

Raman spectroscopic study of the solubility mechanisms of F in glasses in the system CaO-CaF₂-SiO₂

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ABSTRACT

To determine the solubility mechanism of F in depolymerized silicate liquids, quenched glasses in the CaO-CaF₂-SiO₂ system were examined with Raman spectroscopy. The systematic changes in the Raman spectra of the glasses accompanying the substitution of F for O (e.g., along the CaSiO₃-CaSiO₂F₂ join) provide evidence for concomitant polymerization of the liquid. These results are consistent with a solubility mechanism in which F forms complexes with otherwise network-modifying Ca rather than with network-forming Si. Formation of Ca-F complexes increases the ratio of network-formers to network-modifiers in the silicate network and polymerizes the silicate portion of the liquid. The similarity of the positions and intensities of bands in the Raman spectra of glasses of different compositions along the two CaF₂-*a*CaO-*b*SiO₂ joins supports this solubility mechanism and, furthermore, provides evidence that bands from vibrations of F-bearing complexes are not detectable in these spectra.

This solubility mechanism has implications for both the phase equilibria and the physical properties of F-bearing systems. The polymerization resulting from the substitution of F for O in depolymerized systems should increase the stability fields of more-polymerized solid phases relative to fields of less-polymerized phases. Furthermore, if the viscosity of silicate liquids is controlled by the overall polymerization of the liquid, substitution of F for O in depolymerized liquids should increase viscosity. In contrast, previous work has shown that in highly polymerized aluminosilicate liquids, the substitution of F for O decreases the polymerization and the viscosity of the liquid. The effect of F on the polymerization of silicate liquids depends on the type of cations present with which F forms complexes. More work is required to evaluate the relative stabilities of complexes of F with network-modifying, charge-balancing, and network-forming cations and the relationship between these complexes and the physical properties of the liquids.

INTRODUCTION

F is a significant component in certain igneous rocks; alkali granites and topaz rhyolites may contain >1 wt% F (Bailey, 1977; Christiansen et al., 1983), and some mica-bearing, high-K rocks have up to 2 wt% F (Aoki et al., 1981). In addition, the formation of complexes with halogens such as F or Cl may be an efficient means of transporting metals both in magmas (Mahood and Hildreth, 1983) and in aqueous fluids (Candela, 1986). It is necessary, therefore, to understand the solubility mechanisms of F in silicate liquids.

Most of the previous work on F in silicate systems (e.g., Wyllie and Tuttle, 1961; Manning, 1981) has concentrated on the effects of F, in addition to water, on phase equilibria in high-silica systems. Some work, however, has been done on the solubility mechanisms of F in the absence of water in silicate systems. Mysen and Virgo (1985a, 1985b) proposed solubility mechanisms for F in silicate liquids in the systems NaF-SiO₂, AlF₃-SiO₂, and Na₂O-Al₂O₃-SiO₂-F₂O₋₁ based on Raman spectroscopic studies. In their model, F dissolves in fully polymerized

glasses along the SiO₂-NaAlSiO₄ join by forming complexes with Na and Al. The formation of Na-F complexes removes charge-balancing Na associated with Al, thereby requiring Al to change from a network-former to a network-modifier and depolymerizing the liquid. When F forms complexes with Al, Al is removed from the network, and Na, no longer required to fulfill a charge-balancing role, becomes a network-modifier, thereby depolymerizing the liquid. Mysen and Virgo (1985b) found no evidence for F bonded to Si in glasses on the SiO₂-NaAlSiO₄ join, in contrast to their findings for the NaF-SiO₂ and AlF₃-SiO₂ joins (Mysen and Virgo, 1985a).

A study of F-doped SiO₂ glass with ¹⁹F NMR spectroscopy (Duncan et al., 1986) provided evidence for SiO₃F and SiO₂F₂ complexes in the glass, but not for SiOF₃ or SiF₄ complexes. Hayashi et al. (1987) interpreted NMR spectra of F-containing Na₂O-Al₂O₃-SiO₂ glasses to indicate the presence of Si-F, Na-F, and Al-F or Na-Al-F structures in the glasses. The resonance attributed to Si-F was absent in the least silica-rich composition (NaAlSiO₄), and that attributed to Na-F was only present in a phase-separated, peralkaline sample.

In contrast to the depolymerizing effect of F in aluminosilicate liquids, the substitution of F for O would polymerize a liquid in which F forms complexes with network-modifiers. This mechanism was suggested by Foley et al. (1986) on the basis of phase equilibria and infrared studies in the $\text{KAlSiO}_4\text{-Mg}_2\text{SiO}_4\text{-SiO}_2\text{-F}_2\text{O}_{-1}$ system. Tsunawaki et al. (1981) interpreted Raman spectra of glasses in the $\text{CaO-CaF}_2\text{-SiO}_2$ system as indicating that the addition of CaF_2 to glasses with $\text{Ca/Si} > 1$ does not break Si-O bonds. Further, they stated that F is present in melts with $\text{Ca/Si} > 1$ as F^- , presumably coordinated to Ca. In contrast, F is present in melts with $\text{Ca/Si} < 1$ both as F^- ions, again presumably coordinated to Ca, and as F coordinated to Si. In this study, glasses in the $\text{CaO-CaF}_2\text{-SiO}_2$ system were studied with Raman spectroscopy to examine the principles of the solubility mechanism of F in depolymerized liquids. Raman spectroscopy, as a sensitive probe of the structure of the silicate network, was used to provide information about the structural effects of F in such glasses.

EXPERIMENTAL METHODS

F may be added to experimental systems either as HF or by direct substitution of F for O. The former is perhaps more geologically relevant, in that magmatic systems may contain both F and water. The presence of H in HF, and of H_2O if an aqueous solution of HF is used, means that the effects of F on the structure of the glass may be difficult to resolve from those of H-bearing species. Addition of F by substitution for O, which may be expressed as the F_2O_{-1} exchange component (Thompson et al., 1982), allows isolation of the effects of F without the complications of the presence of H. Thus, this study focuses on the effects of this substitution.

Glasses for this study were made in two stages. Appropriate proportions of spectroscopically pure CaCO_3 and SiO_2 were ground together in an agate mortar under ethanol for ~ 1.5 h and placed in a Pt crucible. The mixture was dried at 800°C for 3–4 h, then fired at 1450°C for 2–3 h. This decarbonated oxide mixture was then ground and refired to ensure that it was dry. One aliquot of this mixture was fused in an unsealed Pt capsule at 1550 to 1600°C , depending on the composition, for 1 h to make the F-free glass. F-bearing glasses were prepared by mixing aliquots of the decarbonated mixture with weighed amounts of CaF_2 by grinding under ethanol for > 1 h. These mixtures were loaded into 3-mm-diameter Pt capsules, dried for 16 h at 400°C , and sealed by arc-welding. Glasses were made by heating the capsules in a vertical-tube, Pt-wound quench furnace at 1550 to 1600°C for 30–60 min and quenching in liquid N_2 or water. The capsules were weighed to confirm that they had not leaked and lost F; then they were opened. The resultant glasses were examined with the petrographic microscope to ascertain that no crystals were present and that the glass had a uniform index of refraction. Homogeneity and the composition of the glasses were confirmed by wavelength-dispersive analysis on a JEOL JSM-35 scanning-electron microprobe. Operating conditions were 15-kV accelerating voltage, 100-nA beam current on C, and 100-s counting time (maximum) per element. Standards were a synthetic diopside-jadeite glass for Ca and Si, and a synthetic F-bearing albite glass obtained from D. B. Dingwell (Dingwell et al., 1985) for F. To minimize volatilization of F, the beam was ras-

tered over a $10\text{-}\mu\text{m}$ area during the analysis, and F was analyzed first.

Raman spectra of the quenched glasses were obtained with the automated Raman system described by Mysen et al. (1982) and Seifert et al. (1982). Small, 2–10-mm³ chips of the glasses were excited by the 488-nm line of a Coherent CR-18 Ar⁺ laser operating at 1.5 to 2.5 W. Other details of the data acquisition and storage and the corrections for instrumental background and for temperature- and frequency-dependent scattering are described by Mysen et al. (1982).

Raman difference spectra were obtained by subtracting two digitally recorded spectra that had been normalized such that the intensity of one band is the same in both spectra, similar to the technique of Matson et al. (1983). Ideally, the band to which the two spectra are normalized should be a band caused by vibrations that are unaffected by the substitution of F for O. There are, however, no bands in these glasses that fulfill this requirement perfectly. The spectra in this paper were normalized to the band at $\sim 970\text{ cm}^{-1}$, which has been attributed by previous workers (cf. review by McMillan, 1984) to symmetric-stretching vibrations involving Si-O bonds in structural units with NBO/T (number of nonbridging oxygens per tetrahedrally coordinated cation) = 2. The consequences of this normalization will be discussed below. The more traditional technique of obtaining Raman difference spectra (e.g., Nelson et al., 1984) with rotating cylinders composed of the two glasses could not be applied in this case because the samples are too small.

RESULTS

The compositions studied are shown in Figure 1 and listed in Table 1. The $2\text{F} \leftrightarrow \text{O}$ substitution occurs along the lines parallel to the CaO-CaF_2 join (Fig. 1), from Wo (CaSiO_3) to WoF50 [$\text{F}/(\text{F} + \text{O}) = 0.50$] and from WL37.5 ($\text{Ca}_{1.29}\text{SiO}_{3.29}$) to WL37.5F56 [$\text{F}/(\text{F} + \text{O}) = 0.56$].

Figures 2 and 3 illustrate the changes in the background-corrected Raman spectra as F is substituted for O in Wo and WL37.5 liquids, respectively. Both series of spectra show similar trends in the $600\text{--}1200\text{-cm}^{-1}$ region. Substitution of 10% F for O in CaSiO_3 liquid results in a decrease in the intensity of the band at $\sim 850\text{ cm}^{-1}$ and an increase in the intensity of the band at $\sim 1050\text{ cm}^{-1}$ relative to the intensity of the $\sim 970\text{-cm}^{-1}$ band (Fig. 2) in the Raman spectra of the quenched glasses. Similarly, as the F content of WL37.5 liquid increases (Fig. 3), the intensities of the bands at ~ 870 and $\sim 910\text{ cm}^{-1}$ decrease, and the intensity of the band at $\sim 1050\text{ cm}^{-1}$ increases relative to the intensity of the band at $\sim 970\text{ cm}^{-1}$ in the spectra of the quenched glasses. Substitution of F for O also causes a decrease in the frequency of the band at $\sim 650\text{ cm}^{-1}$ for both compositions. The small band at $\sim 1280\text{ cm}^{-1}$ in the WoF10 and the WL37.5F24 spectra results from stretching vibrations of CO_2 present in the glass, probably from the CaCO_3 used in the initial synthesis.

For comparison, the Raman spectra of three compositions on the F-free CaO-SiO_2 join are shown in Figure 4. As the Ca/Si ratio decreases from 1.29 in WL37.5 to 1.00 in Wo to 0.842 in SW84, the intensities of the bands at ~ 850 and $\sim 900\text{ cm}^{-1}$ decrease, and the intensity of the band at $\sim 1050\text{ cm}^{-1}$ increases. These changes are

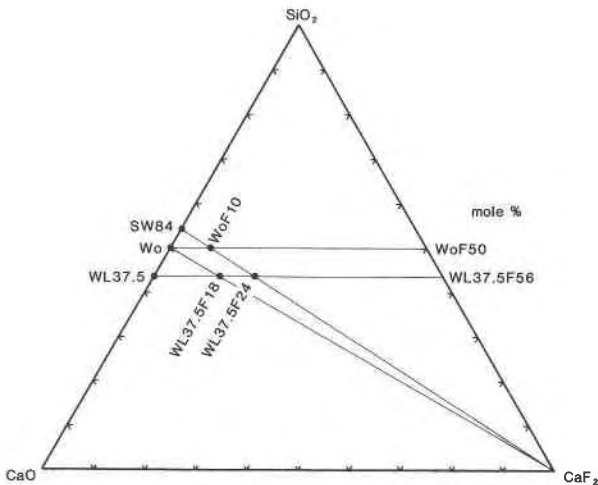


Fig. 1. Compositions of glasses studied in the system CaF_2 - CaO - SiO_2 . Abbreviations: Wo = wollastonite; F10 means that the molar ratio $\text{F}/(\text{F} + \text{O}) = 0.10$.

similar to those observed as F is substituted for O in the Wo and WL37.5 samples (Figs. 2, 3). The low-frequency band at $\sim 650 \text{ cm}^{-1}$ shifts to lower frequency with decreasing Ca/Si (Fig. 4), as it does with increasing substitution of F for O (Figs. 2, 3).

DISCUSSION

Spectroscopic effects of F substitution

To use these results to understand the solubility mechanisms of F in silicate liquids, one must understand the effect of substitution of F for O in SiO_4^{4-} tetrahedra on the frequency of Raman bands caused by vibrations involving these tetrahedra. In addition, the possibility of Raman bands arising from F-containing complexes must be addressed.

Substitution of F for either bridging or nonbridging oxygens will distort the electronic environment of the Si because of the higher electronegativity of F relative to O. This distortion will weaken the remaining Si-O bonds in these tetrahedra, decreasing the force constants and the frequencies of vibrations involving these Si-O bonds. The primary determinant of the frequency of the Raman bands in the $800\text{--}1200\text{-cm}^{-1}$ region is the force constant for the Si-NBO (nonbridging oxygen) bond (Dowty, 1987). Formation of Si-F bonds, therefore, would be expected to give rise to lower-frequency bands in the $800\text{--}1200\text{-cm}^{-1}$ region from Si-NBO vibrations relative to the F-free analogue. If the distortion of the electronic environment resulting from the exchange of F for O is negligible, substituting F for a bridging oxygen is equivalent to increasing the NBO/T of these tetrahedra, which would also increase intensities of lower-frequency bands in the $800\text{--}1200\text{-cm}^{-1}$ region. Substitution of F for a NBO in such a case would have no effect on the intensities of the bands in this region. This argument assumes that the Si-F bond behaves like an Si-O bond, which is consistent with the lack of dis-

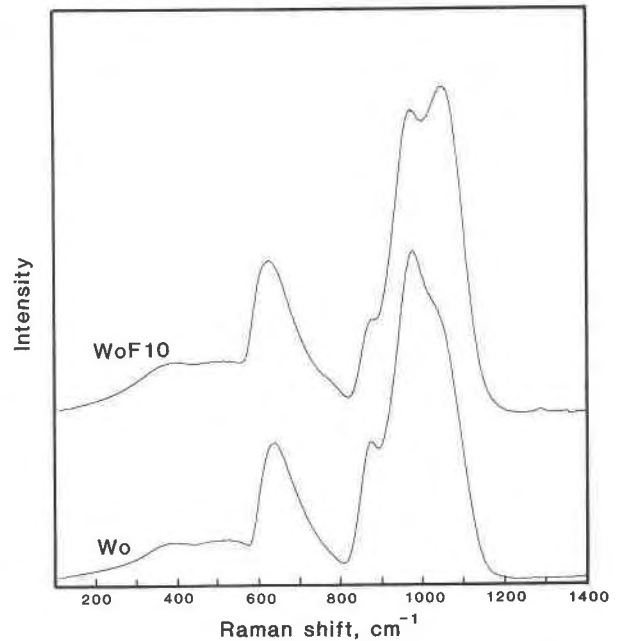


Fig. 2. Unpolarized Raman spectra of glasses along the $\text{CaSiO}_3\text{-F}_2\text{O}_{-1}$ join.

cernible change in the high-frequency region of the Raman spectrum of silica glass upon the addition of F (Dumas et al., 1982). Therefore, the effects of the formation of Si-F bonds on vibrations involving Si-O bonds cannot explain the systematic increase in the intensity of *higher-frequency* bands in the $800\text{--}1100\text{-cm}^{-1}$ region at the expense of lower-frequency bands that accompanies the substitution of F for O.

The frequency of the band resulting from a Si-F stretching vibration in SiO_3F tetrahedra in F-bearing silica glass is $\sim 945 \text{ cm}^{-1}$ (Dumas et al., 1982; Yamamoto et al., 1983). For the F-containing glasses of this study, it is not possible to rule out a small contribution of such a band, because of overlap with bands resulting from Si-O vibrations in the same region. Increasing F/O in $\text{SiO}_x\text{F}_{4-x}$ complexes decreases the frequency of the resultant band in the Raman spectrum by $\sim 50 \text{ cm}^{-1}$ per oxygen replaced by F (Yamamoto et al., 1983; Mysen and Virgo, 1985a, 1985b). The decrease in intensity of the spectrum at $< 970 \text{ cm}^{-1}$ with increasing substitution of F for O (Figs. 2, 3) provides evidence that no Si-(O,F) complexes with $\text{F}/[\text{F} + \text{O}] > 0.25$ are detectable. If the intensity of this

TABLE 1. Compositions (mole percent) of glasses studied

Composition	SiO_2	CaO	CaF_2
SW84	54.29	45.71	—
Wo	50.00	50.00	—
WoF10	50.00	42.10	7.90
WL37.5	43.67	56.33	—
WL37.5F18	43.67	43.67	12.66
WL37.5F24	43.67	39.17	17.16

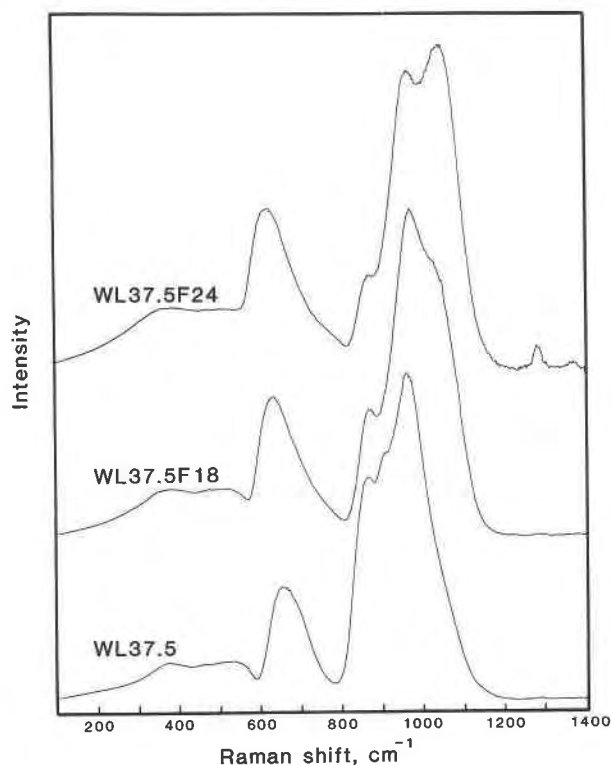


Fig. 3. Unpolarized Raman spectra of glasses along the $\text{Ca}_{1.29}\text{SiO}_{3.29}\text{-F}_2\text{O}_{-1}$ join.

band is low, it is possible, however, that some of these complexes could form.

Another possible Si-F complex is SiF_6^{2-} , which has a symmetric stretching vibration at 663 cm^{-1} (Nakamoto, 1978; Mysen and Virgo, 1985b). The presence of the large silicate band at $\sim 650\text{ cm}^{-1}$ may obscure a contribution of this vibration of SiF_6^{2-} complexes to the Raman spectrum, but there is no evidence of additional, well-defined bands in this region.

Finally, symmetric stretching vibrations of CaF_2 should generate a band at $\sim 485\text{ cm}^{-1}$ (Nakamoto, 1978); such a band is not observed in the F-bearing glasses. Because the Ca-F bond is highly ionic, the intensity of bands in the Raman spectrum from vibrations involving these complexes will be low. Thus, vibrations from F-containing complexes do not contribute detectably to the Raman spectra of these glasses.

TABLE 2. Frequency dependence of symmetric stretching vibrations of units with different NBO/T

NBO/T of structural unit	Frequency (cm^{-1})
4	850-880
3	900-920
2	950-1000
1	1050-1100

Note: After Mysen et al. (1980), McMillan (1984).

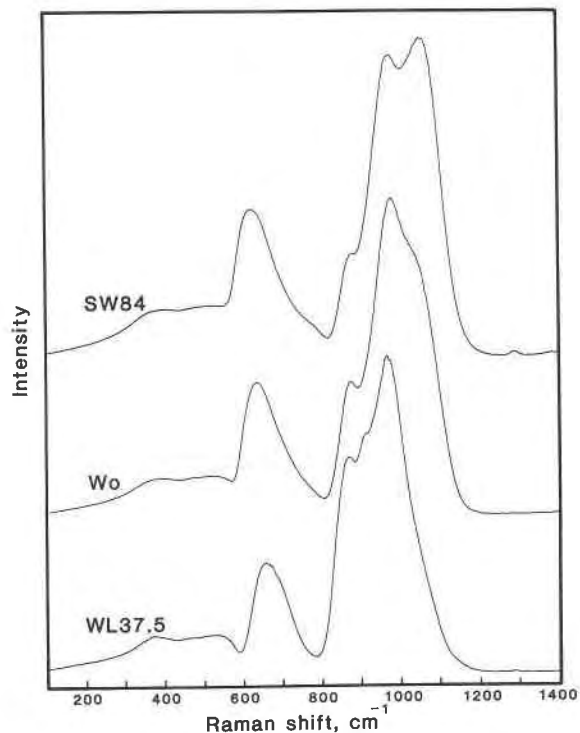


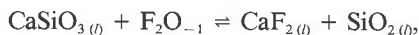
Fig. 4. Unpolarized Raman spectra of glasses along the CaO- SiO_2 join.

Solubility mechanism of F

The systematic changes in the spectra along the CaO- SiO_2 join as Ca/Si decreases and those in the spectra of Wo and WL37.5 glasses as F is added are strikingly similar and may have a common cause. The systematic increase in the intensity of higher-frequency bands as the composition becomes more SiO_2 -rich along the CaO- SiO_2 join has been attributed to increasing proportions of species with fewer nonbridging oxygens as the bulk degree of polymerization increases (Brawer and White, 1977; Mysen et al., 1980; Furukawa et al., 1981; McMillan, 1984). The frequency of bands caused by symmetric-stretching vibrations involving Si-O bonds (Table 2) is a systematic function of the NBO/T of structural units in the melt. At present, there is debate about the size of such units (e.g., discussion by McMillan, 1984). The increase in the intensity of the 1050-cm^{-1} band, accompanied by the decrease in the intensity of the $\sim 870\text{-}$ and $\sim 910\text{-cm}^{-1}$ bands, with increasing silica content along the CaO- SiO_2 join is consistent with increasing amounts of units with NBO/T = 1 at the expense of units with NBO/T = 3 and 4. The identical trends in the intensities and frequencies of bands with substitution of F for O in the Wo and WL37.5 glasses suggest that the substitution of F for O causes an increase in bulk polymerization of the glass.

A solubility mechanism consistent with polymerization accompanying the substitution of F for O is the formation of Ca-F complexes. Formation of such complexes

would remove Ca from a network-modifying role, as illustrated schematically by the reaction



in which polymerization of the silicate network is represented by the presence of $\text{SiO}_2(\text{f})$ on the right-hand side of the reaction.

This mechanism predicts that glasses along a join from CaF_2 to a point on the CaO-SiO_2 join contain identical silicate networks and differ from each other only in the relative proportion of Ca-F complexes to silicate network. Therefore, if the vibrational modes from Ca-F complexes are not Raman-active, the spectra of different glasses along such joins should be identical.

The similarity of the spectra for the samples along the CaF_2 -SW84 join (Fig. 5) and the CaF_2 -Wo join were examined. The only differences are the heights of the peak at $\sim 1280 \text{ cm}^{-1}$, which depends on the amount of residual CO_2 in the sample, and the increase in intensity of the 650-cm^{-1} band relative to the intensity of the $\sim 850\text{-}$, $\sim 970\text{-}$, and $\sim 1050\text{-cm}^{-1}$ bands with substitution of F for O. The vibrations that generate the Raman band at $\sim 650 \text{ cm}^{-1}$ are not well understood (cf. McMillan, 1984), but are associated with the presence of Si-O-Si linkages. The increase in the intensity of this band may result from rearrangement of the overall structure and from changes in the nature or abundance of the Si-O-Si linkages. Without a more thorough understanding of the vibrational modes responsible for this band, the change in intensity accompanying the substitution of F for O cannot be explained. SiF_6^{2-} complexes would give rise to a band near 650 cm^{-1} , but their presence is unlikely for the reasons discussed above. Furthermore, such a band would be unlikely to cause an increase in the intensity over the wide frequency range observed. In addition, the removal of Si from a network-forming role, required by the formation of SiF_6^{2-} complexes, would depolymerize the liquid, which would increase the intensities of the lower-frequency bands at ~ 850 and $\sim 970 \text{ cm}^{-1}$ relative to the intensity of the band at $\sim 1050 \text{ cm}^{-1}$, in contrast to the observed changes.

The difference spectra of the F-bearing glasses relative to the F-free glass along the CaF_2 -SW84 and the CaF_2 -Wo joins are essentially featureless (Figs. 6, 7), supporting the idea that the silicate networks along each of these joins do not vary. The slight differences that are observed probably result from the selection of the $\sim 970\text{-cm}^{-1}$ band as the normalization band. The similarity of the spectra along each of these joins also indicates that there are no detectable contributions in the Raman spectra from either Ca-F or Si-F vibrations.

The difference spectrum for two glasses related by a $2\text{F} \leftrightarrow \text{O}$ substitution (WL37.5F24 - WL37.5, Fig. 8), on the other hand, shows the increase in intensity of the band at 1050 cm^{-1} and the decrease in intensity of the band at 850 cm^{-1} relative to the $\sim 970\text{-cm}^{-1}$ band that accompanies the substitution of F for O. The peak at $\sim 600 \text{ cm}^{-1}$ in the difference spectrum reflects the shift of the $\sim 650\text{-cm}^{-1}$ band to lower frequencies with this sub-

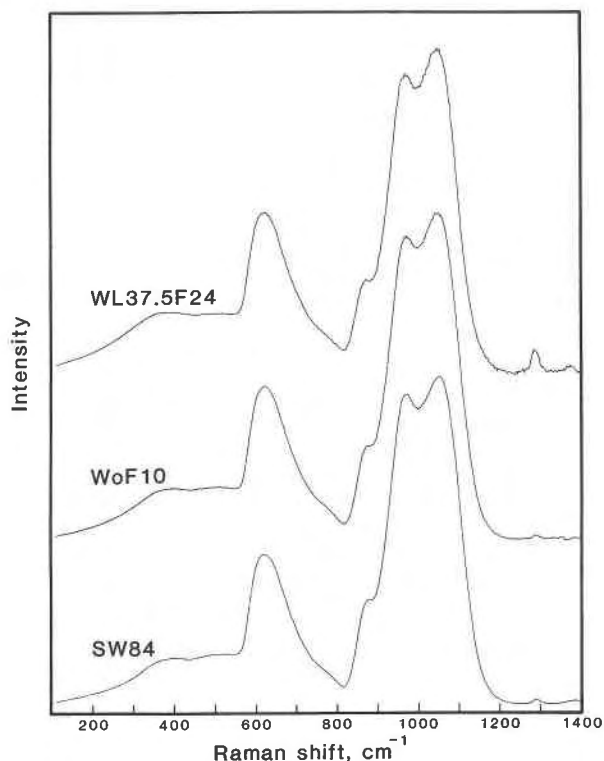


Fig. 5. Unpolarized Raman spectra of glasses along the CaF_2 -SW84 join.

stitution. The differences between this difference spectrum and those in Figures 6 and 7 also support the hypothesis that F complexes predominantly with Ca rather than with Si, and it increases the average polymerization when substituting for O.

Because of the similarity in the Raman spectra along the CaF_2 - $a\text{CaO} \cdot b\text{SiO}_2$ joins and because of the large region of immiscibility in the $\text{CaO-CaF}_2\text{-SiO}_2$ ternary system (Mukerji, 1965), the possibility that two immiscible liquids are formed in the experiments requires evaluation. If the CaF_2 -rich glass had no Raman-active vibrational modes, the Raman spectra of different proportions of a two-phase mixture should be identical, consistent with the data discussed above. All of the F-bearing glasses were synthesized outside of the two-liquid region as delineated by Mukerji (1965, Fig. 3). Further, there is no macroscopic or microscopic evidence of immiscibility in these glasses. In contrast, glasses with higher F contents are milky white and, in the petrographic microscope, clearly show the presence of two isotropic phases, one dispersed as round globules in the other. The Raman spectrum of $\text{CaF}_2 \cdot \text{SiO}_2$ (WoF50, Fig. 1), a sample that is phase-separated, has a small band at ~ 700 and a large band at $\sim 940 \text{ cm}^{-1}$ that are absent from the spectrum of SiO_2 glass. There are other differences in the region below 600 cm^{-1} that are evident as well. The $\sim 940\text{-cm}^{-1}$ band can be attributed to the Si-F stretching vibration in SiO_3F tetrahedra, as discussed previously, that may be present

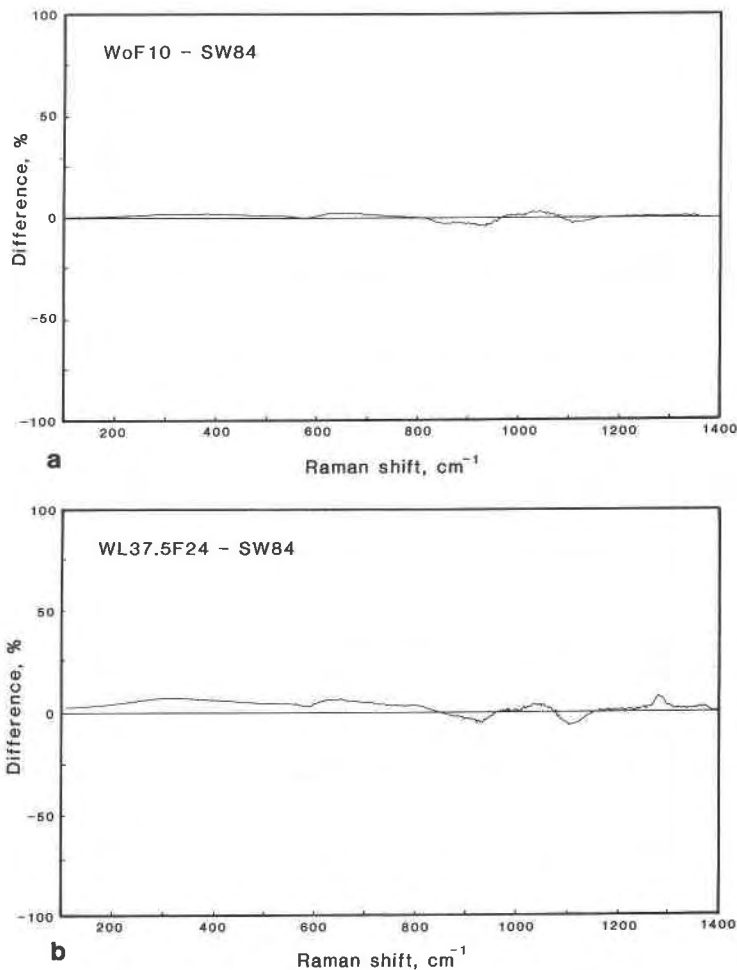


Fig. 6. Difference spectra of glasses along the CaF_2 -SW84 join. (a) WoF10 - SW84. (b) WL37.5F24 - SW84.

in either liquid. It is not known at present what vibrational mode is responsible for the $\sim 700\text{-cm}^{-1}$ band. Nevertheless, the appearance of new bands in this two-phase sample contrasts with the absence of new bands in the other glasses and is supporting evidence that the other glasses were single-phase.

Comparison to more polymerized compositions

The polymerization of the glass accompanying the substitution of F for O found in this study contrasts with the depolymerization observed as F is substituted for O in more polymerized glasses along the NaAlO_2 - SiO_2 join (Mysen and Virgo, 1985b). In both cases, however, F forms complexes with cations other than Si in the liquid. Mysen and Virgo (1985b) found that F forms complexes with Na and Al, but not with Si, in glasses along the NaAlO_2 - SiO_2 join. It should be noted that Hayashi et al. (1987) found resonances in ^{19}F NMR spectra attributed to Si-F complexes as well as to Al-F and Na-F complexes. The formation of Na-F complexes depolymerizes the glass by removing Na from the role of charge-balancing Al in network-forming coordination, and Al becomes a net-

work-modifier. Similarly, the formation of Al-F complexes removes Al from a network-forming role, and Na becomes a network-modifier rather than a charge-balancing cation, again, depolymerizing the glass. If equal amounts of Na and Al are removed from the network, however, there would be no change in the polymerization of the network. The Raman spectra of Mysen and Virgo (1985b) show evidence of depolymerization as F is substituted for O, so this latter possibility can be eliminated, at least for the NaAlO_2 - SiO_2 join. In contrast, in depolymerized glasses in the $\text{CaO-SiO}_2\text{-F}_2\text{O}_{-1}$ system, the glass becomes more polymerized with substitution of F for O because of the formation of Ca-F complexes. This difference reflects the contrast between the roles of metal cations in fully polymerized and depolymerized glasses; metals charge-balance Al in the former, but are network modifiers in the latter.

Implications for phase equilibria and liquid properties

The polymerization of initially depolymerized glasses accompanying the substitution of F for O has implications for the effect of this substitution on phase equilibria

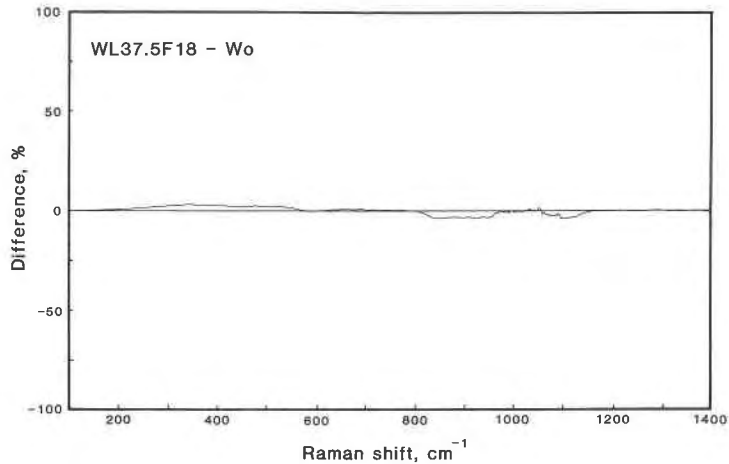


Fig. 7. Difference spectrum of WL37.5F18 - Wo glasses.

and the physical properties of silicate liquids. First, however, the extrapolation of the results from glasses to liquids must be addressed. As reviewed recently by McMillan (1984), a number of workers have compared the Raman and infrared spectra of corresponding glasses and melts and found the spectra to be similar. It is therefore a reasonable assumption that the structures that give rise to vibrational spectra are similar in glasses and melts.

Increased polymerization of the melt should increase the stability field of polymerized minerals at the expense of less-polymerized minerals (Kushiro, 1975). For example, the stability field of orthopyroxene increases relative to the field of olivine in the presence of CO_2 in a model peridotite system (Eggler, 1978). This effect was attributed to the polymerizing effect of the dissolution of CO_2 in the silicate liquid. In an analogous fashion, cotectic boundaries with minerals of differing polymerization should shift away from the more polymerized mineral

with increasing substitution of F for O. The behavior of the enstatite-forsterite cotectic in the system $\text{KAlSiO}_4\text{-Mg}_2\text{SiO}_4\text{-SiO}_2\text{-F}_2\text{O}_{-1}$ at 28 kbar is consistent with this prediction, as discussed by Foley et al. (1986).

If the controlling factor for viscosity in silicate systems is the bulk polymerization of the liquid, the results in the $\text{CaO-SiO}_2\text{-F}_2\text{O}_{-1}$ system suggest that the polymerization of the liquid by the substitution of F for O should be accompanied by an increase in the viscosity of the liquid. This hypothesis cannot be evaluated with available data. Viscosity data for liquids in the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-F}_2\text{O}_{-1}$ system at 1 atm (Dingwell et al., 1985) provide evidence that the substitution of F for O, even in liquids off the fully polymerized $\text{NaAlO}_2\text{-SiO}_2$ join, decreases the viscosity of the liquid. At 75 mol% SiO_2 , the viscosity of albite melt at 1400 °C is depressed more by the substitution of F for O (0.26 \log_{10} units per wt% F) than is the viscosity of either a peralkaline liquid (0.16 \log_{10} units

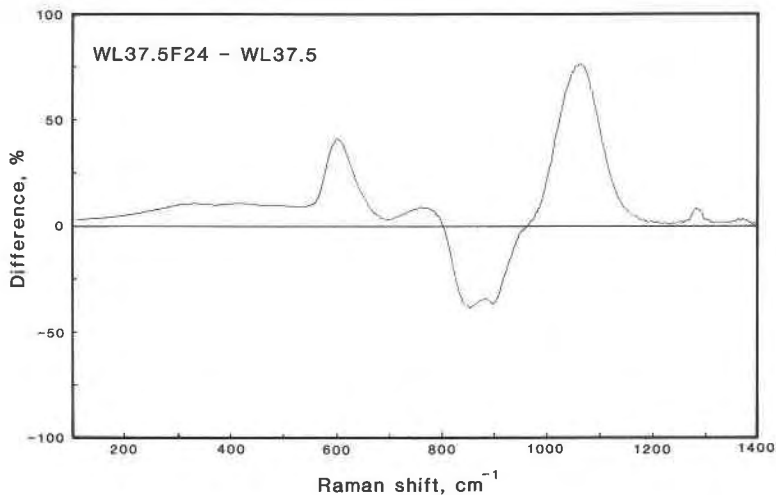


Fig. 8. Difference spectrum of WL37.5F24 - WL37.5 glasses, showing effects of substituting F for O. See text for interpretation of peaks.

per wt% F), or a peraluminous liquid ($0.14 \log_{10}$ units per wt% F). The decrease in the effect of F in the peralkaline and peraluminous liquids is consistent with F forming complexes preferentially with charge-balancing and network-modifying cations rather than with network-forming cations.

In an Al-free liquid in the system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{SiO}_2$, Bacon et al. (1944) observed a decrease in the viscosity of the melt with increasing substitution of F for O. These data cannot be used to test the above prediction, however, because as F increases in their glasses, so does the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio. This change increases the bulk NBO/T, assuming that F formed complexes with Ca, Mg, or Na, and removes a stoichiometric amount of one of these cations from the silicate network. With this assumption, as F increases from 0.0 to 3.6%, the bulk NBO/T increases from 0.66 to 0.78. This change may be sufficient to decrease the viscosity of the liquid, independent of any effect of F. More data are required to address the question of whether polymerization, as gauged by bulk NBO/T, controls the viscosity of F-containing liquids.

Finally, the ease with which F-bearing glasses can be synthesized at 1-atm pressure has some implications for the effects of F in natural systems. Unlike H_2O , which is sparingly soluble at 1 atm in silicate liquids, F is quite soluble; glasses with 10 wt% F can be synthesized without the use of high pressures (Mysen and Virgo, 1985a, 1985b; this study). Therefore, F may remain dissolved in magmas to low pressures and influence their structure and eruptive and crystallization behavior.

For example, the mode of eruption of topaz rhyolites may, in part, result from the different behavior of H_2O and F at low pressure. Rhyolitic magmas with high water contents tend to erupt explosively because of the exsolution of water, forming tuff deposits. Similar magmas with little water but a high F content, in contrast, may not erupt explosively, because the F does not exsolve as much at low pressure. These magmas would be emplaced as domes or flows. Magmas with both high water and high F contents may initially erupt explosively, forming tuffs, until the water is scavenged from the magma, and then erupt quiescently, emplacing the F-rich magma as flows or domes. The effect of F on the lowering of the viscosity of these highly polymerized, Al-bearing liquids may influence whether a dome or a flow is formed; the higher the F content, the lower the viscosity and the greater the tendency for the magma to form a flow (e.g., Dingwell et al., 1985).

In contrast to the F-rich rhyolites just discussed, relatively depolymerized, F-rich ultrapotassic magmas may be more likely to erupt explosively if, as suggested above, the presence of F in depolymerized liquids increases the viscosity of the liquid relative to the F-free liquid. Studies on the effect of F in depolymerized liquids are required to test this hypothesis.

Despite the recent work on F in silicate glasses and liquids, there remain fundamental questions concerning the behavior of F in silicate liquids. Little is known about

the combined effects of F and water on the structure of the liquid, nor is anything known about the effect of F on the structure of depolymerized liquids containing Al. This latter case is a more realistic model of many natural magmas than either the fully polymerized or depolymerized cases studied to date. Study of the effects of F on such compositions will provide information on the relative stabilities of complexes of F with network-formers like Al and with charge-balancing and network-modifying cations like Na and Ca. The relative stability of these complexes will control whether addition of F will polymerize or depolymerize the liquid and will likely control the effects of F on the physical and chemical properties of the melt.

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