Network oxygen sites in calcium aluminoborosilicate glasses: results from $^{17}\text{O}\{^{27}\text{Al}\}$ and $^{17}\text{O}\{^{11}\text{B}\}$ double resonance NMR

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Abstract

^{11}B , ^{17}O , and ^{27}Al NMR has widely been used to quantify numerous aspects of oxide glass structure, but many issues remain to be resolved, including basic issues of assignment of overlapping ^{17}O resonances. Double resonance NMR, involving cation spin pairs such as ^{27}Al and ^{11}B , has provided further details of network connectivities in some multicomponent glasses; very recent work on ^{27}Al - ^{17}O has allowed unique identification of non-bridging oxygen (NBO) on aluminum cations in lanthanum aluminoborosilicate glasses [1]. Here we have explored $^{17}\text{O}\{^{27}\text{Al}\}$ and $^{17}\text{O}\{^{11}\text{B}\}$ TRAnsfer of Population in DOuble-Resonance (TRAPDOR) NMR experiments in several calcium aluminosilicate and aluminoborosilicate glasses. We have demonstrated clear distinction among resonances for ^{17}O associated with boron and/or aluminum, including quantification of NBO associated with boron, aluminum and silicon in these multicomponent glasses. Additionally, spectral components for bridging oxygens and non-bridging oxygens with aluminum, boron, and silicon can also be at least in part separated, allowing for comparison to proportions expected if cations were connected via random mixing.

1. Introduction

Oxide glass structures are typically viewed as networks of strongly bonded, small, low coordination, network forming cations such as B^{3+} , Si^{4+} , Al^{3+} , P^{5+} , and Ge^{4+} , connected to each other by “bridging oxygens” (BO). The network is interrupted by “non-bridging oxygens” (NBO) which are shared between a network former and multiple network modifying cations, which are larger, and have lower charges such as Na^{+} , Ca^{2+} . The latter often act as well to balance partial negative charges on BO.

Nuclear Magnetic Resonance (NMR) spectroscopy has become very useful for elucidating short to medium range structure in oxide glasses, most often on isotopes of network cations such as B, Al, Si or P, but also on other components [2–6]. ^{17}O NMR has become an important complement to NMR studies of cation environments. Standard one-dimensional (1D) magic-angle spinning (MAS) NMR can often directly quantify proportions of NBO vs. BO, NBO bonded to various network formers and modifiers, and in some cases can reveal information on abundances of BO species, thus leading to conclusions about order/disorder in the network [1,7–10]. However, in some systems, such as multicomponent aluminoborosilicate glasses, the ^{17}O resonances associated with various oxygen species are overlapped due to insufficient separation in chemical shifts. ^{17}O triple-quantum magic-angle spinning (3QMAS) NMR has been shown to enhance resolution and allow quantification of both BO and NBO in aluminosilicate [11–14], borosilicate, and more complex compositions [15,16]. But in glasses where there are multiple network forming cations, such as many technologically important aluminoborosilicates, 3QMAS is often unable to pull apart the large number of different oxygen species with overlapping signals.

Double resonance (DR) NMR can reveal more direct information on the proximity of cation-cation and cation-anion pairs in oxide glasses and can yield more structural details in multicomponent systems with overlapping resonances [17]. This approach relies most commonly on nuclear dipole-dipole couplings, which depend strongly on the distance between the two spins, r , and their gyromagnetic ratios, $\gamma_{(1)}$ and $\gamma_{(2)}$, and is proportional to $\gamma_{(1)}\gamma_{(2)}/r^3$. DR NMR is mostly commonly known in solid-state NMR in the form of Cross Polarization (CP) MAS, for example in hydrous glasses, where this method can highlight species such as Al that are closest to ^1H , which has especially strong dipolar couplings [18,19]. Most applications of double

resonance methods to anhydrous oxide glasses have, in contrast, been for other strongly coupled spin pairs such as ^{11}B - ^{27}Al and ^{11}B - ^{31}P , where a great deal has been learned about network ordering and connectivity [20–25]. Some limited double resonance NMR work has been done on spin pairs involving ^{17}O [26,27], including very recent work on $^{29}\text{Si}\{^{17}\text{O}\}$ cross-polarization heteronuclear correlation spectroscopy (CP-HETCOR) in Ca/Mg silicates [28].

Recently, another type of DR experiment, $^{17}\text{O}\{^{11}\text{B}\}$ Rotational Echo Double Resonance (REDOR) NMR, helped define BO bonded to boron in borosilicate glasses by observing the ^{17}O spectrum with and without dephasing of the ^{11}B spins [29]. In this notation, the first nuclide of the pair is directly observed, the second, in brackets, is irradiated during the experiment to dephase these spins and restore the dipolar interaction with the observe nuclide that is otherwise removed by magic angle spinning. In another study, a related experiment, $^{17}\text{O}\{^{27}\text{Al}\}$ TRANSfer of Population in DOuble-Resonance (TRAPDOR) clearly selected NMR signals from oxygen sites bonded to aluminum in lanthanide aluminosilicates, and showed that Al-NBO play an unexpectedly important role in these structures [1]. Both of these studies are notable in that they show the practicality of obtaining useful structural data in glasses from DR NMR involving quadrupolar nuclides ^{17}O (spin 5/2) and cations ^{11}B (spin 3/2) and ^{27}Al (spin 5/2).

Both of these applications of TRAPDOR and REDOR produce a selective ^{17}O spectrum as a difference $\Delta S = (S_0 - S)$ where S_0 is a control ^{17}O spectrum and S is an ^{17}O spectrum whose intensity is diminished by dephasing of the cation nucleus. Both methods rely on the through-space dipolar interaction to provide coupling. For an experiment involving ^{17}O this coupling is substantially reduced by the relatively low γ for this nuclide, but first-neighbor cation-oxygen distances are short (typically 0.15 to 0.18 nm), giving substantial dephasing in a reasonable time. Distances from oxygen to second neighbor cations are more than 2 times greater, reducing the

coupling constants by at least 8 times, and second-neighbor coupling thus causes negligible dephasing. It is thus possible to tune the experiment to see only one-bond couplings.

In this study we use a combination of $^{17}\text{O}\{^{27}\text{Al}\}$ and $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR NMR to produce selective ^{17}O spectra for oxygens bonded to ^{11}B or to ^{27}Al . We examine the network structures of three calcium aluminoborosilicate glasses, after systematic testing and optimization on several simpler binary and ternary compositions. We chose glasses with varying aluminum, boron and silicon contents to give large variations of oxygen speciation and differing levels of expected NBO. The latter species is especially interesting, as although it is commonly assumed to be primarily bonded to Si it can also be present on other network cations. Proportions of some of the many permutations of bridging oxygens in these complex systems are also examined in detail. We show that these experiments can be effectively used to quantify oxygen speciation even in systems with highly overlapped ^{17}O resonances, and demonstrate its promise for complex glass compositions.

2. Experimental Procedures

2.1 Glass Synthesis and Characterization

Glass compositions are listed in Table 1. All are ^{17}O -enriched. The BB [30], CAS [8], and CABS1 [31] samples are the same as have been described in previous ^{17}O NMR studies. The new CABS2 glass is similar to the CABS7 composition previously studied by Du [32] and Wu [33], and the new CABS3 is of similar composition to CABS1 described by Morin [34]. CABS2 and CABS3 glass samples (700 mg each) were made using CaO , Al_2O_3 , ~40% ^{17}O -enriched SiO_2 (made as described in [35]), and B_2O_3 (CABS3) or ^{17}O -enriched B_2O_3 (CABS2, made as described in [36]). The Al_2O_3 , the ^{17}O enriched silica, and the CaO were dried overnight at

1000°C and used immediately. To speed spin-lattice relaxation, 0.2 wt% cobalt oxide was added. CABS3 was melted in a Pt/10%Rh crucible at 1400°C for 15 minutes in an Ar atmosphere and quenched by immersing the bottom of the crucible in water; CABS2 was heated in a sealed Pt tube (to limit ^{17}O loss) at 1500°C for 30 minutes and quenched via immersing the tube in water. Weight losses during both syntheses were below 2%. Experimental glass samples were examined with polarized light microscopy at 400x: all were homogeneously isotropic with no observed crystalline material.

2.2 Solid-State NMR

^{11}B , ^{17}O , and ^{27}Al MAS NMR experiments were carried out using a Varian/Chemagnetics T3 HXprobe with a Varian Unity/Inova 600 spectrometer (14.1 T), at Larmor frequencies of 192.4 MHz, 81.4 MHz, and 156.3 MHz, respectively. Samples, weighing 35-50 mg, were packed into 3.2 mm zirconia rotors and spun at the magic angle at 20 kHz. Chemical shifts are reported in ppm relative to 1.0 M boric acid at 19.6 ppm, 20% ^{17}O -enriched H_2O at 0 ppm, and 0.1M acidified $\text{Al}(\text{NO}_3)_3$ at 0 ppm, respectively. Recycle delays ranging from 0.1 - 0.2 s were used with a single 0.3 μs pulse, corresponding to a radiofrequency (rf) tip angle of less than one-third of the solid 90° pulse duration, with rf powers of approximately 100 kHz. $^{17}\text{O}\{^{27}\text{Al}\}$ and $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR spectra were collected with the same spectrometer using a Varian/Chemagnetics T3 HXY probe following procedure similar to Jaworski et al. [1]. Samples weighing 140-220 mg were packed into 5 mm zirconia rotors and spun at 10-12 kHz, which was sufficiently high to move spinning sidebands outside the spectral region occupied by the central transition signals in most cases. The pulse sequence used involved a spin echo and central-transition selective 180° pulse on the ^{17}O channel in the absence (S_0) and presence (S) of

a high-power recoupling pulse on the secondary channel (^{11}B or ^{27}Al). The spin echo periods and the nutation frequency of ^{27}Al (58 kHz) and ^{11}B (25 kHz) were optimized to provide maximum dephasing for one-bond couplings. The exact dephasing for these conditions was determined with model glass compositions as described below. In typical experiments, high-power recoupling pulse periods of 2.5 to 3 ms were used, corresponding to 28 to 32 integral rotor periods. The peak area of the difference spectrum $\Delta S = (S_0 - S)$, adjusted for dephasing efficiency, represents the abundance of each oxygen species.

2.2.1 Fits for Solid-State NMR spectra

Peak areas were determined from fits to spectra with the program “DMFIT” [37], using Gaussian line shapes only, chosen as a useful approximation assuming predominance of chemical shift distributions over quadrupolar line shapes at this high magnetic field. Difference spectra for both $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR and $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR were fitted with multiple Gaussian components to reproduce the NBO and BO lineshapes. Individual $^{17}\text{O}\{^{11}\text{B}\}$ or $^{17}\text{O}\{^{27}\text{Al}\}$ difference spectra were each fitted with a single Gaussian under the position expected for the NBO peaks, ranging from 80-140 ppm, and with three Gaussians under the larger peak associated with bridging oxygens, accounting for the expected three permutations of bridging oxygens associated with either Al or B. The three BO peaks were initially assigned positions, widths and heights manually and then were allowed to covary in position, width and height using DMFIT’s built-in fitting optimization program. This procedure was run multiple times with varying starting parameters to determine different possible combinations of three Gaussians that fit the bridging oxygen peaks in the difference spectra for $^{17}\text{O}\{^{11}\text{B}\}$ and $^{17}\text{O}\{^{27}\text{Al}\}$. Fits

containing Gaussian parameters with widths greater than those typically observed in single component line shapes were discarded.

The potential fitted components for the $^{17}\text{O}\{^{27}\text{Al}\}$ difference spectra were then multiplied by a correction factor of 1.05 to account for 95% efficiency of aluminum dephasing irradiation, as determined in results of test experiments described below. ^{11}B has a natural isotopic abundance of 80%, so the potential fitted components for the $^{17}\text{O}\{^{11}\text{B}\}$ difference spectra were multiplied by 1.27 for the non-bridging oxygen peak and 1.11 for the bridging oxygen peak to account for both the 93% efficiency of the boron irradiation and the 80% abundance of ^{11}B , as explained further in the Results and Discussion section below. After correction, fits that did not contain a Gaussian BO peak shared between $^{17}\text{O}\{^{11}\text{B}\}$ and $^{17}\text{O}\{^{27}\text{Al}\}$, representing B-O-Al, were also discarded. For the remaining fits, both difference spectra were then overlain and compared to the reference spectra. Combined fits that had intensities in areas not seen in the reference spectra were discarded.

Any intensity remaining in the reference spectrum after addition of both difference spectra was attributed to oxygen connected only to silicon, and was manually fitted as a single Gaussian under the bridging oxygen peak, representing Si-O-Si, and a single Gaussian under the area associated with non-bridging oxygens, representing Ca-O-Si (i.e. Si-NBO).

3. Results and Discussion

3.1 ^{11}B and ^{27}Al MAS NMR

The CABS1, CABS2 and CABS3 glasses studied here had ^{11}B MAS spectra (not shown) similar to those previously reported [31,32,34]. Signals from ^{13}B and ^{10}B groups were well-resolved, as is typical for data at 14.1 T. From the integrations of these two peaks, it was possible

to calculate values of N_4 (fraction of total B as $^{[4]}\text{B}$) of 0.03 for CABS1, 0.11 for CABS2 and 0.12 for CABS3. The values for CABS2 and CABS3 are similar to previously reported values for water-quenched glasses with high NBO content [33,38,39].

^{27}Al MAS NMR on the CAS, CABS2 and CABS3 glasses (not shown) can be similarly used to differentiate between $^{[4]}\text{Al}$ and $^{[5]}\text{Al}$, and closely resemble those previously published on similar compositions. [8,32,34] The latter species produces a smaller shoulder at 35 ppm on the main $^{[4]}\text{Al}$ peak. These spectra indicate that more than 85% of aluminum in these glasses is tetrahedrally coordinated.

3.2 TRAPDOR on test systems

3.2.1 Testing of experimental conditions for $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR

To test power levels and efficacy of the TRAPDOR experiment for selecting signal for ^{17}O sites with ^{11}B first neighbors, we used a barium borate glass, BB. All oxygen anions in this glass have one boron (NBO) or two boron (BO) neighbors, so this glass can be used to yield information about what fraction of ^{17}O signal is dephased with the ^{11}B pulse. The ^{17}O TRAPDOR NMR reference spectrum (Figure 1A) shows a peak associated with BO, centered at 85 ppm, and an NBO peak, centered at 180 ppm, which overlaps with the edge of the spinning sideband centered at 230 ppm. The spectrum collected with the ^{11}B pulse has much lower intensity, demonstrating that most of the ^{17}O spins were suitably close to a ^{11}B neighbor to be affected by the recoupling pulse. The difference spectrum highlights signals from oxygen anions with one or two ^{11}B neighbors.

Since all of the oxygens in this glass are directly bonded to boron, we expected the recoupling pulse to eliminate most of the signal. ^{11}B has a natural isotopic abundance of 80%,

indicating that 20% of the total boron in this sample would be unperturbed by the irradiating pulse targeting only ^{11}B . This would statistically imply that 20% of total NBO and 4% of total BO would be adjacent to only ^{10}B and that signal from these oxygens would therefore remain after ^{11}B irradiation, if the ^{11}B dephasing pulse was 100% efficient. Any remnant ^{17}O signal above these values can therefore be used to calculate the actual efficiency of ^{11}B dephasing at the conditions used in this experiment. Gaussian fitting of the dipolar dephased spectrum (Figure 1A) yields a total remnant signal equal to 11% of the total BO intensity, suggesting that the actual efficiency of the ^{11}B pulse was approximately $93\pm 1\%$, with a correspondingly smaller than expected difference spectrum. This 93% dephasing efficiency is also in reasonable agreement with the size of the remnant signal in the NBO area of this spectrum (accounting again for the 80% isotopic abundance of ^{11}B), though exact quantification of this peak is difficult due to size and overlap with the spinning sidebands. As noted in the experimental section, we used this estimate of 93% efficiency to correct fitted peak areas for oxygens associated directly with ^{11}B .

We also tested maximum possible power levels for the $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR sequence in preliminary experiments on a calcium aluminoborosilicate glass, CABS1. The spectrum of this glass, which contains a relatively low amount of B_2O_3 , was expected to undergo minimal changes as a result of the irradiating ^{11}B pulse. The ^{17}O reference spectrum for this glass, shown in Figure 1B, contained a peak centered around 50 ppm, representing bridging oxygens connected to boron, aluminum and silicon, and a peak centered at 135 ppm, representing non-bridging oxygens. At the optimized ^{11}B pulse level the integrated intensity of the TRAPDOR spectrum's bridging oxygen peak was 80% of the same peak in the reference spectrum. Upon fitting the difference spectrum, a peak corresponding to 16% of the total bridging oxygen peak can be attributed to bridging oxygens connected to at least one ^{11}B .

3.2.2 Experimental conditions for $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR

In order to test the efficacy of the $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR pulse sequence in reducing signal from ^{17}O anions with ^{27}Al cation neighbors, we studied a calcium aluminosilicate glass, CAS. This glass, which has been previously described [8], has an unusually high Al/Si ratio (=6). Its ^{17}O spectrum clearly shows NBO peaks for both Si (energetically favorable, centered at 120 ppm), and Al (energetically less favored, but required due to composition, centered at 150 ppm). There is also a large BO peak centered at 70 ppm, which must contain signal for mostly Al-O-Al and Al-O-Si, just by composition.

The $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR results for this glass, seen in Figure 2, show loss of the peak associated with Al-NBO, and almost all of the BO signal, as expected from the presence of Al in first shell for these oxygen anions. As in previous paper on ^{17}O MAS NMR of this glass [8], the reference spectrum could be fitted to obtain NBO speciation, but the TRAPDOR results allow Si-NBO to be more clearly resolved. The difference spectrum similarly allows for direct viewing of signal for oxygen connected to at least one aluminum cation. Upon fitting these data (Figure 3), it is possible to measure the relative abundances of NBO coordinated to Al (46%) and Si (54%). These percentages, with a strong energetic favoring of Si-NBO relative to a random distribution on Al and Si, agree with those suggested by previously published work [8]. It was also possible to determine relative abundances of bridging oxygens connected to Al (either as Al-O-Al or Al-O-Si, 94% of BO). 6% of the total area under the bridging oxygen peak was not affected by the ^{27}Al pulse. Due to the low abundance of SiO_2 in this glass and measured intensity of Si-NBO, stoichiometrically this cannot all be attributed to Si-O-Si BO, which can account for a maximum of 1% of total BO in this composition. Instead, this is either a result of

heterogeneities present within the sample or by inefficiencies in the ^{27}Al pulse similar to those seen in the ^{11}B pulse. Given that no heterogeneities were visible under 400x light microscope, we concluded that there was a $95\pm 1\%$ efficiency in the pulse and used a multiplication factor of 1.05 to adjust amplitudes of fits determined from the difference spectra.

From analyses of the results for BB, CABS1 and CAS glasses, it is therefore clear that both $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR and $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR can, with appropriate power levels and pulse lengths, be used to select components of ^{17}O spectra with specific first neighbor cations, with high, if slightly imperfect, efficiency.

3.3 TRAPDOR NMR on 4-component glasses

In ^{17}O MAS NMR spectra of complex, multicomponent glasses, signals from different oxygen species may strongly overlap, especially those for BO. Some of these overlapping resonances have been more clearly viewed in multiple quantum magic-angle-spinning (MQMAS) NMR [15,16] but there still remain difficulties in quantification resulting from species with resonances that remain overlapped in MQMAS (and other technical issues unique to MQ spectroscopy such as very long experimental times). TRAPDOR NMR allows for direct observation of these oxygen species in a way that MAS and MQMAS NMR does not provide. The use of both $^{17}\text{O}\{^{11}\text{B}\}$ and $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR NMR on the same glass could help differentiate between oxygens coordinated with ^{11}B or ^{27}Al . Here we explore the potential of this experiment to help unravel these complexities in two carefully selected Ca aluminoborosilicate compositions, for which we can independently examine oxygen interactions with aluminum and boron neighbors. With extensive testing and calibration using model systems to determine pulse

strengths, times, delays and efficiencies, TRAPDOR NMR can yield quantitative information on oxygen speciation.

3.3.1 $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR

3.3.1.1 CABS2

The CABS2 composition, similar to commercial E-glass, has a high silicon content and much lower concentrations of Al and B. Its ^{17}O reference spectrum (Figure 4) is in agreement with previously published spectra of glasses of similar composition [32]. The main BO peak, centered at 35 ppm, contains signal for a large number of different bridging linkages, potentially all permutations of oxygen connected to Si, Al, ^{13}B and ^{14}B (although ^{11}B MAS NMR of this glass indicates 89% ^{13}B). The peak associated with Si-NBO is prominent at around 100 ppm. The expected peak associated with B-NBO is partially obscured by the spinning sideband centered at 155 ppm.

The $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR spectrum (Figure 4) looks similar to the ^{17}O reference spectrum, as is expected for a high-silica, low-boron glass. The difference spectrum shows the oxygen anions that have ^{11}B cations as neighbors. Notably, there is the B-NBO peak centered around 130 ppm, now separated from the sideband, as the latter is comprised mostly of signal from oxygen anions without boron neighbors and is “edited out” by this method. This B-NBO peak can be fitted with a Gaussian, yielding the relative abundance of B-NBO, as seen in Table 2. Also visible is a broad BO feature centered at 55 ppm, with abundance shown in Table 3, corresponding to oxygen anions with either one or two ^{11}B neighbors, which was selected out of the overlapping BO region. This component is on the higher frequency (higher chemical shift) side of the BO peak, in agreement with a previous MQMAS study of a glass of similar

composition [15], which found that the center of gravity of the peak assigned to B-O-Si had a higher chemical shift in the MAS dimension and a more negative shift in the 3Q isotropic dimension. In that paper, peaks for B-O-Al and B-O-B were assumed to be much smaller and were not resolved, but new TRAPDOR NMR results allow for further discussion of those species below.

3.3.1.2 CABS3

The CABS3 composition was chosen to have much higher boron and aluminum contents as well as a much higher NBO content. The ^{17}O reference spectrum for this glass (Figure 5) shows a peak associated with BO, centered at 60 ppm, and a large area associated with NBO, spanning from 100 to 150 ppm. The observed NBO content, Table 2, and oxygen species are consistent with those expected from ^{11}B spectra [34] and stoichiometric constraints. The spectrum collected with the ^{11}B recoupling pulse has much reduced intensity, as expected from the higher boron content of this glass. The difference spectrum again clearly selects the oxygen sites with first neighbor ^{11}B cations, in both the bridging oxygen and the non-bridging oxygen peaks. The NBO peak associated with boron is the higher frequency portion of the large NBO area, centered at 130 ppm. For the BO, the higher frequency part of the peak is again dominated by oxygen with 1 or 2 ^{11}B neighbors, indicating a higher average chemical shift for these oxygen sites, as noted above for CABS2 and in ^{17}O 3QMAS spectra on other Ca aluminoborosilicates [15].

3.3.2 $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR

3.3.2.1 CABS2

As was seen for the $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR results, the overall features of the CABS2 reference and $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR spectra (Figure 6) are similar, as expected from the relatively low Al content. The difference spectrum shows a broad peak for BO with 1 or 2 Al neighbors, strongly overlapped with other BO peaks, as was seen in 3QMAS data when projected in the MAS dimension [15]. There is a shoulder at 110 ppm corresponding to Al-NBO, which has not been previously observed in this composition.

3.3.2.3 CABS3

For CABS3, there is a much more drastic effect of $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR (Figure 7), as was expected due to an Al content much higher than that of CABS2. The NBO peaks were partially perturbed, but there was a large reduction in the BO peak, as expected if most of the BO have at least one Al neighbor. The difference spectrum again shows oxygen anions with aluminum first neighbors. The BO peak in the $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR difference spectrum is shifted slightly down in frequency from the BO peak of the reference spectrum, and overlaps to great extent with the BO peak seen in $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR difference spectrum. In this glass there is also a more prominent feature near to 120 ppm, indicating some Al-NBO.

It is in the combination of the $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR and $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR spectra that the power of this method is illustrated. By combining the difference spectrum for $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR, showing oxygens with one or two boron neighbors, and the difference spectrum for $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR, showing oxygens with one or two aluminum neighbors, it is possible to select the signal for oxygens with no boron and no aluminum neighbors, such as Si-O-Si. It also allows for observation of all three types of NBO, with measured abundances and resonance shifts as listed in Table 2, even for compositions that have low NBO abundance and partially

overlapping signals. Fully exploiting this potential requires detailed analysis of the spectra, however, as described in the next section.

3.4 Fits and species abundance

We have demonstrated that the TRAPDOR experiments can isolate partially resolved ^{17}O signals from NBO, and from unresolved BO bonded to either boron or aluminum. The question remains as to whether this combination of experiments could be utilized to further unravel complex BO distributions with many combinations of boron, aluminum and silicon neighbors. To do this we fit the Al- or B-selective TRAPDOR spectra with multiple, highly overlapped components hypothesized to be associated with distinct signals for different BO species (i.e. Al-O-Al, Al-O-Si, Al-O-B for ^{27}Al and B-O-B, B-O-Al, and B-O-Si for ^{11}B) as described in the experimental procedures. This process resulted in unique combined fits for both CABS2 and CABS3 as can be seen in Figures 8 and 9, respectively. The integrated values for these Gaussians can be seen in Table 3. The intensities of some of the component peaks, e.g. those for Al-O-Al and B-O-B in CABS2 and Si-O-Si in CABS3, are quite low and their positions and areas may have relatively large uncertainties.

The actual physical meanings of the derived proportions of BO species can be given a simple initial test by comparison with a model based on random connections among the network cations in a given composition, after accounting for the experimentally measured proportions of NBO associated with B, Si, or Al and the (relatively low) proportions of ^{41}B from the ^{11}B MAS data. Simple bond counting allows the proportions of each BO species for a random cation distribution to be calculated, combining estimates for ^{31}B and ^{41}B neighbors as we have not attempted to distinguish this in the experiments. Results for this model in comparison to the

integrated fits of the experimental results are shown in Table 3. The majority of the fitted results are within 5% (relative) of the percentages expected from the random model, which is similar to the uncertainty in our estimates arising from fitting and experimental errors. The largest deviations arise for species that are often considered to be energetically unfavorable because of their high formal charges, such as Al-O-Al, though Ca^{2+} is expected to stabilize these BO more so than alkali cations.

Among the few systems where ordering caused by ‘aluminum avoidance’ has been quantified by NMR are the $\text{SiO}_2\text{-Na}_2\text{Al}_2\text{O}_4$ and $\text{SiO}_2\text{-CaAl}_2\text{O}_4$ pseudobinaries [13,40,41], for which the results were treated with a simple thermodynamic order parameter. For comparison, we consider simply the TRAPDOR results for BO involving only Si and Al, normalized to 100%. These can then be compared to predictions from the model of Lee and Stebbins [40] for the same Si/Al ratio. From this comparison, we find significant differences in both minor species (aluminum avoidance in calcium aluminosilicates predicts 1% Al-O-Al in CABS2, whereas we found 4%) and in major species (a calcium aluminosilicate of CABS3 ratios would be expected to have 63% Si-O-Al from Lee’s model while our fits show 46% of that species in that composition). Thus, it does appear that the results from the TRAPDOR experiments indicate a more disordered distribution of at least Si and Al than is expected from models based on simple aluminosilicate binaries. This could be related to the high NBO content of the glasses studied here, and/or to changes in network structure upon addition of boron, both of which will affect the distributions of charge-balancing Ca^{2+} cations. The effects on network cation ordering of these compositional variables have not been well-quantified, and both are important in many technological as well as geological glasses.

Although we consider the application of the TRAPDOR NMR method to oxygen speciation in glasses, and the analysis of such complex results, to be in its early stages, the agreement between experimentally derived speciation and the most simple random (apart from non-random NBO distributions) model of network mixing is quite promising for future, more detailed studies of compositional, temperature, and pressure effects on network order/disorder.

4. Conclusions

In this study we have tested $^{17}\text{O}\{^{11}\text{B}\}$ and $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR NMR on several simple glass compositions and have found that it can select out ^{17}O signals for oxygen not bonded to ^{11}B or ^{27}Al , allowing for observation, by difference, of oxygen bonded to ^{11}B or ^{27}Al or both. The combination of the results from these two techniques was successfully used to highlight oxygen bonded only to Si.

This technique allowed for new resolution for network species in calcium aluminoborosilicate glasses, where signal for various types of BO and NBO overlap to great extent. Through TRAPDOR NMR it was possible to estimate concentration of NBO connected not only to predominant Si, but also aluminum and boron, as well as estimates of permutations of BO shared between these three network forming cations. Initial work on two calcium aluminoborosilicate glasses indicates that distribution of BO among these species is closer to random than suggested by models based on a simple $\text{SiO}_2\text{-CaAl}_2\text{O}_4$ pseudobinary. Note that the fit parameters for the component peaks were derived independently for the two glass compositions, and without constraint by the compositions themselves (e.g. B/Al/Si ratios), to more carefully test this method. Shared constraints across multiple compositions, and accounting

for glass stoichiometry, could be a useful approach when analyzing further data for more samples with more systematic compositional variation.

Future directions for this work involve more systematic exploration of the effects of composition on both NBO and BO distributions as well as effects of the field strength of the network modifying cation. This method could allow a more in depth look into technologically important alkali aluminoborosilicates. The addition of double resonance NMR with ^{17}O and ^{29}Si , may allow for observation of the complete picture of bonding in these compounds.

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Table 1. Nominal composition of samples, in mol%

Label	BaO	CaO	Al ₂ O ₃	B ₂ O ₃	SiO ₂
BB	40	0	0	60	0
CAS	0	58.5	29.4	0	11.8
CABS1	0	30.4	32.9	10	26.8
CABS2	0	20	8	7	65
CABS3	0	43.4	14.1	21.3	21.3

Table 2. Non-bridging oxygen species concentrations, as percent of total NBO, from fitting of TRAPDOR spectra. Uncertainty in measurement is $\pm 2\%$. Values in parenthesis represent peak center of fitted Gaussian in ppm.

Label	Al-NBO	B-NBO	Si-NBO
CABS2	8.5	24.2	67.3
(peak center)	(99.9)	(132.8)	(100.6)
CABS3	14.5	47.2	38.3
(peak center)	(100.0)	(132.7)	(104.4)

Table 3. Bridging oxygen species concentrations, as percent of total BO, random model vs. results of fitting and combination of TRAPDOR spectra. Uncertainty in measurement is $\pm 2\%$. Values in parenthesis represent peak center of fitted Gaussian in ppm.

Label		B-O-B	B-O-Al	B-O-Si	Al-O-Al	Al-O-Si	Si-O-Si
CABS2	random model	1.2	3.9	15.7	3.2	25.6	50.4
	experimental	1.0	2.8	14.8	3.0	27.4	51.0
	(peak center)	(83.0)	(65.5)	(48.0)	(48.6)	(37.6)	(27.8)
CABS3	random model	15.0	29.6	17.9	14.6	17.7	5.2
	experimental	13.0	30.4	17.7	15.9	17.8	5.2
	(peak center)	(74.3)	(66.5)	(58.6)	(61.5)	(47.5)	(45.4)

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402

Figure 1: $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR NMR collected at 14.1 T. ^{17}O observed reference spectrum is solid black, spectrum with ^{11}B irradiation (dipolar-dephased spectrum) in dashed line. Difference spectrum (reference spectrum – dipolar-dephased spectrum) in dotted line. (A) BB. Area between 0 and 140 ppm associated with bridging oxygens. Area between 200 and 140 ppm associated with non-bridging oxygens. (B) CABS1 glass. Area between 0 and 90 ppm associated with bridging oxygens. Area between 200 and 140 ppm associated with non-bridging oxygens. Spinning sideband designated with stars.

Figure 2: $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR NMR of CAS glass. Collected at 14.1 T, ^{17}O observed reference spectrum in solid black, dipolar-dephased spectrum with ^{27}Al irradiation in dashed line. Difference spectrum (reference spectrum – dipolar-dephased spectrum) in dotted line. Area between 90 and -10 ppm associated with bridging oxygens. Area between 200 and 90 ppm associated with non-bridging oxygens. Spinning sideband designated with stars.

Figure 3: Simulated fit for $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR NMR of CAS glass. The upper black line represents the ^{17}O reference spectrum. The lower solid red line represents the combination of the four Gaussians. The two red dashed lines represent Al-NBO (centered at 150 ppm) and Al-BO (centered at 70 ppm, Al-O-Al and Al-O-Si). The green dot/dash line represents Si-NBO (centered at 116 ppm,). The remnant black Gaussian (centered at 72 ppm,) is too intense to be associated with Si-O-Si and so was assigned as remnant signal resulting from inefficiency in aluminum pulse. Spinning sideband designated with stars.

425 Figure 4: $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR NMR of CABS2 glass. Collected at 14.1 T, ^{17}O observed
426 reference spectrum in solid black, dipolar-dephased spectrum with ^{11}B irradiation in dashed line.
427 Difference spectrum (reference spectrum – dipolar-dephased spectrum) in dotted line. Area
428 between 90 and -10 ppm associated with bridging oxygens. Area between 200 and 90 ppm
429 associated with non-bridging oxygens. Spinning sideband designated with stars.

430

431 Figure 5: $^{17}\text{O}\{^{11}\text{B}\}$ TRAPDOR NMR of CABS3 glass. Collected at 14.1 T, ^{17}O observed
432 reference spectrum in solid black, dipolar-dephased spectrum with ^{11}B irradiation in dashed line.
433 Difference spectrum (reference spectrum – dipolar-dephased spectrum) in dotted line. Area
434 between 90 and -10 ppm associated with bridging oxygens. Area between 200 and 90 ppm
435 associated with non-bridging oxygens. Spinning sideband designated with stars.

436

437 Figure 6: $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR NMR of CABS2 glass. Collected at 14.1 T, ^{17}O observed
438 reference spectrum in solid black, dipolar-dephased spectrum with ^{27}Al irradiation in dashed line.
439 Difference spectrum (reference spectrum – dipolar-dephased spectrum) in dotted line. Area
440 between 90 and -10 ppm associated with bridging oxygens. Area between 200 and 90 ppm
441 associated with non-bridging oxygens. Spinning sideband designated with stars.

442

443 Figure 7: $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR NMR of CABS3 glass. Collected at 14.1 T, ^{17}O observed
444 reference spectrum in solid black, dipolar-dephased spectrum with ^{27}Al irradiation in dashed line.
445 Difference spectrum (reference spectrum – dipolar-dephased spectrum) in dotted line. Area
446 between 90 and -10 ppm associated with bridging oxygens. Area between 160 and 90 ppm
447 associated with non-bridging oxygens. Spinning sideband designated with stars.

448
449 Figure 8: CABS2 fit. The upper black line represents the ^{17}O reference spectrum. The lower solid
450 red line represents the combination of the simulated Gaussians. Solid blue lines indicate oxygen
451 connected to boron, including B-NBO (centered at 130 ppm), B-O-B (small, centered at 90 ppm)
452 and B-O-Si (large, centered at 50 ppm). Dotted purple line indicates oxygen shared between
453 boron and aluminum (centered at 65 ppm). Dashed red lines indicate oxygen connected to
454 aluminum, including Al-NBO (small, centered at 100 ppm), Al-O-Al (small centered at 50 ppm)
455 and Al-O-Si (large, centered at 38 ppm). Dot-dashed green lines indicate oxygen connected to
456 silicon, including Si-NBO (centered at 100 ppm) and Si-O-Si (centered at 25 ppm). Spinning
457 sideband designated with stars.

458
459 Figure 9: CABS3 fit. The upper black line represents the ^{17}O reference spectrum. The lower solid
460 red line represents the combination of the simulated Gaussians. Solid blue lines indicate oxygen
461 connected to boron, including B-NBO (centered at 130 ppm), B-O-B (medium, centered at 70
462 ppm) and B-O-Si (large, centered at 50 ppm). Dotted purple line indicates oxygen shared
463 between boron and aluminum (centered at 65 ppm). Dashed red lines indicate oxygen connected
464 to aluminum, including Al-NBO (small, centered at 115 ppm), Al-O-Al (medium centered at 60
465 ppm) and Al-O-Si (large, centered at 45 ppm). Dot-dashed green lines indicate oxygen connected
466 to silicon, including Si-NBO (centered at 100 ppm) and Si-O-Si (centered at 30 ppm). Spinning
467 sideband designated with stars.

468

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure 7:

Figure 8:

Figure 9: