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Water solubility mechanism in hydrous aluminosilicate glasses: Information from ^{27}Al MAS and MQMAS NMR

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Abstract—New ^{27}Al NMR data are presented in order to clarify the discrepancies in the interpretation of the previous ^{27}Al Magic Angle Spinning (MAS) spectra from hydrous aluminosilicate glasses. The ^{27}Al MAS data have been collected at much higher magnetic field (14.1 and 17.6 T) than hitherto, and in addition, multiple quantum (MQ) MAS NMR data are presented for dry and hydrous nepheline glasses and $\text{NaAlSi}_{7.7}\text{O}_{17.4}$ glass that, according to the model of Zeng et al. (Zeng Q., Nekvasil H., and Grey C. P. 2000. In support of a depolymerisation model for water in sodium aluminosilicate glasses: Information from NMR spectroscopy. *Geochim. Cosmochim. Acta* **64**, 883–896), should produce a high fraction (up to 30%) of Al in Al Q³-OH on hydration. Although small differences in the MAS spectra of anhydrous and hydrous nepheline glasses are observed, there is no evidence for the existence of significant (>~2%) amounts of Q³ Al-OH in these glasses in either the MAS or MQMAS data. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

Dissolved water has a great effect on many physical properties of silicate melts and glasses (e.g., viscosity, density, liquidus, and glass transition temperatures), and to link this influence with the microscopic state, many studies on water solubility mechanisms have been performed in the past. Despite all efforts, the water dissolution mechanisms in silicate melts and glasses are still a matter of discussion (e.g., McMillan, 1994; Kohn, 2000). We now know that above the glass transition temperature (T_g), the water speciation changes toward higher OH and lower H₂O concentrations (e.g., Nowak and Behrens, 1995; Shen and Keppler, 1995), but it is also clear that the glass structure frozen in on cooling through T_g is the same as that of the melt at T_g (Behrens and Schmidt, 1998; Withers and Behrens, 1999; Withers et al., 1999). Therefore, detailed studies of glass structures remain a crucial starting point for the understanding of water dissolution mechanisms in silicate melts at elevated temperatures.

Although it is widely accepted that dissolved water depolymerizes the network of silica and alkali silicate glasses (e.g., Stolen and Walrafen, 1976; McMillan and Remmele, 1986; Mysen and Virgo, 1986; Farnan et al., 1987; Kümmerlen et al., 1992; Schaller and Sebald, 1995; Zotov and Keppler, 1998), the water dissolution mechanisms in hydrous aluminosilicate glasses is less clear and has been a matter of discussion for more than a decade. One of the most debated points is the question whether or not the aluminosilicate network depolymerizes on hydration by the rupture of Si-O-Si and Si-O-Al bonds leading to the formation of terminal T-OH groups (T = Si/Al). Such a mechanism was proposed in most of the water solubility models based on vibrational spectroscopy or thermodynamic data (e.g., Burnham, 1975; Bartholomew et al., 1980;

Mysen et al., 1980; Stolper, 1982; McMillan et al., 1983, 1993; Sykes and Kubicki, 1993). However, on the basis of multinuclear NMR spectroscopic studies, Kohn et al. (1989, 1992, 1998) found no conclusive evidence for significant depolymerization of the structure of hydrous albite ($\text{NaAlSi}_3\text{O}_8$) anorthite-quartz ($\text{CaAl}_2\text{Si}_{6.6}\text{O}_{17.3}$) or nepheline (NaAlSiO_4) glasses. These authors concluded that water dissolution causes only small changes in the aluminosilicate network (less than 1% silicon atoms are in Si-OH) and that water is associated with sodium. Kohn et al. (1989) proposed a water solubility model that involves the replacement of a charge balancing Na^+ by a proton, thus forming a bridging hydroxyl group on a Si-O-Al linkage. The exchanged Na^+ forms complexes with OH^- and/or molecular H₂O. Recent ^{17}O NMR spectroscopy results on the study of the water solubility mechanisms in silicate glasses are also not fully conclusive. Maekawa et al. (1998) and Kohn et al. (1997) observed no significant changes on hydration of albite glasses with static ^{17}O and ^{17}O multiple quantum Magic Angle Spinning (MAS) NMR, respectively. However, some differences in ^{17}O NMR spectra of dry and hydrous albite glasses were reported by Xu et al. (1998). On the basis of their ^{17}O multiple quantum (MQ) MAS NMR and ^1H - ^{17}O cross-polarization MAS NMR data, these authors suggested the presence of Si-OH groups in the hydrous glass. The discrepancy between the data of Kohn et al. (1997) and Xu et al. (1998) remains to be explained, but it should be emphasized that the differences between the ^{17}O spectra of dry and hydrous Ab glasses of Xu et al. (1998) are very small. More recently, Oglesby et al. (2001, 2002) studied hydrous silicate and aluminosilicate glasses as well as crystalline compounds containing silanol groups and protonated bridging oxygens with ^{17}O NMR but also reported no direct evidence of the presence of either Al-OH or any other OH sites.

However, Zeng et al. (1999), on the basis of ^1H single-pulse MAS and $^1\text{H}/^{27}\text{Al}$ and $^1\text{H}/^{23}\text{Na}$ TRAPDOR NMR data, came to a different conclusion about the question of depolymerization in hydrous aluminosilicate glasses. They concluded that hy-

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drous glasses along the join $\text{NaAlSiO}_4\text{-NaAlSi}_8\text{O}_{18}$ have three different proton OH resonances, which they assigned to Si Q³-OH, Al Q³-OH, and to another, more strongly hydrogen bonded Q³-OH unit. Zeng et al. (2000) proposed a quantitative model of water dissolution in alkali aluminosilicate glasses. The model is based on multinuclear NMR spectroscopic data (²³Na, ²⁷Al, ²⁹Si, ¹H-²⁹Si cross-polarization), together with the ¹⁷O NMR data of Xu et al. (1998) and thermodynamic considerations. The model involves several reactions of water with the aluminosilicate network such as breaking of Si-O-Si, Si-O-Al, and Al-O-Al linkages and formation of Si-OH and Al-OH groups, but also a cation exchange between H⁺ and Na⁺. It should be emphasized that the depolymerization reactions are the dominant water dissolution mechanisms within this model and that with decreasing Si/Al ratio the concentration of Al-OH species increases and becomes equivalent to that of Si-OH at Si/Al close to 1. Thus, according to this model and in contrast to the model of Kohn et al. (1989), the formation of Al-OH groups is a very important water dissolution mechanism for haplogranitic aluminosilicate compositions.

Zeng et al. (2000) supported their hypothesis by simulation of ²⁷Al MAS NMR spectra of hydrous $\text{NaAlSi}_3\text{O}_8$ glasses with different water contents (up to 6.5 wt%) at a magnetic field (B_0) of 8.45 T. Although only a single asymmetric line was observed in the spectrum, it was simulated assuming two sites corresponding to Al Q⁴ with a quadrupolar coupling constant, C_Q , of 3.5 MHz and Al Q³-OH ($C_Q = 5$ MHz) with a ratio $Q^3/(Q^3 + Q^4)$ up to 0.22 for the highest water content sample. According to Zeng et al. (2000), the predicted fraction of hydroxyl groups present in Al Q³-OH could exceed 30% for the most favorable compositions. This is in contrast to the interpretation of ²⁷Al NMR data by Schmidt et al. (2000, 2001a), who studied a number of glasses along the joins $\text{Qz}_{28}\text{Ab}_{72}\text{-Qz}_{90}\text{Ab}_{10}$ and $\text{Qz}_{28}\text{Ab}_{72}\text{-Qz}_{34}\text{Or}_{66}$ (Qz = quartz, Ab = albite, Or = orthoclase) and a haplogranite glass ($\text{Ab}_{39}\text{Or}_{32}\text{Qz}_{29}$, AOO). They found a constant mean isotropic chemical shift δ_{iso} and decreased mean quadrupolar coupling constant C_Q for ²⁷Al on hydration, suggesting only minor changes in the Al environment and thus that formation of Al-OH is not an important water-dissolution mechanism.

The aim of this study is to provide further information on the changes at the aluminum environment on hydration in aluminosilicate glasses. The detection of a signal from Al Q³-OH units would support the depolymerization model proposed by Zeng et al. (2000) and the absence of any trace of a second aluminum environment would suggest that hydration causes no aluminum depolymerization of the aluminosilicate network. To improve the resolution of the ²⁷Al NMR data published previously, two different approaches were used: acquisition of single-pulse MAS NMR data at a much higher magnetic field (17.6 T), and acquisition of ²⁷Al multiple quantum MAS NMR data. Multiple quantum MAS NMR experiments have been shown to give highly resolved NMR spectra of quadrupolar nuclei such as ¹⁷O or ²⁷Al. With this technique, signals with strongly overlapping character in single-pulse MAS NMR spectra, such as the resonances of 4-, 5-, and 6-coordinated aluminum in some aluminosilicate or aluminate systems (e.g., Baltisberger et al., 1996; Peeters and Kentgens, 1997) or different oxygen environments (e.g., Si-O-Si, Si-O-Al, Al-O-Al, nonbridging oxygen) in silicate glasses, can be clearly sepa-

rated (e.g., Dirken et al., 1997; Xu et al., 1998; Stebbins et al., 1999; Oglesby et al., 2001). The experiment produces a 2D spectrum with one axis free of second-order quadrupolar broadening, allowing the projection in a pure isotropic axis that often shows higher resolution than the normal MAS NMR spectrum. No ²⁷Al MQMAS NMR data of hydrous aluminosilicate glasses have been reported in the literature to date, although this technique should be most promising for the detection of the signal of Al Q³-OH units.

The samples studied here were chosen to favor the probability of formation of Al-OH groups according to the model of Zeng et al. (2000). Dry and hydrous nepheline (Ne) glasses have a degree of Al avoidance of ~0.95 (Lee and Stebbins 2000). Therefore, the structure of dry Ne glass consists predominantly of Si Q⁴(4Al) and Al Q⁴(4Si) units, and thus the number of Si-O-Al linkages is maximal. In addition to Ne glass, we studied a Qz-Ab glass ($\text{Qz}_{52}\text{Ab}_{48}$, $\text{NaAlSi}_{7.7}\text{O}_{17.4}$), which, according to the model of Zeng et al. (2000), should produce an even higher fraction of Al in Al Q³-OH (Al Q³-OH/total Al) on hydration.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation

The dry starting glasses were melted at 1600°C and 1 atm from mixtures of high-purity powdered SiO₂, Al₂O₃, and Na₂CO₃. After a first melting and quenching, the glasses were ground and remelted to obtain more homogeneous samples. The chemical compositions of the anhydrous glasses were determined by electron microprobe to be $\text{NaAlSi}_{7.7}\text{O}_{17.4}$ (Q52-D) and $\text{Na}_{1.03}\text{AlSi}_{1.1}\text{O}_{4.22}$ (Ne-D). Hydrous glasses were prepared from the dry starting glasses and deionized distilled water. The desired proportions of water and dry glass were sealed into Pt capsules for hydration experiments at water-undersaturated conditions. The hydrous $\text{NaAlSi}_{7.7}\text{O}_{17.4}$ glass (Q52-6H) was synthesized in an internally heated pressure vessel operating in vertical configuration (Institut für Mineralogie, Universität Hannover) at 5 kbar, 1300°C, and 80 h experimental duration. The sample was quenched isobarically to give a clear, bubble-free glass. The water content was determined by Karl-Fischer titration to be 5.70 wt%. The hydrous $\text{Na}_{1.03}\text{AlSi}_{1.1}\text{O}_{4.22}$ glass (Ne-6H) was synthesized in a piston cylinder apparatus at 10 kbar, 1400°C, with a 3/4-inch NaCl/Pyrex assembly. After 20-h experimental duration, the sample was quenched isobarically to give a clear and bubble-free glasses. The water content was measured by ¹H-NMR against two different standards used previously by Schmidt et al. (2001b), giving a water content of 5.97 wt%.

2.2. NMR Spectroscopy

MAS and MQMAS spectra were measured for ²⁷Al with a Chemagnetics Infinity 360 at a frequency of 93.83 MHz with a Bruker 4-mm MAS probe capable of achieving spinning speeds up to 14 kHz, a Chemagnetics Infinity 600 at a frequency of 156.38 MHz with a Chemagnetics 3.2-mm MAS probe capable of achieving spinning speeds up to 25 kHz and a Bruker ASX 750 at a frequency of 195.46 MHz at a spinning speed of 24 kHz.

MAS spectra were acquired by using a single pulse corresponding to a selective $\pi/6$ pulse length and a recycle delay of 1 s. MQMAS spectra were acquired by using the split- t_1 pulse sequence (Brown and Wimperis, 1997). The first and second excitation pulses of the sequence were 2.8 μs and 0.9 μs , respectively, applied with the highest allowable power, corresponding to a radio frequency field strength of 150 kHz. The t_2 spectral width was set in the range of 50 to 65 kHz, and the t_1 spectral width was set to 50 kHz. We acquired 128 or 256 free induction decays for each slice. The delay between the second and third pulse was set to be an integer multiple of the period of the spinning speed to ensure that the echo was totally refocused and free of additional artefacts (e.g., dephasing of the spinning sidebands). The 2D spectra were referenced following the procedure explained by Amou-

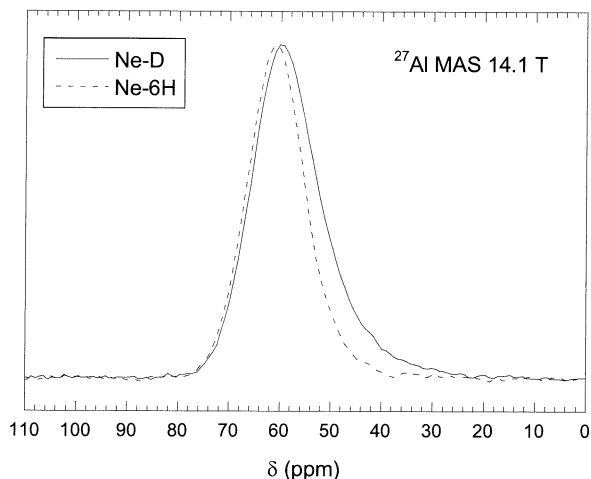


Fig. 1. Single pulse ^{27}Al MAS NMR spectra of dry and hydrous nepheline glasses at 14.1 T. Spectra are normalized to the same peak heights for comparison.

reux and Fernandez (1998). The MAS dimension (F_2) was referenced in the usual way to the external aqueous standard. For a spin 5/2, the spectrometer frequency in the isotropic dimension (F_1) was set to $-17/31 \nu_0$ in a 3QMAS and $85/34 \nu_0$ in a 5QMAS experiment, where ν_0 is the carrier frequency. By using the fact that the isotropic chemical shift is the same for both dimensions, we set the shift in parts per million at the carrier frequency in F_1 at the same value as the shift in parts per million at the carrier frequency in F_2 . Aqueous $\text{Al}(\text{NO}_3)_3$ 1 M was used as external reference for ^{27}Al NMR spectra.

3. RESULTS

Figure 1 shows the ^{27}Al MAS spectra of dry and hydrous nepheline glasses at 14.1 T. The spectra show a single featureless line around 60 ppm corresponding to the conventional chemical shift for tetrahedrally coordinated aluminum without any signal from five or six coordinated sites, similar to previously published ^{27}Al NMR results of nepheline glasses (Kohn et al., 1992). The spectral line narrows on hydration, suggesting a decrease in the quadrupolar interaction. This observation is consistent with those made by Schmidt et al. (2000, 2001a) and more recently by Oglesby et al. (2002) for aluminosilicate glasses with different compositions. Because of the amorphous nature of the glass, the recorded spectral line lacks any structure, making the direct extraction of the chemical shift and quadrupolar interaction from a spectrum at one field very ambiguous. There are only small differences between the spectra of the dry and hydrous glasses. On hydration, the resonance is moved to higher frequencies by less than 1 ppm, but the width of the line shows some narrowing. The depolymerization model of Zeng et al. (2000) predicts that for this composition, more than 30% of the hydroxyls are present in Al-OH units. Assuming that Ne-6H contains 2 wt% water as hydroxyl groups, $\sim 10\%$ of all Al should be Al $\text{Q}^3\text{-OH}$. However, there is no evidence of a second aluminum site in the MAS spectrum.

The hydrous $\text{Qz}_{52}\text{Ab}_{48}$ glass (Q52-6H) should, within the Zeng model, contain an even higher fraction of Al $\text{Q}^3\text{-OH}$ sites. The water speciation of this sample was determined with static $^1\text{H-NMR}$ at low temperature (130 K) following the procedure described in Schmidt et al. (2001b) to be 1.7 wt% water as

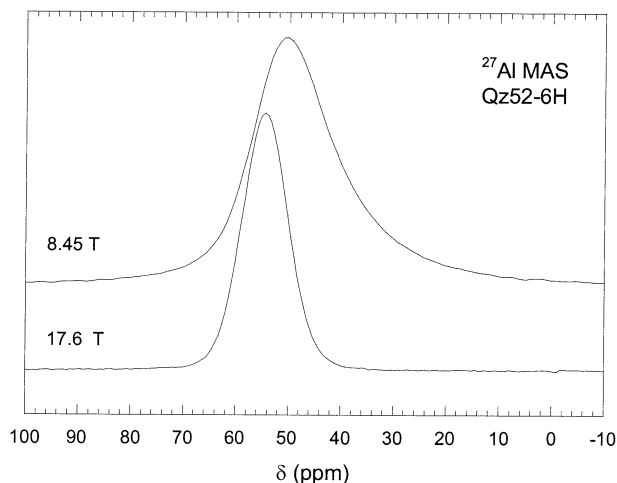


Fig. 2. Single-pulse ^{27}Al MAS NMR spectra of hydrous $\text{Qz}_{52}\text{Ab}_{48}$ glass (Q52-6H) at 8.45 and 17.6 T.

hydroxyl groups and 4.0 wt% molecular H_2O . Following the model of Zeng et al. (2000), $\sim 25\%$ of the hydroxyl groups should be present in Al-OH, which would result in a fraction of 27% of all Al in $\text{Q}^3\text{-OH}$. As for the hydrous Ne-glass, no second aluminum site could be detected in the conventional ^{27}Al MAS spectra of Q52-6H collected at 8.45 and 17.6 T (Fig. 2).

As a result of the inverse proportionality of the second order quadrupolar broadening with the external magnetic field (B_0), higher resolution is normally achieved at a higher B_0 . The low field spectrum in Figure 2 contains a broad, strongly asymmetric resonance with a tail extending to lower frequency. This tail is indicative of the presence of a distribution of quadrupolar parameters, arising from the disordered nature of the glass. Increasing the external magnetic field from 8.45 to 17.6 T (a factor of 2.08) renders the resonance very symmetric and increases the spectral line width in hertz by a factor of 1.15 but decreases it in parts per million from 19.3 to 10.2 ppm. Because the second-order quadrupolar interaction is inversely proportional to the magnetic field, the increase of the line width in hertz suggests the presence of a significant chemical shift distribution. The width from this distribution is directly proportional to the external magnetic field and in a first approximation the widths determined by quadrupolar effects and the chemical shift distribution can be calculated by

$$\begin{aligned} \text{FWHM}_1^2 &= W_q^2 + W_{\text{csd}}^2 \\ \text{FWHM}_2^2 &= \frac{B_1^2}{B_2^2} W_q^2 + \frac{B_2^2}{B_1^2} W_{\text{csd}}^2 \end{aligned} \quad (1)$$

where B_1 and B_2 are the lower and the higher magnetic fields, and FWHM_1 and FWHM_2 are the full width at half maximum at these fields. The two constants in Eqn. 1 are the width contribution due to quadrupolar coupling, W_q , and the width due to the chemical shift dispersion, W_{csd} . Applying Eqn. 1 to the data for Q52-6H shows that at 8.45 T, the quadrupolar interaction dominates the width of the line (Table 1). However, at 17.6 T, the contribution from the quadrupolar coupling is reduced and the width of the line is mainly the result of

Table 1. The ^{27}Al MAS peak width and analysis for the Q52-6H glass.

B_0	W_q (Hz)		W_{csd} (Hz)		W_{csd} (ppm)
	8.45 T	17.6 T	8.45 T	17.6 T	
	1563	750	914	1906	9.75 ^a

^a Value is valid for both fields.

chemical shift dispersion (~ 10 ppm). The symmetric nature of the resonance obtained at the higher field suggests the presence of a single site only, corresponding to a Al Q^4 (4Si) unit.

For quadrupolar nuclei, such as ^{27}Al , sites that are overlapping in MAS spectra can often be resolved in a 2D MQMAS experiment because anisotropic contributions to the line broadening are not present in the isotropic dimension and the quadrupolar shift is different in the two dimensions (Amoureux and Fernandez, 1998). Figure 3 shows the ^{27}Al 3QMAS spectra of dry and hydrous nepheline glasses. The spectra are similar and give no indication of a second signal. (Note that the lowest contour line is at 1.5% intensity.) Figure 4 shows the 3QMAS spectra from our dry and hydrous $\text{QZ}_{52}\text{Ab}_{48}$ glasses. Once again, the spectra of the dry and hydrous glasses are similar,

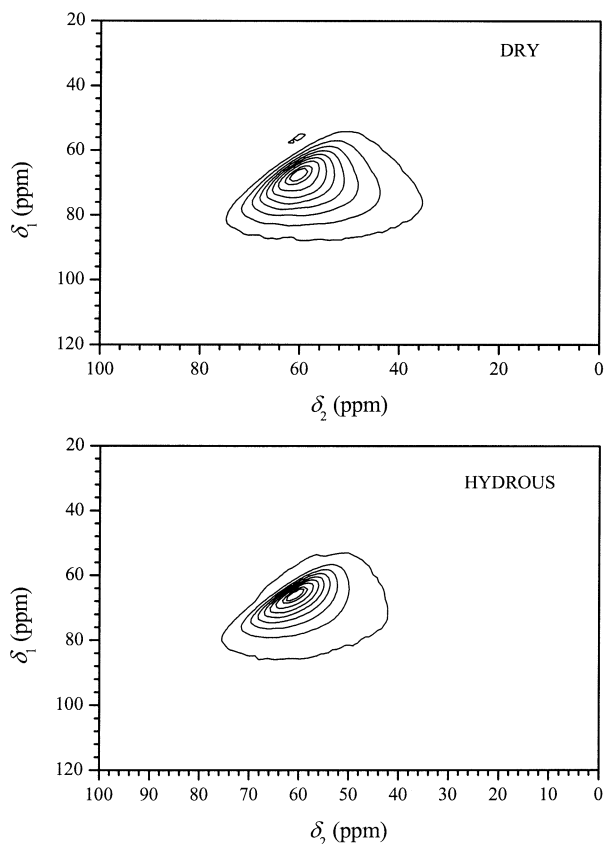


Fig. 3. ^{27}Al 3QMAS spectra of (a) dry and (b) hydrous nepheline glass at 14.1 T. The contour lines are at levels from 1.5 to 98% in 9.4% steps. The plots displays only the region containing any signal; the spectra were acquired with a large spectrum width (50 kHz) in the F1 dimension.

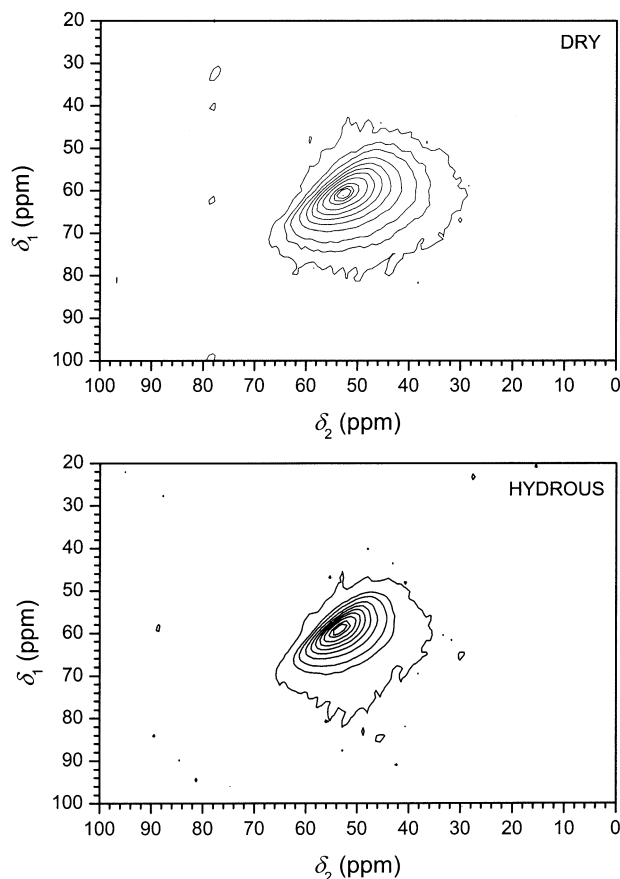


Fig. 4. ^{27}Al 3QMAS spectrum of (a) dry and (b) hydrous $\text{QZ}_{52}\text{Ab}_{48}$ glass at 14.1 T. The contour plot displays nine equally spaced levels from 1.5 to 98%

with the hydrous glass showing a slightly narrower resonance than the dry glass but with similar chemical shift and no sign of a second site.

Even higher resolution enhancements have been postulated by using higher-order MQMAS experiments by Amoureux and Fernandez (1998) (see also Pike et al., 2000), although the quantum coherence transfer in a 5QMAS experiment is smaller than in a 3QMAS experiment and a much weaker signal is observed ($< 20\%$ of 3QMAS). Figure 5 shows the ^{27}Al 5QMAS spectrum from Q52-6H. The 5QMAS experiment also shows only the presence of a single line, which is symmetric in both dimensions although the noise level in this case is at 5.5% of the signal. It should be noted that in a 5QMAS experiment, the lines might sometimes appear narrower because the MQMAS efficiency curves, becoming narrower when the quantum order is increased. This narrowing could be particularly important when the sample has a large distribution of C_Q and δ_{iso} . However, for the small range of C_Q values expected for our samples (3.5 to 5.0 MHz), the difference in the efficiency of the excitation would not have a big effect on the spectrum.

4. DISCUSSION

In agreement with previous observations, the ^{27}Al MAS spectra from the dry and hydrous nepheline glasses at $B_0 =$

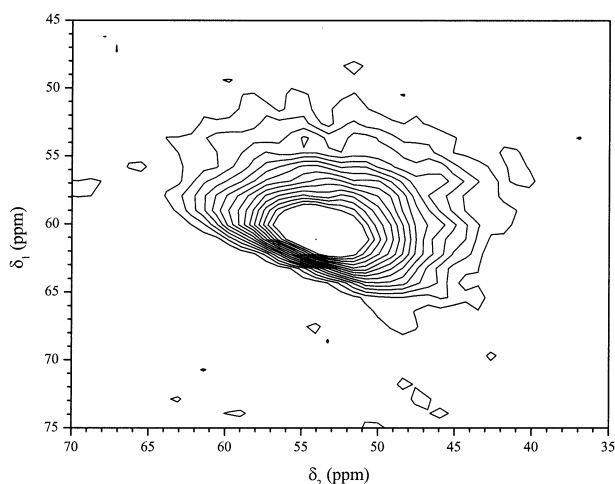


Fig. 5. ^{27}Al 5QMAS spectrum from the hydrous $\text{Qz}_{52}\text{Ab}_{48}$ sample at 14.1 T. The 15 contour lines are plotted at equally spaced levels starting at 5.0% and finishing at 75%.

14.1 T show only very small changes in the spectral position on hydration, with the difference in the center of gravity of the peaks recorded after water dissolution being <1 ppm. For Al, the main difference between the two water solubility models (depolymerization vs. nondepolymerization) is the existence of Al $\text{Q}^3(3\text{Si})\text{-OH}$ groups. Although Kohn et al. (1989, 1992) and Schmidt et al. (2000, 2001a) did not see any evidence for the existence of Al $\text{Q}^3(3\text{Si})\text{-OH}$ groups by ^{27}Al MAS for a number of different aluminosilicate compositions, Zeng et al. (2000) simulated MAS spectra of Ab glasses at 8.45 T, similar to those observed by Kohn et al. (1989), by adding a second Al site that was assigned to Al $\text{Q}^3\text{-OH}$. Assignment of ^{27}Al NMR peaks is typically based on the comparison with related compounds with known structures. Unfortunately, the absence of crystalline aluminosilicate model compounds containing OH groups attached to AlO_4 tetrahedra makes the interpretation of the ^{27}Al chemical shift data more difficult. The resonance from an Al Q^3 unit is presumed to have a more positive chemical shift than a Q^4 group. Kohn et al. (1989) used the chemical shift of $\text{Q}^3\text{Al-O}^-$ unit in a crystalline sheet silicate (70 ppm) as an approximation of $\text{Q}^3\text{Al-OH}$ in a glass. Zeng et al. (2000) suggested the possibility that $\text{Q}^3(3\text{Si})\text{-OH}$ in aqueous solution (65 ppm) is more suitable. In such aluminosilicate solutions, increasing depolymerization of AlO_4 tetrahedra causes a deshielding of ^{27}Al δ_{iso} of ~ 5 ppm per nonbridging oxygen (Mueller et al., 1981). Bearing in mind the strong correlation between ^{27}Al and ^{29}Si chemical shifts of silicates, aluminates, and aluminosilicates (e.g., Mueller et al., 1981; Jacobsen et al., 1989), it can be expected that also in aluminosilicate glasses depolymerization at AlO_4 -sites results in some deshielding of ^{27}Al δ_{iso} . However, if Al Q^4 and $\text{Q}^3(3\text{Si})\text{-OH}$ in our samples have very similar chemical shifts (which we think is very unlikely), then the detection of Al-OH would be very difficult from δ_{iso} alone.

From ^{27}Al MAS and MQMAS, the major difference between the dry and the hydrous nepheline glasses is the narrowing of the resonance. This result is consistent with previous studies of aluminosilicate glasses. The decrease in width could be because

of a decrease in the mean C_Q or in the chemical shift dispersion. For Qz-Ab-Or glasses, Schmidt et al. (2000, 2001a) suggested that the addition of water leads to an average decrease of the electric field gradient around Al and thus to an average increase of the local symmetry around the Al sites, which in turn suggests the absence of significant amounts of Al-OH. A similar effect has been also observed by Oglesby et al. (2002) for calcium aluminosilicate glasses. Such reasoning was already used by Kohn et al. (1992), who argued against the existence of Al-OH units because their formation should impose an axial symmetry, increasing the local distortion, thus leading to an increase in C_Q . If the presence of Al $\text{Q}^3\text{-OH}$ groups were significant, this would produce an increment in the spectral line width, in contrast to what is observed. Zeng et al. (2000) also assumed that Al $\text{Q}^3\text{-OH}$ have higher C_Q than Al Q^4 , but they argued that the decrease in the line width could be associated with a change in the level of disorder, which could cause the decrease of the line width on hydration. On the other hand, Sykes and Kubicki (1993) suggested that for albite glasses C_Q of Al $\text{Q}^3\text{-OH}$ is smaller than that of Al Q^4 .

For quadrupolar nuclei such as ^{27}Al , the experimental peak positions are shifted from their true isotropic chemical shifts. The extent of the shift depends strongly on the quadrupolar coupling constant and the resonance frequency, that is, magnetic field. For a spin 5/2, the center of gravity of the line, δ_{cg} , is related to the true isotropic chemical shift (δ_{iso}) by

$$\delta_{\text{cg}} = \delta_{\text{iso}} - \frac{3 P_Q^2}{500 \nu_0^2} 10^6 \quad (2)$$

where ν_0 is the resonance frequency and P_Q is the quadrupolar coupling product.

$$P_Q = C_Q \sqrt{1 + \frac{\eta_Q^2}{3}} \quad (3)$$

where C_Q is the quadrupolar coupling constant and η_Q is the asymmetry parameter, which can vary between 0 and 1.

By using these equations, we can calculate the positions (center of gravity) of the two aluminum sites (Q^4 and Q^3) in the ^{27}Al MAS spectrum of Q52-6H using the parameters from the simulations of Zeng et al. (2000) for hydrous albite glass. These authors obtained δ_{iso} ranging from 57.8 to 62.1 ppm for Q^4 Al and 65.0 to 65.8 ppm for Q^3 Al, respectively. Similar to Zeng et al. (2000), we consistently used $\eta_Q = 0.0$ for the calculations so that $C_Q = P_Q$. For the glass with a water content close to ours (6.4 wt%), Zeng et al. (2000) simulated the experimental data with the highest δ_{iso} . At $B_0 = 17.6$ T, the position of the two lines would then be $\delta_{\text{cg}} = 60.2$ ppm ($\delta_{\text{iso}} = 62.1$ ppm, $C_Q = 3.5$ MHz) for the Q^4 Al and $\delta_{\text{cg}} = 61.9$ ppm ($\delta_{\text{iso}} = 65.8$ ppm, $C_Q = 5$ MHz) for the Q^3 Al. From Figure 2, it is obvious that the experimental spectrum cannot be fitted with such lines because the experimental spectrum is located at lower frequency (centered at 55 ppm).

Instead, we consider the isotropic chemical shift estimated from the field-dependent measurements for this sample by Schmidt et al. (2000) to describe the Q^4 unit ($\delta_{\text{iso}} = 56.9$ ppm). By using $\delta_{\text{iso}} = 56.9$ ppm and $C_Q = 3.8$ MHz for the Q^4 unit and the values from the Zeng et al. (2000) simulation for $\text{Q}^3\text{-OH}$ ($\delta_{\text{iso}} = 65.0$ ppm, $C_Q = 5$ MHz), the $\text{Q}^3\text{-OH}$ resonance would have a center of gravity of 48.0 ppm in the MAS spectra

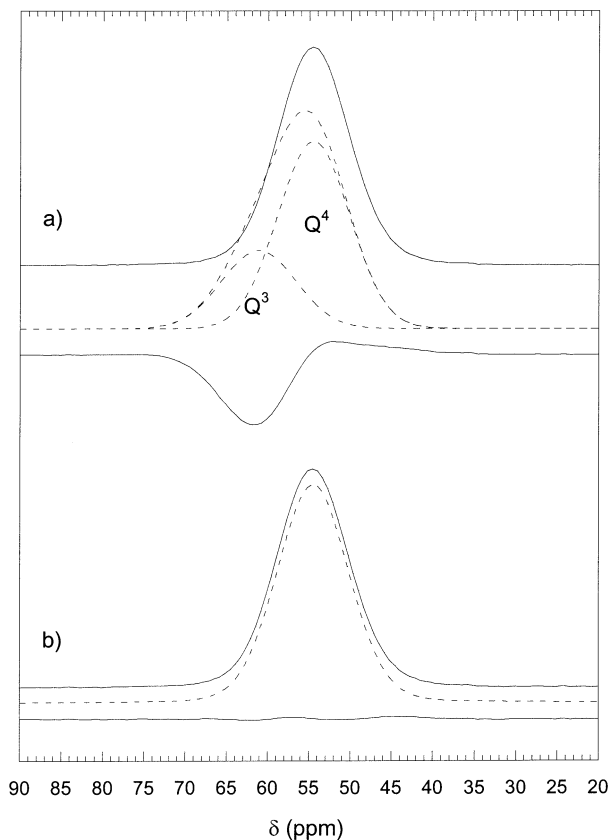


Fig. 6. (a) ^{27}Al MAS spectra (top line) of Q52-6H at 17.6 T showing a simulation of the spectrum (dashed line) with two lines representing Al Q^4 and $\text{Q}^3\text{-OH}$ units. The relative signal intensity of $\text{Q}^3\text{-OH}$ (27%) was adjusted according to the depolymerization model of Zeng et al. (2000), and the NMR parameters were also taken from these authors. The bottom line corresponds to the residual from the simulation. (b) Fit (dashed line) of the same experimental spectrum (top line) with a single line representing the Al Q^4 unit. Bottom line corresponds to the residual from the simulation.

at 8.45 T, completely overlapping with the spectral line from Al Q^4 (4Si) groups of $\delta_{\text{cg}} = 48.9$ ppm. However, at 17.6 T, the effect of the second-order quadrupolar shift is smaller, and the resonances are observed closer to their δ_{iso} . At this magnetic field, δ_{cg} of the predicted $\text{Q}^3\text{-OH}$ line is at 61.1 ppm, whereas the δ_{cg} of the Q^4 line is 54.3 ppm. The spectrum at this field was simulated with two gaussian lines defined by three parameters: the position (δ_{cg}), the intensity, and the width of the line (Fig. 6). The position of the two lines was set to the values used by Zeng et al. (Table 2). As shown above, chemical shift dispersion is the major contribution to the width of the line at

17.6 T. If we neglect the differences in W_q between the two sites and consider that the broadening produced by chemical shift dispersion is similar for both lines, we can assume the same width for both species. The area of the lines was fixed to ensure a contribution of 27% of $\text{Q}^3\text{-OH}$ and 73% of Q^4 to the total intensity as estimated from the model of Zeng et al. (2000) for this glass composition and water content. We varied the width and the intensity of both lines to best fit the experimental data. The fit obtained with these parameters is very poor (shown in Fig. 6a). With the increase in resolution from going to a higher field, the presence of a deshielded Q^3 resonance would make the resonance asymmetric toward the high-frequency side, which is not observed. Figure 6b shows a much better simulation, with a single line at the position of the Al Q^4 . The quality of the simulation with a single line makes it very difficult to support the possibility of a second aluminum site with the values expected by Zeng et al. (2000). It should be noted that if a smaller C_Q than the one used by Zeng et al. (2000) (as suggested by Sykes and Kubicki, 1993) is used to simulate the position of an Al-OH unit, the resonance would be at even higher frequency, making the separation between the Q^4 and Al-OH even larger and easier to detect. If we allow the position of the Q^4 and Q^3 to vary, the presence of a second line is always clear unless the difference in position (δ_{cg}) between Q^3 and Q^4 is smaller than 3.5 ppm. In such a hypothetical case, a 1D NMR experiment is not likely to be able to help in the detection of these two units. The existence of a significant amount of Al sites with a very large C_Q and thus invisible even at 17.6 T can be discounted because earlier experiments at 14.1 T on dry and hydrous $\text{QZ}_{52}\text{Ab}_{48}$ (Schmidt et al., 2000) showed that, to within experimental error ($\pm 5\%$), all of the aluminum was being observed.

The same kind of attempt can be made with the MQMAS data. A single MQMAS experiment allows the determination of the isotropic chemical shift, δ_{iso} , and an estimation of the quadrupolar interaction. This is possible thanks to the different scaling factors of the shift in the MAS (F_2) and isotropic dimension (F_1). For a spin of 5/2 in a 3QMAS experiment, the observed peak position in the isotropic dimension can be described as

$$\delta_1 = \delta_{\text{iso}} + \frac{3}{850} \frac{P_Q^2}{\nu_0^2} 10^6 \quad (4)$$

In the MAS dimension, the observed shift of the center of gravity is the same as the position observed in a standard MAS experiment (Eqn. 2). The values of δ_{iso} and P_Q can be extracted by combining data from both dimensions in a MQMAS experiment. At the same time, Eqns. 2 and 4 can be used to position a line in the 2D plot if we know its δ_{iso} and P_Q .

In the 3QMAS experiment at 14.1 T, the resonance of

Table 2. ^{27}Al NMR parameters used in the simulation of the ^{27}Al MAS NMR data of the Q52-6H glass at 17.6 T.

	Q^4				$\text{Q}^3\text{-OH}$				$\text{Q}^3/(\text{Q}^3 + \text{Q}^4)$
	P_Q (MHz)	δ_{iso} (ppm)	δ_{cg} (ppm)	FWHM (Hz)	P_Q (MHz)	δ_{iso} (ppm)	δ_{cg} (ppm)	FWHM (Hz)	
Fig. 6a	3.8	56.9	54.3	2000	5.0	65.0	61.1	2000	0.27
Fig. 6b	3.8	56.9	54.3	1993	—	—	—	—	0

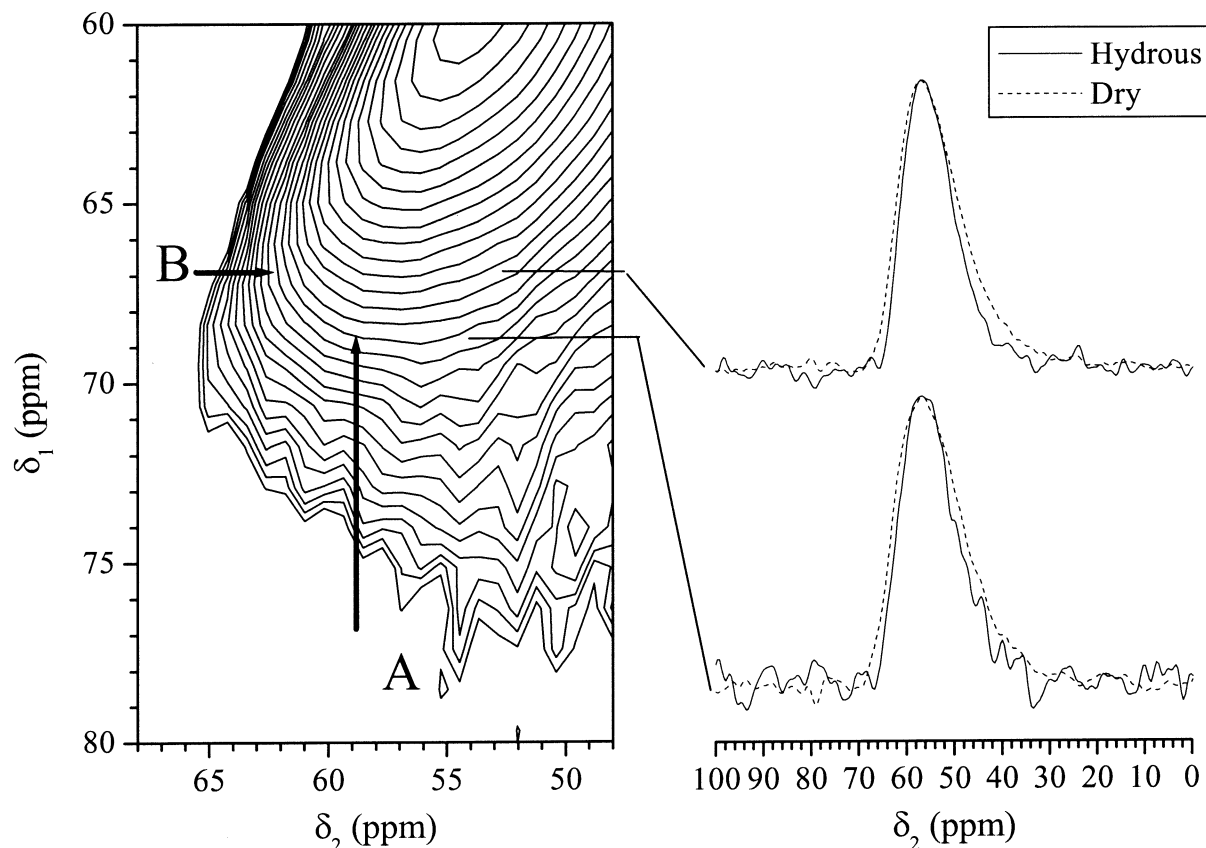


Fig. 7. Expanded view of the ^{27}Al 3QMAS spectrum from Q52-6H sample at 14.1T. The contour lines are plotted emphasizing the low-intensity levels by having a multiplication factor of 1.15 starting at 2% (2.0, 2.3, 2.6, 3.0, 3.5, 4.0, 4.6, 5.3, 6.1...%). The site A and B represent the expected position of the Al $\text{Q}^3\text{-OH}$ unit using parameters of Zeng et al. (2000) and Sykes and Kubicki (1993), respectively. Right plots show the MAS slices at the position of sites A and B. The MAS slices at the same positions of the dry glass are superposed for comparison.

$\text{Q}^3\text{-OH}$ with the parameters used by Zeng et al. (2000) ($\delta_{\text{iso}} = 65$ ppm, $C_Q = 5$ MHz) would have a chemical shift of $\delta_2 = 58.9$ ppm in the F_2 dimension (the same as in a MAS spectrum), whereas in the isotropic dimension, δ_1 would be 68.6 ppm. Figure 7 shows the 3QMAS of Q52-6H with the expected position of the Al-OH group marked as "site A." In this experiment, the resonances from Q^4 and $\text{Q}^3\text{-OH}$ should be better resolved than in a MAS experiment. We could also assume a smaller C_Q for a $\text{Q}^3\text{-OH}$ following the molecular calculations by Sykes and Kubicki (1993) but still lying within the Al C_Q range of 3.5 to 5.0 MHz, as determined by Zeng et al. (1999) by $^1\text{H}/^{27}\text{Al}$ TRAPDOR NMR experiments. By using a value of $C_Q = 3.5$ MHz and the isotropic chemical shift suggested by Zeng et al. (2000) of 65 ppm, the resonance should be visible at $\delta_2 = 62.0$ ppm and $\delta_1 = 66.8$ ppm (marked as "site B" in Fig. 7).

The contour plot shows no sign of distortion around the position where the Q^3 resonance is expected, indicating that if there is any additional intensity in this region, it must be small. Figure 7 also shows the slices taken along the horizontal MAS axis at the position of sites A and B. We can see that compared with the same slices from the dry glass, here also, there is no evidence of a second line. Similarly a projection along the (vertical) isotropic axis consists of a single symmetric reso-

nance that shows no evidence of any other line. It should be emphasized that the noise level in Figure 7 is at the 2.0% level, and for the range of C_Q expected for the Al $\text{Q}^3\text{-OH}$ unit, both Q^4 and Q^3 resonances would be nearly equally excited in a 3QMAS experiment. Thus, any $\text{Q}^3\text{-OH}$ units with the predicted parameters can only be present at a very low concentration. The nepheline hydrous glass gave a very similar 3QMAS spectrum; no distortions are observed in the contour plot or in the MAS slices. In contrast to $\text{Qz}_{52}\text{Ab}_{48}$ glass, nepheline glasses consist of more than 95% of Al-O-Si units, so absence of Al-OH also means absence of Si-OH unless formation of Si-O-Si occurs. These results strongly support those of Kohn et al. (1992).

These two examples demonstrate that the only possibility for the existence of the $\text{Q}^3\text{-OH}$ unit is that it possesses similar NMR parameters (δ_{iso} and quadrupolar interaction) to the Q^4 unit. We think that this possibility is very remote because the inclusion of an OH group at the aluminum site should induce significant changes detectable by NMR.

5. CONCLUSIONS

In summary, ^{27}Al MAS and MQMAS have been used to study the aluminum environments in dry and hydrous aluminosilicate glasses. New and improved ^{27}Al NMR data have

been presented for dry and hydrous nepheline and $\text{Qz}_{52}\text{Ab}_{48}$ glasses. From both the ^{27}Al MAS and MQMAS data, we have no evidence of network depolymerization according to the model proposed by Zeng et al. (2000). A fit to ^{27}Al MAS data at 17.6 T was not possible using the range of parameters proposed by Zeng et al. (2000) to describe the Al $\text{Q}^3\text{-OH}$ units, nor was there any evidence in the MQMAS spectrum of an extra line. The data strongly suggest that aluminum is only present as Al $\text{Q}^4(4\text{Si})$ units for the glasses studied unless Al $\text{Q}^3(3\text{Si})\text{-OH}$ units have a very similar δ_{iso} and P_{Q} so they cannot be resolved. For the particular case of nepheline glasses consisting predominantly of Al-O-Si units, the absence of Al $\text{Q}^3\text{-OH}$ also suggests the absence of Si $\text{Q}^3\text{-OH}$ (considering a water dissolution mechanism such as $\text{Si-O-Al} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{Al-OH}$), which is consistent with the ^{29}Si -NMR data of Kohn et al. (1992). Following this line of reasoning, our ^{27}Al NMR data for nepheline glass suggest the absence of any significant depolymerization of such glasses on hydration.

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