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

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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 (⁴⁰Si) with O in these glasses until the content of P₂O₅ reaches about 32 mol%, at which sixfold coordinated Si (⁶⁰Si) first appears. The proportion of ⁴⁰Si increases qualitatively with increase in the content of P₂O₅. However, several P₂O₅-rich glasses contain ⁴⁰Si only, possibly pointing to a dependence of ⁴⁰Si content on quench rate. These results are consistent with ⁴⁰Si MAS NMR spectra for silicate-phosphate glasses of similar composition. To estimate further the relative proportions of ⁴⁰Si and ⁶⁰Si in these glasses using Si K-edge spectra, model composite materials of α-SiO₂, containing ⁴⁰Si only, and c-SiP₂O₅, containing ⁶⁰Si only, were used to establish the correlation of area ratio for ⁴⁰Si and ⁶⁰Si edge features with bulk composition. The regression equation may be used for semiquantitative estimation of relative proportions of ⁴⁰Si and ⁶⁰Si 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 (⁴⁰Si) with O in silicates of the Earth's crust but becomes sixfold coordinated (⁶⁰Si) 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 ⁴⁰Si structures dominant in the upper mantle and ⁶⁰Si 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-SiP₂O₅) 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 optical 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 (⁴⁰Si) 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; Raman Chakraborty and Condrate 1985; Gan and Hess 1992; Gan et al. 1994; Myssen et al. 1981; Nelson and Tallant 1984; Shibata et al. 1981), MAS NMR (Dickinson and De Jong 1988; Dupree et al. 1987, 1989; 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 ⁴⁰Si in P₂O₅-rich glasses is controversial. Chakraborty and Condrate (1985) and Dupree et al. (1987, 1989) reported ⁴⁰Si in sodium silicate-phosphate glasses.
with P₂O₅ greater than about 30 mol%, and Sekiya et al. (1988) observed a strong dependence of τ₆(rs) on Na₂O content, with τ₆(rs) decreasing to zero at composition SiO₂-PrO₂. Also, Chakraborty and Condrate (1985) reported that only τ₆(rs) was present in glass of composition SiO₂-PrO₂, and similarly Weeding et al. (1985) did not observe τ₆(rs) in glasses in the SiO₂-PrO₂ system. However, Dupree et al. (1989) observed a small amount of τ₆(rs) in glass of SiO₂-PrO₂, and similarly Weeding et al. (1985) did not observe τ₆(rs) in the SiO₂-PrO₂ system. Also, Dupree et al. (1989) observed a strong dependence of τ₆(rs) on Na₂O content, with τ₆(rs) decreasing to zero at composition SiO₂-PrO₂.

In a previous paper, we reported Si K- and L-edge XANES of SiO₂-PrO₂ and Na₂O-SiO₂-PrO₂ 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-SiPrO₂), we establish a correlation between the relative intensities of τ₆(rs) and τ₆(rs) edge peaks and bulk composition and are able to estimate semiquantitatively the relative proportions of τ₆(rs) and τ₆(rs) in these two glass series.

**Experimental methods**

Crystalline silicon diphosphate (c-SiPrO₂) 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 P₂/n phase by powder X-ray diffraction (XRD). Glasses in the system Na₂O-SiO₂-P₂O₅ were prepared from mixtures of Na₂SiO₃, c-SiPrO₂, 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-SiPrO₂, a-SiO₂, and P₂O₅ contained as above, heated at 1400-1500 °C for 5-7 min, and quenched in water.

### Table 1. Si K- and L-edge features and compositions of SiO₂-P₂O₅ and Na₂O-SiO₂-P₂O₅ glasses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na₂O (mol%)</th>
<th>SiO₂ (mol%)</th>
<th>P₂O₅ (mol%)</th>
<th>C₆₄(rs)</th>
<th>C₆₄(rs)</th>
<th>A₅₄(rs)</th>
<th>A₅₄(rs)</th>
<th>C₆₄(rs)</th>
<th>A₅₄(rs) + A₅₄(rs)</th>
<th>A₅₄(rs)</th>
<th>A₅₄(rs)</th>
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</thead>
<tbody>
<tr>
<td>50</td>
<td>93</td>
<td>31.8</td>
<td>58.9</td>
<td>1848.9(1.81)</td>
<td>1848.9(0.95)</td>
<td>1848.9(0.84)</td>
<td>1056.8</td>
<td>106.7</td>
<td>107.8</td>
<td>0.344</td>
<td>0.188</td>
</tr>
<tr>
<td>51</td>
<td>10.9</td>
<td>31.8</td>
<td>57.2</td>
<td>1848.9(1.86)</td>
<td>1848.9(0.95)</td>
<td>1848.9(0.83)</td>
<td>1056.8</td>
<td>106.5</td>
<td>107.8</td>
<td>0.338</td>
<td>0.181</td>
</tr>
<tr>
<td>52</td>
<td>17.6</td>
<td>43.1</td>
<td>39.7</td>
<td>1848.9(1.86)</td>
<td>1848.9(0.95)</td>
<td>1848.9(0.83)</td>
<td>1056.8</td>
<td>106.5</td>
<td>107.8</td>
<td>0.338</td>
<td>0.181</td>
</tr>
</tbody>
</table>

* * Edge position (eV) with integrated area (arbitrary units) in parentheses.
** A₅₄(rs) is edge feature; A₅₄(rs) represents estimated area of feature.

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/I₀, where I is the intensity of the TEY signal and I₀ 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-SiP₂O₅ model composite materials

Figure 1 shows the Si K-edge XANES spectra of a-SiO₂, c-SiP₂O₅, and the model composite materials prepared from mixtures of a-SiO₂ and c-SiP₂O₅. The spectrum of a-SiO₂, which contains [⁴⁰]Si only, is dominated by a major peak at 1846.9 eV, whereas the spectrum of c-SiP₂O₅, which contains [⁶⁰]Si 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-[⁴⁰]Si increases and the relative intensity of peak C-[⁶⁰]Si 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-[⁶⁰]Si in c-SiP₂O₅ 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 t₁ 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-[⁶⁰]Si 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 [⁴⁰]Si and [⁶⁰]Si 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-SiP₂O₅. Peak C-[⁶⁰]Si in the Si K-edge spectrum of a-SiO₂ (solid line) was normalized to the height of peak C-[⁴⁰]Si 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 [⁶⁰]Si. The absorption features for both [⁴⁰]Si and [⁶⁰]Si were fitted into the Gaussian components, as shown in Figures 2b and 2c, respectively. The upper dot lines are absorption features for [⁴⁰]Si and [⁶⁰]Si, 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 [⁴⁰]Si-edge peak (C-[⁴⁰]Si) and the [⁶⁰]Si-edge peak (C-[⁶⁰]Si) in the spectra of all model composite materials were derived from the fitting procedures. The normalized areas for [⁴⁰]Si (squares) and [⁶⁰]Si (dots) edge peaks are plotted against the content (mole percent) of [⁴⁰]Si and [⁶⁰]Si, respectively, in Figures 3a and 3b. The error for the quantity [⁴⁰]Si/[⁴⁰]Si + [⁶⁰]Si is estimated to be about 5%, and the errors for the areas of [⁴⁰]Si- and [⁶⁰]Si-edge peaks are estimated to be about 8%.

The correlation between the area for the [⁶⁰]Si-edge peak and the composition is inferior to that for [⁴⁰]Si, partly because the absorption features for [⁶⁰]Si 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 [⁴⁰]Si-edge peak with proportion of [⁶⁰]Si in the model composite materials is markedly nonlinear (Fig. 3). This may be attributable simply to a higher absorption cross section for [⁶⁰]Si than for [⁴⁰]Si. If this is the case, the calibration curves of Figure 4 could be used to determine [⁶⁰]Si content in all materials, regardless of their bulk composition. Theoretically, the absorption coefficient, μ, is proportional to the number of absorbing Si atoms, N₆.
and the absorption cross section, $\sigma$, $N_{\text{tot}}$ is dependent on the concentration of Si in the samples and on experimental conditions. In our technique for the quantification of $^{28}\text{Si}$ and $^{30}\text{Si}$, 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 all model materials and glasses. In this case, $N_{\text{tot}}$ is related only to the concentration of Si in the samples. On the other hand, the absorption cross section, $\sigma$, is different for $^{28}\text{Si}$ and $^{30}\text{Si}$ and is actually unknown theoretically. The Si $K$-edge spectra of the model a-SiO$_2$ and c-SiP$_2$O$_5$ materials indicated that $\sigma$ is generally larger for $^{30}\text{Si}$ than for $^{28}\text{Si}$, even though the exact values of $\sigma$ for $^{28}\text{Si}$ and $^{30}\text{Si}$ cannot be derived. Thus, the absorption intensity is not expected to be linearly correlated with the concentration of $^{28}\text{Si}$ and $^{30}\text{Si}$ species.

However, our experience suggests that the present calibration may be applied only to materials of bulk composition similar to the SiO$_2$-P$_2$O$_5$ system. As one comparison, the Si $K$-edge XANES spectrum of wadite-structured K$_5$Si$_4$O$_9$ (Swanson and Prewitt 1983) gives 22% $^{30}\text{Si}$ from a simple comparison of the areas of the C-[28]Si and C-[30]Si 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-SiO$_2$ and c-SiP$_2$O$_5$ are 2.19 and 3.05 g/cm$^3$, 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
their effects are minimized by using the peak-area ratio in Figure 4. The error in the quantities $A^{60}\text{Si}/(A^{60}\text{Si} + A^{40}\text{Si})$ and $A^{60}/(A^{60} + A^{40}\text{Si})$ 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 $y = A^{60}\text{Si}/(A^{60}\text{Si} + A^{40}\text{Si})$; $x = A^{60}/(A^{60} + A^{40}\text{Si})$. This correlation equation may be used to estimate the relative proportions of $A^{60}\text{Si}$ and $A^{40}\text{Si}$ 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 Na$_2$O-SiO$_2$-P$_2$O$_5$ glasses**

Figure 5 shows Si K-edge XANES spectra of $\text{SiO}_2-\text{P}_2\text{O}_5$ (Fig. 5a) and Na$_2$O-SiO$_2$-P$_2$O$_5$ (Fig. 5b) glasses. For both series of glasses, when the content of $\text{P}_2\text{O}_5$ is less than about 32 mol\%, only peak $C^{40}\text{Si}$ is observed, indicating that Si remains fourfold coordinated. When the content of $\text{P}_2\text{O}_5$ is greater than 32 mol\%, the other two prominent peaks $C^{60}\text{Si}$ and $E^{40}\text{Si}$ are observed, indicating that some Si atoms are in octahedral coordination with $O$. The assignments of peaks $C^{40}\text{Si}$, $C^{60}\text{Si}$, and $E^{40}\text{Si}$ are similar to those described in the last section (Li et al. 1994b). Qualitatively, the relative intensities of both peaks $C^{60}\text{Si}$ and $E^{40}\text{Si}$ increase with increase in $\text{P}_2\text{O}_5$ content, indicating an increase in the relative proportion of $^{40}\text{Si}$.

Figure 6 shows the corresponding Si L-edge XANES spectra of these $\text{SiO}_2-\text{P}_2\text{O}_5$ (Fig. 6a) and Na$_2$O-SiO$_2$-P$_2$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 $\text{P}_2\text{O}_5$ is less than about 32 mol\%, only peaks $A^{40}\text{Si}$ and $C^{60}\text{Si}$ are evident, indicating that Si is fourfold coordinated (see also Li et al. 1994a). When the content of $\text{P}_2\text{O}_5$ is greater than 32 mol\%, another prominent peak $A^{60}\text{Si}$ is observed, indicating that some Si atoms are in octahedral coordination. As described in our previous paper (Li et al. 1994a), peak $A^{40}\text{Si}$ is assigned to the transition of $^{40}\text{Si}$ 2p electrons to the unoccupied $^{40}\text{Si}$ 3s-like $a_1$ states, and peak $C^{40}\text{Si}$ to the transition of $^{40}\text{Si}$ 2p electrons to the unoccupied $^{40}\text{Si}$ 3p-like $t_2$ states. Also, peak $A^{60}\text{Si}$ is assigned to the transition of $^{60}\text{Si}$ 2p electrons to the unoccupied $^{60}\text{Si}$ 3s-like $a_1$ 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 Na$_2$O-SiO$_2$-P$_2$O$_5$ glasses when the content of $\text{P}_2\text{O}_5$ increases beyond 32 mol\%, and the content of $^{40}\text{Si}$ increases in proportion to the increase in the content of $^{60}\text{Si}$. The Si K-edge peak of silicate minerals containing only $^{40}\text{Si}$ has been shown to shift to higher energy with increase in the polymerization of $\text{SiO}_4$- 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 $^{40}\text{Si}$ in the glasses investigated remain essentially constant in energy positions (see Table 1) and have similar line widths, indicating that the $\text{SiO}_4^-$ cluster has similar polymerization and distortion, even though the content of
SiO₂ ranges between 32 and 72 mol%. All these results are in good agreement with ²⁹Si 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 ⁴⁰Si and ⁶⁰Si in these glasses, the Si K-edge XANES spectra were reduced as described in the previous section for the model composite materials. Peak C for ⁴⁰Si in the spectrum of a-SiO₂ was normalized to the height of peak C for ⁶⁰Si in the spectrum of each glass, so that the difference spectrum between the glass sample and a-SiO₂ represents the absorption features for ⁶⁰Si. The absorption features for both ⁴⁰Si and ⁶⁰Si were fitted into the corresponding Gaussian components, and the areas (or relative absorption intensities) for both ⁴⁰Si and ⁶⁰Si edge peaks were derived. Then the empirical equation derived from the model composite materials was used to calculate the relative proportions of both ⁴⁰Si and ⁶⁰Si (Table 1).

Figure 7 shows the variation of the proportion of ⁶⁰Si with the content of P₂O₅ in both SiO₂-P₂O₅ and Na₂O-SiO₂-P₂O₅ 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 P₂O₅ content. However, beyond about 32 mol%, a bimodal distribution is evident. About one-half of our P₂O₅-rich glasses yielded spectra with ⁶⁰Si, giving a composition-dependent distribution similar to that in Figure 5 ofDupree et al. (1989) for glasses of composition Na₂O-2SiO₂-4P₂O₅ (p = 0.26-4.0). However, other samples in both glass series investigated did not have features of ⁶⁰Si 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 ⁶⁰Si because either the content of ⁶⁰Si 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 P₂O₅-rich glasses and resorted to the sealed silica glass-tube technique to confine the P₂O₅ vapor. Dupree et al. (1989) clearly showed that quench rate exerts an important control on ⁶⁰Si content for glasses of the same composition. Their results for Na₂O-2SiO₂-4P₂O₅ suggest that ⁶⁰Si is either not stable or present in greatly reduced amounts in the P₂O₅-rich silicate-phosphate melt and forms preferentially in the solid (glass and crystalline) products. Therefore, the bimodal distribution of structural states in the present P₂O₅-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 $^{17}$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 $^{30}$Si MAS NMR

The technique of $^{30}$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 indicate that a proportion of the Si atoms is present in octahedral coordination in both SiO$_2$-P$_2$O$_5$ and Na$_2$O-SiO$_2$-P$_2$O$_5$ glasses containing more than 32 mol% P$_2$O$_5$, and qualitatively the content of $^{17}$Si increases proportionately with increase in the content of P$_2$O$_5$. These results are consistent with $^{30}$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 SiO$_2$-P$_2$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 $^{30}$Si MAS NMR spectroscopy. In general, $^{30}$Si MAS NMR requires a larger sample size (~1 g), because of the low natural abundance of $^{28}$Si, but gives greater spectral resolution of $^{17}$Si and $^{18}$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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