Sodium environments in dry and hydrous albite glasses: Improved ^{23}Na solid state NMR data and their implications for water dissolution mechanisms

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Abstract—The sodium environments in albite glasses with water concentrations ranging from 0 to 60 mol% were studied using ^{23}Na off-resonance quadrupole nutation and magic angle spinning (MAS) NMR spectroscopy. Crystalline albite was used as a model compound to demonstrate that off-resonance nutation is a suitable method for determination of the quadrupole coupling constant (C_q) for ^{23}Na . Off-resonance nutation experiments gave a mean $C_q = 1.75 \pm 0.2$ MHz for all the albite glasses studied here. MAS NMR experiments were performed at three magnetic fields, 7.05 T, 9.4 T, and 14.1 T in order to deduce the mean isotropic chemical shift, δ_{iso} , and to provide an independent measurement of the values of C_q . The mean isotropic chemical shift is a strong function of dissolved water concentration, but the mean C_q is essentially constant at $2.1\text{--}2.2 \pm 0.2$ MHz over the water concentration range studied. The distributions of both chemical shift and quadrupolar interactions decreases markedly with increasing water concentration, consistent with earlier suggestions that the hydrous glasses have a much more ordered structure. These new data using off-resonance nutation and faster MAS combined with higher applied magnetic fields supersede the ^{23}Na NMR data of Kohn et al. (1989a) and should be used in preference in devising or testing models for water dissolution mechanisms in albite melts and glasses. Our revised data provide no evidence for a change in water dissolution mechanism at 30 mol% H_2O , but the other conclusions of Kohn et al. (1989a) and the principal features of the dissolution mechanism developed by Kohn et al. (1989a, 1992, 1994) are essentially unchanged. Copyright © 1998 Elsevier Science Ltd

1. INTRODUCTION

The presence of water in silicate melts has long been recognised as an important control on the behaviour of igneous systems (Bowen, 1928; Goranson, 1931; Burnham, 1975). Water dissolution has dramatic effects on phase equilibria (Kushiro, 1969; Pichavant et al., 1992) and on the physical properties of melts (e.g., Lange, 1994; Dingwell et al., 1996; Richet et al., 1996; Schulze et al., 1996) and is, therefore, crucially important in a wide range of geological processes as diverse as partial melting of the mantle and explosive silicic volcanism. In order to rationalize the effects of water on the physical and chemical properties of melts, it is important to have an understanding of the mechanisms of dissolution of water in melts of different compositions. One approach to this goal is to perform spectroscopic and diffraction measurements on hydrous silicate glasses and melts, and many such studies have been published (e.g., Farnan et al., 1987; Okuno et al., 1987; Kohn et al., 1989b; Silver and Stolper, 1989; Kümmerlen et al., 1992; Mysen, 1992; McMillan et al., 1993; Nowak and Behrens, 1995; Shen and Keppler, 1995; Holtz et al., 1996; Zotov et al., 1996). However, despite the large literature on the subject and numerous attempts to explain phase equilibria, solubility measurements and spectroscopic data in terms of a physical mechanism for water dissolution, no model has yet found universal acceptance (McMillan, 1994).

Kohn et al. (1989a) proposed a new model for the dissolution mechanism of water in albite melts, which represented a major departure from all earlier models. The model was based on multinuclear NMR measurements on glasses, the principal observations being (1) only very small changes in the spectra of ^{29}Si and ^{27}Al were seen; (2) the ^1H spectra were consistent with the $\text{OH}/\text{H}_2\text{O}$ ratio in glasses determined from infra-red by Silver and Stolper (1989); (3) major changes in ^{23}Na spectra as a function of dissolved water concentration were seen. The NMR data were interpreted in terms of a model whereby the aluminosilicate framework of the glass is not depolymerised by rupture of T-O-T linkages, but instead a $\text{Na}^+ \leftrightarrow \text{H}^+$ cation exchange occurs, leading to aluminate tetrahedra charge balanced by H^+ , and an equal number of Na^+OH^- complexes. Such a configuration can also be thought of in terms of bridging hydroxyl groups ($\text{Al-OH}_{(\text{br})}\text{-Si}$). The model proposed was in marked contrast to all previous models in which rupture of T-O-T linkages to give T-OH was universally advocated. Additional data on other framework aluminosilicate compositions (Kohn et al., 1992) were fully consistent with the Kohn et al. (1989a) model. Kohn et al. (1992) also attempted to rationalise changes in the vibrational spectra and physical properties of hydrous aluminosilicate melts. More recently Sykes and Kubicki (1993) have proposed an alternative model partially based on MO calculations of aluminosilicate clusters, but also relying heavily on the Kohn et al. (1989a) ^{23}Na quadrupole coupling constant data. Sykes and Kubicki (1993) suggested that over the range 0–30 mol% water, the dissolution mechanism involves breakage of Al-O-Al bridges to give Al-OH. Above 30

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mol%, they suggested that the mechanism changes to the one proposed by Kohn et al. (1989a). The value of 30 mol%, which is central to the model of Sykes and Kubicki (1993), is based solely on the discontinuity in the ^{23}Na quadrupole coupling constant (C_q) data presented by Kohn et al. (1989a). Other more recent contributions also cite the discontinuity in the ^{23}Na C_q as a crucial piece of evidence in elucidating the water dissolution mechanism in albite melt (Zeng and Nekvasil, 1996; Tossell and Sàghi-Szabó, 1997; Sykes et al., 1997).

As changes in C_q and the isotropic chemical shift (δ_{iso}) for ^{23}Na are central to some models of water dissolution mechanisms, obtaining detailed and accurate knowledge of changes in these parameters is very important. In this paper we will present new data using the techniques of off-resonance nutation NMR spectroscopy and fast magic angle spinning (MAS) over a range of magnetic fields. The technique of off-resonance nutation NMR spectroscopy has recently been used to determine the quadrupole coupling constant C_q ($= e^2qQ/h$, where eq is the maximum component of the electric field gradient at the nuclear site and eQ is the nuclear electric quadrupole moment). In a study of a series of aluminosilicate glasses it was demonstrated that off-resonance nutation can be used in amorphous systems to get information about the average quadrupole parameters (Dirken et al., 1995). Due to the fact that off-resonance nutation mainly relies on line intensities to discriminate between different sites well resolved spectra can still be obtained in systems (e.g., glasses) where a distribution of quadrupolar interactions is present. Thus, the average C_q can be obtained from nutation, but there is no straightforward information about the details (i.e., width and shape) of its distribution.

The other technique we have used is to measure changes in the centre of gravity of fast MAS NMR spectra as a function of the Larmor frequency to extract estimates of both the isotropic chemical shift (δ_{iso}) and C_q . This is essentially an improved version of the technique used by Kohn et al. (1989a) which was an early example of a multiple field study of a quadrupolar nucleus in an amorphous solid. In the intervening years there have been great improvements in both the understanding of how the NMR interactions are related to the spectral features in amorphous materials and in the experimental technology available, allowing better, more unambiguous extraction of the NMR interaction parameters.

For MAS NMR resonances from quadrupole nuclei where there is a distribution of interaction parameters, both their width and position can be strong functions of applied magnetic field and MAS rate. For a nucleus such as ^{23}Na that experiences a substantial quadrupolar interaction it is usually only the central ($1/2, -1/2$) transition which is observed and this experiences second-order broadening. This has two important implications for the study of such nuclei in solids; (1) the width (in Hz) is inversely proportional to the applied magnetic field and (2) the maximum narrowing which can be attained using MAS at 54.7° is a factor of about 3.4–4, and to achieve this factor the MAS rate must exceed the residual second-order quadrupolar width. For a glass, where there will be a distribution of environments and hence quadrupolar interactions, slow MAS speed will only narrow those environments with the smallest values of C_q , as these will have the smallest residual width. As the spinning speed is increased more sites narrow but these have larger

residual linewidths so that the MAS linewidth increases. This has been observed in other studies of quadrupolar nuclei (e.g., ^{27}Al) in glasses (Sato et al., 1991). To observe the true lineshape it is important that the spinning speed is fast enough to exceed the residual width of the largest C_q -components, and this turned out not to be the case in the original 4.7 T data of Kohn et al (1989a). Calculations of the MAS NMR lineshapes of quadrupolar nuclei in glasses have shown that the characteristic tail to low frequency which is often observed, results from the distribution of quadrupolar interactions (Phillips et al., 1988; Jäger et al., 1993). The relationship of the peak position to the centre of gravity depends on the size and nature of the distribution, and for such asymmetric lineshapes it is important to use the centre of gravity rather than the peak maximum (which was used by Kohn et al., 1989a) of the resonance to evaluate the mean interaction parameters from the multiple magnetic field data.

2. NMR METHODOLOGY

2.1. Off-Resonance Quadrupole Nutation NMR

The basic idea of the nutation NMR experiment is to examine the response of the spin system to an r.f. pulse. This response is a function of the ratio of the quadrupole frequency ν_q ($= 3C_q/2I(2I-1)$ where I is the nuclear spin quantum number) and the precession rate of the magnetisation in the applied rf-field ν_1 ($= \gamma B_1/2\pi$, where γ is the gyromagnetic ratio of the nucleus and B_1 the rf field strength) (Samoson and Lippmaa, 1983). This was refined into a two-dimensional NMR experiment which means that in different time periods of the experiment the magnetisation evolves under different interactions, giving effectively two separate time domains, so that on double Fourier transformation the magnetisation is labelled in the nutation experiment by its normal spectral frequency and the frequency of its response to the rf-pulse (Kentgens et al., 1987; Samoson and Lippmaa, 1988). Unfortunately, nutation spectroscopy yields just one line when $\nu_q/\nu_1 \geq 1$, setting an upper limit on the quadrupolar constants that can be recovered from the spectra. To overcome this problem the off-resonance nutation experiment was introduced. Here, a resonance offset is present during the rf irradiation period of the 2D nutation experiment (Kentgens, 1993). The evolution of the quadrupolar spin system in the rotating frame then occurs in an effective field which is the vector sum of the resonance offset $\Delta\nu$ and the applied rf field ν_1 . The effective field can be much greater than the applied rf field itself, thus it is possible by an appropriate choice of offset to get a structured nutation spectrum and hence deduce C_q from powders with values of C_q that would give a single peak using ν_1 alone. From this experiment a 2D spectrum is obtained, and the projection of this spectrum along the F2-axis is the static NMR spectrum of the central transition with some distortions to the lineshape because the spectra are processed in magnitude mode. The projection along the F1-axis is the so-called nutation spectrum of the lines whose features critically depend on the ratio ν_q/ν_{eff} (where $\nu_{\text{eff}} = (\nu_1^2 + \Delta\nu^2)^{1/2}$). A detailed theoretical description of off-resonance nutation and a number of experiments on some model compounds has been previously presented (Kentgens, 1993). Theoretical nutation spectra were calculated by numerically diagonalising the appropriate Hamiltonians (Kentgens et al., 1987;

Table 1. List of samples studied, together with their synthesis conditions and the NMR techniques used to study them.

Sample	mol% Water	Apparatus	P/kb	T/°C	Run duration/hrs	MAS or nutation
AB5	0	LVF	0.001	~1500		MAS + QN
AB7	29	IHPV	0.5	1270	4	MAS + QN
AB4B	40	IHPV	1	1300	7	QN
AB4A	50	IHPV	2	1300	6	QN
AB5G	60	IHPV	5	900	3	MAS
AbB4	0	LVF	0.001	1200	1.75	MAS
AbB2	41	PC	12	1200	4	MAS
AbB3	56	PC	12	1200	4	MAS

LVF = large volume furnace; IHPV = internally heated pressure vessel; PC = solid media piston cylinder apparatus; MAS = magic angle spinning; QN = quadrupolar nutation.

Kentgens, 1993). The spectra were calculated as full 2D data sets and processed similarly to the experimental spectra.

2.2. Field Dependent MAS NMR

As has been outlined (vide supra) at appropriately fast MAS speeds, exceeding the residual second-order quadrupolar broadening the magnetic field dependence of the centre of gravity of the resonance can be used to extract the mean C_q and δ_{iso} using

$$\delta_{cg} = \delta_{iso} - (C_q^2/40\nu_o^2)(1+\eta^2/3). \quad (1)$$

(1) Hence a plot of δ_{cg} against ν_o^{-2} (where $\nu_o = \gamma B_o/2\pi$) will give C_q from the gradient and δ_{iso} from the intercept that corresponds to infinite applied magnetic field. If no indication of the asymmetry parameter η can be obtained from the lineshape it is often assumed to be 0, which can introduce a maximum error of only 13% in the value of C_q deduced from the above plot.

3. EXPERIMENTAL DETAILS

Nine samples have been investigated: crystalline Amelia albite (from the Natural History Museum, specimen number BM 1962, 439) which was used as a model compound for which δ_{iso} and C_q are known; two dry albite glasses, AB5 which was used previously by Kohn et al. (1989a), and AbB4 which was a portion of AB5 glass remelted at 1200°C for this study; four of the hydrous samples of Kohn et al. (1989a) AB7, AB4B, AB4A, and AB5G containing 29, 40, 50, and 60 mol% H₂O (on an 8 oxygen basis), respectively; and two new hydrous glasses, AbB2 and AbB3, containing 41 and 56 mol% H₂O, respectively, which were newly synthesised and used as a check on the integrity of the older samples. A summary of the preparation methods of the glassy samples and the NMR techniques which were used to study each sample are listed in Table 1. More details on the samples studied by Kohn et al. (1989a) can be found in the original reference. AbB4 and AbB2 were synthesised using the same starting material as the other samples, but AbB3 was a ¹⁷O-enriched sample which was slightly deficient in Al compared to ideal stoichiometry (Dirken et al., 1997). The water concentrations in the AbB2 and AbB3 are assumed to correspond to the amounts weighed into the capsules, as these samples were undersaturated with respect to water at the run conditions.

The nutation spectra of AB5, AB7, AB4B, and AB4A were carried out on a Bruker AM 500 spectrometer equipped with a solid-state accessory at a magnetic field of 11.7 T. The spectra were collected static using a home-built high power probehead equipped with a 2.5 mm coil capable of rf-fields up to 200 kHz. In these experiments the magnetisation is initially prepared perpendicular to the effective rf field using frequency stepped adiabatic half passage (Kentgens, 1993) im-

plemented with the Spinguide hardware (van Os et al., 1991). The nutation was performed for the crystalline sample with $\nu_1 = 155$ kHz and an offset of 247 kHz using 128 t_1 increments of 0.8 μ s with twenty-eight scans coadded per increment with a recycle delay of 60 s. For the glassy samples $\nu_1 \sim 180$ kHz and an offset of 195 kHz, with 128 t_1 increments of 0.7 μ s were used with 1200 scans coadded at each increment with a recycle delay of 0.5 s. The signals were processed using NMRi software running on a SUN microcomputer.

MAS NMR was performed at three magnetic fields of 7.05, 9.4, and 14.1 T on Chemagnetics CMX-300 and 400 and Varian VXR-600 spectrometers operating at frequencies of 79.5, 105.3, and 158.7 MHz and with magic angle spinning in excess of 17, 30, and 12 kHz, respectively. In the analysis of the data the centre of gravity of the peaks was used rather than the peak maximum (used previously, see Fig. 3 of Kohn et al., 1989a). In all cases short, small tip angle pulses were used ($\pi/12$ with 1-2 s recycle delays to produce unsaturated, rf-distortion free spectra. Additionally some MAS spectra were run with high power ¹H decoupling. The spectra were referenced to 1M NaCl at 0 ppm either directly against this primary reference or solid NaCl at 7.2 ppm. An MAS NMR spectrum of crystalline Amelia albite was obtained on a Bruker DMX-300 spectrometer operating at 79.4 MHz and simulation of the second-order quadrupole lineshape was performed using the Bruker Winfit program on a PC.

4. RESULTS

Nutation spectroscopy was used to obtain the quadrupole interaction in these albite glasses. Initially a well characterised sample of crystalline Amelia albite was studied by both MAS and 2D nutation NMR. The MAS NMR spectrum at 7.05 T (Fig. 1a upper) shows a well defined second-order quadrupolar powder pattern which could be closely simulated (Fig. 1a lower) using the parameters previously published in the literature of $C_q = 2.6$ MHz and $\delta_{iso} = -8$ ppm (Phillips et al., 1988). The full two-dimensional nutation data set is shown (Fig. 1b) along with the projections. This nutation spectrum is highly structured and can be fully simulated in the sense that the main frequency features of the nutation response (F1) are correctly predicted along with the two-dimensional distribution of intensities (Fig. 1c). The simulation yields a value for C_q of 2.6 MHz. The agreement between the MAS and nutation on this model compound lends confidence to the values extracted from nutation for the glasses. The nutation spectra were run on a series of albite glasses with results shown for the dry and AB4A (50 mol% H₂O) albite glasses (Fig. 2). As can be judged from Fig. 2, there is good correspondence between experimental and simulated spectra, with the frequency response (F1)

Fig. 1. ^{23}Na NMR spectra of Amelia Albite. (a) 7.05 T MAS NMR spectrum (upper) and simulation (lower), (b) 11.7 T two-dimensional off-resonance quadrupole nutation spectrum and (c) simulation of nutation data. The nutation data was collected with $\nu_1 = 155$ kHz and $\Delta\nu = 247$ kHz.

correctly predicted, although there are some small intensity differences at negative frequencies. These discrepancies are attributed to lineshape distortions as a result of the magnitude processing. Moreover, the calculations assume ideal pulses. For a number of model compounds it has been established, however, that if one concentrates on the main signal intensities of the spectra (in the positive frequency regime) reliable values may be obtained for the quadrupole parameters (Kentgens, 1993). This is further demonstrated by the good agreement of the calculated and experimental spectra of crystalline albite in the present study. A subsequent off-resonance nutation study of aluminosilicate glasses showed that one can obtain the average

quadrupole coupling constants from amorphous systems, but no information about the distribution in these parameters (Dirken et al., 1995). There it was shown that the simulations with a single C_q -value do not differ significantly from those simulated with a distribution in C_q of up to 1-1.5 MHz. In the present study we simulated the spectra using a single C_q value, which should be interpreted as the average C_q value in the glass. The off-resonance nutation spectra from all the glass samples look very similar and could all be simulated with $C_q \sim 1.75$ MHz (AB5 1.75 MHz; AB7, 1.7 MHz; AB4B, 1.65 MHz; AB4A, 1.75 MHz) and $\eta \sim 0.7$. As was already stressed, this C_q value should be interpreted as an average C_q . Although the simula-

Fig. 2. Projections of the 11.7 T off-resonance quadrupole nutation spectra of albite glasses. (a) dry and (b) 50 mol% H_2O . In each case the upper spectrum is the experimental data, the lower is a simulation. The nutation data was collected with $\nu_1 = 175$ kHz and $\Delta\nu = 195$ kHz.

tions already show small differences when changing C_q by 0.05 MHz, we estimate the accuracy of simulation of the main (F1) spectral features from the nutation method to be ± 0.2 MHz, however, the width of the distribution in C_q is different for the various glasses and may be as large as 1–1.5 MHz.

Given the nutation spectra showed very little variation in the average value of C_q with dissolved water content a more detailed MAS NMR study was demanded, taking advantage of the improved experimental methodology which has become available since the study of Kohn et al. (1989a). All ^{23}Na MAS NMR spectra from the albite glasses consisted of a single centreband that was accompanied by a series of small sidebands. A typical set of spectra, those obtained at 7.05 T, are shown in Fig. 3. The most striking thing about this set of spectra is that the resonance from the dry sample is broad and shows asymmetry while in the wet samples the resonance becomes increasingly narrow and much more symmetric. All the ^{23}Na MAS NMR data obtained in this study are summarised in Table 2. It is immediately clear that the centres of gravity and linewidths are strong functions of applied magnetic field (B_0).

The importance of using fast MAS for quadrupolar nuclei particularly at low field is well illustrated by ^{23}Na in these albite glasses. Figure 4 compares the centres of gravity (a) and linewidths (full width half maximum) (b) at 7.05 T for AbB3 (56 mol% H_2O) and AbB4 (dry) glasses as a function of spinning speed. It is quite clear that the behaviour of the two samples is very different. The centre of gravity for AbB3 decreases by only 4.7 ppm from the static spectrum to MAS at 17.5 kHz, and indeed reaches a steady value at 13 kHz. In contrast, for AbB4 there is initially a sharp decrease of ~ 11 ppm between 0 and 7 kHz, then a levelling off before a further decrease at the highest speeds used. It is only at the highest speed that truly representative shifts of the samples are recorded; for the dry sample even spinning at 17.5 kHz at 7.05 T appears not to be sufficiently fast. However, at this speed the centre of gravity should be approaching its limiting value, and this is certainly true at the MAS rates used at 9.4 and 14.1 T. There is also an interesting difference between the behaviours of the linewidths for the two samples. In both samples initially there is a rapid decrease in linewidth until about 3 kHz. At higher speed the linewidth for AbB3 remains relatively constant whereas that of AbB4 rises significantly with increased spinning speed. The observations of both the linewidth and position as a function of spinning speed are consistent with a wide distribution of C_q s in the dry glass, with progressively larger values being narrowed as the spinning speed increases, whereas for the hydrous glass this distribution is very much more limited.

At the highest field used here (14.1 T), there is a wide variation in the peak positions with water content so that it can already be seen that there is a large variation in the isotropic chemical shifts, the second-order quadrupole contribution to the isotropic position being much reduced at these fields. To check that the changing residual linewidth is not related to the

Fig. 3. ^{23}Na MAS NMR data for albite glasses obtained at a magnetic field of 7.05 T and with MAS at 17 kHz; (a) AbB4, dry glass, (b) AbB2, 41 mol% H_2O , and (c) AbB3, 56 mol% H_2O .

Table 2. Summary of ^{23}Na MAS NMR data at three different magnetic fields from albite glasses and the C_q and δ_{iso} deduced from them.

Sample	mol% H_2O	7.05 T		9.4 T		14.1 T		$\delta_{\text{iso}} \pm 2$ ppm	$C_q \pm 0.2$ MHz
		$\delta_{\text{cg}} \pm 1.5$	$\Delta_{1/2} \pm 0.2$	$\delta_{\text{cg}} \pm 1.5$	$\Delta_{1/2} \pm 0.2$	$\delta_{\text{cg}} \pm 1.5$	$\Delta_{1/2} \pm 0.2$		
AbB4	0	-36.8	3.7	-26.5	2.7	-19.3	2.5	-13.4	2.25
AB5	0	-35.7	3.5	—	—	-19.4	2.7	-13.9	2.17
AB7	29	-29.6	2.9	—	—	-14.2	2.6	-9	2.11
AbB2	41	-27.5	2.7	—	—	-12.0	2.3	-6.8	2.12
AbB3	56	-24.6	2.1	-17.1	1.6	-8.9	1.9	-4.4	2.12
AB5G	60	—	—	—	—	-9.0	0.83	—	—

δ_{cg} is the centre of gravity in ppm and $\Delta_{1/2}$ is the fullwidth at half maximum in kHz. C_q was calculated using $\eta = 0.7$, the error is estimated from a least squares analysis and allowing for the fact that η can vary between 0.5 and 1.

dipolar coupling to ^1H , some additional spectra were acquired at 11.7 T with ^1H high power decoupling. Identical spectra were obtained with and without decoupling indicating that the fast MAS employed here is sufficient to effectively remove all the dipolar contributions.

In Fig. 5 the position of the centre of gravity of the line vs.

Fig. 4. Effect of spinning speed on (a) the centre of gravity (δ_{cg}) and (b) the linewidth (FWHM) of the 7.05 T ^{23}Na MAS spectra for the dry and hydrous albite glasses, AbB4 and AbB3, respectively.

ν_0^{-2} is plotted. Equation 1 was employed to obtain the values of isotropic chemical shift and mean C_q given in Table 2. The mean C_q values for AB5, AbB4, AB7, AbB2, and AbB3 are all in the range $2.1\text{--}2.2 \pm 0.15$ MHz. These values were calculated assuming $\eta = 0.7$. This is the asymmetry parameter deduced from the nutation spectra and should, therefore, be a better assumption than taking $\eta = 0$ (Kohn et al., 1989a), although a possible range of $\eta = 0.5\text{--}1.0$ was considered when estimating the errors in the values of C_q . The very small variation in C_q as a function of dissolved water concentration is consistent with the results of the nutation experiments, although the absolute values are different (vide infra). The isotropic chemical shifts vary with molar water concentration in the glasses in an approximately linear manner, ranging from -13.4 in the dry glass to -4.4 in the glass containing 56 mol% H_2O .

Another NMR approach that has recently been introduced is examination of the noncentral or satellite transitions. Satellite transition spectroscopy was introduced since for certain transitions and spins there is a reduction in the second-order quadrupolar broadening and hence improved resolution (e.g., $\pm 3/2$, $\pm 1/2$ for $I = 5/2$, Samoson, 1985). A further advantage of this technique is that the intensity of the sideband envelope is much more sensitive to the mean C_q and the distribution, than the centreband lineshape (Jäger et al., 1993), and this approach has been used to characterise highly amorphous flash calcined aluminas (Kunath-Fandrei et al., 1995). Given that there is interest here in obtaining alternative confirmation of the variation in the mean C_q and the distribution the satellite transition approach should in principle work for ^{23}Na in glasses. All these albite samples were examined in a series of satellite transition experiments but no satellite transition spectra could be obtained.

5. DISCUSSION

The previous ^{23}Na work of Kohn et al. (1989a) made three major observations relating to sodium, namely (1) C_q remained constant at around 0.7 MHz up to 30 mol% and then rose sharply to ~ 1.8 MHz at 60 mol%, (2) there was a continuous change in δ_{iso} of $+15$ ppm with increasing water content, and (3) the dry glass had a considerable distribution of both quadrupolar and chemical shift interactions whereas the 60 mol% H_2O glass has a very narrow distribution of C_q and δ_{iso} . These observations were made in the context of the 4.7 T data which used insufficient spinning speed to cause full narrowing. Con-

Fig. 5. Centre of gravity of ^{23}Na MAS NMR centrebands plotted as a function of the square of the inverse Larmor frequency (ν_o^{-2}). The lines shown are the linear least squares fits through the data for AbB4, Ab7, AbB2, and AbB3, with the gradients and intercepts being used to estimate the average values of C_q and δ_{iso} .

sequently, both the peak position (and centre of gravity) and linewidth from the data are only representative of a subset of sodium sites in these samples. Furthermore, the peak position rather than the centre of gravity of the resonances was used. The much faster spinning used here and the higher applied magnetic fields mean that the spectra are essentially fully narrowed. The values of C_q and δ_{iso} reported here are compared with those of Kohn et al. (1989a) in Fig. 6. The trend in δ_{iso} is fairly similar, but displaced by several ppm. The most important difference, however, is in the mean value of C_q , which has been shown by the two independent techniques used in this study to be independent of water concentration over the range 0–56 mol% dissolved water. The field dependent centre of gravity and nutation data indicate an approximately constant value of C_q of $2.1\text{--}2.2 \pm 0.2$ MHz and 1.75 ± 0.2 MHz, respectively. Although the values from the field-dependent centre of gravity and nutation experiments do not produce exactly the same value, this result is consistent with the study of Dirken et al. (1995) who observed that in aluminosilicate glasses the values of C_q obtained from nutation experiments were always smaller than those from the field-dependent shift. This is probably a consequence of the different ways the techniques sample the distributions. However, the change in the C_q data from a constant value below 30 mol% and a rapidly changing value above 30 mol% reported by Kohn et al. (1989a) is now unambiguously shown to be an artefact of using insufficiently fast magic angle spinning. Our NMR studies of albite glasses, therefore, provide no evidence for a sudden change in water dissolution mechanism at 30 mol%.

A number of factors could in principle cause the changes in δ_{iso} observed here. For example, δ_{iso} has been shown to change systematically with coordination number (Xue and Stebbins, 1993). However in the light of the ^{29}Si and ^{27}Al NMR data on hydrous albite glasses (Kohn et al., 1989a) it seems likely that the changes are due to the association of Na with either hydroxyl, molecular water, or both. The fact that C_q is constant is not inconsistent with this model, as many different coordination environments can give the same C_q (see for example Fig. 8 of Koller et al., 1994).

Observations of the spinning sidebands also provide some interesting information in that these come only from the $(1/2, -1/2)$ transition. No satellite transition spectra were observed in any of these glasses. The conditions necessary to observe satellite transitions have not been investigated in detail yet, but given that the distribution of environments in the highest water content glasses is small, it cannot be a distribution that broadens the sidebands. A more likely explanation is that in such glasses there is sufficient motion on the NMR timescale (probably very localised) to interfere with the formation of the rotational echo, so the satellites are not observed.

The distribution in C_q and δ_{iso} also changes markedly across the series with the linewidth of the wettest glass essentially determined by a single quadrupolar interaction and no chemical shift dispersion. The dry albite has a significant distribution of both the quadrupolar interaction and chemical shift dispersion as concluded previously by Kohn et al. (1989a). The significant decrease in the distributions of δ_{iso} and C_q with increasing water-content is consistent with the increased order of hydrous albite glass compared with the dry glass, also observed in X-ray radial distribution functions (Okuno et al., 1987). However, the higher degree of order could be associated with the lower T_g for the hydrous glasses rather than directly related to the presence of water in the structure.

The principal aim of this paper has been to report revised data concerning the local environments of Na in dry and hydrous albite glass. It is, therefore, beyond the scope of this paper to review in detail the large literature pertaining to the dissolution mechanisms of water in silicate melts. Nonetheless two important points need to be made. First, our new data have important implications for the water dissolution model of Sykes and Kubicki (1993). Their suggestion that the mechanism of dissolution changes at 30 mol% dissolved water was based on the kink in the C_q data of Kohn et al. (1989a). As we have shown in the present paper, there are virtually no changes in C_q with increasing H_2O concentration, the kink at 30 mol% being an experimental artefact. There is, therefore, no evidence for a change in dissolution mechanism at 30 mol% H_2O which was one of the main pieces of evidence used in the formulation of the Sykes and Kubicki (1993) model. Although the MO calculations of the stabilities and vibrational frequencies of possible structural units in hydrous glasses (e.g., Sykes and Kubicki, 1993) are of interest, we stress that the ^{29}Si and ^{27}Al data from hydrous glasses are not consistent with breakage of Al–O–Al linkages (discussed in detail by Kohn et al., 1994), nor are Al–O–Al linkages likely to be present in dry albite glass (shown by ^{17}O NMR; Dirken et al., 1997) which is the essential underlying assumption of the Sykes and Kubicki (1993) model. Furthermore, new ^{17}O multiple quantum MAS NMR studies of hydrous albite glass seem to rule out the presence of Al–OH in hydrous albite glass (Kohn et al., 1997 and in prep.).

The second important point which must be mentioned here is the question of whether detailed studies of hydrous glasses such as this are relevant to understanding the dissolution mechanisms of water in melts. It is now well known that there are changes in the speciation of water as a function of temperature (Dingwell and Webb, 1990; Nowak and Behrens, 1995; Shen and Keppler, 1995; Zhang et al., 1995), and there is currently a

Fig. 6. Changes in (a) the mean isotropic chemical shift and (b) the mean quadrupole coupling constant for ^{23}Na as a function of dissolved water concentration. The squares are the values of C_q from quadrupole nutation (this study), and the circles are values of δ_{iso} and C_q deduced from MAS experiments at two or more magnetic fields. Note the differences between the data from this study (filled circles) and the original determinations of Kohn et al. (1989a) (open circles).

large research effort aimed at quantifying such effects. However, it will be many years before the effects of temperature on hydrous silicate melts can be studied in the necessary degree of detail. Until then, studies of hydrous silicate glasses, which can give a detailed picture of the structure of the melt at T_g , will continue to contribute vital information on the structure and properties of silicate melts.

To summarize, the data presented here do not change the broad features of the mechanisms of water dissolution developed from NMR data, and we stress that the mechanism appears to be different for different glass compositions (Kohn et al., 1994). Silica (Farnan et al., 1987; Kohn et al., 1989b) and alkali and alkaline earth silicates (Kohn, Smith, and Dupree, unpubl. data, 1989; Dupree et al., 1990; Kummerlen et al., 1992; Schaller and Sebald, 1995) are depolymerised by water via the reaction $\text{Si-O-Si} + \text{H}_2\text{O} \leftrightarrow 2\text{Si-OH}$. In contrast, fully polymerised aluminosilicate compositions (Kohn et al., 1989a, 1992, 1997) do not appear to be depolymerised by water,

but instead a more subtle interaction occurs which involves $\text{Na}^+\text{Na} \leftrightarrow \text{H}^+$ exchange.

6. CONCLUSIONS

Remeasurement of the ^{23}Na MAS NMR spectra of hydrous albite glasses reveals some modification of the trends presented by Kohn et al. (1989a). We find that the mean isotropic chemical shift changes from -13.4 ppm in the dry glass to -4.4 ppm in the glass containing 56 mol% water. These values represent a small modification from the earlier analysis of a more limited data set, but the broad features of the original and revised analyses are the same, i.e., there is a continuous change in the mean environment of Na as a function of water concentration. The major difference between the data presented here and the original data of Kohn et al. (1989a) is that the mean quadrupole coupling constant appears to be constant (shown by two independent methods), whereas our earlier study suggested a constant value of C_q from 0 to 30 mol% water then a rapid increase from 30 to 60 mol%. Nonetheless the most important feature of the model developed by Kohn et al. (1989a, 1992, 1994) for aluminosilicate glasses, i.e., that water does not break T-O-T bonds to give terminal T-OH groups is unaffected by the new data presented here.

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