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1Geophysical Laboratory and Center for High Pressure Research, Carnegie Instn. Washington, 5251 Broad Branch Rd., NW., Washington, DC 20015, USA
2CRSCM-CNRS, 1a, rue de la Ferollerie, 45071 Orleans, France
3Department de Geologie, URA 10 du CNRS, Universite Blaise Pascal, 5, rue Kessler, 63038 Clermont-Ferrand, France
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Abstract—Solution mechanisms of P in metaluminous to peraluminous quenched, hydrous (~9 wt% H2O) and anhydrous glasses in the system CaO-Na2O-K2O-Al2O3-SiO2-P2O5 have been examined with microRaman spectroscopy. The principal aim was to examine relative stability of phosphate complexes as a function of bulk chemical composition. Increasing peraluminosity was accomplished by increasing Al3+ and Ca2+ proportions with constant SiO2 content. The molar ratio Al2O3/(CaO + Na2O + K2O) (A/CNK) ranged from 1 (metaluminous) to ~1.3 (peraluminous).

In all compositions P5+ is bonded to Al3+ to form AlPO4 complexes. The principal solution mechanism is one where depolymerized species (Q3−), involving Al3+ both within and outside the aluminosilicate network, interact with P to form the AlPO4 complex together with Q4 species. The mechanism does not involve alkali metals or alkaline earths. In anhydrous compositions, the spectra are interpreted to suggest Si-O-P cross-linking in the structure. In hydrous compositions, evidence for Si-O-P bonding is less evident. In such glasses, there is, however, possible spectroscopic evidence for Si-OH bonding and possibly P-OH bonding resulting from breakage of cross-linking Si-O-P bonds existing in the anhydrous glasses. Therefore, the water content of peraluminous aluminosilicate melts is likely to affect the solubility behavior of P, and conversely, the solubility behavior of H2O is affected by P in such melts.

1 INTRODUCTION

The geochemical behavior of phosphorus in both mafic and silicic magmas is receiving increasingly detailed attention (e.g., Ryerson and Hess, 1980; Watson and Capobianco, 1981; Harrison and Watson, 1984; Pichavant et al., 1992; Toplis et al., 1994a; Wolf and London, 1994). Although generally present in comparatively low concentrations in natural magmas (less than ~2–3 wt% P2O5), even in this abundance range P strongly modifies both physical and chemical properties of silicate liquids (Wyllie and Tuttle, 1964; Kushiro, 1975; Watson, 1976; Visser and Koster Van Groos, 1979; Ryerson and Hess, 1980; London, 1987; Dingwell et al., 1993; London et al., 1993; Toplis et al., 1994a; Toplis and Dingwell, 1996).

In silicic magmas, the P concentration generally is buffered by the solubility of apatite. Early studies (Ryerson and Hess, 1980; Watson and Capobianco, 1981; Harrison and Watson, 1984) have determined that apatite solubility in felsic melts is dependent primarily on temperature and melt SiO2 content and generally is small for crustal temperatures and melt compositions (e.g., 0.02 wt% P2O5 for a melt having 75 wt% SiO2 at 800°C, Harrison and Watson, 1984). Recent studies, however, have revealed that apatite solubility depends in a complex way on other melt compositional parameters such as the balance between Al and alkali plus Ca (i.e., A/CNK = Al2O3/(CaO + Na2O + K2O), molar (Pichavant et al., 1992; Richard et al., 1992; Wolf and London, 1994), and FeO/Fe2O3 ratio (Richard et al., 1992). For constant melt SiO2 content and temperature, apatite solubility is increased dramatically for peraluminous liquids (A/CNK > 1). Solubilities of up to several wt% P2O5 for peraluminous silicic liquids in equilibrium with apatite at 750–1000°C have been reported (Pichavant et al., 1992; Richard et al., 1992; Wolf and London, 1994). To be interpreted, such results require a better understanding of the structural role of P with the aid of detailed structural studies of multi-component P-bearing aluminosilicate melt compositions.

Most P-bearing silicate melt compositions studied in the glass literature are peralkaline, i.e., molar contents of alkali greatly exceed that of Al (A/CNK < 1). For such compositions, results of spectroscopic studies have shown that the addition of P increases polymerization of silicate network. In those melts alkali metals associate with P to form phosphate complexes and the number of nonbridging oxygens decreases (Nelson and Tallant, 1984; Dupree et al., 1988, 1989). In contrast, for both subaluminous (A/CNK < 1) and peraluminous (A/CNK > 1) melts, it has been suggested that P speciation is characterized by the presence of AlPO4-like units (Mysen et al., 1981; Kosinski et al., 1988; Dupree et al., 1989; Gan and Hess, 1992). Complexing of P5+ with Al3+ in peraluminous aluminosilicate melts would account for the strong increase of apatite solubility found experimentally (Pichavant et al., 1992; Wolf and London, 1994). However, none of the different spectroscopic studies

* Present address: Inst. Mineralogie, Univ. Hannover, Welfengarten 1, D-30167 Hannover, Germany.
so far available have been conducted on compositions approaching either natural peraluminous or experimental melts showing elevated apatite solubility.

Here, we present room temperature Raman spectroscopic data on the mechanisms of solution of P2O5 in peraluminous quenched melts (glass) in the system SiO2-Al2O3-Na2O-K2O-CaO-P2O5 with and without H2O. The data concern two series of glasses, one with a Ca/P ratio of 5/3 (i.e., same as in apatite) and the other with Ca/P = 1, thus enabling to test the possible preference of P to coordinate with Ca rather than with Al.

2. EXPERIMENTAL AND ANALYTICAL METHODS

2.1. Preparation of Glasses

Starting materials were P2O5-free gels (or glasses). Nominally, these have constant SiO2 content of 75 wt% and constant Na/K of 1. In each series of four compositions (1: Ca/P = 5/3 and 2: Ca/P = 1), Al and Ca progressively increase (along with P concentration), whereas the total alkali contents decrease, resulting in compositions becoming progressively more peraluminous (A/CKN = 1.0, 2.1. Preparation of Glasses

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The glasses were initially synthesized hydrous at high pressure and temperature. The source of P2O5 was an H3PO4 solution. The glasses were loaded in Pt capsules, together with the H3PO4 solution and a small additional amount of demineralized doubly-distilled water added so that glasses contain 9-10 wt% H2O. Two batches of eight hydrous glasses (about 200 mg each) were synthesized in internally-heated pressure vessels, respectively, at 1100°C, 8 kbar for 7-9 days (see description of apparatus by Vielzeuf and Montel, 1994), and 1300°C, 4 kbar for 3 days (see Roux et al., 1994, for description of apparatus). The samples were contained in sealed Pt containers.

All glasses were analyzed with a Cameca SX 50 electron microprobe to check for their composition and chemical homogeneity. Analytical conditions and standards were those established previously for P2O5-bearing glasses of similar compositions (Pichavant et al., 1992) using the precautions described by Pichavant (1987) for analysis of hydrous alkali aluminosilicate glasses. Results are given in Table 1 and recalculated to 100% to compare with nominal compositions. Macusani glass was used as P2O5 standard. The water contents of two of the glasses, 245 and 248, were determined with Karl Fischer titration (Behrens, 1995; Holtz et al., 1995). The analyzed values (8.53 and 8.27 wt% H2O, respectively) compare well with the maximum water contents from the proportions of the reactants (8.9-9.1 wt%).

The Raman microspectroscopic analyses of the dry compositions were performed from small chips of hydrous glasses that were slowly dehydrated in situ in a Pt wire furnace of the type developed by Mysen and Frantz (1992) for high-temperature, in situ micro-Raman spectroscopy. Complete dehydration was taken as that where there was no longer Raman intensity near 3600 cm⁻¹ (OH stretching) corresponding to less than 0.1 wt% H2O in the glass (M. O. Mysen and D. Virgo, unpubl. data). The Raman analyses of hydrous glasses were carried out on small glass chips.

Raman spectra were recorded with a Dilor XY confocal microRaman spectrometer equipped with a cryogenic Wright Model CCD
05-11-0-202 charge-coupled detector (CCD). The excitation source was the 514 nm line of a Coherent Innova Model 90-5 Ar+ laser operating at several hundred mW at the sample. Integration times ranged from 60 to 300 s. The spectra were recorded in the frequency ranges 200–1800 cm$^{-1}$ and 3000–4000 cm$^{-1}$.

The high-frequency portion of the spectra was deconvoluted with lines of Gaussian shape as is normally done with Raman spectra of silicate glasses (See Mysen, 1992, for detailed discussion). Prior to deconvolution of the spectra, the instrumental background was subtracted by using a line obtained by least-square fitting of the data points at frequencies where no Raman scattering was observed. The spectra were then corrected for temperature- and frequency-dependent scattering intensity (Long, 1977) and the intensities were normalized to the absolute maximum intensity. The curve-fitting is based on the minimization of the squares of the deviations between the observed and calculated Raman envelopes using the algorithm described by Davidon (1966) (see also Seifert et al., 1982; Mysen, 1992, for details). The line parameters were treated as independent variables. The number of lines was determined statistically to be that number where additional lines did not improve the quality of the fit significantly. A significant shift in $\chi^2$ corresponds to a 10% or more improvement when increasing the number of independent variables by (Hamilton, 1965). As three independent variables are needed to describe one line, a 10% improvement in $\chi^2$ is required to justify an increase in the number of fitted lines by one.

3. RESULTS

The Raman spectra can be divided into two frequency regions. The low-frequency region between 200 and 1300 cm$^{-1}$ contains the first order Raman bands associated with the aluminosilicate network (see Fig. 2 for examples). That between 3000 and 4000 cm$^{-1}$ contains the O-H stretch vibrations from hydroxyl groups and molecular H$_2$O in samples containing dissolved H$_2$O (Fig. 3). The presence of molecular H$_2$O in the glass samples is evidenced by the weak band near 1600 cm$^{-1}$ assigned H-O-H bending.

3.1. Low-Frequency Region (200–1300 cm$^{-1}$)

The Raman spectra of anhydrous glasses (e.g., Fig. 2) overall show similar topology with a broad band centered near 1100 cm$^{-1}$. This maximum is asymmetric toward lower frequency. There is another strong maximum near 500 cm$^{-1}$ with additional spectral detail near 600 cm$^{-1}$. There is also a distinctive band near 800 cm$^{-1}$. The overall topological features resemble those of other highly polymerized aluminosilicate glasses (e.g., McMillan et al., 1982; Seifert et al., 1982; Matson et al., 1986).

Fig. 1. Relationship between peraluminisity (A/CNK) and P$_2$O$_5$ content of the glasses.

Fig. 2. Examples of unpolarized Raman spectra in the low-frequency region of nominally P-free (244) and P-bearing (247) glasses anhydrous (A) and hydrous (B).

Fig. 3. Unpolarized Raman spectra in the spectral region of OH stretching.
In the 200–1300 cm\(^{-1}\) region, the principal spectral effect resulting from added H\(_2\)O to the samples is the appearance of a broad strong band near 900 cm\(^{-1}\) (Fig. 2), an observation consistent with those of Mysen and Virgo (1986a) and McMillan et al. (1993). In both the P-free and P-bearing samples, the difference spectra (hydrous–anhydrous samples) also reveal a shoulder near 990 cm\(^{-1}\) (Fig. 4).

Addition of phosphorus to both hydrous and anhydrous samples, whether at Ca/P \(\approx\) 5/3 or Ca/P \(\approx\) 1, results only in subtle spectral changes (Fig. 2a, cf. spectrum 244, which is nominally P-free, and spectrum 247, which contains nearly 3 wt\% P\(_2\)O\(_5\)). There appears to be a shoulder slightly below 1100 cm\(^{-1}\), a feature more clearly shown as a maximum near 1070 cm\(^{-1}\) in the difference spectra (P-bearing–P-free; see Fig. 4). In anhydrous samples with the highest Ca/P (\(\approx\) 5/3; samples 245–247), a subtle intensity increase near 940 cm\(^{-1}\) with increasing phosphorus content may also be discerned (Fig. 5d). This latter effect is less clear in the samples with Ca/P \(\approx\) 1 (samples 249–251; Fig. 5c). In the spectra of the hydrous glasses (Fig. 5a,b), this latter effect is obscured by the significant intensity increase near 970–990 cm\(^{-1}\) (see also Fig. 4). These spectral changes near 940 and 1100 cm\(^{-1}\) are qualitatively analogous to those of other P-bearing aluminosilicate glasses (e.g., Gan and Hess, 1992). The presence of phosphorus in the glasses also results in an intensity increase in the Raman spectra of such samples near 1210–1220 cm\(^{-1}\) (marked as 1210 in Fig. 5).

The spectra of P-bearing, hydrous samples (see Fig. 2b, for example) show the same overall topological features as the spectra of P-free hydrous samples. It is evident, however, that the intensity near 900 cm\(^{-1}\) diminishes with increasing P-content (and concomitant increase in peraluminosity; see Fig. 5a,b).\(^1\) Increasing P-content also results in enhanced intensity near 1070 cm\(^{-1}\) for the Ca/P \(\approx\) 1 series. This intensity change is less pronounced for hydrous samples with Ca/P \(\approx\) 5/3 (Fig. 5a,b).

3.1.1. Curve-fitted spectra

The spectral region between \(\sim\) 850 and 1250 cm\(^{-1}\) was fitted to Gaussian bands with the number of bands statistically determined as described above (experimental methods). Typical examples are shown in Fig. 6. A summary of the frequencies and areas of these bands is given in Table 2.

The spectra of P-free, anhydrous glasses were fitted to a very weak band near 900 cm\(^{-1}\), and three strong bands near 1000, 1100, and 1200 cm\(^{-1}\), respectively, similar to other Raman data from highly polymerized aluminosilicate glasses (e.g., Seifert et al., 1982).\(^2\) For the anhydrous, P-bearing samples, the frequencies of the latter three bands are only very subtly dependent on the phosphorus content (Table 2). In the spectra of hydrous, both P-free and P-bearing samples, the frequencies of these latter three bands are distinctly higher (by as much as 20–30 cm\(^{-1}\)) than in the spectra of the equivalent anhydrous samples. This observation accords with other spectroscopic data on the effect of H\(_2\)O content on Raman frequencies in this frequency range for aluminosilicate glasses (Mysen and Virgo, 1986a).

In the presence of H\(_2\)O (e.g., Fig. 6b,d; see also Tables 2 and 3 for complete set of data), a strong band occurs near 900 cm\(^{-1}\) in accord with other Raman and infrared spectroscopic data of hydrous aluminosilicate glasses (e.g., Mysen et al., 1980; Remmele et al., 1986; Mysen and Virgo, 1986a,b; Silver and Stolper, 1989; McMillan et al., 1993; Holtz et al., 1996). A band near 970 cm\(^{-1}\) is also observed (Fig. 6, see also Table 2). In the spectra of P-containing glasses, whether hydrous or anhydrous, two additional bands near 1100 and 1210 cm\(^{-1}\), respectively, are needed to satisfy the spectral envelope (e.g., Fig. 6). In the hydrous, phosphorus-bearing samples, a band near 940 cm\(^{-1}\) could also be fitted. This band is less evident in spectra of anhydrous, P-bearing samples (Table 3). In all cases, whenever present the frequencies of the 940, 1100, and 1210 cm\(^{-1}\) bands appear insensitive to H\(_2\)O and P concentrations (Table 2).

3.2. High-Frequency Region (3000–4000 cm\(^{-1}\))

The high-frequency region between 3000 and 4000 cm\(^{-1}\) of the spectra of all the hydrous samples is quite similar (Fig. 3) with a broad intensity maximum near 3600 cm\(^{-1}\), asymmetric toward lower frequencies and with a small shoulder near \(\sim\) 3300 cm\(^{-1}\). This spectral topology is similar to that of other hydrous, highly polymerized aluminosilicate glasses (e.g., Mysen et al., 1980; Mysen and Virgo, 1986a,b; McMillan et al., 1993).

3.2.1. Curve-fitted spectra

In the curve-fitted spectra, four Gaussian bands near 3300, 3500, 3600, and 3650 cm\(^{-1}\) were inserted (Fig. 7). Their

\(^1\) This effect appears as an increasingly deep valley in the difference spectra in Fig. 5A,B.

\(^2\) The anhydrous, P-free glasses (no. 244 and 248; see Table 1) have NBO/T values of 0.022 and 0.027, respectively. Thus any contribution from nonbridging oxygen is not likely to be detected in the Raman spectra.
frequencies, with the exception of the band near 3300 cm\(^{-1}\), are insensitive to Ca/P, A/CNK, and phosphorus content (Table 4). The lowest-frequency band, near 3300 cm\(^{-1}\), exhibits a slight frequency decrease as the phosphorus content is increased (Table 4). The relative band areas vary systematically with \(P_2O_5\) content (Fig. 8). Notably, in the Ca/P \(\sim 5/3\) series, the band near 3500 cm\(^{-1}\) grows and those near 3300 and 3600 cm\(^{-1}\) diminish, whereas the opposite trends with P-content is observed in the spectra of the Ca/P \(\sim 1\) series of glasses (Fig. 8). The band near 3650 cm\(^{-1}\) is quite weak in all spectra ranging in relative area from 1.3 to 2.2% of the total area of the envelope.

Fig. 5. Difference spectra illustrating the effect of increased phosphorus content for the two series of samples both anhydrous and hydrous. (A) The series Ca/P \(\sim 1\) with approximately 10 wt% H\(_2\)O in solution. The spectra 249, 250, and 251 were subtracted from spectrum 248 (nominally P-free). (B) As A, but for the series Ca/P \(\sim 5/3\). In this series spectra 245, 246, and 247 were subtracted from the nominally P-free spectrum 244. (C) As A, but for anhydrous samples. (D) As B, but for anhydrous samples.
3.3. Band Assignments and Structural Interpretation

The starting point for interpretation of the aluminosilicate glass spectra is that of vitreous SiO₂ where two average structures differing in the number of tetrahedra in the threedimensionally interconnected rings are commonly suggested (Mammone et al., 1981; Galeener, 1982; Seifert et al., 1982, 1983; Revesz and Walrafen, 1983). These two ring structures give rise, for example, to the two bands near 1150 and 1200 cm⁻¹ both of which are assigned to Si-O⁶ stretch vibrations. A detailed analysis of spectra of glasses along the join SiO₂-Na₂O₅ led Seifert et al. (1982) to conclude
### Table 2. Experimental results—line parameters in 700–1300 cm⁻¹ region.

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<tr>
<td>0.13</td>
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<td>941</td>
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<td>870</td>
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<td>1.11</td>
<td>1.15</td>
<td>745</td>
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<td>223</td>
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<td>740</td>
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<td>253</td>
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<td>609</td>
<td>98</td>
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<td>2.86</td>
<td>1.32</td>
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<td>103</td>
<td>4291</td>
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<tr>
<td>~10 wt% H₂O</td>
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<tr>
<td>0.15</td>
<td>1.04</td>
<td>1281</td>
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<td>819</td>
<td>66</td>
<td>1820</td>
<td>49</td>
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<td>1.16</td>
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<td>37</td>
<td>367</td>
<td>61</td>
<td>572</td>
<td>121</td>
<td>1000</td>
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</table>
Table 3. Area of 940 cm\(^{-1}\) band relative to total area\(^a\) of high-frequency envelope (850–1300 cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Wt% P(_2)O(_5)</th>
<th>A/CNK*</th>
<th>Hydrous (±1σ)</th>
<th>Anhydrous (±1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/P~5/3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.11</td>
<td>1.15</td>
<td>0.024 (4)</td>
<td>n.d.</td>
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<tr>
<td>2.11</td>
<td>1.24</td>
<td>0.030 (10)</td>
<td>0.003 (2)</td>
</tr>
<tr>
<td>2.55</td>
<td>1.34</td>
<td>0.027 (9)</td>
<td>0.004 (5)</td>
</tr>
<tr>
<td>Ca/P~1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.08</td>
<td>1.15</td>
<td>0.042 (6)</td>
<td>n.d.</td>
</tr>
<tr>
<td>2.24</td>
<td>1.24</td>
<td>0.046 (4)</td>
<td>n.d.</td>
</tr>
<tr>
<td>2.86</td>
<td>1.34</td>
<td>0.042 (7)</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

* The area of the 970 cm\(^{-1}\) band not included.


\(^a\) Molar Al\(_2\)O\(_3\)/(CaO + Na\(_2\)O + K\(_2\)O).

that a similar structural environment existed as Al\(^{3+}\) substituted for Si\(^{4+}\) in glasses along this join. The frequencies of the bands near 1150 and 1200 cm\(^{-1}\) in spectra of vitreous Si\(_2\)O\(_3\) decreased systematically with increasing Al/(Al + Si). In the present spectra of anhydrous, P-free glasses, bands assigned to (Si,Al)-O\(^\circ\) stretching, occur near 1090 and 1160 cm\(^{-1}\), respectively (Table 2; see also Fig. 6a).

The assignment of the ~900 cm\(^{-1}\) band in spectra of all hydrous samples (whether P-bearing or nominally P-free) as well as in published spectra of other hydrous aluminosilicate glasses has been the subject of debate. One assignment is to (Si,Al)-OH stretch vibrations (e.g., Remmele et al., 1986; McMillan et al., 1993). From multinuclear NMR (\(^{23}\)Na,\(^{27}\)Al,\(^{29}\)Si), Kohn et al. (1989, 1992) concluded, however, that in melt of albite composition there is no evidence for Al-OH or Si-OH bonding but, rather that the principal OH-formation is through interaction with alkalis. Thus, the inference from the NMR data is inconsistent with the assignment of the 900 cm\(^{-1}\) band to (Si,Al)-OH stretching. The observation (Mysen and Virgo, 1986a) that the intensity of this band increases continuously with increasing H\(_2\)O content (up to 8–10 wt% H\(_2\)O) also is inconsistent with an assignment to (Si,Al)-OH. This inconsistency is because in hydrous aluminosilicate glasses with total H\(_2\)O content above ~3 wt% results from IR spectroscopy (e.g., Stolper, 1982; Silver and Stolper, 1989; Silver et al., 1990) show that any additional H\(_2\)O is dissolved in molecular form. Thus, one would not expect the 900 cm\(^{-1}\) band intensity to increase if it was assigned to any kind of vibration associated with structurally bound OH groups. Others have assigned the 900 cm\(^{-1}\) band to (Si,Al)-O\(^\circ\) stretching arising from the presence of nonbridging oxygen in the hydrous samples (e.g., Mysen and Virgo, 1986a). Such proposed nonbridging oxygen could be as the result of formation either of M-OH or Al-OH complexes. By forming M-OH complexes, the charge-balance requirement of Al\(^{3+}\) in tetrahedral coordination is no longer met. By forming Al-OH complexes, there would be an excess M-cations. In either case, nonbridging oxygen would be formed. (This effect is illustrated with Eqns. 9 and 10 and Table V in Mysen and Virgo, 1986a.) Although clearly more information is needed before the issue can be fully resolved, in the absence of evidence to the contrary, we assign the 900 cm\(^{-1}\) band to (Si,Al)-O\(^\circ\) stretching in a depolymerized structural unit (probably of Q\(^2\) type). The spectral interpretation is also consistent with results from anhydrous peralkaline melts and glasses in, for the example, the system Na\(_2\)O-Al\(_2\)O\(_3\)-Si\(_3\)O\(_5\). Spectra of melt and glasses in

![Fig. 7. Examples of curve-fitted spectra in the region of OH stretching.](image-url)
Table 4. Experimental results—line parameters in the 3000–4000 cm\(^{-1}\) region.

<table>
<thead>
<tr>
<th>Wt% (P_2O_5)</th>
<th>A/CNK*</th>
<th>Frequency</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3300</td>
<td>3500</td>
</tr>
<tr>
<td>Ca/P = 5/3</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.13</td>
<td>1.05</td>
<td>3316</td>
<td>3484</td>
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<tr>
<td>1.11</td>
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<td>3495</td>
</tr>
<tr>
<td>2.11</td>
<td>1.24</td>
<td>3279</td>
<td>3487</td>
</tr>
<tr>
<td>2.55</td>
<td>1.34</td>
<td>3245</td>
<td>3488</td>
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<tr>
<td>Ca/P = 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.05</td>
<td>3268</td>
<td>3481</td>
</tr>
<tr>
<td>1.08</td>
<td>1.15</td>
<td>3268</td>
<td>3485</td>
</tr>
<tr>
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<td>1.24</td>
<td>3256</td>
<td>3471</td>
</tr>
<tr>
<td>2.86</td>
<td>1.34</td>
<td>3258</td>
<td>3477</td>
</tr>
</tbody>
</table>

* Molar \(Al_2O_3/(CaO + Na_2O + K_2O)\).

this system reveal significant reduction in frequencies of bands assigned to Si–O\(^+\) stretching as the \(Al/(Al + Si)\) of the system is increased (Mysen and Frantz, 1994).

The relative intensity of the 900 cm\(^{-1}\) band could then be a measure of degree of polymerization of the melts. Interestingly, the area of this band is greater in all the spectra of samples from the Ca/P \(-1\) series. Furthermore, in both series, its relative area decreases somewhat with increasing phosphorus content (Fig. 9). Consequently, one may suggest that in hydrous aluminosilicate melts, P acts as a polymerizing agent analogous to the structural role of phosphorus in anhydrous depolymerized melts (Dupree et al., 1988, 1989; Mysen, 1992). The actual value of NBO/T contributing to the 900 cm\(^{-1}\) band intensity may be estimated with the method proposed by Mysen and Virgo (1986a). From such calculations, it would appear that solution of \(\sim 9\)–\(10\) wt\% \(H_2O\) has increased the NBO/T from near 0 for anhydrous samples to about 0.7 in the hydrous glasses, a value similar to that of trisilicate glasses, for example. There is a 10–25% decrease in this NBO/T-value as phosphorus is dissolved (Table 5).

The Raman band fitted near 970–975 cm\(^{-1}\) in the spectra of hydrous glasses, with composition-independent frequency, is assigned to Si–OH stretching (e.g., Stolen and Walrafen, 1976). The presence of Si–OH bonding in these glasses is also consistent with the band near 3650 cm\(^{-1}\) in the high-frequency envelope (e.g., Fig. 7, see also Table 4) as OH stretch vibrations at this high frequency has not been associated with hydroxyl formation involving the other metal cations (\(Al, Ca, Na, K\)) in the present system (e.g., Aines and Rossman, 1984; Mysen and Virgo, 1986a,b). The dominant intensity in the 3000–4000 cm\(^{-1}\) range at lower frequency

![](image1.png)

Fig. 8. Variations in areas of individual bands in the OH stretch region relative to the total area of the envelope, \(\Sigma A\), as a function of wt\% \(P_2O_5\) (and A/CNK, see Fig. 1).

![](image2.png)

Fig. 9. Relationship between phosphorus content (and A/CNK) the area of the 900 cm\(^{-1}\) band (\(A_{900}\)) relative to the total area of bands assigned to vibrations not including OH (970 cm\(^{-1}\)) and P (1120 and 1210 cm\(^{-1}\)). \(\Sigma A = A_{900} + A_{1120} + A_{1210} + A_{2500}\).
The latter two bands are observed only when there is P in the system. It is suggested that the band fitted in accord with Gan and Hess (1992), leading to the suggestion that glasses to form perhaps P-O-Al linkages in a three-dimensional structure (see also Mysen et al., 1981).

Published Raman and NMR data (Chakraborty and Condrate, 1985) could be assigned to coupled vibrations of Si-O and P-O stretching coordinates, Chakraborty and Condrate (1985) on this basis concluded that this was evidence for Si-O-P linkages in their Na2O-SiO2-P2O5 glasses. Additionally, Kosinski et al. (1988) reported 31P NMR evidence for Si-O-P linkages in P-bearing alkali silicate glasses.

In a vibrational spectroscopic study that included Raman data for the glasses along the join NaOH-SiO2, this latter frequency, however, is about 20 cm⁻¹ lower than that observed in many crystalline orthophosphates and also in spectra of other P-bearing glasses where independent spectroscopic evidence indicates that orthophosphate complexes exist (e.g., Nelson and Tallant, 1986). Further, Raman spectra of CaO-SiO2-P2O5 and Na2O-SiO2-P2O5 glasses show the band assigned to P-O stretching in orthosilicate units as a narrow band between 960 and 965 cm⁻¹ (Mysen, 1992, 1996). In the present system, with similar metal cations, one would, therefore, expect the frequency to be near 960 cm⁻¹ and not 940 cm⁻¹ as observed. It should also be noted that despite this inconsistency, if the 940 cm⁻¹ band was due to P-O stretching in orthosilicate units in the hydrous glasses, from a comparison of the intensity data from the system Na2O·9SiO2 (NBO/Si = 0.22) with 2 mol% P2O5 in solution with the present intensity relationships, it would be suggested that even in the most P-rich sample, only about 10% of the dissolved P2O5 would exist as orthophosphate.

An alternative interpretation may be related to the observation above (e.g., Fig. 7, 8) that the abundance of P-O-Si relative to P-O-Al linkages decreases as H2O is dissolved in the glasses. This structural change might imply that P-O-Si oxygen bridges have been broken by H2O. Such breakage could lead to formation of Si-OH and P-OH bonds (analogous to the breakage of Si-O-Si bridges to form two Si-OH bonds in SiO2·H2O glasses and melts; see, for example, Wasserburg, 1957; Stolen and Walrafen, 1976). It is possible that the 940 cm⁻¹ might be assigned to an equivalent P-OH vibration.

In the study of Mysen and Virgo (1986b), the area of the band near 3500 cm⁻¹ was found particularly sensitive to Ca/Si ratio (in spectra of glasses along the join Ca(OH)2-SiO2), whereas the area of lower-frequency band, near 3300 cm⁻¹, appeared positively correlated with Na/Si (in spectra of glasses along the join NaOH-SiO2). This latter frequency region also, however, exhibits increased intensity with increasing abundance of molecular H2O so interpretation of the intensity variations in this region of spectra from the more complex aluminosilicate glasses should be conducted with caution. A band near 3600 cm⁻¹ occurred in spectra of glasses along both the joins Al(OH)3-SiO2 and SiO2·H2O (Mysen and Virgo, 1986b). Relative intensity variations re-

<table>
<thead>
<tr>
<th>Ca/P~5/3</th>
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</tr>
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<tbody>
<tr>
<td>0.13</td>
<td>1.05</td>
<td>0.76 (8)</td>
</tr>
<tr>
<td>1.11</td>
<td>1.15</td>
<td>0.59 (6)</td>
</tr>
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<td>1.24</td>
<td>0.72 (8)</td>
</tr>
<tr>
<td>2.55</td>
<td>1.34</td>
<td>0.65 (7)</td>
</tr>
</tbody>
</table>

| 0.15 | 1.05 | 0.74 (8) |
| 1.08 | 1.15 | 0.65 (7) |
| 2.24 | 1.24 | 0.64 (7) |
| 2.86 | 1.34 | 0.65 (7) |

* Molar Al2O3/(CaO + Na2O + K2O).
reflecting possible variations in abundance of Al-OH and Si-
OH bonding is, therefore, not feasible. It is tentatively sug-
gested, however, that the intensity variations among the 3500
and 3300 cm⁻¹ bands (Fig. 8) might reflect relative impor-
tance of Ca-OH and alkali-OH bonding. If so, it appears Ca/
P ~ 5/3 series with increasing CaO and P₂O₅ content, Ca-
OH bonding becomes more important relative to OH groups
bonded to alkali metals. In the Ca/P ~ 1 series of glasses,
this trend is less evident.

4. DISCUSSION

4.1. Solution Mechanism of Phosphorus in Anhydrous Peraluminous Glasses

The mechanism of incorporation of P in peraluminous
glasses is first detailed for the dry compositions. The spectro-
scopic data are interpreted to suggest that phosphorus is
present in the two series of glasses studied primarily as
AlPO₄ species. There is also evidence for P-O-Si bonding
thus suggesting cross-linking between the phosphate com-
plexes and the aluminosilicate network. From Raman spec-
troscopic data, the presence of phosphate units with double-
bonded oxygen can be ruled out (they should appear as
peaks at ~1320 cm⁻¹, e.g., Kosinski et al., 1988, and no
Raman intensity was observed in this spectral range).

The Al that participates in the formation of AlPO₄ units
may come from two distinct structural positions. One is
where Al³⁺ is charge-balanced with alkalis and possibly Ca.
In one case, this mechanism results in the formation of non-
bridging oxygen as illustrated with the following schematic
equations (for monovalent and divalent charge-balancing
cations):

\[
2\text{M}^+\text{AlSi}_3\text{O}_{20-2} + \text{P}_2\text{O}_5 = 2\text{AlPO}_4 + 2\text{M}^+\text{Si}_3\text{O}_{20-3} \quad (1)
\]

\[
\text{M}^{2+}\text{AlSi}_3\text{O}_{20+4} + \text{P}_2\text{O}_5 = 2\text{AlPO}_4 + \text{M}^{2+}\text{Si}_3\text{O}_{20+1} \quad (2)
\]

Toplis and Dingwell (1996) suggested an alternative mecha-
nism to form AlPO₄ complexes where one may envision
exchange of alkalies (or alkaline earths) between charge-
balanced Al³⁺ and phosphate complexes:

\[
\text{M}^+\text{AlO}_2 + \text{P}_2\text{O}_5 = \text{AlPO}_4 + \text{M}^+\text{PO}_4^-(1a)
\]

\[
\text{M}^{2+}\text{AlO}_4 + 2\text{P}_2\text{O}_5 = 2\text{AlPO}_4 + \text{M}^{2+}(\text{PO}_4^2-) \quad (2a)
\]

In the case illustrated by Eqns. 1 and 2, P solution would
involve the production of network modifiers (alkalis and Ca),
resulting in depolymerization of the melt. This model
would have a large influence on the framework structure,
which is not observed in the Raman spectra. We, therefore,
view this possibility as unlikely. An important implication
of this observation is that P incorporation in these aluminosi-
licate glass systems has little influence on the aluminosilicate
network.

Phosphate complexing according to the mechanisms 1a or
2a, or both, does not affect the NBO/T of the aluminosilicate
network. However, in this mechanism the Al/(Al + Si) of
the aluminosilicate must decrease as phosphorus is dis-
solved. This postulated decrease in Al/(Al + Si) will result
in an increase in frequency of the (Si,Al)-O° stretch vibra-
tions near 1000, 1090, and 1160 cm⁻¹ in the P-free glasses
(Seifert et al., 1982; Neuville and Mysen, 1996) as P is
dissolved. Such a frequency increase is not observed. Fur-
ther, from a stoichiometric point of view, only metaphos-
phate (PO₃) units can be formed without generating excess
Al which might result in additional nonbridging oxygen in
the melts. The frequency of P-O° stretching in PO₃ units
in crystalline NaPO₃ is near 1165 cm⁻¹ (Nelson and Tallant,
1986). There is no evidence for such a band in the Raman
spectra. The mechanisms proposed by Toplis and Dingwell
(1996) and illustrated with expressions 1a and 2a are not,
therefore, consistent with the data.

An alternative is a conceptually similar model with the
phosphate complexes less polymerized than that of PO₄.
Such a model can be illustrated with the expressions:

\[
8\text{M}^+\text{AlO}_2 + 3\text{P}_2\text{O}_5 = 2\text{AlPO}_4 + 2\text{M}^+4\text{P}_2\text{O}_7 + 6\text{Al}^{3+} \quad (1b)
\]
$$3M^+\text{AlO}_2 + P_2\text{O}_5$$

$$= \text{AlPO}_4 + M^+\text{PO}_4 + 2\text{Al}^{3+}(\text{excess})$$  \hspace{1cm} (1c)

where $\text{Al}^{3+}(\text{excess})$ represents $\text{Al}^{3+}$ in excess of that for which alkali charge-compensation would be available. Analogous expressions could be written with divalent cations (e.g., alkaline earths).

Mechanism 1b is unlikely because P-O$^-$ stretching in pyrophosphate units results in Raman bands near 1020 cm$^{-1}$ (Nelson and Tallant, 1985), which have not been observed in the spectra. Mechanism 1c (orthophosphate complexing) will be considered in more detail because there is a very, very weak band near 940 cm$^{-1}$ in the nominally anhydrous samples. By using the Raman data from Mysen (1996) for the purpose of estimating relations between Raman intensity and P concentration, with the $\approx 0.5\%$ of the intensity of the 940 cm$^{-1}$ band relative to the strongest band in the high-frequency envelope of the anhydrous samples, this intensity would correspond to $\approx 0.5\%$ of the total amount of dissolved P$_2$O$_5$ in the form of orthophosphate units. It would seem, therefore, that none of the mechanisms involving alkali or alkaline earth exchange between aluminate and phosphate are consistent with the Raman data for these glasses.

In the second possible case, P is structurally bonded with excess Al$^{3+}$ present. This Al$^{3+}$ may be linked either to Si- or Al-bearing Q$^3$ species, themselves connected to the network. This mechanism is consistent with the phosphorus solubility data of Wolf and London (1994), for example. In that study, it was observed that there was a 1:1 correlation between P solubility and Al content whenever the P/Al = 1. Phosphorus incorporation in such glasses can then be described by the following homogeneous equilibrium:

$$\text{Al}_2\text{SiO}_3 + \text{P}_2\text{O}_5 \rightarrow \text{Al}_2\text{P}_2\text{SiO}_{10}$$  \hspace{1cm} (3)

If some of the original excess Al$^{3+}$ existed in a non-network-forming structural position, the process involves an overall reduction of the NBO/T and the formation of Q$^1$ species, i.e., polymerization. The Q$^1$ silicate tetrahedra and charge-balanced AlO$_4$ tetrahedra forming the network remain unaffected, implying that the structural roles of alkali and Ca do not need to be affected. The total amount of P present in our glasses can be incorporated completely with the above mechanism, because the amount of excess Al$^{3+}$ present exceeds the amount of phosphorus dissolved. This solution mechanism is consistent with the P diffusion data for quite similar bulk compositions in the same system as reported by Wolf and London (1994). Wolf and London (1994) found that there was no absolute or relative change in Na and K concentration in the apatite diffusion aureole compared with the original melt, which is exactly what would be expected from the structural model of P solution proposed here. In other words, the compositions are so Al-rich and peraluminous that there is no need to involve those Al$^{3+}$ atoms charge-balanced by alkalis or Ca$^{2+}$ and forming part of the network (see Table 1).

If, in fact, there is also interaction between P and charge-balanced Al$^{3+}$, the structural scenario illustrated with Eqns. 1 and 2 requires consideration. Mechanisms 1a,b,c and 2a will not be considered further for the reasons discussed above. In scenarios 1 and 2, nonbridging oxygen will be generated. Relevant Raman bands reflecting increasing depolymerization of the structure as P is dissolved cannot be discerned in the spectra although the sensitivity of the spectra of these samples to such structural features is somewhat difficult to establish quantitatively. A very conservative estimate of the sensitivity might be derived in the following manner. The Raman cross-sections of (Si,Al)-O$^-$ stretch vibrations is on the order of 1 order of magnitude greater than those of (Si,Al)-O$^-$ stretching vibrations in these systems (e.g., Mysen, 1995). Therefore, if, for example, a sample contained 5% of structural units containing nonbridging oxygen and 95% fully polymerized units, the Raman intensities from the depolymerized units should be about 50% of the maximum intensity of the high-frequency envelope. This would be easily observed but was not detected in the spectra. A conservative estimate of sensitivity to nonbridging oxygen from this discussion is, therefore, 5% of the total.

4.2. The Role of H$_2$O in P-Bearing Glasses

The spectroscopic information on hydrous, P-free glasses is consistent with solution of water via association with alkali or alkaline earths, possibly with Al, and probably with Si. There is also molecular water in the glasses. This conclu-
sion is consistent with previously suggested models for H₂O solution mechanisms in aluminosilicate melts and glasses (e.g., Mysen and Virgo, 1986b; Silver et al., 1990; Kohn et al., 1992; Holtz et al., 1996).

The Raman spectra of H₂O- and P-bearing glasses differ from both the anhydrous, P-bearing and P-free anhydrous glasses in (1) the presence of a distinct Raman band near 940 cm⁻¹ and (2) a considerably larger value of the area ratio, A₁₁₂₀/(A₁₁₂₀ + A₁₁₂₀) (Fig. 10). The latter observation is consistent with previously suggested models for H₂O solution mechanisms in alumino-silicate melts and glasses from both the anhydrous, P-bearing and P-free anhydrous (e.g., Mysen and Virgo, 1986b; Silver et al., 1990; Kohn et al., 1992; Holtz et al., 1996).

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It is possible that the ~940 cm⁻¹ band observed in the Raman spectra of hydrous, P-bearing samples might then be assigned to P-OH vibrations analogous to the 970 cm⁻¹ that is assigned to Si-OH stretching. Consequently, in this solution model of water into P-bearing peraluminous glasses has the effect of isolating the AlPO₄ complexes from the silicate network through the formation of P-OH bonds. A consequence of this solution model for P in hydrous peraluminous glasses is that most likely the solubility of H₂O in P-bearing melts would differ from that in the same melt without phosphorus. Such an effect was demonstrated experimentally by Wolf and London (1994).

$$\text{Al}_2\text{P}_2\text{SiO}_{10} + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{P}_2\text{SiO}_9(\text{OH})_2$$

5. CONCLUDING REMARKS

Raman spectra of peraluminous granitic glasses are consistent with Al-O-P bonding, perhaps in an AlPO₄-type complex, being a principal solution mechanism of P. These complexes are linked with the silicate network over Si-O-P bridges. In hydrous systems, the Si-O-P bridges are broken and replaced with OH-groups attached to Si-OH and probably P-OH. Therefore, the water content of peraluminous aluminosilicate melts are likely to affect the solubility behavior of P, and conversely, the solubility behavior of H₂O is affected by P in such melts.

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