Oxygen triclusters in crystalline CaAl$_4$O$_7$ (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$_4$O$_7$ and monoaluminate, CaAl$_2$O$_4$. 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$_4$O$_7$ 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$^{14+}$, 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$_2$O$_4$–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$_2$Si$_2$O$_7$ 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$_2$O$_4$ 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$_3$Si) and/or O(Al$_2$) 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 ($\delta$ iso) and quadrupolar coupling constant ($C_Q$) and asymmetry parameter ($\eta$) are rapidly becoming accurate enough to be predictive (Vermillion et al. 1998; Xue and Kanzaki 1999). Calcium dialuminate (grossite, CaAl$_4$O$_7$), in which one of four O sites is a simple tricluster with three [5]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$_4$O$_7$ 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$_4$O$_7$. 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$_4$O$_7$ at a field of 18.8 Tesla also clarify previous results for [5]Al–O–[5]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.
**EXPERIMENTAL METHODS**

CaAl\(_2\)O\(_4\), enriched in \(^{17}\)O was synthesized from CaCO\(_3\) and isotopically-enriched Al\(_2\)O\(_3\) (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\(_2\)O\(_4\) (Stebbins et al. 1999) might contain a significant amount of CaAl\(_2\)O\(_4\) 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\(_2\)O\(_4\) 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\(_2\)O\(_4\). Synthesis of the calcium aluminosilicate glass ("CAS") was also described previously (Stebbins et al. 1999); its nominal composition lies on the CaAl\(_2\)O\(_4\)–SiO\(_2\) join with a Si/Al ratio of 0.5 (CaAl\(_2\)SiO\(_5\)).

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/Czemagnetics 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\(_2\)O. 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\(_2\)O\(_7\) 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\(_2\)O\(_4\) 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 \(\delta_{iso}\), \(C_\eta\), and \(\eta\) can in some cases be derived by fitting well-defined 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 \(\delta_{iso}\), \(C_\eta\), and \(\eta\) 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

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* \(\pm 2\) ppm for CaAl\(_2\)O\(_7\), \(\pm 1\) ppm for CaAl\(_2\)O\(_4\).  
† For CaAl\(_2\)O\(_4\), table shows \(C_\eta = C_\eta(1 + \eta^2/3)^{1/2}\), which is 0 to 15% greater than \(C_\eta\).  
‡ 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 \(C_\eta\) values for the two peaks to be determined.
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 ($\delta_{\text{iso}}$ within 0.5 ppm) (Skibsted et al. 1993), but not with another (Gervais et al. 2001), where $\delta_{\text{iso}}$ values are 7 to 10 ppm lower for unknown reasons, possibly a simple error in frequency referencing in the latter publication.

The original CaAl$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ (Fig. 4) and suggesting that it is unique to CaAl$_2$O$_4$. The NBO peak became narrower and shifted slightly after recrystallization, suggesting that it was now present in a crystalline, Ca-rich aluminate, possibly Ca$_3$Al$_2$O$_6$ (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 CaAl₂O₄ 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 Cₒ 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_mа и Cₒ (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 Cₒ 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 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 ¹⁷O MAS and 3QMAS in three glass compositions on the CaAl₂O₄-SiO₂ 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 Ca²⁺ cations (Stebbins 1995; Stebbins et al. 1997). In contrast, the ¹⁷O NBO peaks described here in Ca-aluminates are centered at about 130 to 135 ppm (δ_mа и 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 (Myseen 1988).

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