected to show large amounts of $^{[5]}$Ti (together with $^{[4]}$Ti). Therefore, a model of coordination mixture involving $^{[4]}$Ti and $^{[5]}$Ti is preferred for these Rb-bearing glasses.

The preedge parameters for ATY2 glasses suggest that $^{[6]}$Ti is important only in the sodic ATY2 glasses (maximum 30 at% in NTG2). Substitution of Si by Ge does not dramatically change the preedge feature, except by slightly decreasing its normalized height. In contrast, the relative amount of $^{[4]}$Ti increases significantly in the order Rb > K > Na, as shown by a regular shift in the preedge position (4970.5 vs. 4970.3 vs. 4969.9 ± 0.1 eV) with increasing size of the alkali. On the basis of the previous models of Ti-coordination mixtures (Table 3), the replacement of Na by Rb increases the relative amounts of $^{[4]}$Ti in ATY2 glasses from <10 to 40 ± 10 at%. In ATY2 glasses, the average Ti coordination varies from ~5.3 ± 0.1 in NTG2 to 4.6 ± 0.1 in RTS2 and RTG2 glasses.

The importance of $^{[5]}$Ti^{4+}

The presence of major amounts of $^{[5]}$Ti in all glasses is consistent with previous structural information about the coordination environment of Ti^{4+} in alkali-bearing silicate glasses, derived using direct techniques such as X-ray and neutron methods (Loshmanov et al. 1975; Yarker et al. 1986; Cormier et al. 1995; Farges et al. 1996b). In these glasses, $^{[5]}$Ti is probably present as square pyramidal polyhedra, the only environment clearly documented for many silicate glasses, synthetic or natural (cf. Farges et al. 1996a, 1996b). This polyhedron is characterized by

TABLE 3. Preedge parameters for models of Ti coordination

	Ti-*K* preedge information				Ti coordination		
	Position (eV) ($\pm$0.1)	Normalized height ($\pm$0.05)	FWHM (eV) ($\pm$0.1)	Area (eV) ($\pm$0.1)	4 (at%) ($\pm$10)	5 (at%) ($\pm$10)	6 (at%) ($\pm$10)
Models of Ti coordination (predicted and measured)							
End-members	4969.7	0.90	0.8	1.2	100	0	0
(Avg. values)	4970.5	0.60	0.8	0.8	0	100	0
	4971.4	0.20	1.3	0.4	0	0	100
2 components	4969.7	0.50	1.2	1.0	50	0	50
	4969.9	0.60	1.1	1.0	50	50	0
	4970.7	0.30	1.2	0.7	0	50	50
NTS glasses							
20.60	4970.4	0.34	1.2	0.6	<10	50	40
40.40	4970.4	0.37	1.1	0.6	<10	55	35
60.20	4970.5	0.40	1.0	0.6	—	65	35
64.16	4970.5	0.42	1.0	0.6	—	70	30
68.12	4970.5	0.46	0.9	0.6	—	75	25
72.08	4970.6	0.48	0.9	0.7	—	75	25
76.04	4970.6	0.52	0.9	0.7	—	80	20
78.02	4970.5	0.56	0.9	0.8	—	85	15
ATY2 glasses							
NTS2	4970.5	0.45	0.8	0.5	<10	75	25
NTG2	4970.5	0.43	0.7	0.5	<10	70	30
KTS2	4970.3	0.54	0.7	0.6	15	85	—
KTG2	4970.3	0.50	0.7	0.6	15	85	—
RTS2	4969.9	0.60	0.8	0.6	40	60	—
RTG2	4969.9	0.55	0.8	0.6	40	60	—

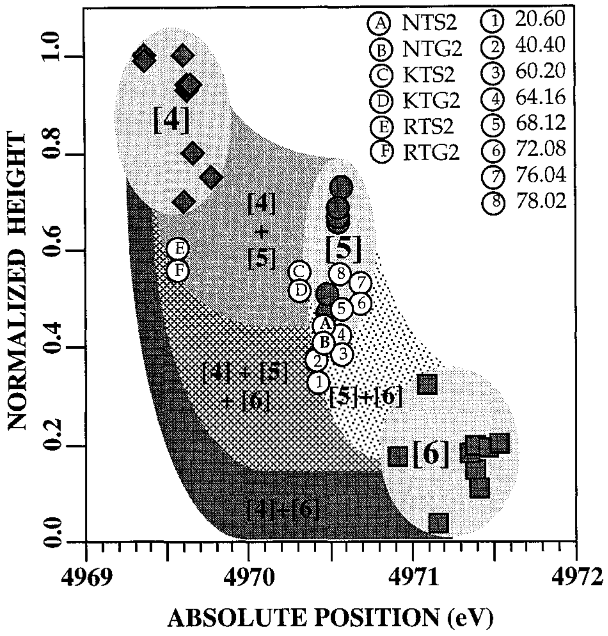

FIGURE 5. Summary of Ti preedge parameters (normalized preedge height vs. absolute energy position) showing regions for pure $^{[4]}$Ti, $^{[5]}$Ti, and $^{[6]}$Ti, the regions for the various mixtures of Ti coordinations (data from Farges et al. 1996a; partial list in Table 2), and the preedge parameters for the 14 glasses.

two sets of Ti-O distances. One short Ti=O distance (near 1.7 Å) is referred to as titanyl, and this bond must connect Ti to a nonbridging O atom because of its very high bond valence (~1.7 vu). Opposite the summit of this square pyramid, four bridging O atoms form four longer Ti-O distances (~1.9–2.0 Å with bond valence of ~0.75 vu). The titanyl-bearing unit ($^{[5]}$TiO^{2+} or "Ty") is always coordinated to four bridging O atoms (bridging to Si, Ge, P, or Ti, depending on the system). The titanyl unit can therefore act as a network former, e.g., TyO_4.

Several Raman scattering studies have also suggested the possibility of $^{[5]}$Ti species in several silicate glasses (Markgraf et al. 1992, 1993; Henderson and Fleet 1995), again in good agreement with XANES and neutron scattering information. However, Henderson and Fleet (1995) found that $^{[4]}$Ti is the most important Ti coordination at the lowest TiO_2 contents (below ~10 mol% TiO_2) in glasses of the Na_2SiO_3-TiO_2 binary (NBO/T ≈ 2). The present XANES data do not clearly show such a trend. However, the glasses investigated in this study are more polymerized than those studied by Henderson and Fleet (1995).

Comparison with other glasses: A model to help in the prediction of Ti coordination in oxide glasses

Direct information about the coordination of Ti^{4+} in oxide glasses was reviewed by Farges et al. (1996a). An attempt to summarize these results is presented in Figure 7, in which the NBO/T ratio is plotted against the average Pauling bond valence for the network modifiers present in the glasses studied (valence divided by coordination). This diagram is valid only for glasses with relatively low TiO_2 contents (<30 mol%; but this limit depends on several factors such as glass composition) because TiO_2 saturation enhances the domain for $^{[6]}$Ti (see Hess 1991). The coordination domains shown represent the most abundant Ti species. However, nonnegligible amounts of, for instance, $^{[4]}$Ti are also likely in the domain for $^{[5]}$Ti, which is close to the boundary with $^{[4]}$Ti.

The diagram shows the importance of the domain for $^{[5]}$Ti in oxide glasses. The possibility that $^{[5]}$Ti bonds to both bridging and nonbridging O atoms makes this coordination highly sensitive to the presence of both network formers and modifiers. Indeed, about four to five network modifiers (usually alkali or alkaline earth atoms) are needed around every NBO of a titanyl unit for charge balancing (see Farges et al. 1996b). On the basis of these observations, an analysis of the crystal structures containing titanyl units shows that K is among the best network modifiers for promoting the presence of $^{[5]}$Ti. When, near Ti, a network modifier is replaced by a larger one (e.g., K replaced by Rb), we can suspect a deficit in bond valence around this Ti that is associated with that substitution. Because of the need for overall electroneutrality in the oxide glass, regardless of its composition, a decrease in the average bond valence around one type of cation should be compensated by an increase in the average bond valence around another cation. Si cannot decrease its coordination below four and is therefore not likely to participate in that mechanism, in contrast to $^{[5]}$Ti.

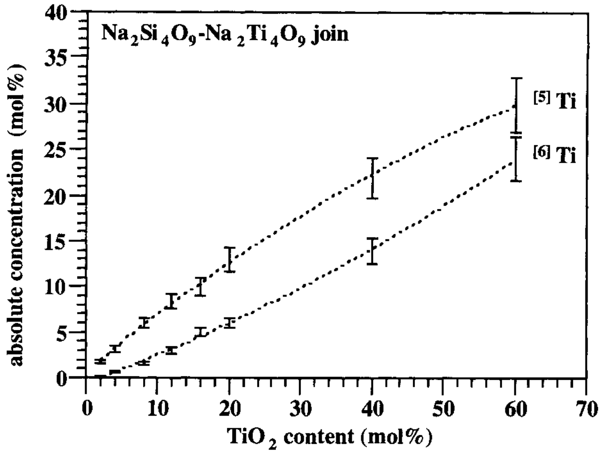

FIGURE 6. Plot of the absolute molar concentrations calculated for [5]Ti and [6]Ti (based on preedge models listed in Table 3) for the NTS glasses. Note the rapid increase of [6]Ti at high TiO_2 contents.

Increasing amounts of [4]Ti are therefore predicted (and observed). In contrast, the replacement of K by Na favors lower Ti-O bond valences because Na shows lower average coordination in oxide glasses than K (~6 and ~9, respectively). This substitution results in higher average alkali-O bond valences, which should be compensated by lower Ti-O bond valences (electroneutrality principle), e.g., higher Ti coordinations (which are also observed). Therefore, the average bond valence of the network modifier is a useful parameter for the derivation of the coordination of Ti.

Tetrahedrally coordinated Ti^{4+} is significant in glasses in which the network modifiers form very ionic bonds (as previously predicted), such as in Rb-bearing glasses. Fourfold-coordinated Ti is also present when NBO/T is near zero (such as Ti in vitreous silica or in silica-rich rhyolite) because of the lack of network modifiers that are needed to form [5]Ti. In contrast, [6]Ti is relatively important when smaller alkaline earth network modifiers (e.g., Ca, Mg) are present, such as in basaltic glasses. Sixfold-coordinated Ti is also important when the TiO_2 content greatly increases (TiO_2 saturation). Natural glasses show mixtures of [4]Ti, [5]Ti, and [6]Ti, depending on the NBO/T ratio (Farges and Brown 1997). This model (which needs further refinement to be more accurate) can be used to help predict the coordination environment of Ti^{4+} in several relevant oxide glasses. When several network modifying cations are present in the glass, the average of the Pauling bond valences for each network modifier can be used. Such a model can also be used to calculate more realistic NBO/T ratios for titanosilicate glasses and melts or to "calibrate" Raman scattering spectra, which are relatively easy to collect (in contrast to XAFS).

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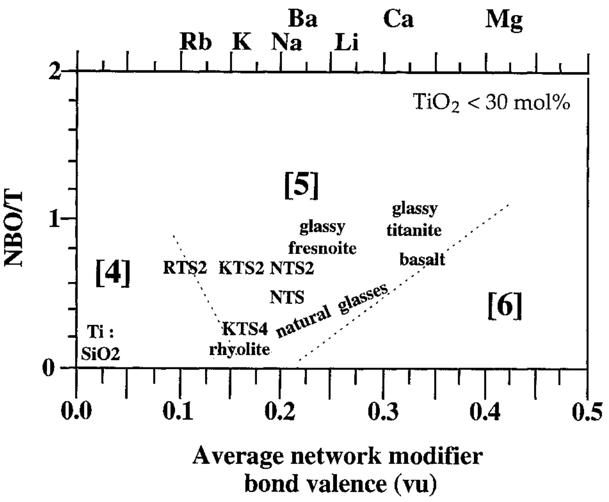

FIGURE 7. Summary of the Ti coordination in silicate glasses as a function of the NBO/T ratio and the (average) Pauling bond valence (valence divided by coordination) for the network modifiers present in the glass. This schematic plot is valid only for glasses without TiO_2-saturation effects (which promote [6]Ti). Coordination information is taken from this study and previous XAFS studies summarized in Farges (1996; glassy fresnoite), Farges and Brown (1996; natural glasses), and Farges et al. (1996b; glassy titanite). The domains shown correspond to the Ti coordination that is estimated to be most abundant. However, nonnegligible amounts of [4]Ti, for instance, are likely in the domain for [5]Ti that is close to the boundary with [4]Ti.

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