

Detection and Identification of Corrosion Products of Sodium Aluminoborosilicate Glasses by ^{23}Na MQMAS and $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS NMR

J. M. Egan and K. T. Mueller*

Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

Received: August 24, 1999; In Final Form: July 3, 2000

^{23}Na multiple-quantum (MQ) MAS NMR is applicable for monitoring the chemical and structural changes resulting from atmospheric exposure of a series of alkali aluminoborosilicate glasses with compositions $R\text{Na}_2\text{O}:1\text{B}_2\text{O}_3:1\text{SiO}_2:0.25\text{Al}_2\text{O}_3$ (where $R = 0.5\text{--}2.5$). Glasses with high alkali concentrations possess greater numbers of nonbridging oxygens within the bulk structure and presumably at the initial surface of a fresh sample, and for three samples with $R \geq 1.5$ sharp resonances are revealed in the isotropic dimension of an MQMAS NMR experiment conducted after prolonged atmospheric exposure. The MQMAS NMR experiments, combined with $^1\text{H} \rightarrow ^{23}\text{Na}$ cross-polarization magic-angle spinning (CPMAS) NMR measurements, indicate that these resonances arise from sodium cations no longer participating in the glass network. Two new phases are formed as corrosion products and have been identified as an anhydrous Na_2CO_3 phase and a $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ phase through comparison with ^{23}Na MQMAS and $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS NMR spectra of crystalline samples. Due to an inherent difficulty with direct quantification of populations based on MQMAS spectra, a simplified approach for quantification of the amount of the new carbonate phase is presented. Values are then calculated for relative amounts of corrosion product formation for different exposure times and bulk glass compositions.

Introduction

Understanding the durability of a glass within a particular compositional series under typical environmental conditions is crucial for basic and advanced technological applications of the material. Borosilicate glasses are considered for various applications including laboratory glassware, nuclear waste disposal and containment, and optical glasses. In each of these applications both understanding and identifying corrosive processes affecting glass networks or surfaces are important, especially for prediction of failure after long-term interactions with the environment. One significant challenge is the development of quantitative methods, and the ease of implementation of those methods, for determination and comparison of the severity of corrosion.

The formation of sodium carbonate on the surface of sodium silicate glasses has long been known and studied. In silicate glass systems, corrosion resistance decreases as the percentage of alkali metal oxide increases.¹ Experimental studies have investigated the formation of Na_2CO_3 on glass surfaces utilizing atomic force microscopy (AFM),^{2–4} electron microscopy,⁵ and secondary ion mass spectrometry (SIMS).⁶ Most importantly, the formation of a surface phase can be observed, and X-ray photoelectron spectroscopy (XPS) has been utilized to identify the phase as Na_2CO_3 . Carter et al.⁴ studied the surfaces of silicate glass via AFM with a “stiffer” tip than normally used (nominal spring constant of 0.064 N/m) and found features on the glass surface that were over 300 nm in height and up to 2 μm in width after just 20 days of exposure to air. They attributed these features to alkali carbonates, a hypothesis consistent with their Auger spectroscopic measurements. However, the presence of alkali silicates could not be ruled out.

In sodium aluminoborosilicate glasses, the sodium cations act as a network modifier and their chemistry is tied to the corrosion behavior and other physicochemical properties of these advanced materials. Thus, sodium is of central interest for corrosion studies. Solid-state magic-angle spinning (MAS) NMR spectra of ^{23}Na nuclei have been published in numerous studies of glass systems.^{7,8} Unfortunately, ^{23}Na MAS NMR spectra are usually uninformative as to the specific identity of environments surrounding the ^{23}Na nuclei in amorphous systems, essentially due to the broad line shapes encountered. Partly responsible for the broad resonances is the distribution of bonding parameters (bond angles and internuclear distances) associated with the amorphous state of a glassy material. Another difficulty encountered in ^{23}Na NMR is the inability of magic-angle spinning to completely average away the effects of second-order quadrupolar interactions, leading to residual linebroadening in ^{23}Na MAS spectra. Improved solid-state NMR techniques are needed for higher resolution ^{23}Na spectra. For example, a recent study using a technique called off-resonance quadrupole nutation has reported the resolution of different sodium environments in hydrous albite glass.⁹

Multiple-quantum (MQ) MAS^{10,11} is another recent experimental development in solid-state NMR that eliminates the quadrupolar broadenings in spectra of half-integer quadrupolar nuclei. MQMAS has the advantage that commercially available MAS probes can be used to acquire higher-resolution spectra. MQMAS is essentially a two-dimensional experiment where spin magnetization evolves along specific multiple- and single-quantum spin coherence pathways during two separate time periods. The two evolution periods allow for the averaging to zero of residual anisotropic broadening while under MAS conditions. The resulting two-dimensional correlation spectrum consists of a dimension free from anisotropic line broadening, with direct correlation to an anisotropic MAS line shape in a

* Author to whom correspondence should be addressed. Fax: (814) 863-8403. E-mail: ktm2@psu.edu.

second dimension. Spectral editing (utilizing the isotropic dimension) coupled with the anisotropic information of the second dimension results in superior site resolution, discrimination, and characterization. Detailed investigations of the theoretical formalism and optimal experimental conditions for MQMAS are found in the literature^{12–14} and are not the focus of this study. In studies of amorphous samples, MQMAS experiments have been used to investigate ¹¹B and ¹⁷O nuclei participating in oxide glass systems, and the results have provided enhanced models of the structures and linkages present.^{15–17} In the past, ²³Na MQMAS studies have been successfully performed on crystalline^{18–23} or highly ordered materials,²⁴ and limited ²³Na MQMAS studies have been focused toward investigations of glass systems.^{15,25} Precise structural analysis is hindered in the glass experiments due to the lack of long-range order found in glasses, so that discussions of these ²³Na MQMAS studies are limited to the broadness of resonances present in both dimensions of the spectra.

This paper reports on the chemical and structural results of the reactions of alkali aluminoborosilicate glasses with a typical laboratory atmosphere. Changes in the local environments surrounding sodium nuclei are monitored after different exposure times and from samples with different bulk glass compositions. Chemical changes are initially revealed by ²³Na MQMAS experiments, and subsequent investigations incorporate ¹H → ²³Na cross-polarization MAS (CPMAS) measurements. New resonances that appear as a function of exposure time are identified on the basis of comparisons to ²³Na MQMAS and ¹H → ²³Na CPMAS spectra of reference carbonate, borate, and silicate compounds. In this study, one advantage to the MQMAS method is that the new phases formed by corrosion contain local environments for sodium that are overall more ordered than the sodium sites in the original glass samples, providing sharper and more easily resolved resonances in MQMAS spectra. The relative extent of chemical reactivity of each glass is quantified through deconvolution of MQMAS spectra, providing analyses that allow comparisons of corrosion across a family of samples with the same reaction products.

Experimental Section

A family of glass samples with batched mole ratios; $R\text{Na}_2\text{O}:1\text{B}_2\text{O}_3:1\text{SiO}_2:0.25\text{Al}_2\text{O}_3$ (where $R = 0.5–2.5$) were prepared. The samples will be referred to by their sodium oxide content (R value) in the text. The raw materials consisted of Na_2CO_3 , calcined alumina, and H_3BO_3 (all purchased from J. T. Baker and used as received), and silica (Min-u-sil from U.S. Silica). The raw materials were crushed and mixed, and then heated in a Pt crucible to 1200 °C, where they were held for 3 h. The melts were then quenched between metal plates and crushed to powder for the NMR experiments. Once the samples were crushed, they were stored in glass vials within a desiccator for varying amounts of exposure times. The uniformly sized glass vials each held 2–3 mL of sample in a total volume of 20 mL. The atmosphere in the vials was the standard laboratory atmosphere. All glass samples were quenched and crushed on the same day and placed in sample vials within a desiccator immediately upon finishing the crushing. Exposure times refer to the time period between the crushing of the glass samples and the start of the NMR experiments, so that time zero corresponds to performing the NMR experiment immediately after crushing the glass sample. Powder X-ray diffraction, performed on a Philips XPert MPD System using $\text{Cu K}\alpha$ radiation, proved that all original samples were amorphous. Sharp peaks indicating crystalline material were only observed

for the highest-alkali content ($R = 2.5$) glass sample after extensive atmospheric exposure. FTIR spectra of selected samples were acquired on a Perkin-Elmer 1600 series instrument.

All solid-state NMR experiments were performed using a Chemagnetics CMX-300 spectrometer operating at a magnetic field strength of 7.0 T. The ²³Na MAS and MQMAS experiments were performed utilizing the low-frequency channel of a 4 mm Chemagnetics HX double-resonance probe. Rotor frequencies of 12,000 kHz were kept constant to within ± 3 Hz with a Chemagnetics MAS speed controller. The ²³Na resonance frequency at this field strength is 78.660 MHz and all spectra are externally referenced to the ²³Na resonance from a 1 M NaCl solution. A 0.5 μs pulse length was used to obtain ²³Na MAS spectra. Recycle delays were 1 s for both MAS and MQMAS experiments.

A three-pulse sequence employing TPPI (time-proportional phase incrementation)²⁶ for two-dimensional data acquisition was used for all MQMAS experiments. The three pulses include a triple-quantum excitation pulse and two pulses for the z-filter pulse scheme.^{14,27,28} The first two pulses were hard, nonselective pulses of 3.5 μs and 1.4 μs duration, while the last pulse was attenuated in order to produce a “soft” pulse, selective for the central transition of the ²³Na nuclei (5.50 μs pulse duration). All pulse lengths were optimized to produce maximum signal for the spectrum of the first t_1 data point of a two-dimensional experiment. The t_1 increment used provided for a 50 kHz sweep width in the first (high resolution) spectral dimension. A total of 936 scans were acquired for each t_1 point, and two-dimensional data sets consisted of either 128 t_1 points \times 256 t_2 points or 256 t_1 points \times 256 t_2 points. All two-dimensional data sets have been processed with a shearing transformation by the reported methods^{12,14} prior to the complex Fourier transformation. Deconvolutions of the MQMAS projections and determinations of the centers of gravity of resonances were performed using GRAMS/32 deconvolution software.²⁹

Additional ¹H → ²³Na CPMAS experiments were performed to identify sodium nuclei that exhibit dipolar connectivity to the hydrogen nuclei present in hydroxyl groups or molecular water. The ¹H resonance frequency at 7.0 T was 297.372 MHz. A sample of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ was utilized to establish the optimum matching condition for the CP experiment. A 1 ms contact time was found to produce maximum signal and a 5 s recycle delay was used between acquisitions. Results of the ¹H → ²³Na CPMAS experiments were pivotal in establishing the identity of phases that were hydrated, as well as indirectly supporting the presence of anhydrous phases (through a lack of ¹H → ²³Na CP signal).

Results and Discussion

²³Na MAS NMR spectra of the $R = 2.5$ glass sample for three different atmospheric exposure times are shown in Figure 1. The ²³Na MAS NMR spectrum of the $R = 2.5$ sample at time zero (Figure 1a) demonstrates the lack of resolution commonly observed for amorphous samples. As the powdered sample is exposed to the atmosphere for further time, the center of gravity of the broad resonance shifts downfield from -31.6 to -20.9 ppm. In addition to a spectral shift, a sharp contribution to the NMR signal begins to appear at $+1.0$ ppm after two weeks of atmospheric exposure. After months of exposure this additional feature in the spectrum becomes more prevalent and is a strong indication of changes occurring in the local environment surrounding some (but obviously not all) of the sodium nuclei. Due to the broad nature of the other portions of the ²³Na MAS

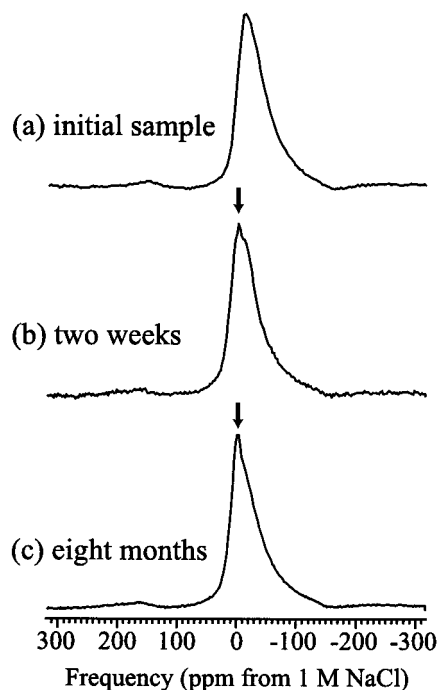


Figure 1. ^{23}Na MAS spectra of an $R = 2.5$ glass sample are shown for three different times of exposure to laboratory atmospheric conditions, as indicated. All spectra were processed by Fourier transformation of 128 transients collected with a 1 s recycle delay. The arrow indicates the sharp singularity that appears as a result of atmospheric exposure.

spectra, it is difficult to quantify or even further characterize the changes occurring from ^{23}Na MAS experiments alone. ^{23}Na MAS spectra of glass samples with different alkali oxide compositions (not shown) that have been exposed for 8 months exhibit broad lineshapes whose centers of gravity range from -37.0 ppm ($R = 0.5$ glass) to -20.9 ppm ($R = 2.5$ glass). The shift becomes more positive as the sodium oxide content increases in the samples. After eight months, only the $R = 2.5$ glass sample clearly shows a visible change in the ^{23}Na MAS spectrum at 7.0 T, with the presence of a "sharp" resonance at $+1.0$ ppm.

MQMAS experiments were performed to aid in the identification of any new species that slowly appear over time in the glass samples. Figure 2 displays a two-dimensional MQMAS correlation spectrum of the $R = 2.5$ sample after exposure to laboratory atmosphere (as described above) for a period of 8 months. The horizontal axis corresponds to the anisotropic MAS dimension and the vertical axis corresponds to the isotropic dimension. Along the isotropic dimension three features can be observed. Two of the features are sharp peaks identifying resonances that have been narrowed significantly by use of the MQMAS experiment, while the remaining feature is a broad resonance that shows little change in line shape when compared to the MAS data. We propose that the two sharp resonances arise from sodium atoms that have been removed from the bulk glass structure and have been incorporated into a more ordered environment compared to the glass network. ^{23}Na MQMAS spectra of an unexposed $R = 2.5$ sample display evidence of neither new site. The positions of these two new resonances are $+2880$ and $+5000$ Hz in the isotropic dimension. The broad resonance represents sodium cations that remain in the structural network of the bulk glass. This sodium resonance shows little or no narrowing because of a distribution of local electromagnetic environments not averaged away by the MQMAS experiment.

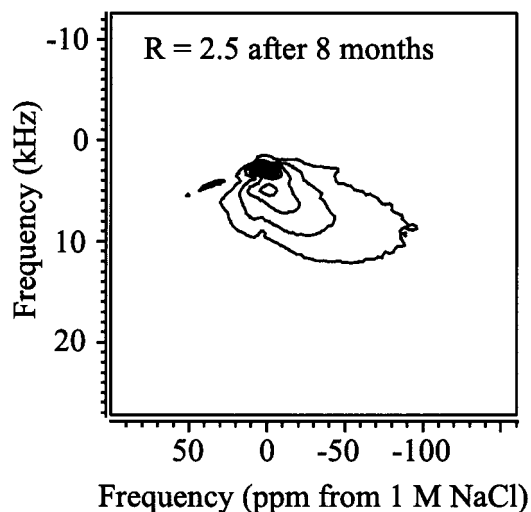


Figure 2. A ^{23}Na two-dimensional MQMAS spectrum of the $R = 2.5$ glass sample exposed for eight months is shown. Contour lines are drawn to indicate 5–95% of signal intensity and are spaced equally apart.

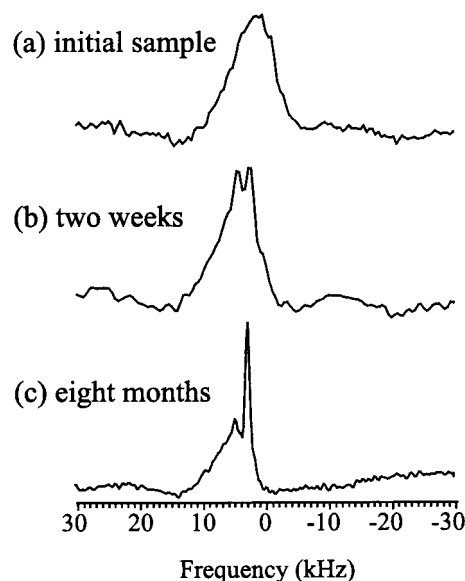


Figure 3. Single-slice projections (taken at $+1.0$ ppm in the MAS dimension) of the ^{23}Na isotropic dimension from two-dimensional MQMAS experiments performed on the $R = 2.5$ sample are shown for three different exposure times, as indicated. These single-slice projections were chosen to display the presence (or absence) of the two sharp peaks from more-ordered sodium environments.

A single slice of the isotropic dimension for the $R = 2.5$ sample (after 8 months total exposure) is shown in Figure 3c. From this projection the two sharp resonances can be clearly observed with the broad component making up the remainder of the spectrum. Also depicted in Figure 3 are single-slice projections obtained at two previous exposure times for the $R = 2.5$ sample. Figure 3a shows no indication of specific narrowed resonances appearing in data from a freshly crushed $R = 2.5$ glass. Figure 3b shows the emergence of the two sharp resonances after two weeks of exposure to the atmosphere. Another characteristic of the $R = 2.5$ glass after two weeks exposure time is the approximately equal intensities of the two narrower peaks. At much longer exposure times the peak at $+2880$ Hz is of greater intensity.

Figure 4 displays full projections along the isotropic dimension for three glass samples with different alkali oxide composi-

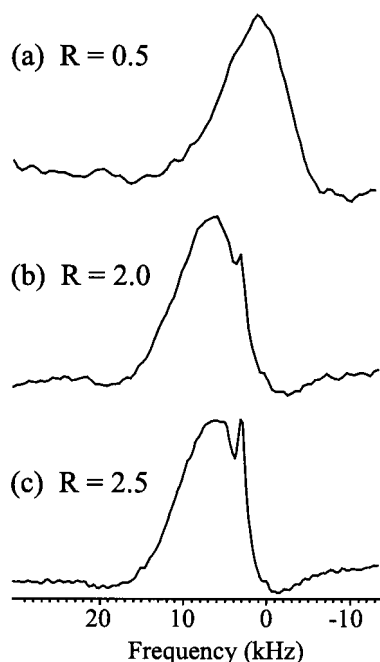


Figure 4. Changes in the ^{23}Na MQMAS spectra are charted with the emergence of one of the sharp resonances in the full isotropic projections as a function of sodium content. No evidence is seen for changes in the sodium environment in (a) the $R = 0.5$ glass, while a new resonance clearly appears in the (b) $R = 2.0$ and (c) $R = 2.5$ glass samples.

tions and after exposure for an 8-month time period. Both the $R = 0.5$ (Figure 4a) and $R = 1.0$ (not shown) samples lack any evidence of singularities in the ^{23}Na MQMAS spectra. These two samples exhibit broad NMR line shapes in both dimensions, consistent with no measurable change in the environment of sodium nuclei. Isotropic projections of the $R = 1.5$ glass sample (not shown) begin to display evidence of a newly formed sodium environment but the full projection does not indicate the presence of any sharp resonances because the bulk glass remains mostly intact and its signal dominates the spectrum. When the glass has a sodium content with $R = 2.0$, full projections indicate the presence of at least one sharp resonance indicative of a highly ordered sodium environment, as well as the remaining broad component from sodium in the bulk glass. The presence of any additional distinct resonances is not obvious in the full projections because the broad component dominates most regions of the spectra.

While the known chemistry for leaching and corrosion of similar glasses indicates the probable formation of carbonate species, determination of the nature and identity of the particular species responsible for the sharp resonances observed in the MQMAS experiment necessitates a comparison of the spectra with results from numerous crystalline samples of potential corrosion products or intermediates. The ^{23}Na MAS spectrum of crystalline Na_2CO_3 is displayed in Figure 5c and does not agree well with a MAS (low-resolution dimension) projection from the $R = 2.5$ sample that is correlated to the sharp resonance at +2880 Hz in the MQMAS spectrum (Figure 5a). A much superior match is observed when a MAS slice is taken (Figure 5b) from the two-dimensional MQMAS spectrum of crystalline Na_2CO_3 at the same frequency shift in the isotropic dimension as the slice from the glass sample. The difference can be explained by the efficiency of the radio frequency pulses in the MQMAS experiments used to excite and convert triple-quantum coherence for various orientations of crystallites or quadrupolar

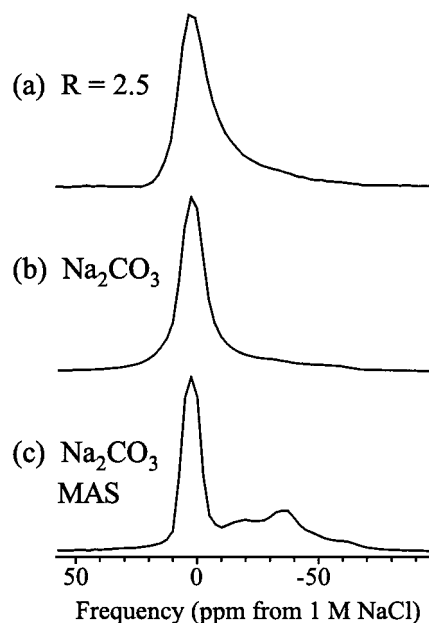


Figure 5. (a) A projection from the ^{23}Na MQMAS spectrum of an $R = 2.5$ glass sample reveals the MAS spectrum of the species that is directly correlated to the sharp resonance at +2880 Hz in the isotropic dimension. (b) A similar MAS projection from the ^{23}Na MQMAS spectrum of pure, crystalline Na_2CO_3 is shown to compare with the phase present in the glass samples. (c) The ^{23}Na MAS spectrum of pure, crystalline Na_2CO_3 is displayed, and its comparison to spectrum (b) underscores the deficiencies of triple-quantum excitation during the MQMAS experiments implemented here.

TABLE 1: Comparison of Measured NMR Parameters^a for Pure Na_2CO_3 and a Putative Na_2CO_3 Phase from a Glass Sample ($R = 2.5$) after Exposure to the Atmosphere

sample	crystalline Na_2CO_3	$R = 2.5$ glass
ν_1' av freq. (Hz)	+3267	+2983
ν_2 av freq. (Hz)	-520	-504
ν_0^Q (Hz)	-291	-271
ν^{CS} (ppm)	+4.5	+4.0

^a See ref 12 for definitions.

interaction parameters.¹² At the radio frequency field strengths utilized in these experiments, only one of the two Na_2CO_3 sites observed can be excited efficiently. Based on the spectra presented in Figure 5, and the fact that this match is the best obtained from any crystalline compound considered, the preliminary assignment of the resonance at +2880 Hz in the MQMAS spectrum is to an anhydrous sodium carbonate phase.

The two-dimensional MQMAS experiment provides two direct quantitative measures of the similarity of the spectra, again providing strong evidence that this predominant reaction product is anhydrous Na_2CO_3 . By measuring the average frequencies in both MQMAS spectral dimensions (here designated as ν_1' and ν_2) we calculate the isotropic quadrupolar and isotropic chemical shift parameters (ν_0^Q and ν^{CS} , respectively).¹² Table 1 lists the average frequencies in both dimensions and the calculated isotropic shift values for crystalline Na_2CO_3 , and values are compared with those from the sharp resonance for the $R = 2.5$ glass. The average frequencies are within 10% of one another in both cases, and discrepancies in the numbers may be explained by the difficulty of determining an accurate center of gravity for the sharp resonance in the isotropic dimension of the glass sample.

Additional analytic techniques also indicate that Na_2CO_3 is present in the $R = 2.5$ glass sample after exposure to atmosphere

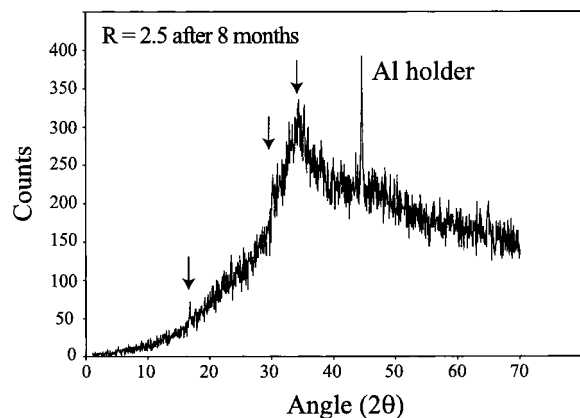


Figure 6. The XRD pattern for the $R = 2.5$ glass exposed for eight months displays minor peaks assignable to crystalline Na_2CO_3 . The arrows indicate positions that have been computer-chosen as peaks via an algorithm supplied with the diffractometer system.

for eight months. Powder X-ray diffraction studies of the glass samples, both exposed and unexposed, contribute little understanding to the bulk glass structure because of the absence of crystallinity. However, the XRD pattern for the $R = 2.5$ glass after exposure for eight months (see Figure 6) does indicate some evidence of a small amount of crystalline material. The peaks identified in Figure 6 were chosen automatically by the XRD software package, and two of the computer-chosen peaks correspond to peaks that exhibit strong intensity for crystalline Na_2CO_3 . While the 2.61 and 2.96 Å peaks are found for Na_2CO_3 , the absence of any other peak match indicates that the concentration of the Na_2CO_3 phase is still at or beyond the detection limits of the technique, or possibly that the phase is not completely crystalline. The monohydrate form of Na_2CO_3 provides an XRD pattern with crystalline peaks that occur at smaller angles than those observed for the glass sample, imparting further support for an anhydrous assignment. XRD patterns for the $R = 1.5$ and 2.0 glasses (8 months exposure time) do not reveal any detectable crystalline peaks, demonstrating that in this instance the NMR methods are more sensitive than XRD.

The presence of the CO_3^{2-} anion in a sample of corroded glass could also be expected to produce modification of the FTIR spectrum of the sample after exposure, revealing an additional stretching vibration from the CO_3^{2-} anion. The main change in the FTIR spectra depicted in Figure 7 between exposed and unexposed glass samples ($R = 2.5$) is the increased intensity in the region of 1430–1460 cm^{-1} . This peak is consistent with the presence of Na_2CO_3 , based on the large spectral intensity observed between 1400 and 1500 cm^{-1} for crystalline Na_2CO_3 . No other significant differences are seen in the FTIR spectra for the two $R = 2.5$ glass samples.

The assignment of the second resonance (at +5000 Hz in the isotropic dimension) presented a more difficult challenge. Two crystalline compounds possessed resonances with very similar frequency shifts in the MQMAS isotropic dimensions that coincide with the +5000 Hz shift observed for the glass sample. Both potential candidates, $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot \text{H}_2\text{O}$, are hydrated compounds. Comparison of the MAS slice of the glass sample at +5 kHz with the ^{23}Na MAS spectra of the two candidates is extremely difficult because of the contribution of the broad sodium background present from the glass that obscures the true line shape of interest. Because both potential compounds share the characteristic of being hydrated, $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS NMR would in principle enable the

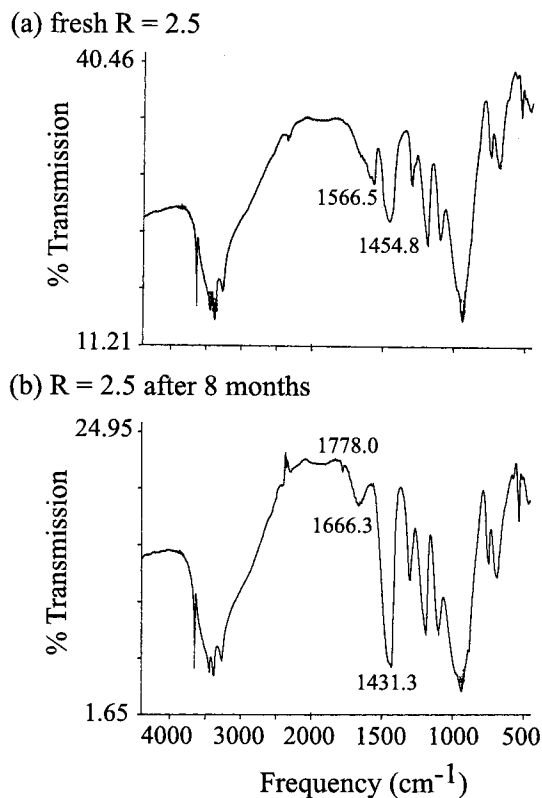


Figure 7. A major difference between the FTIR spectra of the (a) fresh and (b) corroded glass (with $R = 2.5$) is the relative intensity of the peak at 1430–1460 cm^{-1} . Pure Na_2CO_3 exhibits a very intense stretching vibration at these wavenumbers.

detection of sodium environments near to (or in the same phase as) H_2O , and thus will provide additional data for identifying the particular species present in the corroded glass samples.

Two conclusions can be made based on the $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS spectra of Figure 8. The first conclusion supports the assignment of the first site at +2880 kHz to an anhydrous Na_2CO_3 phase. In the CPMAS spectrum from the $R = 2.5$ glass (Figure 8a), no resonance peak is observed around +1.0 ppm, indicating a lack of proton or H_2O interactions with the sodium in the putative Na_2CO_3 phase. The second conclusion is the assignment of the other corrosion product to a sodium metaborate monohydrate compound. Comparison of the CPMAS spectrum of the glass to the CPMAS spectra of $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (Figure 8b,c, respectively) illustrates the superior match between the glass and borate resonances. The frequency shift of maximum intensity occurs at identical positions in both spectra 8a,b, and the line shapes of both samples coincide closely with one another. The $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS spectrum of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and the MAS spectrum of $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ are shown in Figure 8d,e for further comparison.

Estimation of the relative percentage of glass that is converted into the major Na_2CO_3 phase in these samples is documented in Table 2. The glasses with $R < 1.5$ are not included in this table because no indication of any new sodium environments is observed. Percentages were determined by deconvolution of the full projections in the isotropic dimension into three peaks: one peak corresponding to the Na_2CO_3 phase, one for the $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ phase (especially prominent at short exposure times), and a third peak, which is considerably broader, representing the sodium remaining in the bulk glass network. The percentages given in Table 2 are not absolute percentages of Na_2CO_3 because the MQMAS experiment is not perfectly

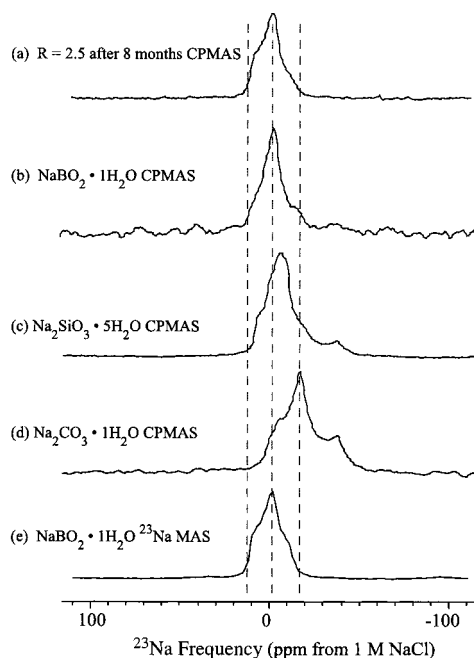


Figure 8. (a) The $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS spectrum of the $R = 2.5$ glass (after eight months of exposure) is shown, and compared to (b) the $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS spectrum of $\text{NaBO}_2 \cdot \text{H}_2\text{O}$. These resonances are very similar in position and line shape, arguing strongly for the assignment of this hydrated species. (c) The $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS spectrum of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ is shown for comparison, as is (d) the $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS spectrum of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. (e) The ^{23}Na MAS spectrum of $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ is also presented for completeness, and compares well with spectrum (a). The dashed lines are drawn as guides for the eye.

TABLE 2: Relative Percentages of Na_2CO_3 Phase in Modified Glasses from Deconvolution of Full Projections of the MQMAS Experiments

R content (exposure time)	freq. of max. intensity (Hz)	% of ^{23}Na MQMAS signal in putative Na_2CO_3 phase ^a
1.5 (8 months)	+2841	2.0
2.0 (8 months)	+2976	3.4
2.5 (2 weeks)	+2386	2.3
2.5 (8 months)	+2945	11.5

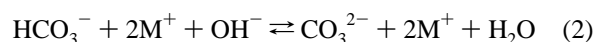
^a Estimated error of 10% in reported values.

quantitative using our experimental conditions. The important purpose of these ratios is to illustrate the *change* in the amount of Na_2CO_3 phase between glasses measured under identical experimental conditions.

Many other NMR studies have been performed on a variety of glass systems investigating the effects of H_2O in the structure. Most often ^1H MAS NMR,^{30–33} or a related technique, has been utilized to probe the hydrogen environments. An unfortunate experimental shortcoming of ^1H MAS NMR is a small chemical shift range, further complicated by the broad resonances often encountered. In many systems, resonances from molecular H_2O can dominate and obscure the remaining resonances in the frequency spectrum. Also, ^1H MAS spectroscopic techniques are limited to investigating structures that are created by corrosion. This disadvantage is common to many analytical tools in that only the created structures are detected or observed. Because corrosion is a dynamic process, it is vital for a complete understanding to simultaneously detect the nature and number of structures created and destroyed in the process. Probing the ^{23}Na environments accomplishes a 2-fold purpose in one experiment. Observing the appearance of resonances can first provide information on the type of corrosion products formed from sodium cations removed from the glass network. Second,

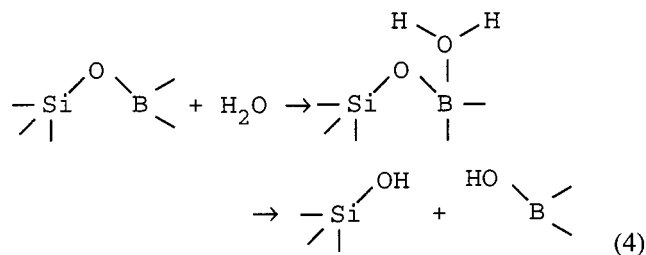
observing the disappearance of resonances is useful for determining the types of sodium environments most susceptible to aqueous attack.

It is commonly believed that two reaction schemes are involved in the atmospheric attack of the aluminoborosilicate glasses considered in this study. Ion-exchange reactions take place between hydrogen and sodium cations involved in the charge balance of the nonbridging oxygens of the silicate network. This aqueous attack on the structural network does not appear at significant (detectable) levels until the glass samples contain alkali contents of greater than $R = 1.0$. Sodium oxide initially associates with the aluminate and borate networks, facilitating conversion to tetrahedral units. Formation of a hydrous layer containing Na^+ and OH^- ions results from the atmospheric water vapor attack. Secondary reactions in the basic surface layer begin to occur with corrosive gases such as CO_2 and progress to form carbonate species:



The fact that the Na_2CO_3 phase is anhydrous indicates that H_2O is not retained by this phase and instead continues to contribute to glass degradation.

Hydrolysis of the network is also occurring in the basic layer by a nucleophilic attack on borosilicate linkages:



and the NMR experiments presented here indicate that sodium metaborate monohydrate is the main product of these hydrolysis reactions.

Although both degradation processes are proceeding during the first two weeks of exposure, as demonstrated by the presence of both new resonances in Figure 3b, it is also observed that ion-exchange is the more dominant mechanism after longer exposure times, while the primary hydrolysis product ($\text{NaBO}_2 \cdot \text{H}_2\text{O}$) appears to reach a maximum concentration at shorter exposure times. This latter conclusion is reached from Figure 3 by comparing the relative intensity of the $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ resonance peak to the intensity of the broad component present for sodium remaining in the glass network (which remains relatively constant).

Sodium resonances that disappear upon interaction with the atmosphere can also be tracked by inspection of Figure 3. Evident in these full projections is a loss of signal intensity for ^{23}Na nuclei with total frequency shifts that appear at more negative values than that of the sharp resonance at +2880 Hz. Spectral intensity at these frequencies represent sodium environments that are initially present in structural units correlated with nonbridging oxygens on silicon, and these environments are expected to be destroyed by the corrosion reactions. Aside from the loss in intensity of the broad component due to sodium remaining in the glass network, there is a gain in ^{23}Na signal

intensity at large positive values of frequency shift for the glasses after atmospheric exposure. The positive frequency shift may be a signature of modified structural units in the glass that still contain sodium cations in close proximity.

Conclusions

The MQMAS NMR technique applied to ^{23}Na nuclei provides resolution and identification of new sodium environments formed from sodium aluminoborosilicate glasses exposed to a common laboratory atmosphere. The appearance of narrowed resonance lines in the isotropic MQMAS dimension leads to the identification of two corrosion products, both containing sodium in more-ordered phases than the glass samples. The enhanced sensitivity of the MQMAS NMR technique in these studies allows for detection of corrosion products before noticeable changes can be observed in MAS or diffraction experiments. Comparisons with MQMAS spectra from crystalline sodium-containing materials indicate that one reaction product in the glasses, predominant at long exposure times, is Na_2CO_3 . $^1\text{H} \rightarrow ^{23}\text{Na}$ CPMAS experiments also provide evidence that the second phase, formed in greater quantities at shorter times, is $\text{NaBO}_2 \cdot \text{H}_2\text{O}$. Both the MQMAS and CPMAS data presented are inconsistent with the formation of detectable quantities of other possible or probable reaction products, including hydrated carbonate species. As the corrosion reaction products are formed, the observed disappearance of sodium environments associated with nonbridging oxygens confirms that sodium nuclei in these environments are most susceptible to attack and removal. Heteronuclear connectivity experiments coupled with MQMAS may provide a more potent tool to fully characterize these systems, and such investigations are currently in progress.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This report is also based upon work supported by the National Science Foundation under Grant No. DMR-9458053 and Grant No. DMR-9413674. The authors also acknowledge the support of the Henry Dreyfus Teacher-Scholar Awards Program. Amy Barnes, Dr. Carlo Pantano, and Dr. Mary Strzelecki are also acknowledged for their helpful discussions.

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