

LETTER

Al coordination in magnesium aluminosilicate glasses

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ABSTRACT

High coordinate (five- and sixfold) Si and Al species have been previously observed by MAS NMR techniques in binary silicate and peraluminous aluminosilicate glasses and gels. For liquids along the charge-balanced joins $\text{SiO}_2\text{-MAlO}_2$ or $\text{SiO}_2\text{-M}'\text{Al}_2\text{O}_4$ (M = alkali metal; M' = alkaline earth), such high coordinate species have not yet been observed experimentally, although their presence has been inferred from molecular dynamics simulations and NMR experiments on high-temperature liquids. In the present study, we report the observation, by ^{27}Al MAS NMR spectroscopy, of AlO_5 and AlO_6 species in glasses with peraluminous compositions near the $\text{SiO}_2\text{-MgAl}_2\text{O}_4$ join.

INTRODUCTION

The coordination behavior of Al in aluminosilicate liquids and glasses is of great importance for understanding the thermochemistry and rheology of natural magmas. For glasses and liquids with compositions $M_2\text{O}/\text{Al}_2\text{O}_3$ or $MO/\text{Al}_2\text{O}_3 \geq 1$ (M = alkali metal; M' = alkaline earth), most structural studies to date have concluded that Al is in tetrahedral coordination, replacing Si in corner-shared aluminosilicate polymers (Taylor and Brown, 1979; McMillan et al., 1982; Mysen et al., 1982, 1983, 1985; Matsson et al., 1986; Oestrike et al., 1987; Merzbacher et al., 1990). Fivefold- and sixfold-coordinated Al species (^{51}Al and ^{61}Al) have been observed using ^{27}Al MAS NMR for some highly peraluminous compositions (Dupree et al., 1985; Risbud et al., 1987; Farnan et al., 1989; Sato et al., 1991a, 1991b), and a signal for minor quantities of ^{61}Al species has recently been reported for $\text{Na}_2\text{Si}_2\text{O}_5$ glass with 6 mol% of Al_2O_3 component (Stebbins and Farnan, 1992). However, to date, only ^{41}Al has been detected in NMR studies of glasses with compositions near the charge-balanced joins with $M_2\text{O}/\text{Al}_2\text{O}_3$ or $MO/\text{Al}_2\text{O}_3 = 1$ (Oestrike et al., 1987; Merzbacher et al., 1990; Sato et al., 1991b; Coté et al., 1992), even for samples prepared at pressures up to 10 Gpa (Stebbins and Sykes, 1990; Sykes et al., in preparation).

Recent molecular dynamics simulations for aluminosilicate liquids with charge-balanced compositions (Scamehorn and Angell, 1991) have found a distribution of fourfold- and fivefold-coordinated Al and Si sites, along with some sixfold-coordinated sites. A recent ^{27}Al NMR study of liquids along the $\text{SiO}_3\text{-CaAl}_2\text{O}_4$ join (Coté et al., 1992) has shown that the chemical shifts of the liquid

samples occur at less positive values than the isotropic chemical shifts of ^{41}Al in the corresponding glasses. This observation also suggests the presence of Al with coordination greater than four.

We present here a ^{27}Al magic angle spinning (MAS) NMR study of glasses with slightly peraluminous compositions close to the $\text{SiO}_2\text{-MgAl}_2\text{O}_4$ join, prepared using solar furnace melting and rapid quench techniques (McMillan et al., 1982). A previous ^{27}Al NMR study of glasses in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system found no evidence for any high coordinate Al species (Merzbacher et al., 1990). However, that study used normal laboratory quenching, a lower H_0 field, and slower MAS spinning frequencies.

EXPERIMENTAL

Samples were prepared from stoichiometric oxide mixes, which were melted into boules by solar heating at approximately 2500–3000 °C (McMillan, 1981; McMillan et al., 1982). Two glass samples [nominally $\text{S}_{90}\text{M}_{10}$ and $\text{S}_{70}\text{M}_{30}$: the subscripts refer to mole percent components SiO_2 (S) and MgAl_2O_4 (M)] were formed by simply removing the sample from the focus of the solar beam, to give a normal quench (NQ) rate of approximately 500 °C/s. Two other glass samples, with normal compositions $\text{S}_{50}\text{M}_{50}$ and $\text{S}_{30}\text{M}_{70}$, were prepared by splat (hammer) quench (SQ) techniques, with a quench rate on the order of $10^6\text{-}10^7$ °C/s. This rapid quench rate was required to vitrify the samples with lower silica content.

The final compositions determined by electron microprobe (Table 1) were slightly peraluminous because of the loss of SiO_2 and MgO during the solar melting experiment (McMillan, 1981; McMillan et al., 1982). The large stan-

TABLE 1. Glass compositions studied

Quench rate*	Sample	MgO	Al ₂ O ₃	SiO ₂	Σ
NQ	S ₉₀ M ₁₀	5.2**	6.2	88.7	98.4
		±2.3†	±3.1	±5.4	±1.6
NQ	S ₇₀ M ₃₀	16.1	18.0	65.9	100.6
		±0.9	±1.1	±1.9	±1.8
SQ	S ₅₀ M ₅₀	26.9	29.6	43.5	100.4
		±0.6	±0.5	±0.7	±1.7
SQ	S ₃₀ M ₇₀	35.6	39.9	24.5	100.6
		±0.4	±0.3	±0.5	±0.8

* Quench rate: NQ = "normal quench," approximately 500 °C/s; SQ = splat quench, 10⁶–10⁷ °C/s.

** Mean in mol% oxide of 20–30 point analyses.

† This value is ±2σ of 20–30 point analyses.

standard deviation in the chemical analysis for the S₉₀M₁₀ sample indicates a lower degree of chemical homogeneity than for the other samples. No microscopic unmixing has been reported in the SiO₂-MgAl₂O₄ glass system, but the enthalpies of mixing indicate a tendency for phase separation at high silica content (Navrotsky et al., 1985). The S₃₀M₇₀ sample contains some quench crystals of MgAl₂O₄ spinel, identified by X-ray diffraction and also detected in the ²⁷Al NMR spectra (Fig. 1). The S₅₀M₅₀ sample originally contained a few crystals, but these were easily removed by hand-picking under a microscope. The sample examined by NMR contains no crystals. The S₉₀M₁₀ and S₇₀M₃₀ samples are also crystal free.

The ²⁷Al and ²⁹Si MAS NMR spectra were obtained for samples of 20 to 30 mg at H₀ = 11.7 T and MAS frequencies of approximately 11 kHz for ²⁷Al and 7 kHz for ²⁹Si. The ²⁷Al chemical shifts are reported in parts per million relative to 1 M aqueous AlCl₃ solution and ²⁹Si chemical shifts relative to tetramethylsilane. Because of unaveraged second-order quadrupolar effects, the ²⁷Al peak maxima do not correspond to the isotropic chemical shifts, but because the H₀ field and MAS spinning frequencies were the same for all samples, the peak positions can be compared. An empty zirconia rotor yields a weak ²⁷Al probe background, which does not affect the results described here.

RESULTS AND SPECTRAL INTERPRETATION

All of the ²⁷Al NMR spectra have a principal asymmetric peak with a maximum at 50–60 ppm, which is caused by ¹⁴AlO₄ sites in the glasses (Fig. 1). This is the only obvious peak or shoulder in the spectrum of the S₇₀M₃₀ sample, but it is broader for this sample than the ¹⁴Al peaks previously observed for aluminosilicate glasses (e.g., Oestrike et al., 1987).

In addition to this principal resonance, the spectrum of the S₅₀M₅₀ sample also contains well-defined maxima near 35 and 10 ppm. Because of the high magnetic field and fast MAS frequencies, these additional peaks are not spinning sidebands and can be assigned to fivefold- and sixfold-coordinated AlO₅ and AlO₆ species, respectively (Dupree et al., 1985; Risbud et al., 1987; Farnan et al., 1989; Brow et al., 1990; Sato et al., 1991a, 1991b; Bunker et al., 1991; Poe et al., 1992). It is unlikely that the peaks

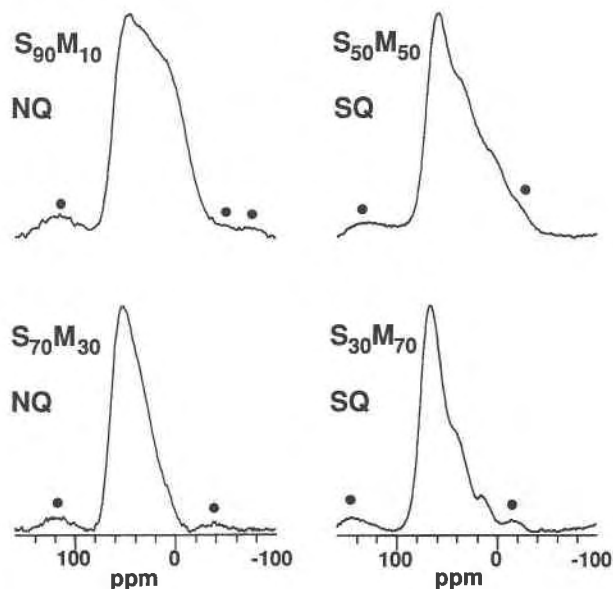


Fig. 1. The ²⁷Al MAS NMR spectra for normal-quenched (NQ) samples S₉₀M₁₀ and S₇₀M₃₀, and splat-quenched (SQ) samples S₅₀M₅₀ and S₃₀M₇₀. Peaks marked with dots are spinning sidebands.

near 35 and 10 ppm represent the more shielded parts of peaks split by unaveraged second-order quadrupolar effects. Such splitting for ²⁷Al NMR peaks appears to be rare for oxide glasses, probably because of the presence of Al sites of each nearest neighbor coordination with a range of quadrupole coupling constants and asymmetry parameters (see references above). Merzbacher et al. (1990) studied a sample close to this composition, prepared by normal quench techniques, and found evidence for only ¹⁴Al species by ²⁷Al MAS NMR spectroscopy.

The overall peak envelope for the S₃₀M₇₀ glass is much narrower than that for the S₅₀M₅₀ sample, but there is a definite shoulder at 35–40 ppm, which indicates the presence of some AlO₅. There is also a weak peak at 14 ppm in this spectrum that is much sharper than the features due to glass. This peak is due to a small amount of crystalline MgAl₂O₄ in the sample. The spectrum for sample S₉₀M₁₀ is very broad, with a broad asymmetric maximum extending from near 50 ppm to 5 ppm. A weak maximum near 35 ppm and a shoulder near 10 ppm suggest the presence of AlO₅ and AlO₆ groups in this sample, and there is clearly a wide range of structural environments.

Because of the small sample sizes we could obtain a ²⁹Si MAS NMR spectrum for only the S₇₀M₃₀ sample. This spectrum contains a single, broad peak near -100 ppm, caused by ¹⁴SiO₄ groups. No peaks due to SiO₅ or SiO₆ species (Stebbins and McMillan, 1989; Xue et al., 1989, 1991) can be resolved at a minimum detection limit of about 1–2%.

DISCUSSION

These results demonstrate that even mildly peraluminous aluminosilicate glasses can contain substantial

amounts of high coordinate Al species. Because the MgO/Al₂O₃ ratio is in fact close to unity (1.1–1.2), these results indicate that ²⁷Al and ²⁹Al species might well be present in glasses along the SiO₂-MgAl₂O₄ join, in agreement with the prediction from the molecular dynamics simulations for liquids along this join (Scamehorn and Angell, 1991), and also with the observations of Coté et al. (1992) for SiO₂-CaAl₂O₄ liquids.

Because these high coordinate Al species, especially AlO₅, are likely to have a positive formation enthalpy relative to ⁴AlO₄ groups, their abundance in the melt should increase with increasing temperature (Stebbins, 1991; Poe et al., 1992). These groups should also be more abundant in glasses prepared with a faster quench rate, which have a higher fictive temperature (Sato et al., 1991a; Poe et al., 1992). Assuming an infinite frequency shear modulus of $G = 10^{10}$ Pa, the measured viscosities of these compositions (Riebling, 1964) define structural relaxation times on the order of 10⁻⁷–10⁻¹⁰ s (Dingwell and Webb, 1990). These relaxation times are shorter than the time scale defined by the quench rate of these glass synthesis experiments (on the order of 10⁻⁶–10⁻⁷ s for the splat-quenched samples, and 10⁻²–10⁻³ s for the normal quench). The amounts of ²⁷Al and ²⁹Al preserved in these glasses are, therefore, a lower limit to their abundance in the high-temperature liquids (Dingwell and Webb, 1990). Thus, it is impossible to use the present results to ascertain, even qualitatively, the effect of silica content on the relative proportions of fourfold-, fivefold-, and sixfold-coordinated species. Because the viscosity of these liquids is a strong function of composition (Riebling, 1964), the degree of structural relaxation during the quench is different for each sample.

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