Oxygen triclusters in crystalline $CaAl_4O_7$ (grossite) and in calcium aluminosilicate glasses: ^{17}O NMR

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ABSTRACT

We present ^{17}O MAS NMR data for crystalline calcium dialuminate (grossite), $CaAl_4O_7$ and monoaluminate, $CaAl_2O_4$. The first of these contains an oxygen tricluster site and serves as a model compound for sites of this type in aluminosilicate glasses. Tricluster site NMR parameters are distinct from those of bridging O atoms (Al-O-Al), allowing partial resolution in triple quantum MAS NMR spectra. Such spectra for calcium aluminosilicate glasses are consistent with the presence of a small fraction of tricluster sites. Observed chemical shifts for non-bridging oxygen (NBO) atoms in an impurity phase in the $CaAl_2O_4$ sample are distinct from those for NBO in Ca-aluminosilicate glasses, indicating that the latter are primarily bonded to Si, not Al.

INTRODUCTION

Oxygen sites with three highly charged, tetrahedral cations as first neighbors (e.g., Al^{3+}, Si^{4+}) are unusual in minerals, but such "triclusters" have long been suspected of playing a role in the structure of Al-rich aluminosilicate glasses and melts (Mysen 1988). For example, to maintain local charge balance in peraluminous liquids, it has been proposed that either triclusters form (Lacey 1963) and/or that some Al cations have five or six O atom neighbors (Riebling 1966). The two mechanisms may not be strictly independent, as the relatively long cation-oxygen bonds expected for triclusters could allow a fifth O atom into one or more of the cation coordination shells.

Recent high-precision measurements in aluminosilicate melts suggest that because viscosity maxima are displaced from the expected ideal "charge compensation" joins (i.e., where Na/Al = 1 or Ca/Al = 0.5), excess non-bridging O atoms (NBO) should be present (Toplis et al. 1997; Toplis and Dingwell 1998). To maintain charge balance, either high-coordinated Al must also be present and/or triclusters must form. Existing structural data on the corresponding glasses suggested low concentrations of $^{[5]}Al$ and $^{[6]}Al$ in these systems, and thus that the latter mechanism predominates (Toplis et al. 1997). High-resolution NMR of ^{17}O in several "charge-compensated" glasses on the $CaAl_2O_4$–SiO_2 join has demonstrated that several per cent of the O atoms are indeed NBO (Stebbins and Xu 1997; Stebbins et al. 2001). Although ^{27}Al NMR has now shown that small amounts of $^{[5]}Al$ are also present in $CaAl_2Si_2O_8$ glass, the concentration of this species is too low to account for the observed NBO (Stebbins et al. 2000). Hence, triclusters are still called for. However, little direct spectroscopic evidence has been presented for their existence, although speculation was made about assigning an "extra" feature in the ^{17}O spectra to such groups (Stebbins and Xu 1997). Formation of triclusters was also suggested to explain changes in Raman spectra of $CaAl_2O_4$ melts at high temperature (Daniel et al. 1996). If triclusters are present, compositional effects on viscosity anomalies in the high silica part of the Na-aluminosilicate system suggested that $O(AlSi_2)$ groups predominate, but that $O(Al_2Si)$ and/or $O(Al_3)$ groups are most important in the Ca-aluminosilicate system (Toplis et al. 1997; Toplis and Dingwell 1998). Local charge balance would seem to favor $O(Al_3)$, as in crystalline mullite $[Al_2(Al_{2+x}Si_{2-x})O_{10-x}]$ (Angel et al. 1993).

To accurately interpret NMR results on glasses, data on representative crystalline model compounds are needed, although ab initio quantum mechanical calculations of NMR observables such as isotropic chemical shift (δ_{iso}) and quadrupolar coupling constant (C_Q) and asymmetry parameter (η) are rapidly becoming accurate enough to be predictive (Vermillion et al. 1998; Xue and Kanzaki 1999). Calcium dialuminate (grossite, $CaAl_4O_7$), in which one of four O sites is a simple tricluster with three $^{[4]}Al$ and no other neighbors, is an excellent potential model for $O(Al_3)$ sites in Ca-aluminosilicate glasses. The remaining O sites in $CaAl_4O_7$ all are "bridging O atoms" ($^{[4]}Al$-O-$^{[4]}Al$), with one or two Ca^{2+} neighbors for charge compensation (Goodwin and Lindop 1970; Ponomarev et al. 1971), and can serve as models for such sites in glasses as well.

Here we present ^{17}O NMR data on $CaAl_4O_7$. We suggest that these results for $O(Al_3)$ triclusters are consistent with their presence in Ca-aluminosilicate glasses, although future work will be needed to confirm this. New, higher resolution spectra for $CaAl_2O_4$ at a field of 18.8 Tesla also clarify previous results for $^{[4]}Al$-O-$^{[4]}Al$ groups (Stebbins et al. 1999): this phase has a "stuffed silica" structure in which all O atoms are in such linkages (Hörkner and Müller-Buschbaum 1976). In addition, new results on NBO in Ca-aluminate crystals and glasses better refine the role of these types of O atoms in glasses.

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EXPERIMENTAL METHODS

$CaAl_4O_7$ enriched in ^{17}O was synthesized from $CaCO_3$ and isotopically-enriched Al_2O_3 (Stebbins et al. 1999). Three cycles of solid-state reaction for 2 h at 1600 °C under Ar, followed by grinding, were required to produce a monophasic (by XRD) sample, but apparently led to significant loss of ^{17}O and a relatively low enrichment level (probably <10%). ^{17}O NMR results on this material (see below) suggested that a previously described sample of ^{17}O-$CaAl_2O_4$ (Stebbins et al. 1999) might contain a significant amount of $CaAl_4O_7$ in addition to the reported non-bridging oxygen-containing (glassy?) impurity noted at the time, apparently missed in the routine powder XRD scan used to characterize the material. Therefore, the $CaAl_2O_4$ sample was reacted with an additional 5 wt% CaO by partially melting under Ar at 1560 °C followed by crystallization for 2 h at 1340 °C in order to eliminate residual glass and $CaAl_4O_7$. Synthesis of the calcium aluminosilicate glass ("CAS") was also described previously (Stebbins et al. 1999); its nominal composition lies on the $CaAl_2O_4$–SiO_2 join with a Si/Al ratio of 0.5 ($CaAl_2SiO_6$).

NMR spectra for ^{17}O were collected at 54.2 MHz with a Varian 400 (9.4 Tesla field) and at 81.3 and 108.4 MHz with Varian Inova 600 and 800 spectrometers (14.1 and 18.8 T). At 9.4 T, a 5 mm MAS probe from Doty Scientific was used with sample spinning rates of about 15 kHz; at 14.1 and 18.8 T, 3.2 mm Varian/Chemagnetics probes were used with spinning rates of 18 to 20 kHz. Radio frequency tip angles of about 15 to 30° were used (0.2 to 0.8 μs); recycle delays of 1 to 5 s were chosen to optimize signal to noise ratios but were tested to ensure that there was no differential relaxation among different sites (no change in the shapes of the spectra with increased delay time); frequencies are reported relative to 20% ^{17}O H_2O. Spectra were fitted with the Varian software "STARS," with manual optimization of the agreement between calculated and observed spectra at one or two magnetic fields as needed. The triple-quantum magic angle spinning (3QMAS) method and the spectra for the CAS glass were previously described (Stebbins et al. 1999). Long spin-lattice relaxation times for the crystalline Ca-aluminates made collection of 3QMAS spectra on these samples impractical. The single-pulse ^{27}Al spectrum for $CaAl_4O_7$ was acquired at 18.8 T (208.3 MHz), and was referenced to 1 M, acidified, aqueous $Al(NO_3)_3$.

RESULTS

Although the relatively low ^{17}O enrichment level and long relaxation time for the $CaAl_4O_7$ resulted in noisy MAS spectra (Fig. 1), it is clear in the data collected at 14.1 T that signals from the expected four distinct O sites are observable. Magic angle spinning does not remove all effects of structural orientation in the NMR spectrum of a quadrupolar (spin = 5/2) nuclide such as ^{17}O in a polycrystalline material or a glass; broadened peaks with complex (often double-peaked) shapes typically result in a fully ordered phase (Kirkpatrick 1988), but these can be accurately calculated given known NMR parameters. These effects are substantially greater at lower magnetic fields, as can be seen in the much worse resolution of the spectrum collected at 9.4 T (Fig. 1). The NMR parameters δ_{iso}, C_Q, and η can in some cases be derived by fitting well-defined
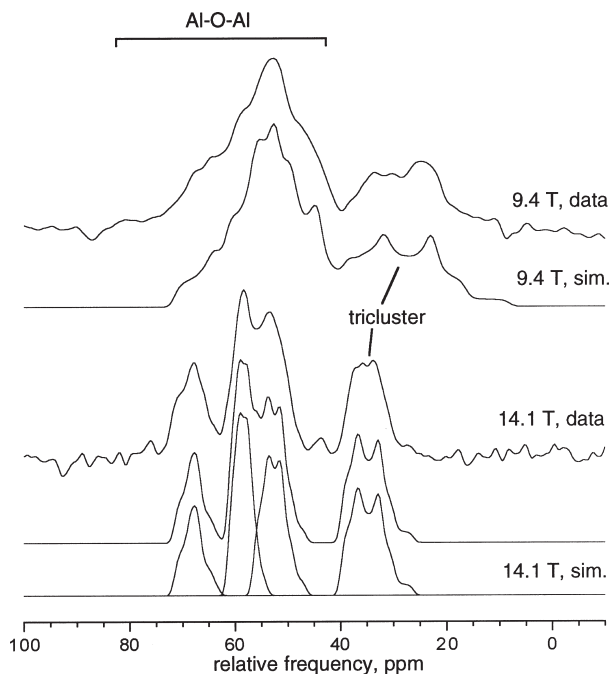

FIGURE 1. ^{17}O MAS spectra for $CaAl_4O_7$ at the fields shown, with simulations using parameters in Table 1.

TABLE 1. NMR parameters for ^{17}O in calcium aluminates, derived from fitting peaks in spectra at 9.4 and 14.1 T ($CaAl_4O_7$) or from peak positions at 14.1 and 18.8 T ($CaAl_2O_4$)

Peak no.	δ_{iso}, ppm*	C_Q, MHz† ±0.2	η ±0.3	Approx. relative area	Assignment
		$CaAl_4O_7$			
1	71.6	1.9	0.7	1	O1
2	61.5	1.8	0.5	2	O2 or O3
3	56.8	2.1	0.5	2	O2 or O3
4	40.6	2.5	0.4	2	O4 (tricluster)
		$CaAl_2O_4$			
1	86.8	1.5	–	1	
2	80.7	1.6‡	–	1	
3	76.2	1.6‡	–	1	
4	72.4	1.6	–	2	
5	69.1	1.3	–	3	
6	66.7	1.6	–	1	
7	61.8	1.4	–	2	
8	57.3	1.4	–	1	

* ±2 ppm for $CaAl_4O_7$, ±1 ppm for $CaAl_2O_4$.
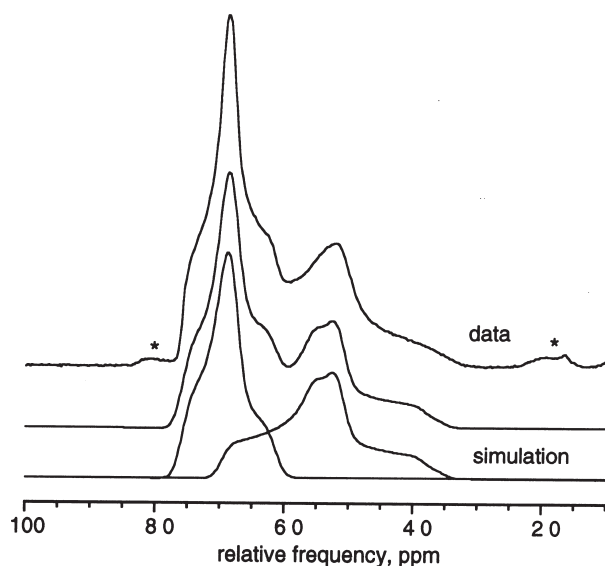† For $CaAl_2O_4$, table shows $P_Q = C_Q(1 + η^2/3)^{1/2}$, which is 0 to 15% greater than C_Q.
‡ This value was that derived previously from 9.4 and 14.1 T data for a single, unresolved peak (Stebbins et al. 1999). Resolution at 14.1 T is insufficient to allow separate C_Q values for the two peaks to be determined.

peak shapes at a single field; the change in shape and position with field can often provide much more certainty, especially in noisy or overlapping spectra. Fitting of the data collected at both fields allowed δ_{iso}, C_Q, and η to be determined (Table 1). The spectral simulations (Fig. 1) were made with the 1:2:2:2 peak ratios as required by the known structure, with the lowest-intensity peak chosen as that with highest frequency by testing various assignments. This peak can thus be assigned to the
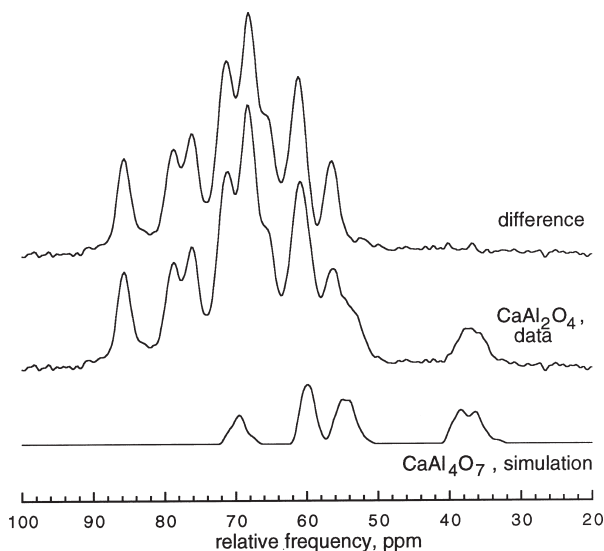
O1 site (Goodwin and Lindop 1970). The [27]Al spectrum at 18.8 T (Fig. 2) is consistent with one previous data set collected at lower field (δ_{iso} within 0.5 ppm) (Skibsted et al. 1993), but not with another (Gervais et al. 2001), where δ_{iso} values are 7 to 10 ppm lower for unknown reasons, possibly a simple error in frequency referencing in the latter publication.

The original $CaAl_2O_4$ as previously described (Stebbins et al. 1999) was examined at 18.8 T. At this "ultra-high" field, the resulting [17]O spectrum is remarkable in resolving peaks or shoulders for at least 8 of the 12 crystallographically distinct O sites (Fig. 3) in contrast to only 5 peaks at 14.1 T; NMR parameters can be refined by comparison with peak positions at 14.1 T (Table 1). C_Q values are small enough so that well-defined quadrupolar peak shapes are not generated at either field.

At both fields, a broad ^{17}O NMR peak centered at about 135 ppm suggested the presence of a significant fraction of NBO in the sample (Fig. 4), probably in a residual, Ca-rich glass: the eutectic in the system is on the CaO side of this composition. This assignment is based on analogy to Ca-silicate crystals and glasses, where NBO sites resonate near 100 ppm (Stebbins 1995; Stebbins et al. 1997). Stoichiometry requires that a minor amount of an Al-rich phase also be present; the identical shape and position of the lowest frequency peak in the spectrum to that in $CaAl_4O_7$ suggests that this is the "contaminant." To test this possibility, 5% excess CaO was added and the sample was recrystallized. The lowest frequency peak disappeared after this treatment, demonstrating that it was not inherent to the $CaAl_2O_4$ (Fig. 4) and suggesting that it is unique to $CaAl_4O_7$. The NBO peak became narrower and shifted slightly after recrystallization, suggesting that it was now

FIGURE 3. [17]O MAS spectra for $CaAl_2O_4$ at 18.8 T, showing also a simulated spectrum for $CaAl_4O_7$ at this field and the difference spectrum obtained by subtracting the latter from the former.
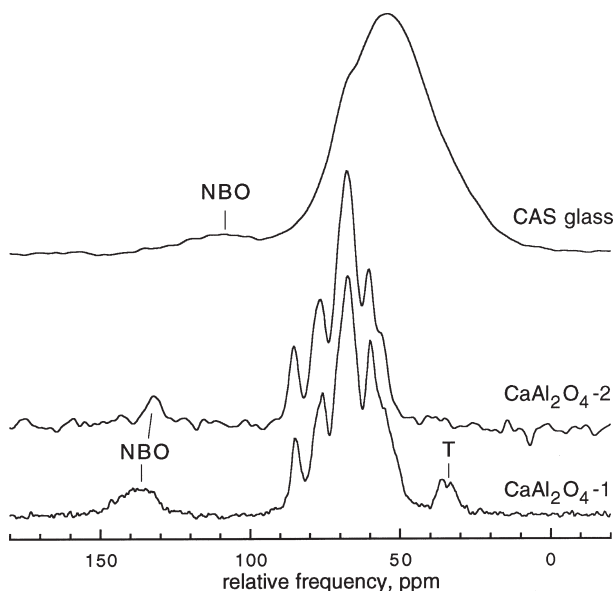
FIGURE 4. [17]O MAS spectra for $CaAl_2O_4$ at 14.1 T, and for a Ca-aluminosilicate glass (see text). $CaAl_2O_4$–1 is the original sample as previously described (Stebbins et al. 1999); $CaAl_2O_4$–2 was produced by adding a small amount of CaO to $CaAl_2O_4$–1 and recrystallizing to eliminate $CaAl_4O_7$.

FIGURE 2. [27]Al MAS spectrum for $CaAl_4O_7$ collected at 18.8 T, with a simulation assuming two sites with equal occupancies (consistent with the crystal structure), with δ_{iso}, C_Q, and η values of 76.0 ppm, 6.25 MHz, 0.88 and 70.0 ppm, 9.55 MHz, and 0.80 respectively. Asterisks mark spinning sidebands.

present in a crystalline, Ca-rich aluminate, possibly $Ca_3Al_2O_6$ (Mondal and Jeffery 1975). This experiment also confirmed that all observed Al–O–Al peaks have chemical shifts in the range of about 50 to 90 ppm and C_Q values below about 2 MHz.

DISCUSSION

In the Ca-aluminates studied, it is clear that the ^{17}O NMR peak with the smallest chemical shift and the largest C_Q is unique

to $CaAl_4O_7$ and thus is most likely to be due to tricluster oxygen. Although [4]Al-O-[4]Al O atoms all seem to have a relatively well-defined range of chemical shifts from about 50 to 90 ppm and C_Q less than about 2 MHz, unique assignment of these peaks to specific crystallographic sites is not yet possible. Ab initio calculations suggest some correlation between Al-O-Al bond angle and δ_{iso} and C_Q (Xue and Kanzaki 1999). However, they also make it clear that other aspects of the local structure, in particular the distance to and number of charge-compensating first neighbor cations, can have large effects, making empirical correlations with simple local structural variables difficult. Such calculations do suggest, however, that C_Q values for tricluster O atoms may be systematically greater than those for Al-O-Al sites, consonant with our peak assignments. Some very recent ab initio calculations predict both C_Q and δ_{iso} values that are in good accord with the data for the $O(Al_3)$ tricluster presented here (M.J. Toplis, written communication).

3QMAS spectra can potentially provide much improved resolution for "quadrupolar" nuclides such as ^{17}O (nuclear spin = 5/2), by eliminating the broadening effect of second-order quadrupolar coupling (Frydman and Harwood 1995). The resulting two dimensional spectra give somewhat distorted versions of the 1-D MAS spectra when projected (summed) in one dimension but highly-resolved "isotropic" spectra when projected in the other. Peak positions in both dimensions depend on both δ_{iso} and C_Q according to well-known equations (Schaller and Stebbins 1998). The ^{17}O 3QMAS spectrum for CAS glass is shown in Figure 5 (modified from Stebbins et al. 1999), together with the "footprint" expected for OAl_3 triclusters with the same parameters as in crystalline $CaAl_4O_7$. The area for the latter is elongated in the MAS dimension by its relatively large C_Q, and is shown with only a narrow range of δ_{iso},

which could be increased by disorder. The range for Al-O-Al sites as defined by the known Ca-aluminates is also shown and is elongated along a line with slope of $-31/17$ as expected for the small and relatively constant C_Q combined with the observed wide range of δ_{iso} (Schaller and Stebbins 1998), the latter probably stemming from local degrees of freedom such as Al-O-Al angle and Ca-O distances that may not affect triclusters. It is clear that there is significant intensity in the tricluster region of the spectrum that is not due to the partially overlapping peak for Si-O-Al sites and seems to be outside the range for Al-O-Al sites as defined by the Ca-aluminates. Although we do not consider this interpretation to be definitive because of the severe peak overlap and our limited knowledge of the effects of structure on chemical shifts, the results do suggest consistency for tricluster-containing models of melt properties and indicate that further work on this question would be worthwhile. Our results neither support nor rule out the presence of triclusters containing one or more Si as proposed for relatively silica-rich Na-aluminosilicates (Toplis et al. 1997); these may not be predominant in silica-poor Ca-aluminosilicate glasses such as that described here (Toplis and Dingwell 1998).

The presence of several (roughly 3-5) percent of NBO has now been observed by ^{17}O MAS and 3QMAS in three glass compositions on the $CaAl_2O_4$–SiO_2 join with Si/Al ranging from 3 to 0.5 (Stebbins and Xu 1997; Stebbins et al. 1999; Stebbins et al. 2001). In all cases, the chemical shifts are in the range of about 100 to 120 ppm, with peaks centered at about 110 ppm, typical of NBO bonded to Si and several Ca^{2+} cations (Stebbins 1995; Stebbins et al. 1997). In contrast, the ^{17}O NBO peaks described here in Ca-aluminates are centered at about 130 to 135 ppm (δ_{iso} are a few ppm higher). The systematic difference indicates that most of the NBO in the aluminosilicate glasses are indeed bonded to Si and not to Al, as has been suggested previously from Raman and other spectroscopic data (Mysen 1988).

REFERENCES CITED

Angel, R.J., McMullan, R.K., and Prewitt, C.T. (1993) Substructure and superstructure of mullite by neutron diffraction. American Mineralogist, 76, 332–342.
Daniel, I., McMillan, P.F., Gillet, P., and Poe, B.T. (1996) Raman spectroscopic study of structural changes in calcium aluminate ($CaAl_2O_4$) glass at high pressure and high temperature. Chemical Geology, 128, 5–15.
Frydman, L. and Harwood, J.S. (1995) Isotropic spectra of half-integer quadrupolar spins from bidimensional magic-angle spinning NMR. Journal of the American Chemical Society, 117, 5367–5368.
Gervais, C., MacKenzie, K.J.D., and Smith, M.E. (2001) Multiple magnetic field ^{27}Al solid-state NMR study of the calcium aluminates $CaAl_4O_7$ and $CaAl_{12}O_{19}$. Magnetic Resonance in Chemistry, 39, 23–28.
Goodwin, D.W. and Lindop, A.J. (1970) The crystal structure of $CaO·2Al_2O_3$. Acta Crystallographica, B26, 1230–1235.
Hörkner, W. and Müller-Buschbaum, H.K. (1976) Zur Kristallstruktur von $CaAl_2O_4$. Journal of Inorganic and Nuclear Chemistry, 38, 983–984.
Kirkpatrick, R.J. (1988) MAS NMR spectroscopy of minerals and glasses. In F.C. Hawthorne, Ed., Spectroscopic Methods in Mineralogy and Geology, p. 341–403. Mineralogical Society of America, Washington, D.C.
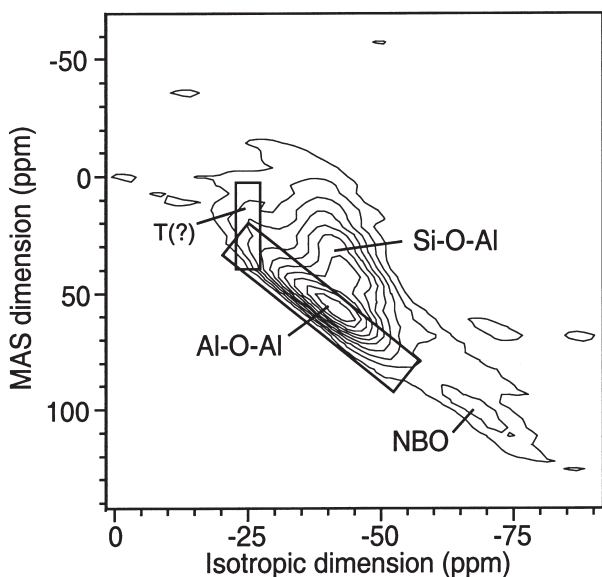Lacey, E.D. (1963) Aluminum in glasses and melts. Physics and Chemistry of Glasses, 4, 234–238.

FIGURE 5. ^{17}O 3QMAS spectrum for a Ca-aluminosilicate glass as in Figure 1 and as previously reported (Stebbins et al. 1999). Ranges for the $O(Al_3)$ tricluster ("T") and Al-O-Al sites, as expected from data on the crystalline Ca-aluminates, are shown, as is the non-bridging O atom peak.

Mondal, P. and Jeffery, J.W. (1975) The crystal structure of tricalcium aluminate, $Ca_3Al_2O_6$. Acta Crystallographica, B31, 689–697.

Mysen, B.O. (1988) Structure and Properties of Silicate Melts, Elsevier, Amsterdam, 354 p.

Ponomarev, V.I., Kheiker, D.M., and Belov, N.V. (1971) Crystal structure of calcium dialuminate, CA_2. Soviet Physics-Crystallography, 15, 995–998.

Riebling, E.F. (1966) Structure of sodium aluminosilicate melts containing at least 50 mol% SiO_2 at 1500 °C. Journal of Chemical Physics, 44, 2857–2865.

Schaller, T. and Stebbins, J.F. (1998) The structural role of lanthanum and yttrium in aluminosilicate glasses: a ^{27}Al and ^{17}O NMR study. Journal of Physical Chemistry B, 102, 10690–10697.

Skibsted, J., Henderson, E., and Jakobsen, H.J. (1993) Characterization of calcium aluminate phases in cements by high-performance ^{27}Al MAS NMR spectroscopy. Inorganic Chemistry, 32, 1013–1027.

Stebbins, J.F. (1995) Nuclear magnetic resonance spectroscopy of silicates and oxides in geochemistry and geophysics. In T.J. Ahrens, Ed., Handbook of Physical Constants, p. 303–332. American Geophysical Union, Washington D.C.

Stebbins, J.F. and Xu, Z. (1997) NMR evidence for excess non-bridging oxygens in an aluminosilicate glass. Nature, 390, 60–62.

Stebbins, J.F., Oglesby, J.V., and Xu, Z. (1997) Disorder among network modifier cations in silicate glasses: new constraints from triple-quantum oxygen-17 NMR. American Mineralogist, 82, 1116–1124.

Stebbins, J.F., Lee, S.K., and Oglesby, J.V. (1999) Al-O-Al oxygen sites in crystalline aluminates and aluminosilicate glasses: high-resolution oxygen-17 NMR results. American Mineralogist, 84, 983–986.

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 ^{27}Al NMR. Journal of Non-Crystalline Solids, 275, 1–6.

Stebbins, J.F., Oglesby, J.V., and Lee, S.K. (2001) Oxygen sites in silicate glasses: a new view from oxygen-17 NMR. Chemical Geology, 174, 63–75.

Toplis, M.J. and Dingwell, D.B. (1998) The structural role of aluminum in highly polymerized 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_2O-Al_2O_3-SiO_2 liquids: the role of triclusters in tectosilicate melts. Geochimica et Cosmochimica Acta, 61, 2605–2612.

Vermillion, K.E., Florian, P., and Grandinetti, P.J. (1998) Relationships between bridging oxygen ^{17}O quadrupolar coupling parameters and structure in alkali silicates. Journal of Chemical Physics, 108, 7274–7285.

Xue, X. and Kanzaki, M. (1999) NMR characteristics of possible oxygen sites in aluminosilicate glasses and melts: an ab initio study. Journal of Physical Chemistry B, 103, 10816–10830.