

Coordination of Si in Na₂O-SiO₂-P₂O₅ glasses using Si K- and L-edge XANES

DIEN LI,^{1,*} G.M. BANCROFT,¹ AND M.E. FLEET²

¹Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada

²Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada

ABSTRACT

Si K- and L-edge X-ray absorption near-edge structure (XANES) of SiO₂-P₂O₅ and Na₂O-SiO₂-P₂O₅ glasses containing P₂O₅ above 30 mol% were investigated using synchrotron radiation. Both Si K- and L-edge spectra indicate that Si remains fourfold coordinated (⁴Si) with O in these glasses until the content of P₂O₅ reaches about 32 mol%, at which sixfold coordinated Si (⁶Si) first appears. The proportion of ⁶Si increases qualitatively with increase in the content of P₂O₅. However, several P₂O₅-rich glasses contain ⁴Si only, possibly pointing to a dependence of ⁶Si content on quench rate. These results are consistent with ²⁹Si MAS NMR spectra for silicate-phosphate glasses of similar composition. To estimate further the relative proportions of ⁴Si and ⁶Si in these glasses using Si K-edge spectra, model composite materials of a-SiO₂, containing ⁴Si only, and c-SiP₂O₇, containing ⁶Si only, were used to establish the correlation of area ratio for ⁶Si and ⁴Si edge features with bulk composition. The regression equation may be used for semiquantitative estimation of relative proportions of ⁶Si and ⁴Si in glasses and other materials of unknown structure with compositions similar to those of the present glass systems.

INTRODUCTION

It is well known that Si is fourfold coordinated (⁴Si) with O in silicates of the Earth's crust but becomes sixfold coordinated (⁶Si) with O at high pressure. For example, silicon dioxide (SiO₂) has numerous polymorphic modifications with 4:2-coordinated structures (e.g., quartz, cristobalite, and tridymite) and occurs as stishovite with 6:3-coordinated structure at high temperature and pressure beyond about 9 GPa. Materials in the Earth's mantle are believed to be Fe-bearing magnesium silicates, with ⁴Si structures dominant in the upper mantle and ⁶Si structures dominant in the lower mantle (e.g., Ito and Takahashi 1987; Jeanloz 1990; Finger and Hazen 1991). The phase transformations of Mg₂SiO₄ and MgSiO₃, two of the most important silicate components of the mantle, have been established as follows (Liu 1975): with increasing pressure, forsterite (Mg₂SiO₄) transforms first to wadsleyite (β spinel), then to ringwoodite (γ spinel), and finally to perovskite plus periclase, whereas enstatite (MgSiO₃) transforms to β spinel plus stishovite and then to perovskite phases. Crystalline silicon diphosphate (c-SiP₂O₇) is one of several compounds in which Si occurs in octahedral coordination with O at atmospheric pressure (e.g., Liebau 1985; Finger and Hazen 1991).

P-bearing silicate glasses and melts have attracted much interest because of their high-technology and geochemical applications. Silica-rich glasses containing P₂O₅ have been recognized as the most promising fiber material for op-

tical communication systems (Miya et al. 1983). P₂O₅ also has a profound effect on the evolution of magma systems (Kushiro 1975; Hess 1991; Ryerson and Hess 1978, 1980; London 1987, 1992; London et al. 1990, 1993). For example, the addition of P₂O₅ to magma leads to liquid immiscibility (Visser and Koster van Groos 1979), significantly depresses the liquidus temperature of magmatic liquids (Wyllie and Tuttle 1964), strongly affects the partitioning of elements between crystals and liquid and between liquid and liquid (Watson 1976), and reduces the viscosity of synthetic granitic liquids (Dingwell et al. 1993).

It has generally been accepted that Si is fourfold coordinated (⁴Si) with O in low-pressure silicate glasses ever since Zachariasen (1932) predicted that the octahedral coordination of Si in glasses would force periodicity and disrupt the vitreous state. Glasses containing P have been studied by IR (Wong and Angell 1976), Raman (Chakraborty and Condrate 1985; Gan and Hess 1992; Gan et al. 1994; Mysen et al. 1981; Nelson and Tallant 1984; Shibata et al. 1981), MAS NMR (Dickinson and De Jong 1988; Dupree et al. 1987, 1989; Gan and Hess 1992; Gan et al. 1994; Sekiya et al. 1988; Weeding et al. 1985), and X-ray absorption near-edge structure (XANES) spectroscopy using synchrotron radiation (Li et al. 1994a, 1995a).

Si appears to remain fourfold coordinated in silicate-phosphate glasses containing <30 mol% P₂O₅ (Dupree et al. 1989; Okura et al. 1990; Li et al. 1995a). However, the existence of ⁶Si in P₂O₅-rich glasses is controversial. Chakraborty and Condrate (1985) and Dupree et al. (1987, 1989) reported ⁶Si in sodium silicate-phosphate glasses

* Present address: National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan.

TABLE 1. Si *K*- and *L*-edge features and compositions of SiO₂-P₂O₅ and Na₂O-SiO₂-P₂O₅ glasses

Sample	Composition (mol%)			Si <i>K</i> edge* (± 0.1 eV)		Si <i>L</i> edge** (± 0.1 eV)			A ⁽⁶³⁾ Si**	⁽⁶³⁾ Si
	Na ₂ O	SiO ₂	P ₂ O ₅	C- ⁽⁴¹⁾ Si	C- ⁽⁶³⁾ Si	A- ⁽⁴¹⁾ Si	A- ⁽⁶³⁾ Si	C- ⁽⁴¹⁾ Si		
SiO₂-P₂O₅ glasses										
52		54.4	45.5	1847.0(3.54)	1848.9(1.29)	105.7	106.6	107.8	0.267	0.139
53		61.7	37.9	1846.9(4.79)	1848.9(0.25)	105.7	106.7	107.8	0.050	0.015
54		50.2	49.6	1847.0(3.59)	1848.9(1.58)	105.7	106.8	107.8	0.306	0.164
5		72.4	27.7	1846.9		105.8		107.9	0	0
Na₂O-SiO₂-P₂O₅ glasses										
40	9.3	31.7	58.9	1846.9(1.81)	1848.9(0.95)	105.6	106.7	107.8	0.344	0.188
43	10.9	31.8	57.2	1846.9(1.68)	1848.9(0.84)	105.6	106.5	107.8	0.333	0.181
45	17.6	49.3	31.7	1846.9		105.6		107.8	0	

* Edge position (eV) with integrated area (arbitrary units) in parentheses.

** A-⁽⁴¹⁾Si is edge feature; A⁽⁴¹⁾Si represents estimated area of feature.

with P₂O₅ greater than about 30 mol%, and Sekiya et al. (1988) observed a small amount of ⁽⁶³⁾Si in glass of SiP₂O₇ composition. However, Chakraborty and Condrate (1985) reported that only ⁽⁴¹⁾Si was present in glass of composition SiP₂O₇, and similarly Weeding et al. (1985) did not observe ⁽⁶³⁾Si in glasses in the SiO₂-P₂O₅ system. Also, Dupree et al. (1989) observed a strong dependence of ⁽⁶³⁾Si on Na₂O content, with ⁽⁶³⁾Si decreasing to zero at composition 2SiO₂·3P₂O₅ and quench conditions.

In a previous paper, we reported Si *K*- and *L*-edge XANES of SiO₂-P₂O₅ and Na₂O-SiO₂-P₂O₅ glasses containing <30 mol% P₂O₅. The results indicated that Si remains fourfold coordinated in these glasses, but Na₂O depolymerizes and P₂O₅ copolymerizes the silicate glasses (Li et al. 1995a). In this paper, we present Si *K*- and *L*-edge XANES spectra of SiO₂-P₂O₅ and Na₂O-SiO₂-P₂O₅ glasses containing >30 mol% P₂O₅. Using model composite materials prepared from mixtures of amorphous silica (a-SiO₂) and crystalline silicon diphosphate (c-SiP₂O₇), we establish a correlation between the relative intensities of ⁽⁴¹⁾Si and ⁽⁶³⁾Si edge peaks and bulk composition and are able to estimate semiquantitatively the relative proportions of ⁽⁴¹⁾Si and ⁽⁶³⁾Si in these two glass series.

EXPERIMENTAL METHODS

Crystalline silicon diphosphate (c-SiP₂O₇) was synthesized by reacting high-purity amorphous SiO₂ (a-SiO₂; commercial vitreous silica) and excess H₃PO₄ in an open silica-glass tube at initially 230 °C and finally about 950 °C. The product was identified as the monoclinic P2₁/n phase by powder X-ray diffraction (XRD). Glasses in the system Na₂O-SiO₂-P₂O₅ were prepared from mixtures of Na₂Si₂O₅, c-SiP₂O₇, and P₂O₅ contained in a silica-glass tube. The starting composition was separated from the silica-glass wall by a sleeve of platinum foil. Each sample was maintained vertically in a box furnace, heated at 1200 °C for about 10 min, and quenched in water. Glasses in the system SiO₂-P₂O₅ were prepared from mixtures of c-SiP₂O₇, a-SiO₂, and P₂O₅ contained as above, heated at 1400–1500 °C for 5–7 min, and quenched in water. Glasses were examined by optical microscopy and pow-

der XRD, and glass compositions were determined by electron microprobe analysis (EMPA) (see Table 1). All glasses were optically transparent, isotropic and inclusion free, X-ray amorphous, and compositionally homogeneous. A series of model composite materials containing both ⁽⁴¹⁾Si and ⁽⁶³⁾Si was made by mechanically mixing accurately weighed proportions of a-SiO₂ and c-SiP₂O₇. The model composite materials and glass samples were ground into very fine powder (about 10 μm) for the Si *K*- and *L*-edge XANES measurements.

Si *K*-edge XANES spectra of the model composite materials and glasses were collected with a double-crystal monochromator (DCM) using InSb(111) monochromator crystals, giving an energy resolution of 0.8 eV at 1840 eV (Yang et al. 1992). Si *L*-edge XANES spectra were recorded using a Grasshopper beamline that employs a grazing incidence system with a grating of 1800 grooves/mm (Bancroft 1992). The resolution of the Grasshopper beamline is about 0.1 eV at 100 eV. For both Si *K*- and *L*-edge measurements, very fine powder samples were spread uniformly on electric carbon tape supported on a stainless steel sample holder. The area covered by the sample was about 10 mm in diameter for Si *K*-edge measurements, and the sample thickness was constant for the measurements of each sample. Both Si *K*- and *L*-edge spectra were recorded by total electron yield (TEY), which measures the sample current of electrons of different energies that escape from the surface because of excitation by synchrotron X-rays. The TEY spectrum is proportional to the absorption coefficient, μ.

All samples were prepared in a similar manner to minimize the effects of sample thickness and particle size on the relative intensity of absorption features. Three measurements were made for each sample. The spectrum for each measurement was normalized by I/I_0 , where I is the intensity of the TEY signal and I_0 is the intensity of the photon flux. The raw spectrum for each sample investigated was averaged from three normalized measurements and smoothed. A linear preedge background was removed from each spectrum. All Si *K*-edge XANES spectra were calibrated against the Si *K* edge of α-quartz at 1846.8 eV, and all Si *L*-edge spectra were calibrated by

the Si *L* edge (peak a) of α -quartz at 105.7 eV (Li et al. 1994b). The fitting of the Si *K*-edge spectra into Gaussian components was carried out using the BAN data analysis program (Tyliszczak 1992).

RESULTS AND DISCUSSION

Si *K*-edge XANES spectra of a-SiO₂-c-SiP₂O₇ model composite materials

Figure 1 shows the Si *K*-edge XANES spectra of a-SiO₂, c-SiP₂O₇, and the model composite materials prepared from mixtures of a-SiO₂ and c-SiP₂O₇. The spectrum of a-SiO₂, which contains ²⁸Si only, is dominated by a major peak at 1846.9 eV, whereas the spectrum of c-SiP₂O₇, which contains ³⁰Si only, is characterized by a major peak at 1848.9 eV. The absorption features are labeled as in our previous work (Li et al. 1994b). It is apparent that, as expected, the relative intensity of peak C-²⁸Si increases and the relative intensity of peak C-³⁰Si decreases with increasing proportion of a-SiO₂ in the model composite materials.

The major peak in the a-SiO₂ spectrum has been assigned by many researchers to a 1s → 3p transition in the SiO₄ tetrahedra of silicate and aluminosilicate materials (Lagarde et al. 1992; Li et al. 1994b; Fröba et al. 1995a, 1995b). Similarly, peak C-³⁰Si in c-SiP₂O₇ has been assigned to a 1s → 3p transition in SiO₆ octahedra (Li et al. 1994b). These peaks are of the same type as the discrete resonances observed in tetrahedral SiX₄ molecules (1s → 3p-like t₂ states) and in the octahedral SiF₆ molecule (1s → 3p-like t_{1u} states; Lagarde et al. 1992; Sutherland et al. 1993). Full multiple-scattering calculations on a SiO₄ cluster can also rationalize these peaks as the result of single-scattering resonances in the SiO₄ tetrahedra (Lagarde et al. 1992). The peaks at higher energy, in the immediate postedge region (e.g., E-³⁰Si at ~1853 eV), result from a combination of multiple-scattering and shape resonances (e.g., Lagarde et al. 1992; Li et al. 1994b; Fröba et al. 1995a).

The Si *K*-edge spectra for the model composite materials were interpreted by subtracting the spectrum for a-SiO₂ and then fitting the features of the separate ²⁸Si and ³⁰Si spectra into the Gaussian components. In Figure 2a, the dotted line is the experimental spectrum of a model composite sample containing 70 mol% a-SiO₂ and 30 mol% c-SiP₂O₇. Peak C-²⁸Si in the Si *K*-edge spectrum of a-SiO₂ (solid line) was normalized to the height of peak C-²⁸Si in the spectrum of the model sample, so that the difference (dashed line) between the model sample and the a-SiO₂ represents the features for ³⁰Si. The absorption features for both ²⁸Si and ³⁰Si were fitted into the Gaussian components, as shown in Figures 2b and 2c, respectively. The upper dot lines are absorption features for ²⁸Si and ³⁰Si, the dashed lines are the fitted Gaussian components, and the solid curves are the envelopes of the fitted components. Backgrounds (lower dot lines) were included in the fitting procedures.

The integrated areas (arbitrary units) for the ²⁸Si-edge peak (C-²⁸Si) and the ³⁰Si-edge peak (C-³⁰Si) in the spectra

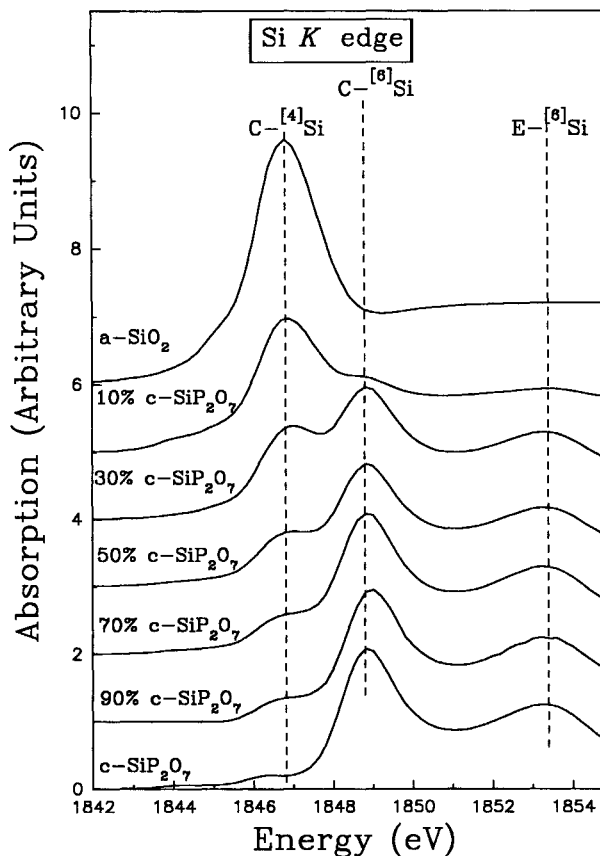


FIGURE 1. Si *K*-edge XANES spectra of model composite materials prepared from mechanical mixtures of a-SiO₂, containing ²⁸Si only, and c-SiP₂O₇, containing ³⁰Si only. The relative intensity of the ²⁸Si edge peak at 1846.8 eV increases, and that of the ³⁰Si edge peak at 1848.9 eV decreases proportionally with increasing a-SiO₂.

of all model composite materials were derived from the fitting procedures. The normalized areas for ²⁸Si (squares) and ³⁰Si (dots) edge peaks are plotted against the content (mole percent) of ²⁸Si and ³⁰Si, respectively, in Figures 3a and 3b. The error for the quantity ³⁰Si/(³⁰Si + ²⁸Si) is estimated to be about 5%, and the errors for the areas of ²⁸Si- and ³⁰Si-edge peaks are estimated to be about 8%. The correlation between the area for the ³⁰Si-edge peak and the composition is inferior to that for ²⁸Si, partly because the absorption features for ³⁰Si were derived from the difference spectrum between the model composite materials and a-SiO₂.

It is evident that the correlation of normalized area of the ³⁰Si-edge peak with proportion of ³⁰Si in the model composite materials is markedly nonlinear (Fig. 3). This may be attributable simply to a higher absorption cross section for ³⁰Si than for ²⁸Si. If this is the case, the calibration curves of Figure 4 could be used to determine ³⁰Si content in all materials, regardless of their bulk composition. Theoretically, the absorption coefficient, μ , is proportional to the number of absorbing Si atoms, N_{Si} ,

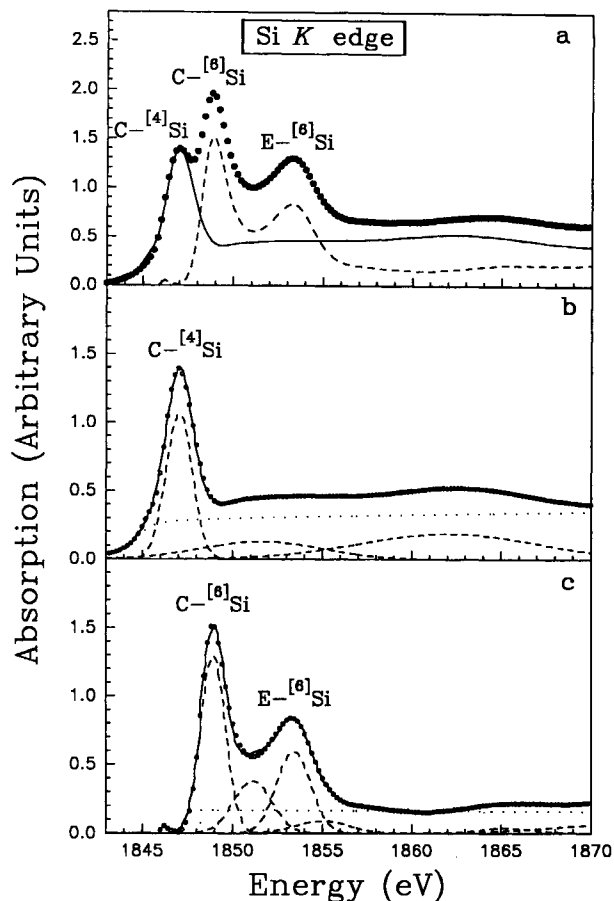


FIGURE 2. Data reduction for Si *K*-edge XANES spectrum of a model composite material containing 70 mol% a-SiO₂ and 30 mol% c-SiP₂O₇. (a) The dotted line is the experimental Si *K*-edge spectrum. Peak C-[⁴Si] in the Si *K*-edge spectrum (solid line) of a-SiO₂ was normalized to the height of peak C-[⁴Si] in the end-member spectrum, so that the difference spectrum (dashed line) represents the absorption features for [⁶Si]. (b and c) The absorption features for [⁴Si] (a-SiO₂) and [⁶Si] (c-SiP₂O₇), respectively, were fitted into the Gaussian components. Upper dot lines are the absorption features for [⁴Si] and [⁶Si]; dashed lines are the fitted Gaussian components; solid lines are the envelopes of the fitted components; lower dot lines are the fitted backgrounds.

and the absorption cross section, σ . N_{Si} is dependent on the concentration of Si in the samples and on experimental conditions. In our technique for the quantification of [⁴Si] and [⁶Si], the experimental conditions (particle size and thickness of samples, and the spot size of the synchrotron X-ray beam) were reasonably constant for the Si *K*-edge measurements of both model materials and glasses. In this case, N_{Si} is related only to the concentration of Si in the samples. On the other hand, the absorption cross section, σ , is different for [⁴Si] and [⁶Si] and is actually unknown theoretically. The Si *K*-edge spectra of the model a-SiO₂ and c-SiP₂O₇ materials indicated that σ is generally larger for [⁶Si] than for [⁴Si], even though the exact values of σ for [⁴Si] and [⁶Si] cannot be derived. Thus,

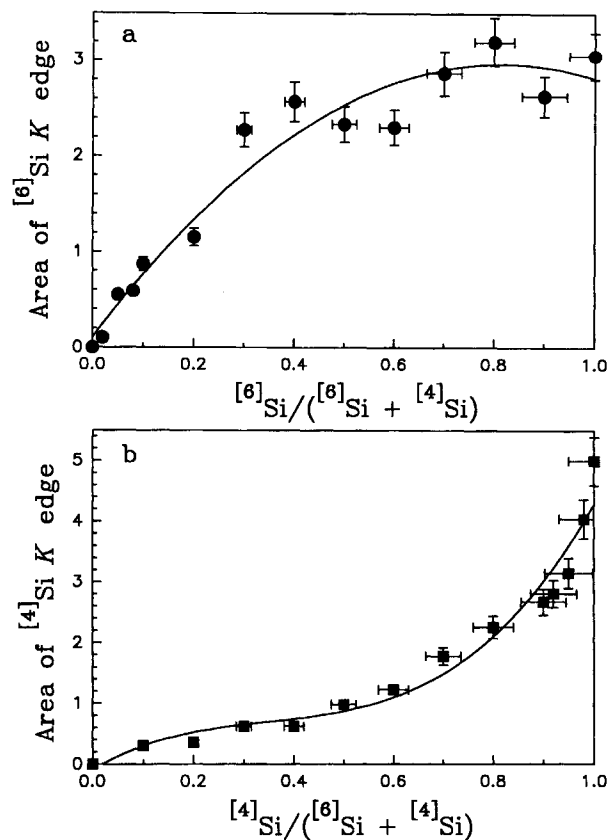


FIGURE 3. The integrated areas (or relative intensities) of [⁶Si] (dots) (a) and [⁴Si] (squares) (b) edge peaks correlated with atomic proportion of species in model composite materials. Error in composition was estimated to be about 5%, and the errors for the integrated areas were estimated to be about 8%. The solid lines were fitted by least-squares regression.

the absorption intensity is not expected to be linearly correlated with the concentration of [⁴Si] and [⁶Si] species.

However, our experience suggests that the present calibration may be applied only to materials of bulk composition similar to the SiO₂-P₂O₅ system. As one comparison, the Si *K*-edge XANES spectrum of wadite-structured K₂Si₄O₉ (Swanson and Prewitt 1983) gives 22% [⁶Si] from a simple comparison of the areas of the C-[⁴Si] and C-[⁶Si] peaks. Figure 4 has the convex-upward form of a typical relative intensity vs. concentration calibration curve for the quantitative analysis of powder mixtures by XRD (e.g., Klug and Alexander 1974). The densities of a-SiO₂ and c-SiP₂O₇ are 2.19 and 3.05 g/cm³, respectively. However, we do not know whether the non-linearity of the present calibration curve is due to attenuation of either primary synchrotron radiation or the Auger electrons and electron cascade.

The absolute values for absorption intensity measured in the spectra are very dependent on sample preparation (particle size and thickness, etc.) and the spot size of the synchrotron radiation beam. It is difficult to keep these experimental parameters constant for each sample, but

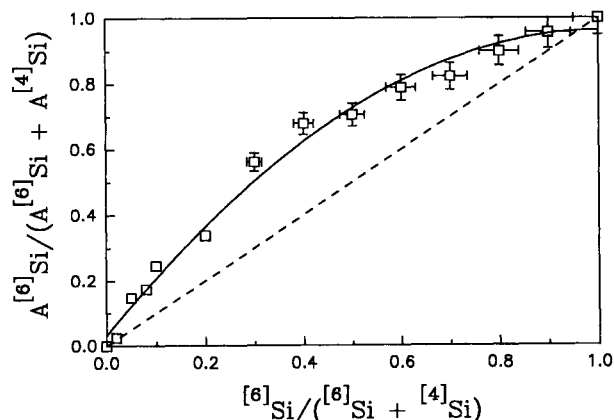


FIGURE 4. Correlation of peak area ratio for ^{16}Si and ^{14}Si with atomic proportion of species in model composite materials. Error in the area ratio was estimated to be about 5%. The solid line was fitted with experimental data (open squares) by least-squares regression, and the dashed line represents the ideal proportional correlation. An empirical equation was derived for the model materials and may be used for the quantification of ^{16}Si and ^{14}Si in glasses and other materials of unknown structure.

their effects are minimized by using the peak-area ratio in Figure 4. The error in the quantities $A^{[6]}\text{Si}/(A^{[6]}\text{Si} + A^{[4]}\text{Si})$ and $^{[6]}\text{Si}/(^{[6]}\text{Si} + ^{[4]}\text{Si})$ shown in this figure was estimated to be about 5%. The solid line is the corresponding correlation curve defined by the regression equation $y = -0.9160x^2 + 1.8476x + 0.0314$, with a correlation coefficient of 0.9947, where $y = A^{[6]}\text{Si}/(A^{[6]}\text{Si} + A^{[4]}\text{Si})$; $x = ^{[6]}\text{Si}/(^{[6]}\text{Si} + ^{[4]}\text{Si})$. This correlation equation may be used to estimate the relative proportions of ^{14}Si and ^{16}Si in glasses and other materials of unknown structure that are closely comparable in composition to the $\text{SiO}_2\text{-P}_2\text{O}_5$ system.

Si K- and L-edge XANES spectra of $\text{SiO}_2\text{-P}_2\text{O}_5$ and $\text{Na}_2\text{O-SiO}_2\text{-P}_2\text{O}_5$ glasses

Figure 5 shows Si K-edge XANES spectra of $\text{SiO}_2\text{-P}_2\text{O}_5$ (Fig. 5a) and $\text{Na}_2\text{O-SiO}_2\text{-P}_2\text{O}_5$ (Fig. 5b) glasses. For both series of glasses, when the content of P_2O_5 is less than about 32 mol%, only peak C- ^{14}Si is observed, indicating that Si remains fourfold coordinated. When the content of P_2O_5 is greater than 32 mol%, the other two prominent peaks C- ^{16}Si and E- ^{16}Si are observed, indicating that some Si atoms are in octahedral coordination with O. The assignments of peaks C- ^{14}Si , C- ^{16}Si , and E- ^{16}Si are similar to those described in the last section (Li et al. 1994b). Qualitatively, the relative intensities of both peaks C- ^{16}Si and E- ^{16}Si increase with increase in P_2O_5 content, indicating an increase in the relative proportion of ^{16}Si .

Figure 6 shows the corresponding Si L-edge XANES spectra of these $\text{SiO}_2\text{-P}_2\text{O}_5$ (Fig. 6a) and $\text{Na}_2\text{O-SiO}_2\text{-P}_2\text{O}_5$ (Fig. 6b) glasses. These are in good agreement with the Si K-edge spectra for both series of glasses. When the content of P_2O_5 is less than about 32 mol%, only peaks A- ^{14}Si and C- ^{14}Si are evident, indicating that Si is fourfold coordinated (see also Li et al. 1994a). When the content of

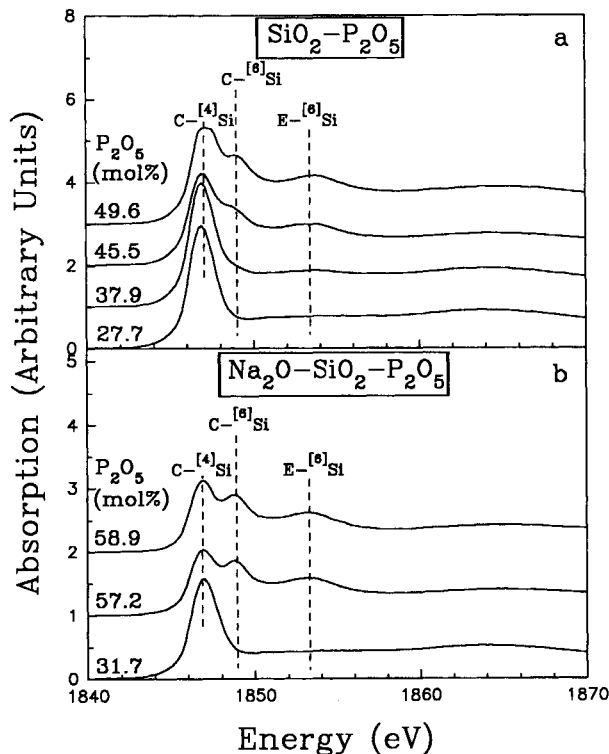


FIGURE 5. Si K-edge XANES spectra of $\text{SiO}_2\text{-P}_2\text{O}_5$ (a) and $\text{Na}_2\text{O-SiO}_2\text{-P}_2\text{O}_5$ (b) glasses. The absorption features are labeled as in our previous paper (Li et al. 1994b).

P_2O_5 is greater than 32 mol%, another prominent peak A- ^{16}Si is observed, indicating that some Si atoms are in octahedral coordination. As described in our previous paper (Li et al. 1994a), peak A- ^{14}Si is assigned to the transition of ^{14}Si 2p electrons to the unoccupied ^{14}Si 3s-like a_1 states, and peak C- ^{14}Si to the transition of ^{14}Si 2p electrons to the unoccupied ^{14}Si 3p-like t_2 states. Also, peak A- ^{16}Si is assigned to the transition of ^{16}Si 2p electrons to the unoccupied ^{16}Si 3s-like a_{1g} states (Li et al. 1994b).

Thus, both Si K- and L-edge XANES spectra indicate a change in coordination of some Si atoms in both $\text{SiO}_2\text{-P}_2\text{O}_5$ and $\text{Na}_2\text{O-SiO}_2\text{-P}_2\text{O}_5$ glasses when the content of P_2O_5 increases beyond 32 mol%, and the content of ^{16}Si increases in proportion to the increase in the content of P_2O_5 . The Si K-edge peak of silicate minerals containing only ^{14}Si has been shown to shift to higher energy with increase in the polymerization of SiO_4^{4-} clusters (Li et al. 1995b). Although the features due to the structural units of different polymerizations are not well resolved, the Si K-edge peak of diopside glass shifts to lower energy and becomes much broader, indicating that the diopside glass contains structural units from Q^0 to Q^4 (Li et al. unpublished manuscript). However, Si K- and L-edge peaks for ^{14}Si in the glasses investigated remain essentially constant in energy positions (see Table 1) and have similar line widths, indicating that the SiO_4^{4-} cluster has similar polymerization and distortion, even though the content of

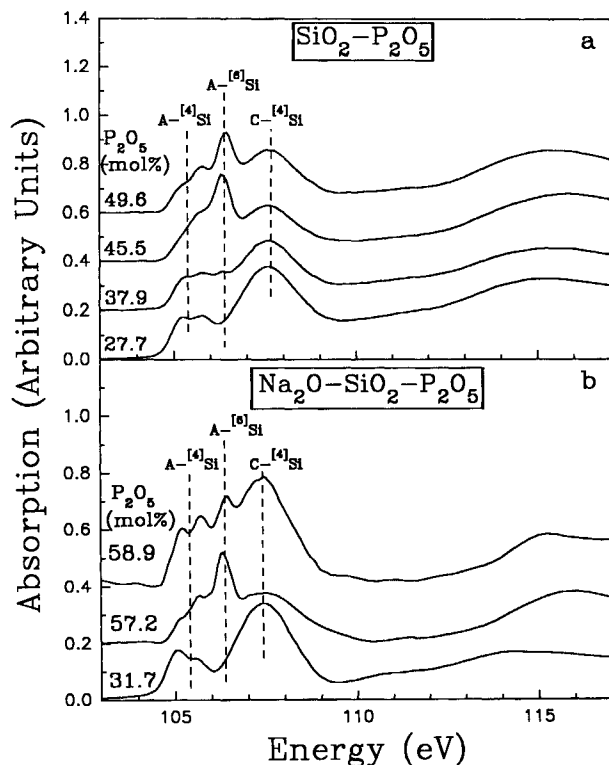


FIGURE 6. Si *L*-edge XANES spectra of $\text{SiO}_2\text{-P}_2\text{O}_5$ (a) and $\text{Na}_2\text{O-SiO}_2\text{-P}_2\text{O}_5$ (b) glasses. The absorption features are labeled as in our previous paper (Li et al. 1994b).

SiO_2 ranges between 32 and 72 mol%. All these results are in good agreement with ^{29}Si MAS NMR spectra of similar silicate-phosphate glass systems (Dupree et al. 1987, 1989; Sekiya et al. 1988).

To estimate more quantitatively the relative proportions of ^{44}Si and ^{66}Si in these glasses, the Si *K*-edge XANES spectra were reduced as described in the previous section for the model composite materials. Peak C- ^{44}Si in the spectrum of a- SiO_2 was normalized to the height of peak C- ^{44}Si in the spectrum of each glass, so that the difference spectrum between the glass sample and a- SiO_2 represents the absorption features for ^{66}Si . The absorption features for both ^{44}Si and ^{66}Si were fitted into the corresponding Gaussian components, and the areas (or relative absorption intensities) for both ^{44}Si and ^{66}Si edge peaks were derived. Then the empirical equation derived from the model composite materials was used to calculate the relative proportions of both ^{66}Si and ^{44}Si (Table 1).

Figure 7 shows the variation of the proportion of ^{66}Si with the content of P_2O_5 in both $\text{SiO}_2\text{-P}_2\text{O}_5$ and $\text{Na}_2\text{O-SiO}_2\text{-P}_2\text{O}_5$ glasses, as determined in this study and by Li et al. (1995a). For both series of silicate-phosphate glasses, Si remained fourfold coordinated with O at low P_2O_5 content. However, beyond about 32 mol%, a bimodal distribution is evident. About one-half of our P_2O_5 -rich glasses yielded spectra with ^{66}Si , giving a composition-dependent distribution similar to that in Figure 5 of Du-

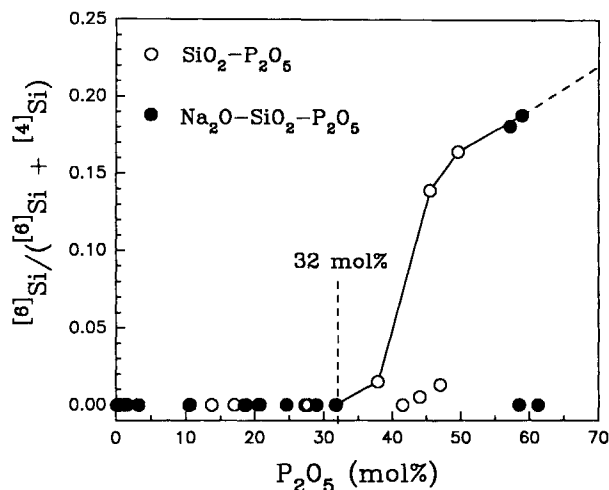


FIGURE 7. Atomic proportion of ^{66}Si as a function of P_2O_5 content in $\text{SiO}_2\text{-P}_2\text{O}_5$ (open circles) and $\text{Na}_2\text{O-SiO}_2\text{-P}_2\text{O}_5$ (solid circles) glasses. The threshold value of P_2O_5 for stabilizing ^{66}Si in these glasses appears to be about 32 mol%. Data for P_2O_5 contents of less than 30 mol% are from Li et al. (1995a).

pree et al. (1989) for glasses of composition $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot p\text{P}_2\text{O}_5$ ($p = 0.26\text{--}4.0$). However, other samples in both glass series investigated did not have features of ^{66}Si in their Si *K*-edge XANES spectra. The XANES spectra for these samples were recollected using new sample aliquots during a subsequent beam time but were unchanged.

There are two possible explanations for this unusual behavior. First, the glass samples in question may have gained moisture, which either degraded the glasses directly or induced surface damage during sample preparation: XANES collected by TEY largely reflect surface and near-surface structure. Second, the glass samples in question may not have contained ^{66}Si because either the content of ^{66}Si in these glass compositions is sensitive to quenching conditions or the starting materials were incompletely reacted. We experienced great difficulty making small amounts of the P_2O_5 -rich glasses and resorted to the sealed silica glass-tube technique to confine the P_2O_5 vapor. Dupree et al. (1989) clearly showed that quench rate exerts an important control on ^{66}Si content for glasses of the same composition. Their results for $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 4\text{P}_2\text{O}_5$ suggest that ^{66}Si is either not stable or present in greatly reduced amounts in the P_2O_5 -rich silicate-phosphate melt and forms preferentially in the solid (glass and crystalline) products. Therefore, the bimodal distribution of structural states in the present P_2O_5 -rich glasses (Fig. 7) could be due to a marked sensitivity to cooling rate during quenching. Even though our samples were quenched in water, they were not quenched in a reproducible manner, largely because quenching was inhibited by the sealed silica glass tube. The absence of intermediate structural states (Fig. 7) at constant composition is surprising and inconsistent with Dupree et al. (1989). The short experiment times required to preserve the integrity of the sealed silica glass tubes may have

resulted in incomplete reaction in the melts of ^{61}Si -bearing glasses. However, this was not evident using the present methods of characterization: All materials investigated were single-phase, homogeneous glasses on the optical, EMPA, and XRD scales of resolution.

Comparison of Si *K*- and *L*-edge XANES with ^{29}Si MAS NMR

The technique of ^{29}Si MAS NMR spectroscopy has been established as a powerful means of studying coordination geometries and local structure of Si and the polymerization of SiO_4 clusters in silicate glasses. As shown above, both Si *K*- and *L*-edge XANES spectra indicated that a proportion of the Si atoms are present in octahedral coordination in both $\text{SiO}_2\text{-P}_2\text{O}_5$ and $\text{Na}_2\text{O-SiO}_2\text{-P}_2\text{O}_5$ glasses containing more than 32 mol% P_2O_5 , and qualitatively the content of ^{61}Si increases proportionally with increase in the content of P_2O_5 . These results are consistent with ^{29}Si MAS NMR spectra for similar silicate-phosphate glasses (Dupree et al. 1987, 1989; Sekiya et al. 1988). Discrepancies with Dupree et al. (1989) for $\text{SiO}_2\text{-P}_2\text{O}_5$ compositions are probably related to the difference in structural state of the glasses in the two studies rather than to the methods of structural characterization. Thus, Si *K*- and *L*-edge XANES spectra can provide information on coordination geometries and local structure of Si (Li et al. 1994a, 1994b, 1995a) and on the polymerization of SiO_4 clusters (Li et al. 1995b) comparable to that from ^{29}Si MAS NMR spectroscopy. In general, ^{29}Si MAS NMR requires a larger sample size (~ 1 g), because of the low natural abundance of ^{29}Si , but gives greater spectral resolution of ^{41}Si and ^{61}Si features. However, Si *K*- and *L*-edge X-ray absorption spectroscopy offers many advantages, particularly, small sample size (~ 10 mg), rapid acquisition of high-resolution XANES spectra, and complementary extended X-ray absorption fine-structure (EXAFS) data.

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