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LETTER

NMR evidence for five- and six-coordinated aluminum fluoride complexes in F-bearing aluminosilicate glasses

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ABSTRACT

Anhydrous glasses of jadeite + NaF and jadeite + cryolite compositions were quenched from melts at 1250 °C and 3.0–3.5 kbar. ^{19}F to ^{27}Al cross-polarization MAS-NMR experiments at a magnetic field of 8.45 T and single pulse ^{27}Al MAS-NMR experiments at 14.1 T demonstrated the presence of $^{[4]}Al$, $^{[5]}Al$, and $^{[6]}Al$ in both glasses. The $^{[5]}Al$ is thought to be present in AlF_5^{2-} complexes, a previously unknown species.

INTRODUCTION

The presence of dissolved volatile components in natural magmas has long been recognized as being of crucial importance in controlling their physical properties and volcanic eruptive behavior. The effect of F is particularly significant in strongly differentiated felsic magmas; it affects phase relations (Wyllie and Tuttle, 1961; Manning, 1981; Foley et al., 1986) and lowers viscosities (Dingwell, 1987). These effects are similar to those of H_2O, and similar dissolution mechanisms for these two volatile components have often been proposed. The phase relations of F-bearing systems combined with thermodynamic arguments have been used to infer structural features such as the presence of AlF_6^{3-} units (Manning et al., 1980; Burnham and Nekvasil, 1986) and the absence of Si-F bonds (Kogarko and Krigman, 1973). Mysen and Virgo (1985) interpreted Raman spectra of glasses of $NaAlSi_3O_{8-x}F_{2x}$ and $NaAlSi_7O_{16-x}F_{2x}$ composition in terms of F^- charge balanced by Na^+, Al^{3+}, and Na_3Al^{6+}, with a resultant depolymerization of the silicate framework and the formation of Q^3-O^- and Q^2-$(O^-)_2$ units in addition to residual Q^4 units. Foley et al. (1986) used phase equilibrium results in the Ks-Fo-Qz + F system, together with infrared studies of quenched glasses to infer the presence of F complexes with K, Mg, and Al. They also stressed that bulk composition crucially affects the solubility mechanism, particularly whether F replaces O or is added as a metal fluoride. This is an important point because the compositions used here were made by adding fluorides, whereas in some other studies addition of F was accompanied by removal of O.

NMR is an ideal technique for studying the structure of glasses (see Kirkpatrick et al., 1986 and Dupree and Holland, 1989 for reviews) as the chemical shift is sensitive to local environment and gives information on coordination numbers. Recently ^{27}Al NMR has been used to demonstrate the presence of $^{[5]}Al$ and $^{[6]}Al$ in a variety of glasses and other amorphous solids in the system Al_2O_3-SiO_2 (Dupree et al., 1985; Risbud et al., 1987; Farnan et al., 1989). In this study we use single-pulse ^{27}Al magic-angle-spinning (MAS) NMR methods at two different magnetic fields (8.45 T and 14.1 T) and ^{19}F-^{27}Al cross-polarization (CP) to study aluminum complexing in glasses quenched from F-bearing melts and to deduce information on the polymerization of such melts.

EXPERIMENTAL DETAILS

A glass of jadeite composition was prepared from SiO_2, Al_2O_3, and Na_2CO_3 by melting at 1500 °C for 3 h and cooling rapidly. Mixtures of this material with NaF (to produce the Jd-NaF glasses) and with cryolite (to produce the Jd-Cry glasses), with or without the addition of H_2O, were melted at pressures between 2 and 3.5 kbar and temperatures of 1200–1300 °C in an internally heated pressure vessel using standard techniques and quenched. Optical examination and X-ray diffraction showed that the two anhydrous glasses were completely free of any crystalline material; however the hydrous glasses contain many tiny ($<10^{-7}$ m) crystals of cryolite, which must have formed during the quench. Essentially all the F in the hydrous glasses is present in the cryolite quench crystals. The presence of quench cryolite crystals in hydrous F-bearing glasses has been used to support the idea that cryolite-like complexes are present in the melt prior to quenching (Manning et al., 1980), and this interpretation could be consistent with the fact that cryolite rather than

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TABLE 1. Conditions of glass synthesis

Sample	Composition	wt % H_2O	Synthesis conditions T/°C	P/kbar	Time/h
Dry Jd-NaF	$Na_3Al_2Si_4O_{12}F$	0	1250	3.5	3.5
Hydrous Jd-NaF	$Na_3Al_2Si_4O_{12}F$	7.5	1270	2.0	2.5
Dry Jd-Cry	$Na_{3.67}Al_{3.33}Si_{6.33}O_{19}F$	0	1250	3.0	6.0
Hydrous Jd-Cry	$Na_{3.67}Al_{3.33}Si_{6.33}O_{19}F$	5.0	1250	3.0	6.0

NaF quench crystals are present even in the hydrous Jd-NaF glass. Only the spectra for the anhydrous glasses will be presented here, and the subsequent discussion will also apply only to the anhydrous glasses. The glasses were analyzed by electron probe microanalysis, and the compositions in terms of Si, Al, and Na were very close to the expected values. The measured concentrations of F were slightly lower than expected (5–10% low), but because there may be difficulties in analyzing volatile bearing glasses, the nominal compositions are assumed to be correct and are given together with the synthesis conditions of the glasses in Table 1. It should be noted that the amount of dissolved F (expressed as the F/(F + O) ratio for example) is considerably lower for the Jd/Cry sample than the Jd-NaF sample. ^{27}Al and ^{19}F-^{27}Al CP-MAS spectra were obtained at a frequency of 93.83 MHz using a Bruker MSL 360 spectrometer. To improve the resolution among the different species present, some additional spectra were obtained at a higher magnetic field using a homemade probe and a Varian VXR 600 (magnetic field 14.1 T) operating at 156.325 MHz. This higher field will narrow the resonance if quadrupolar broadening, arising from the electric field gradient at the nucleus, is a major contribution to the linewidth. Fitzgerald et al. (1989) have used previously a 14.1 T spectrometer to obtain significantly improved data for $^{[5]}$Al in dehydrated pyrophyllite.

RESULTS AND DISCUSSION

The MAS-NMR spectrum of F-free, anhydrous jadeite glass (Fig. 1a) consists of a single peak at ~55 ppm due to $^{[4]}$Al, which is broadened to the more shielded side of the peak. This line shape is typical of ^{27}Al in glasses or materials where a distribution of electric field gradients is present (Phillips et al., 1988; Kohn et al., 1989). The addition of NaF (Fig. 1b) results in a significant narrowing of the main part of the tetrahedral peak and the appearance of an additional peak at −5 ppm, a typical chemical shift for $^{[6]}$Al. In addition there appears to be a change in slope of the right hand edge of the tetrahedral peak at about 30 ppm. In the absence of other data, this shoulder could result from a relatively narrow peak with an isotropic chemical shift of about 25 ppm or a much broader feature with an isotropic shift similar to that of the tetrahedral peak, broadened to more negative shifts.

The changes in the ^{27}Al spectrum on the addition of cryolite (Fig. 1c) are very small, although it again seems that the tetrahedral peak is narrowed, that there is a change in its slope at around 30 ppm, and that a very small octahedral peak is produced.

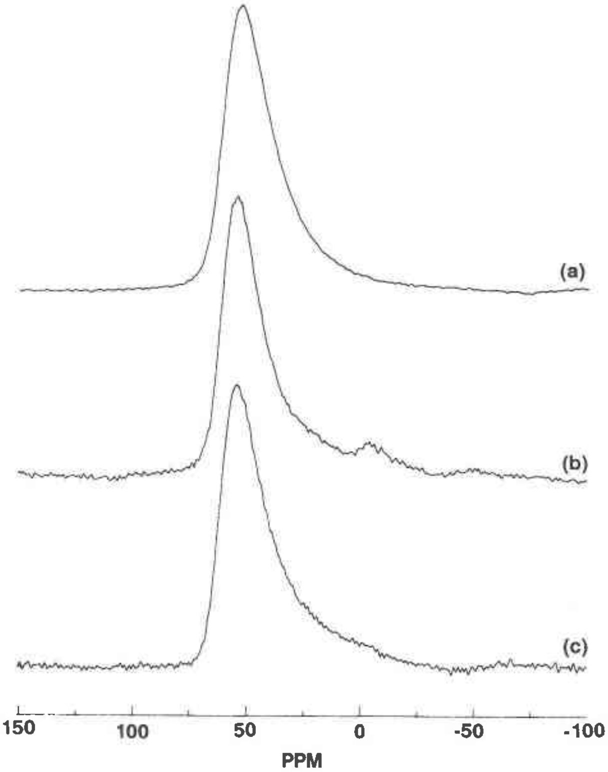

Fig. 1. The ^{27}Al MAS-NMR spectra obtained at 93.83 MHz, using a pulse length of 1 μs ($\pi/12$) and a recycle delay of 2 s. (**a**) F-free jadeite glass, 1600 pulses; (**b**) Jd-NaF glass, 500 pulses; (**c**) Jd-Cry glass, 400 pulses.

Cross-polarization from ^{19}F to an abundant nucleus such as ^{27}Al is effectively a method of spectral editing because it enhances the signal from Al nuclei near F nuclei relative to the signal from other Al nuclei. The ^{19}F-^{27}Al CP spectra for both the F-bearing glasses (Fig. 2) consist of three peaks at 57 ppm, ~22 ppm, and −1 ppm. The 57 ppm and −1 ppm peaks are clearly due to $^{[4]}$Al and $^{[6]}$Al, respectively. However, the position of the 22 ppm peak is outside the normal ranges for either. F does not appear to have a large effect on the chemical shift of $^{[6]}$Al, since AlO_6, AlF_6, and AlO_4F_2 (in topaz, our unpublished data) all have similar shifts, near 0 ppm, therefore the 22 ppm peak seems likely to be caused by $^{[5]}$Al. Furthermore, because the peak is enhanced in the CP spectrum, it must have F in its coordination shell. As the peak has a relatively narrow resonance, it can probably be assigned to AlF_5^{2-} because mixed pentahedra would probably have large electric field gradients and give a very broad line. An alternative possibility, which could conceivably give rise to a small field gradient, is a mixed O and F pentahedron, with a either a trigonal arrangement of three O atoms and two *trans* F atoms, or the same arrangement with the F and O transposed, i.e., three F atoms and two O atoms. In addition it should be noted that the shift is significantly different from that of AlO_5 groups, which have isotropic shifts in the range 30–40 ppm. We have

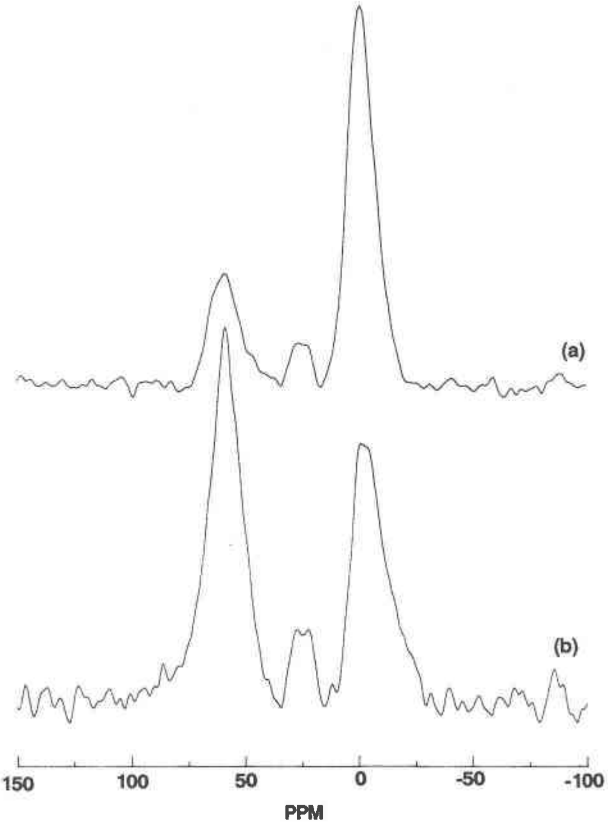

Fig. 2. The ^{19}F-^{27}Al CPMAS-NMR spectra obtained using a ^{19}F pulse length of 5 μs, a contact time of 1 ms, and a recycle delay of 10 s. (**a**) Jd-NaF glass, 3000 pulses; (**b**) Jd-Cry glass, 2308 pulses.

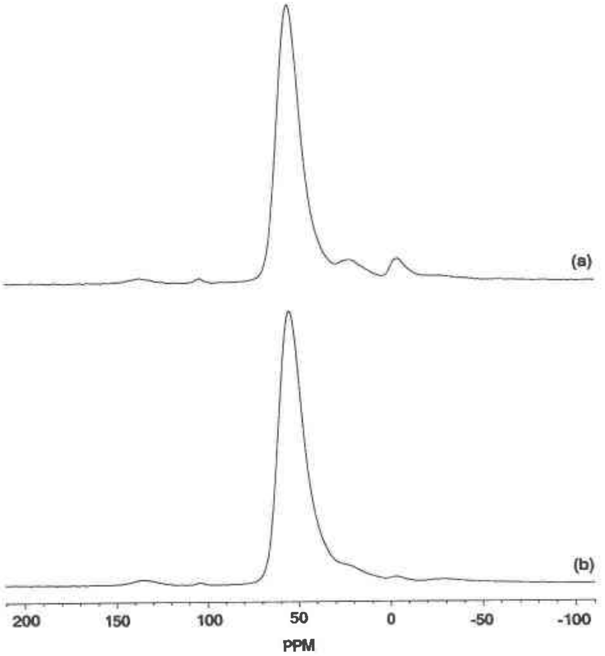

Fig. 3. The ^{27}Al MAS-NMR spectra obtained at 156.325 MHz, using a pulse length of 2 μs ($\pi/12$) and a recycle delay of 0.5 s. (**a**) Jd-NaF glass, 1632 pulses; (**b**) Jd-Cry glass, 1824 pulses.

also performed variable contact-time experiments on the Jd-NaF glass. For shorter contact times than the 1 ms illustrated in Figure 2a the $^{[5]}$Al peak is relatively larger, and the $^{[4]}$Al peak is relatively smaller, compared with the $^{[6]}$Al peak. For longer contact times, the opposite is true. This shows that most of the $^{[4]}$Al peak is due to Al not directly coordinated to F, because AlF$_4^-$ units would have shorter Al-F bonds and hence would be likely to have shorter optimum contact times than AlF$_5^{2-}$ and AlF$_6^{3-}$. However, a significant $^{[4]}$Al peak can be seen for contact times as short as 0.1 ms, suggesting that some AlF$_4^-$ may be present. The fact that the $^{[5]}$Al peak is increased in intensity relative to the $^{[6]}$Al peak for shorter contact times indicates that the Al-F distance is shorter in the $^{[5]}$Al complex, as would be expected. There are interesting differences in the relative intensities of the three peaks for the 1 ms contact time spectra of the two samples. Although the overall intensity for the Jd-Cry sample is less than that for the Jd-NaF sample, it has larger $^{[4]}$Al/$^{[6]}$Al, $^{[4]}$Al/$^{[5]}$Al, and $^{[5]}$Al/$^{[6]}$Al ratios.

As the three peaks observed in the CP experiments on the anhydrous F-bearing glasses were not resolved in our 8.45 T single pulse experiments, we also obtained single pulse spectra at 14.1 T, the highest available field on a commercial spectrometer. These spectra are shown in Figure 3. The spectrum for the Jd-NaF glass contains three clearly resolved peaks at 56 ppm ($^{[4]}$Al), 22 ppm ($^{[5]}$Al), and −4 ppm ($^{[6]}$Al). The Jd-Cry glass appears to yield the same three peaks, although the $^{[5]}$Al peak is not as well resolved because the $^{[5]}$Al/$^{[4]}$Al ratio is smaller and the $^{[4]}$Al peak is broader than that in the Jd-NaF glass. The position of the $^{[5]}$Al peak is the same as that in the CP spectrum, despite the difference in applied magnetic field; this indicates that the true isotropic chemical shift is close to the peak position. Accurate quantification of the 14.1 T data is difficult because of problems with fitting the line shapes, possible loss of signal from broad components during the dead time of the spectrometer, etc. However an estimate gives the following figures for the percentage of Al in each coordination state:

Jd-NaF glass,

$$^{[4]}\text{Al} = 93.5\%, \quad ^{[5]}\text{Al} = 2.7\% \quad ^{[6]}\text{Al} = 3.8\%;$$

Jd-Cry glass,

$$^{[4]}\text{Al} = 98.1\%, \quad ^{[5]}\text{Al} = 1.3\%, \quad ^{[6]}\text{Al} = 0.7\%.$$

Note that the $^{[4]}$Al/$^{[6]}$Al, $^{[4]}$Al/$^{[5]}$Al, and $^{[5]}$Al/$^{[6]}$Al ratios are all larger for the Jd-Cry glass than the Jd-NaF glass, the same result as from the CP spectra.

Although we would not wish to overemphasize the significance of these figures, it appears that in both cases some F is present in a form other than AlF$_5^{2-}$ or AlF$_6^{3-}$ complexes (approximately 30% for the Jd-NaF glass and around 60% for the Jd-Cry glass). As discussed above, some may be present as AlF$_4^-$ complexes or as $^{[4]}$Al in the framework with one or more F atoms replacing bridging O atoms, or alternatively in complexes with Na or attached to framework Si. The presence of the Al-F complexes implies the presence of nonbridging O atoms, probably attached to framework Si. This would be consistent with our ^{29}Si data (not shown), as the shift in anhydrous Jd-NaF glass is −89.5 ppm compared with −93 ppm in the jadeite glass.

The presence of a ^{27}Al peak at about 22 ppm, which we have assigned to AlF_5^{2-}, is a very unexpected feature. We know of no crystalline compounds containing $^{[5]}Al$ coordinated by F, therefore this appears to be the first observation of this species in any material. However, a recent computer simulation has suggested the presence of small concentrations of the AlF_5^{2-} species in cryolite melt in addition to the major species, Na^+, AlF_6^{3-}, AlF_4^-, and F^- ions (Qiu and Xie, 1988). The observation of a new species in a glass is not unprecedented; for example $^{[5]}Si$ has been observed in $K_2Si_4O_9$ glass quenched from high pressure, whereas it is not known in any crystalline silicates (Stebbins and McMillan, 1989).

These results may help explain some previous observations on the effect of F in aluminosilicate systems. For example, Luth and Muncill (1989) have shown that the presence of F in anhydrous plagioclase melts decreases the activity of the anorthite component relative to the albite component. They suggested that this result is due to F preferentially complexing Ca rather than Na. The results reported here (and also some unpublished results for the $NaAlSi_3O_7F_2$ composition) suggest that much of the F is involved in complexes with Al. An alternative explanation of Luth and Muncill's (1989) results is that the remaining Al (that which is not in fluoride complexes) is preferentially charge balanced by Na rather than Ca [due to the relative stabilities of the $NaAlO_2$ and $Ca_{0.5}AlO_2$ complexes (Navrotsky et al., 1982)], in effect resulting in a decreased activity of anorthite in the melt.

In conclusion this work has shown that the solution mechanism of F appears to be entirely different from that of H_2O (Kohn et al., 1989). The broad similarity in the effects of H_2O and F on viscosity and phase relations would therefore appear to be coincidental. Further work is currently underway to investigate changes in the solubility mechanisms when F is added as F_2O_{-1} instead of NaF or Na_3AlF_6, and the roles of varying Al/Si and bulk NBO/T ratios.

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