# LETTER

# Fivefold-coordinated aluminum in tectosilicate glasses observed by triple quantum MAS NMR

# MICHAEL J. TOPLIS,<sup>1,\*</sup> SIMON C. KOHN,<sup>2</sup> MARK E. SMITH,<sup>3</sup> AND IAIN J.F. POPLETT<sup>3</sup>

<sup>1</sup>CRPG-CNRS, BP20, F-54501, Vandoeuvre-lès-Nancy, France <sup>2</sup>Department of Earth Sciences, University of Bristol, Wills Memorial Building, Bristol, BS8 1RJ U.K. <sup>3</sup>Department of Physics, University of Warwick, Coventry, CV4 7AL, U.K.

## ABSTRACT

Eight glasses with molar Mg/2Al  $\approx$  1 in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> have been studied by magic angle spinning (MAS) NMR spectroscopy. Using triple quantum (3Q) NMR techniques we find evidence for significant concentrations of Al coordinated to five O atoms in all glasses, the proportion increasing with decreasing Mg/Al and decreasing silica content. In glasses with Mg/2Al = 1, up to 6% of the Al is estimated to be coordinated to five rather than four O atoms. Calculations of the polymerization state of these liquids made assuming that all aluminum is in tetrahedral coordination charge balanced by magnesium are thus seriously in error. Such errors may be of even greater importance at the high temperatures and pressures relevant to the Earth and materials sciences.

#### INTRODUCTION

The continuous random network model (Zacharaisen 1932) has been a remarkably useful basis for understanding the structure and properties of silicate melts. An essential feature of this model is the assignment of cations to network forming and network modifying roles (e.g., Mysen 1988). The former are generally small, highly charged cations tetrahedrally coordinated to oxygen, while the latter are larger monovalent and divalent cations which are coordinated to more than four O atoms. This concept may be used to quantify the "polymerization" of the melt, for example, by taking the ratio of the number of non-bridging O atoms (NBO) to the number of tetrahedrally coordinated network forming cations (T). This molar ratio "NBO/T" has been extensively used to rationalize the variation of physical and thermodynamic properties of silicate melts as a function of composition. The distinction between network forming and network modifying is somewhat artificial as there is obviously a continuum of behavior between these two extremes. Furthermore, it is difficult to account for unusual coordination states within this framework. Nonetheless it provides a simple starting point, upon which a more sophisticated treatment can be built. For Al3+, which has an intermediate charge and radius, it is generally assumed that association with "charge balancing" cations ( $M^{n+}$ , e.g.,  $Na^+$ , Ca<sup>2+</sup>) will stabilize aluminum in tetrahedral coordination wherever possible (Mysen 1988). Therefore, addition of aluminum to a depolymerised silicate melt will remove metal cations from network modifying roles until no more non-bridging O atoms remain. If all Al is incorporated in this way, NBO/T will fall to zero when the molar ratio  $M^{n+}/nAl = 1$  (the "charge balanced join"). If further Al is added, the "excess" Al may play a network modifying role, thus depolymerising the network, or alternatively may remain tetrahedrally coordinated, but associated with a three coordinated oxygen in a configuration known as a tricluster (Lacy 1963). It has been recently proposed that such triclusters may even occur in compositions with  $M^{n+}/nAl \ge 1$ (Toplis et al. 1997; Stebbins and Xu 1997). On the other hand no evidence for more than 1% high coordinated Al has been reported in glasses with  $M^{n+}/nAl = 1$  (Baltisberger et al. 1996; Stebbins et al. 2000), although early 1D <sup>27</sup>Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of magnesium aluminosilicate glasses with Mg/2Al slightly less than 1 demonstrated that five and six coordinated aluminum (VAI and <sup>VI</sup>Al) are present (McMillan and Kirkpatrick 1992).

To establish whether Al with a high coordination number is present in glasses with Mg/2Al > 1 we applied state-of-the-art NMR techniques to study the local environment of Al in glasses

<sup>\*</sup> E-mail: mtoplis@crpg.cnrs-nancy.fr

from the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. The compositions were chosen to determine how the proportion of highly coordinated Al varies as a function of Mg/Al ratio and silica content.

#### **EXPERIMENTAL METHODS AND RESULTS**

Three series of glasses at fixed silica content (nominally 50, 67, and 75 mol%) were synthesized, each one spanning the charge balanced join (Mg/2Al = 1) from compositions with an excess of Mg to an excess of Al. For each series two end-member glasses were made from mixtures of reagent grade oxides fused at 1600 °C at one atmosphere. Intermediate compositions were mixtures of weighed proportions of the two end-members, mechanically stirred at 1600 °C for periods up to 12 hours to ensure homogeneity. Of the 24 glasses synthesized in this way, four with 50 mol% SiO<sub>2</sub> and two each with 67 and 75 mol% SiO<sub>2</sub> were examined here. Sample compositions were determined using an SX50 electron microprobe (Nancy, France) running at 15kV, 10nA, and a defocused beam diameter of 20 micrometers.

All <sup>27</sup>Al NMR spectra were collected using a Chemagnetics Infinity 600 operating at a resonance frequency of 156.38 MHz and a 3.2 mm magic angle spinning (MAS) probe with MAS at ~18 kHz. The 1D MAS spectra (Fig. 1) were collected under excitation and relaxation conditions that ensured the quantitative integrity. The resulting spectra show evidence for <sup>v</sup>Al in



FIGURE 1. <sup>27</sup>Al MAS NMR spectra of glasses with 50 mol% SiO<sub>2</sub>.

addition to <sup>IV</sup>Al, but because of quadrupolar broadening of the peaks, it is not possible to quantify their relative proportions. To resolve the two components of the spectra, triple quantum (3Q) MAS NMR was used (Medek et al. 1995). The phase modulated split-t1 method (Brown and Wimperis 1997) was employed, with a 145 kHz excitation on resonance radio frequency (r.f.) field. The spectra were accumulated with an echo time of 0.5 ms with ~1000 scans for each of the 80 to 100 slices spaced by 20 ms. A relaxation delay of 0.5 s was used with total spectral widths of 50 and 65 kHz in the F1 and F2 directions respectively. Resonance and MAS frequencies were those employed for the 1D MAS spectra. The 3Q <sup>27</sup>Al spectra confirm that <sup>v</sup>Al is present in all of the studied glasses, but no evidence for <sup>VI</sup>Al was found (Fig. 2).

The concentrations of <sup>IV</sup>Al and <sup>V</sup>Al were quantified by projecting the 2D 3Q data onto the isotropic axis, then fitting the resulting one-dimensional spectrum with two Gaussian peaks (Fig. 3). One potential problem in extracting quantitative information from MQ MAS spectra is that the efficiency of exciting multiple quantum coherence depends in a complex way on the magnitude of the quadrupole coupling constant and the r.f. field (Iuga et al. 1999). The NMR interactions can be estimated from the positions of the signals in both spectral dimensions (Brown and Wimperis 1997) and give mean values for the quadrupole interaction ( $C_0$ ) of ~6 MHz for <sup>IV</sup>Al and  $\leq$ 5 MHz for <sup>v</sup>Al. The main problem with this approach in amorphous materials is the asymmetry of the lineshape in the F2 dimension resulting from the distribution of interactions, which makes it difficult to estimate the center of gravity. However these values for  $C_0$  agree well with those determined for the same units in yttrium and lanthanum aluminosilicate glasses (Schaller and Stebbins 1998). Therefore, the values of <sup>V</sup>Al/<sup>IV</sup>Al + <sup>V</sup>Al (Table 1) probably require a correction of less than 20%.

## DISCUSSION

#### Comparison with simple structural models

When the measured proportion of fivefold-coordinated aluminum (Table 1) is compared with the prediction of currently employed structural models (which assume that wherever possible, all Al will be tetrahedrally coordinated charge balanced by metal cations) several discrepancies are apparent (Fig. 4). First, up to 6% (relative) five coordinated aluminum is shown to exist in glasses with Mg/2Al>1 where none would be expected. Second, although the concentration of VAl systematically increases with decreasing Mg/Al ratio at constant silica content, the measured number of <sup>v</sup>Al in glasses with the lowest Mg/Al ratio studied is significantly less than the total number of "excess" Al required by stoichiometry (Fig. 4). This result implies that in this compositional range some of the Al present in tetrahedral coordination is not associated with charge balancing Mg ions. The most plausible mechanism for this fraction is as part of a tricluster (Lacy 1963) as recently proposed for sodium and calcium aluminosilicate glasses (Toplis et al. 1997; Stebbins and Xu 1997). Third, the concentration of <sup>v</sup>Al decreases with increasing SiO<sub>2</sub> at constant Mg/Al. This observation can be explained if incorporation of VAl requires association with "normal" tetrahedral Al (thus there is more at high



FIGURE 2. <sup>27</sup>Al 3Q MQ MAS spectra of samples MAS 50:54 and MAS 50:44.

total Al content), or alternatively may be due to some anomalous behavior of  $Mg^{2+}$ , for example a higher proportion of  $Mg^{2+}$ behaving as a network forming cation at high MgO concentrations (Angell et al. 1987).

The structural role of the observed <sup>v</sup>Al should be considered. At one extreme, <sup>v</sup>Al may play a purely network forming role, i.e., all five Al-O bonds are bridging to other network forming Al or Si. In this case, two positive charges (i.e., an  $Mg^{2+}$  cation) are required to stabilize the Al in pentahedral coordination. Transformation of a tetrahedrally coordinated Al (charge balanced by  $0.5Mg^{2+}$ ) to a network forming <sup>v</sup>Al therefore requires consumption of an additional 0.5 network modifying Mg ion. The observed increase in proportion of <sup>v</sup>Al in glasses with decreasing number of available Mg ions is therefore inconsistent with this hypothesis. This latter observation suggests that the structural role of <sup>v</sup>Al in these glasses does not require the presence of Mg at all, and we therefore infer that one or more of the Al-O bonds may be network modifying in character.

If it is assumed that each observed <sup>v</sup>Al is associated with one non-bridging O atom, the recalculated value of NBO/T at the charge balanced join along the 50 mol% silica isopleth is 0.12, because of the presence of the 6 mol% NBO. If such NBO play a similar role to those associated with addition of mono and divalent metal cations, melt transport properties (Hess et al. 1996; Liang et al. 1996), volatile solubilities (Brooker et al. 2000), and element partitioning (Kohn and Schofield 1994) are likely to be affected. For example, at 1273 K, addition of 6 mol% NBO associated with alkalis and alkaline earths to a haplogranitic melt results in a decrease in viscosity of 2 to 4 orders of magnitude (Hess et al. 1996).

#### How common is <sup>v</sup>Al?

The presence of <sup>v</sup>Al in all the glasses studied here contrasts with other glasses close to the charge balanced join, such as anorthite, where less than 2% have been found (Stebbins et al. 2000; Baltisberger et al. 1996). The greater proportion of <sup>v</sup>Al



**FIGURE 3.** (a) Projection of 2-D data (obtained using the same conditions as in Fig. 2) for sample MAS 50:47 onto the isotropic axis; (b) simulation of this projection; (c) the two Gaussian components and (d) the difference between a and b.

in magnesium aluminosilicate glasses may be related to the relatively low stability of tetrahedral aluminate complexes charge-balanced by magnesium compared with those charge-balanced by K<sup>+</sup>, Na<sup>+</sup>, or Ca<sup>2+</sup> (Roy and Navrotsky 1984). This finding is also consistent with ion dynamics simulations of aluminate compositions which predict greater concentrations of  $^{v}$ Al in magnesium compared to calcium bearing compositions (Poe et al. 1993). An alternative explanation is that some proportion of the Mg has a low coordination number (Angell et al.

TABLE 1. Compositions and measured proportion of VAI

Sample	wt% SiO <sub>2</sub>	wt% Al <sub>2</sub> O <sub>3</sub>	wt% MgO	Mol% SiO <sub>2</sub>	Mg*	% <sup>v</sup> Al/ΣAl
MAS50:54	48.78(61)	34.90(45)	16.21(25)	52.2	54.0	2.3
MAS50:50	47.59(46)	36.83(49)	14.85(13)	52.2	50.5	6.0
MAS50:47	46.46(19)	39.55(39)	13.84(20)	51.4	46.9	8.4
MAS50:44	45.17(60)	41.70(38)	12.73(26)	50.9	43.6	8.9
MAS67:53	62.28(25)	26.11(46)	11.43(26)	65.8	52.6	2.8
MAS67:48	61.98(42)	27.52(49)	10.03(23)	66.5	48.0	6.3
MAS75:51	71.58(31)	19.74(37)	8.04(15)	75.2	50.7	2.9
MAS75:49	71.22(37)	20.40(27)	7.62(13)	75.3	48.6	1.0
Notes: Mg* is 100	0 times the molar ratio N	IgO/(MgO+ Al <sub>2</sub> O <sub>3</sub> ). Numb	ers in parentheses cor	respond to uncertainty	in terms of the le	east units cited.



**FIGURE 4.** The uncorrected  ${}^{V}Al/({}^{V}Al + {}^{V}Al)$  ratio determined by fitting the MQ projections (Fig. 3) plotted as a function of the MgO/ (MgO + Al<sub>2</sub>O<sub>3</sub>) ratio of the glass. The solid line is the predicted ratio assuming that all Mg<sup>2+</sup> charge balances  ${}^{IV}Al$  and that any "excess" aluminum is  ${}^{V}Al$ .

1987; Waseda and Toguri 1990) and acts as a network forming cation, leading to a reduced availability of Mg as a charge-balancing cation for Al<sup>3+</sup>.

It should not be forgotten that the structure of a glass is essentially the same as that of the equivalent liquid at the glass transition temperature and that at higher temperature and/or pressure the relative proportions of <sup>v</sup>Al and <sup>Iv</sup>Al in MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses may be different from those measured here (Fig. 4). Ion-dynamics simulations and in-situ high temperature NMR spectroscopy have both been used to suggest that high coordinate Al is favored with increasing temperature (Poe et al. 1994). Furthermore, because of their smaller volume <sup>v</sup>Al should be also favored over <sup>Iv</sup>Al with increasing pressure. This would imply that the proportions of <sup>v</sup>Al measured here represent lower bounds for the proportions of highly coordinated Al present at the temperatures and pressures relevant to geological processes. Also, although <sup>v</sup>Al has not been described in other charge balanced glasses, highly coordinated aluminum is common in molecular dynamics simulations of liquids at very high temperature (Scamehorn and Angell 1991; Stein and Spera 1995), and has been inferred from viscosity measurements in the system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> at 1600 °C (Toplis and Dingwell 1998). Future studies should be aimed at determining if network modifying <sup>v</sup>Al is a general feature of silicate liquids at temperatures well above the glass transition.

### ACKNOWLEDGMENTS

R.J. Kirkpatrick and two anonymous reviewers are thanked for their thoughtful comments. S.C.K. acknowledges NERC for provision of an advanced research fellowship, and M.E.S. thanks EPSRC and HEFCE for support of NMR facilities at Warwick. This work is CRPG contribution no. 1477.

#### **REFERENCES CITED**

- Angell, C.A., Cheeseman, P.A., and Kadiyala, R.R. (1987) Diffusivity and thermodynamic properties of diopside and jadeite melts by computer simulation studies. Chemical Geology, 62, 83–92.
- Baltisberger, J.H., Xu, Z., Stebbins, J.F., Wang, S., and Pines, A. (1996) Triple quantum two-dimensional <sup>27</sup>Al magic angle spinning nuclear magnetic resonance spectroscopic study of aluminosilicate and aluminate crystals and glasses. Journal of the American Chemical Society, 118, 7209–7214.
- Brooker, R.A., Kohn, S.C., Holloway, J.R., and McMillan, P.F. (2000) Structural controls on the solubility of CO<sub>2</sub> in silicate melts. Part I: Bulk solubility data. Chemical Geology, in press.
- Brown, S.P. and Wimperis, S. (1997) Two dimensional multiple-quantum MAS NMR of quadrupolar nuclei: a comparison of methods. Journal of Magnetic Resonance A, 128, 42–61.
- Hess, K.-U., Dingwell, D.B., and Webb, S.L. (1996) The influence of excess alkaline-earth oxides (BeO, MgO, CaO, SrO, BaO) on the viscosity of a haplogranitic melt: systematics of non-Arrhenian behaviour. European Journal of Mineralogy, 8, 371–381.
- Iuga, D., Simon, S., de Boer, E., and Kentgens, A.P.M. (1999) A NMR study of amorphous and crystalline lanthanum aluminates. Journal of Physical Chemistry B, 103, 7591–7598.
- Kohn, S.C. and Schofield, P.F. (1994) The importance of melt composition in controlling trace element behaviour. Chemical Geology, 117, 73–87.
- Lacy, E.D. (1963) Aluminium in silicate glasses and melts. Physics and Chemistry of Glasses, 4, 234–238.
- Liang, Y., Richter, F.M., Davis, A.M., and Watson, E.B. (1996) Diffusion in silicate melts.1. Self diffusion in CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> at 1500 °C and 1 GPa. Geochimica et Cosmochima Acta, 60, 4353–4367.
- McMillan, P.F. and Kirkpatrick, R.J. (1992) Al coordination in magnesium aluminosilicate glasses. American Mineralogist, 77, 898–900.
- Medek, A., Harwood, J.S., and Frydman L. (1995) Multiple quantum MAS NMR: A new method for the study of quadrupolar nuclei. Journal of the American Chemical Society, 117, 12779–12787.
- Mysen, B.O. (1988) Structure and Properties of Silicate Melts. Elsevier, Amsterdam.
- Mysen, B.O., Virgo, D., and Seifert, F.A. (1982) The structure of silicate melts: implications for chemical and physical properties of natural magma. Reviews in Geophysics and Space Physics, 20, 353–383.
- Poe, B.T., McMillan, P.F., Coté, B., Massiot, D., and Coutures, J.P. (1993) Magnesium and calcium aluminate liquids: In-situ high-temperature <sup>27</sup>Al NMR spectroscopy. Science, 259, 786–788.
- ——(1994) Structure and dynamics in calcium aluminate liquids: High temperature <sup>27</sup>Al NMR and Raman spectroscopy. Journal of the American Ceramic

Society, 77, 1832-1838.

- Roy, B.N. and Navrotsky, A. (1984) Thermochemistry of charge-coupled substitutions in silicate glasses: The systems M<sub>1/n</sub><sup>n+</sup>AlO<sub>2</sub>-SiO<sub>2</sub> (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Pb). Journal of the American Ceramic Society, 67, 606–610.
- Scamehorn, C.A. and Angell, C.A. (1991) Viscosity-temperature relations and structure in fully polymerized aluminosilicate melts from ion dynamics simulations. Geochimica et Cosmochima Acta, 55, 721–730.
- Schaller, T. and Stebbins, J.F. (1998) The structural role of lanthanum and yttrium aluminosilicate glasses: a <sup>27</sup>Al and <sup>17</sup>O MAS NMR study. Journal of Physical Chemistry B, 102, 10690–10697.
- Stebbins, J.F. and Xu, Z. (1997) NMR evidence for excess non-bridging oxygen in an aluminosilicate glass. Nature, 390, 60–62.
- Stebbins, J.F., Kroeker, S., Lee, S.K., and Kiczenski, T.J. (2000) Quantification of five- and six-coordinated aluminum in aluminosilicate and fluoride-containing glasses by high-field, high-resolution <sup>27</sup>Al NMR. Journal of Non-Crystalline Solids, in press.
- Stein, D.J. and Spera, F.J. (1995) Molecular dynamics simulations of liquids and glasses in the system NaAlSiO<sub>4</sub>-SiO<sub>2</sub>: Methodology and melt structures. American Mineralogist, 80, 417–431.
- Toplis, M.J. and Dingwell, D.B. (1998) The structural role of aluminum in highly polymerised silicate melts: New insights from shear viscosity measurements.

Proceedings of the XVIII International Congress on Glass, Session D5. CD-ROM 6 p.

- Toplis, M.J., Dingwell, D.B., and Lenci, T. (1997) Peraluminous viscosity maxima in Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> liquids: The role of triclusters in tectosilicate melts. Geochimica et Cosmochima Acta, 61, 2605–2612.
- Waseda, Y. and Toguri, J.M. (1990) Structure of silicate melts determined by X-ray diffraction. In F. Marumo, Ed., Dynamic processes of material transport and transformation in the Earth's interior, p. 37–51. Terra Scientific, Tokyo.
- Zachariasen, W.H. (1932) The atomic arrangement in glass. Journal of the American Ceramic Society, 54, 3841–3851.

MANUSCRIPT RECEIVED APRIL 21, 2000 MANUSCRIPT ACCEPTED JULY 10, 2000 PAPER HANDLED BY ANNE M. HOFMEISTER