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LETTERS

Al-O-Al oxygen sites in crystalline aluminates and aluminosilicate glasses: High-resolution oxygen-17 NMR results

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ABSTRACT

We report ^{17}O magic-angle spinning (MAS) NMR data for crystalline $NaAlO_2$ and $CaAl_2O_4$ at external magnetic fields of 9.4 and 14.1 T, as model compounds for Al-O-Al sites in tetrahedral networks. The former contains one peak with isotropic chemical shift (δ_{iso}) = 30.9 ppm and quadrupolar coupling constant (C_Q) ≈ 1.8 MHz. The latter contains several peaks with δ_{iso} ranging from 39 to 87 ppm and C_Q ≈ 1.5 to 2.4 MHz. Triple-quantum MAS (3QMAS) spectra of sodium and calcium aluminosilicate glasses with Si/Al < 1 show clearly resolved peaks for Al-O-Al sites, removing ambiguity in the use of such spectra to explore the extent of aluminum avoidance in both glassy and crystalline materials. We also report ^{23}Na and ^{27}Al NMR data for the crystalline phases.

INTRODUCTION

In glasses and magmas that are most common in and on the Earth's continental crust, in the most commonly used technological glasses, and in crystalline framework silicates that dominate the mineralogy of the crust and of oxide ceramics most or all of the oxygen atoms are shared between two SiO_4 or AlO_4 tetrahedra. For compositions with Si/Al ≥ 1, Al-O-Al linkages are generally considered to be energetically unfavorable and thus to have low concentration (Tossell 1993). Such "aluminum avoidance" may be imperfect in disordered crystalline phases, especially those with alkaline earth interstitial cations, and particularly in phases quenched from high temperature or metastable syntheses. Incomplete aluminum avoidance is also suspected in aluminosilicate glasses, and has been sought by vibrational spectroscopy (McMillan et al. 1982; McMillan and Wolf 1995) and NMR methods (Murdoch et al. 1985; Lee and Stebbins 1999). When a significant proportion of the Al-O-Al species is present, it can have important effects on the energy and entropy of the material, particularly if its concentration changes with temperature. A direct way of measuring its concentration is thus desirable.

High-resolution ^{17}O NMR has great potential for the detection and quantification of different types of bridging oxygen sites in framework aluminosilicates, as demonstrated by recent work on zeolites and on glasses (Dirken et al. 1997; Xu et al. 1998; Xu and Stebbins 1998). However, detection of minor amounts of Al-O-Al has been hampered by the lack of data on this kind of site in crystalline model compounds. NMR parameters for this and other bridging O atoms have been predicted by ab initio calculations (Tossell 1993), but such results must be tested and refined by experiment. Al-O-Al linkages must, of course, become common in tetrahedral networks as Si/Al decreases below one, as in the crystalline phases of $NaAlO_2$ and $CaAl_2O_4$. These have "stuffed tridymite" structures and thus are entirely constructed of corner-shared AlO_4 groups (Théry et al. 1961; Hörkner and Müller-Buschbaum 1976). Here we report ^{17}O data on these phases, which allow us to definitively assign newly-observed NMR peaks in aluminous glasses to Al-O-Al sites.

EXPERIMENTAL PROCEDURE

The ^{17}O-enriched (about 20%) Al_2O_3 was produced by hydrothermal exchange between enriched H_2O and $Al(OH)_3$ at 400 °C and 0.5 kb for about 5 days, followed by drying under Ar at 800 °C. Crystalline $CaAl_2O_4$ was synthesized from $CaCO_3$ and ^{17}O-Al_2O_3 by decarbonation followed by melting at 1635 °C in Ar and crystallization at 1535 °C. About 0.2 wt% Co_3O_4 was added to the batch prior to melting to speed spin-lattice relaxation. Powder XRD showed only single-phase $CaAl_2O_4$. $NaAlO_2$ reagent was hydrothermally exchanged with ^{17}O-enriched H_2O at 400 °C and 0.5 kb for about 5 days. The powder XRD pattern matched previous reports for β-$NaAlO_2$ (Théry et al. 1961).

Two glasses were synthesized (Lee and Stebbins 1999) from Na_2CO_3 or $CaCO_3$, Al_2O_3, 0.2 wt% Co_3O_4, and ^{17}O-enriched SiO_2, by decarbonation and melting under Ar at 1600 °C for the CAS glass and 1700 °C for the NAS glass. Nominal compositions are on the aluminate-silica joins, with Si/Al = 0.7 for the sodium aluminosilicate ("NAS") and Si/Al = 0.5 for the calcium aluminosilicate ("CAS"). Both samples appeared completely amorphous at 400X in a petrographic microscope; the latter contained a fraction of a per cent of corundum, as detected by ^{27}Al MAS NMR.

Single-pulse MAS (magic-angle spinning) NMR experiments were done on a modified Varian VXR 400S spectrom-

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eter (9.4 T magnet), or on a Varian Inova 600 spectrometer (14.1 T). For the former, a Doty Scientific, Inc., 5 mm MAS probe was used with spinning rates of about 12 kHz, for the latter, a Varian/Chemagnetics 3.2 mm MAS probe was used, with spinning rates to 19 kHz. External references of aqueous NaF (for ^{23}Na), aqueous $Al(NO_3)_3$, (for ^{27}Al), and tap water (for ^{17}O) were used. Excitation was done with short pulses (<30° radiofrequency tip angle), and delays between pulses were chosen to ensure that spectra were free of distortion by differential relaxation among different sites.

Two dimensional, high-resolution, triple-quantum MAS (3QMAS) spectra were collected for the two glass samples, using the two-pulse technique previously described (Stebbins and Xu 1997; Frydman and Harwood 1995). Pulse lengths of 5 and 9 μs, corresponding to rf tip angles of about 180 ° and 360°, were used. Delays between acquisitions were chosen to allow nearly complete relaxation: The spin-lattice relaxation times for the CAS and NAS glasses were estimated at 5 and 0.7 s, respectively. Data were shear transformed prior to plotting, to produce two dimensional spectra that are isotropic in the ω1 dimension (i.e., free of second-order quadrupolar broadening) and that portray somewhat distorted MAS spectra in the ω2 dimension. Spectra are plotted with axis conventions described previously (Baltisberger et al. 1996). Spectra collected with a three-pulse sequence including a "soft" echo pulse were similar but of somewhat lower quality.

RESULTS

The ^{17}O MAS spectra for both $NaAlO_2$ and $CaAl_2O_4$, particularly at 14.1 T, are primarily comprised of narrow, symmetrical peaks that are approximately Gaussian in shape (Fig. 1). This finding is surprising in light of the large quadrupolar broadening typical of Si-O-Al and Si-O-Si peaks in aluminosilicates. However, narrow ^{17}O peaks are common in more ionically bonded oxides in which the quadrupolar coupling constant (C_Q) is often less than about 2 MHz (Stebbins 1995). The observed peak positions (δ_{MAS}) are shifted from the isotropic chemical shift (δ_{iso}) by a factor that depends on the Larmor frequency (in MHz, ν_0) and thus on the external magnetic field, with $\delta_{MAS} = \delta_{iso} - 6000\,(P_Q)^2/\,(\nu_0)^2$. For typical oxygen sites in which the quadrupolar asymmetry parameter $\eta < 0.5$, P_Q is only 0 to 4% greater than the quadrupolar coupling constant C_Q, with $P_Q = C_Q\,(1 + \eta^2/3)^{1/2}$. Peak positions acquired at the two magnetic fields (ν_0 of 81.30 and 54.2 MHz) can thus be compared to estimate δ_{iso} and P_Q (Table 1). For $NaAlO_2$, the single narrow peak suggests that either all O sites are identical or are nearly so. For $CaAl_2O_4$, the complex manifold of peaks is expected from the presence of 12 distinct sites in the structure, with Al-O-Al bond angles ranging from about 115 to 132° (calculated from data in Hörkner and Müller-Buschbaum 1976; note that Skibsted et al. 1993 reported discrepancies between bond angles calculated from these data and those listed in the original paper, suggesting the possibility of some minor errors in the original tabulation). For this phase, the listed NMR parameters for the larger peaks thus average together several sites.

The MAS spectra for the NAS glass at both fields was featureless and slightly asymmetrical (Fig. 1). No distinction between Si-O-Al and Al-O-Al sites is obvious, even though this sample must contain at least 17.6% of the latter because of its composition (Lee and Stebbins 1999). In contrast, the CAS glass spectrum shows a distinct shoulder at 66 ppm (at 14.1 T), in the same location as the most intense peak for $CaAl_2O_4$, suggesting that it is due to Al-O-Al sites.

TABLE 1. NMR results for crystalline aluminates

Sample	No. of sites	Peak max. at 14.1 T	Peak max. at 9.4 T	δ_{iso}, ppm ±0.5	P_Q MHz ±0.1
$CaAl_2O_4$, ^{17}O	NBO(?)*	138	134	≈141	≈1.9
$CaAl_2O_4$, ^{17}O	1	84.9	82.0	87.2	1.60
$CaAl_2O_4$, ^{17}O	2	76.3	73.6	78.5	1.54
$CaAl_2O_4$, ^{17}O	4	67.7	64.0	70.7	1.81
$CaAl_2O_4$, ^{17}O	4	59.9	57.3	62.2	1.60
$CaAl_2O_4$, ^{17}O	1	34.8†	28.4†	39.3	2.4
$NaAlO_2$, ^{17}O	all‡	27.9	24.2	30.9	1.81
$NaAlO_2$, ^{23}Na	1	—	—	24.9§	2.30§
$NaAlO_2$, ^{27}Al	1	79.0	—	79.8‖	0.9‖

Notes: Peak positions in parts per million. Number of sites represented is based on approximate relative areas: Individual sites within each peak are not resolved.

* Broad peak, possibly for NBO in residual glass or metastable Ca-rich phase.

† Quadrupolar doublet, peak-shape fitted with C_Q = 2.3 MHz, η = 0.4 at both fields.

‡ Single, symmetrical peak with FWHM of 5.5 ppm.

§ Based on fit to well-defined quadrupolar peak shape at 14.1 T, C_Q = 2.15 MHz, η_Q = 0.6.

‖ Based on positions of central peak (symmetrical, FWHM = 3.5 ppm) and satellite sidebands at 14.1 T.

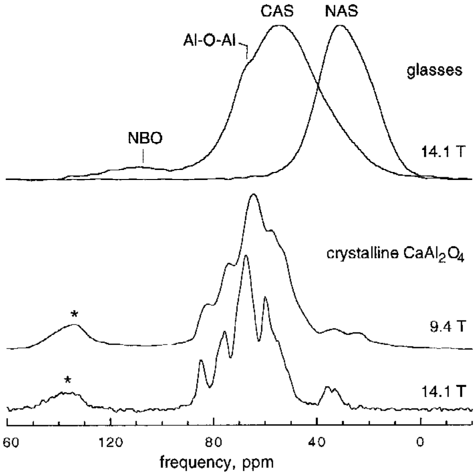

FIGURE 1. Various ^{17}O MAS NMR spectra of crystalline $CaAl_2O_4$, and of CAS and NAS glasses. Magnetic fields at which data were acquired are shown. Asterisk marks a peak that may be due to a second phase in the $CaAl_2O_4$ sample, and probably is due to Al-O-Ca sites.

The spectrum for the CAS glass also contains a low peak at about 108 ppm that is almost certainly due to a small fraction (about 4 to 6%) of non-bridging O atoms, which have also recently been reported in $CaAl_2Si_2O_8$ glass (Stebbins and Xu 1997). This species, although unexpected in conventional models of "fully polymerized" aluminosilicate glasses (i.e., those on the SiO_2-aluminate joins), is expected from recent studies of viscosity (Toplis et al. 1997).

The ^{17}O 3QMAS spectrum of the NAS glass (Fig. 2) contains two well-resolved peaks centered at about –13 and –30

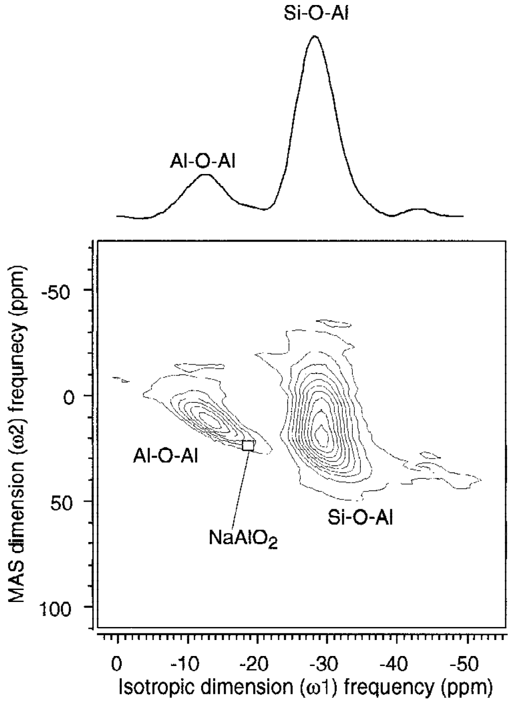

FIGURE 2. Various ^{17}O 3QMAS spectra for NAS glass at 9.4 T. Contour lines of intensity are equally spaced with the lowest level set at 6% of the maximum. The position of the peak center predicted for crystalline $NaAlO_2$ is marked. The total projection in the isotropic dimension is shown above the two-dimensional plot, with the same scale.

ppm in the isotropic dimension. The first of these is similar in position to that predicted by the two-field MAS data on $NaAlO_2$, and thus is clearly assignable to Al-O-Al sites. The shape of the peak (a narrow ridge aligned along a slope of about –31/17) indicates a range of δ_{iso} with a roughly constant C_Q (Stebbins et al. 1997; Schaller and Stebbins 1998). If we approximate the center of this peak as its maximum at –13 ppm in the 3QMAS dimension and 12 ppm in the MAS dimension, mean values of δ_{iso} and P_Q can be calculated as 19 ± 2 ppm and 1.85 ± 0.05 MHz (Baltisberger, et al. 1996). P_Q is the same as that observed for $NaAlO_2$, but δ_{iso} is about 10 ppm lower than in the crystalline model. The second major peak is similar in position to Si-O-Al peaks previously reported in 3QMAS studies of $NaAlSi_3O_8$ glass (Dirken et al. 1997; Xu et al. 1998) and for the zeolite stilbite (Xu and Stebbins 1998). If significant amounts of Si-O-Si sites were present, a third peak at lower frequency in the isotropic dimension would be observed, but the concentration of this species is expected to be low in this composition.

In the CAS glass (Fig. 3), a clearly defined ridge attributable to Al-O-Al sites is again seen, although its resolution from the Si-O-Al is not as good as in the NAS glass because of overlapping chemical shift ranges. The non-bridging oxygen (NBO) peak is also clearly seen, as recently reported for $CaAl_2Si_2O_8$ glass (Stebbins and Xu 1997). The peak maximum for Al-O-Al (–41 and 56 ppm in isotropic and MAS dimensions) can again be used to estimate mean δ_{iso} and P_Q values as about 68 ppm and 2.4 MHz. The former is similar to the most common value in crystalline $CaAl_2O_4$, although the latter is significantly higher than the data for all but one of the sites in the crystal.

DISCUSSION

The P_Q values observed here for the aluminates are the lowest reported for bridging O atoms (Stebbins 1995). C_Q measures the electric field gradient at the nucleus under observation, and for ^{17}O, is at least roughly correlated with the deviation from an ideal, tetrahedral or octahedral environment of the coordination of the O site by first neighbor cations. Thus, Si-O-Si atoms, with highly asymmetric, twofold coordination, have relatively high C_Q values of 5 to 6 MHz (Stebbins 1995). Al-O-Si sites, which are in addition coordinated by one or more low-charge cations such as Na^+ or Ca^{2+}, have lower C_Q values, typically 3.4 to 4 MHz. Non-bridging O atoms generally have even lower values, 2 to 3.5 MHz. The low C_Q values for Al-O-Al sites seem to continue this trend, as predicted by ab initio calculations, which estimated C_Q for such sites as low as 2.3 MHz (Tossell 1993). The even lower experimental values probably reflect the greater coordination number of the Al-O-Al sites by Na^+ or Ca^{2+} in the real crystals, which may reduce the Al-O-Al angle further and increase the local charge symmetry.

Isotropic chemical shifts for ^{17}O are not well understood. However, some broad trends are clear. The offset of δ_{iso} between the sodium- and calcium-bearing crystals and glasses is expected from similar effects for non-bridging O atoms (Florian et al. 1996; Stebbins, et al. 1997) and for Si-O-Al sites (Stebbins and Xu 1997; Xu, et al. 1998). For Si-O-Si sites in coesite, there appears to be no simple correlation between δ_{iso} and the Si-O-Si angle, although correlations between C_Q and angle are well known (Grandinetti et al. 1995). For Al-O-Si sites in the zeolite stilbite, C_Q and δ_{iso} are positively correlated (Xu and Stebbins 1998), suggesting that Al-O-Si angle may explain at least some of the variance in δ_{iso}. If this trend is applicable to

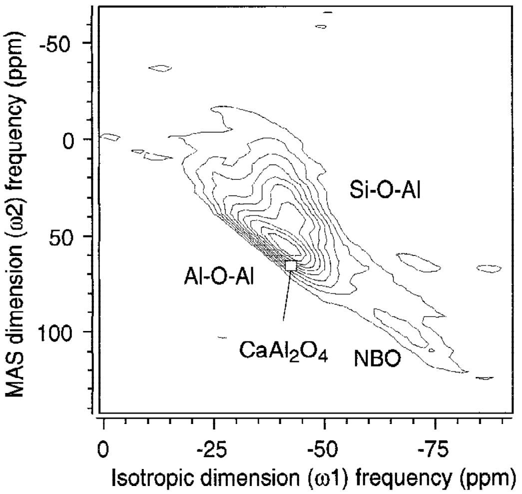

FIGURE 3. Various ^{17}O 3QMAS spectra for CAS glass at 9.4 T. Contours as in Figure 2. The predicted position of the most intense peak for crystalline $CaAl_2O_4$ is shown.

Al-O-Al sites, then the peak in the $CaAl_2O_4$ spectrum with the lowest δ_{iso} value would correspond to the site with the narrowest angle [O6, with an angle of about 115° (Hörkner and Müller-Buschbaum 1976)]. The two highest frequency peaks, with relative areas of about 1:2, would then correspond to O7 (132°) and O2 + O9 (both about 130°). However, the relatively large C_Q of the lowest frequency peak would seem to be inconsistent with this speculation. In any case, other structural factors, such as number and proximity of Ca^{2+} neighbors, are also likely to have significant effects on δ_{iso} and C_Q.

By composition alone, about 17.6% of the O atoms in the NAS glass (Si/Al = 0.7) are expected to be Al-O-Al; in the CAS glass (Si/Al = 0.5) the fraction is expected to be about 33.3%. A recent ^{29}Si MAS NMR study of a series of NAS and CAS glasses suggested that, particularly for the latter, somewhat more Al-O-Al sites are expected as the result of greater disorder than allowed by strict "aluminum avoidance" (Lee and Stebbins 1999). However, in these Al-rich samples, predicted Al-O-Al fractions are not too different from the minimum allowed by composition: 18.4 to 21.4% for the NAS glass, 36.7 to 38% for the CAS glass.

These 3QMAS spectra are, in principle, not precisely quantitative, because the efficiency of triple quantum excitation, and that of reconversion to the observed NMR signal, depend significantly on C_Q (Frydman and Harwood 1995; Amoureux et al. 1996). However, for relatively small variations in C_Q, spectra can be at least semi-quantitative, as illustrated for the Si-O-Al and Si-O-Si sites in $NaAlSi_3O_8$ glass (Dirken et al. 1997; Xu et al. 1998). In the isotropic projection for the 3QMAS spectrum for the NAS glass (Fig. 2), the Al-O-Al peak area is about 20 ± 2% of the total, in good agreement with the expected value. Assessment of the areas of such peaks in spectra for CAS glasses is made difficult by their overlap with Si-O-Al peaks. However, it is clear in the ^{17}O 3QMAS spectrum of $CaAl_2Si_2O_8$ glass previously published (Stebbins and Xu 1997) that an Al-O-Al peak is present, as the "tail" of such a ridge-shaped feature is visible at an isotropic dimension position of about –25 ppm. This finding qualitatively supports our recent conclusion, based on ^{29}Si spectra, that aluminum avoidance is significantly violated in such glasses (Lee and Stebbins 1999).

Recent ^{17}O 3QMAS studies of $NaAlSi_3O_8$ (albite) glass have reported that Al-O-Al sites were not detected (Dirken et al. 1997; Xu et al. 1998). The position of this peak reported here confirms that it should be well-resolved and detectable at a level of a few percent or better. A fully random model of Al/Si distribution predicts about 6% Al-O-Al at this composition, which can probably be ruled out (Lee and Stebbins 1999). However, some violation of Al avoidance is allowed by current detection limits. In the future, more detailed studies should enable the extent of Al avoidance, and its importance to the overall energetics of both glassy and crystalline materials, to be more accurately assessed than has previously been possible.

Finally, we note that detection and eventual quantitation by NMR of Al-O-Al sites in glassy, and perhaps in crystalline, aluminosilicates, may help constrain assignments of bands in Raman spectra, which has been somewhat controversial (McMillan et al. 1982, 1998). Such a result would be particularly helpful in interpreting vibrational spectra acquired under conditions (e.g., ultra-high pressure) where NMR on solid materials is difficult or impossible (McMillan and Wolf 1995).

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