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THE CONNECTIVITY OF SILICON SITES IN SILICATE GLASSES, AS DETERMINED BY TWO-DIMENSIONAL ^{29}Si NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY *

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The application of two-dimensional silicon-29 homonuclear shift correlated magic angle spinning nuclear magnetic resonance (COSY MAS NMR) spectroscopy to silicate glasses prepared using silica isotopically enriched in silicon-29 is reported. Two sodium silicate glass compositions and a sodium phospho-silicate glass were examined. The results suggest that a substantial proportion of the four coordinate silicate sites in sodium silicate glasses (Q^2/Q^3 and Q^3/Q^4) are interconnected on a nearest neighbor level. Experiments with the sodium silicate glasses prepared with varying levels of isotopic enrichment reveal a correlation between the intensity of the cross peak and the percentage of silicon-29 in the sample, confirming this observation. No cross peaks were observed for the sodium phospho-silicate glass, implying that the Q^4 and six coordinate silicate sites present are not linked together at the nearest neighbor level.

1. Introduction

It has long been appreciated that a full understanding of the short and medium range structure of amorphous materials, such as silicate glass, is a vital prerequisite for understanding, and indeed predicting, their macroscopic properties. Such an understanding requires knowledge not only of the type of silicate site present, but also the relative concentration of these sites and their spatial distribution. Although solid state ^{29}Si NMR spectroscopy has in recent years proved invaluable in quantifying the relative amounts of the various types of silicate sites present in silicate glasses, it has fallen short of providing information on how these sites are interconnected. Thus both Dupree et al. [1] and Stebbins [2] have recently used ^{29}Si NMR spectroscopy to show that sodium silicate glasses are composed of a variety of four coordinate, tetrahedral silicon sites (Q sites), the distribution of which is a function of the Na : Si ratio. Moreover, Dupree et al. [3] have also shown that sodium phospho-silicate glasses can contain high proportions of both four and six coordinate silicate sites. However, as de Jong recently noted [4]:

"The principal remaining issue in explaining the physical properties of amorphous alkali silicates is how these different (silicate) species are connected..."

The connectivity of the various silicate sites in an amorphous glass is, in principle, amenable to the same spectroscopic procedures that have proved so successful in determining the connectivity, and hence structure, of non-crystallizable proteins in solution, i.e. two-dimensional shift correlated (COSY) NMR spectroscopy. Although more commonly applied to the ^{1}H nucleus, shift correlated NMR spectroscopy may be used whenever sites with different chemical environments, and consequently different chemical shifts, interact with each other [5]. This interaction may occur either through chemical bonds (scalar or "J" coupling) or through space (dipolar coupling). By

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increasing the number of magnetically active ^{29}Si nuclei in a glass by means of isotopic enrichment, one may expect to observe scalar coupling between any interconnected silicate sites present. If, on the other hand, the different silicate sites are not substantially interconnected, but are grouped together in areas rich in one site or another, as has been suggested [6], no interaction between sites of different chemical shift would be expected.

We show here that two dimensional shift correlated ^{29}Si NMR spectroscopy is capable of shedding light on the connectivity of silicate sites within silicate glasses, revealing their short range structure on an atomic, or nearest tetrahedral neighbor, level. Using this technique we provide the first direct evidence that the various types of four coordinate silicate sites occurring in sodium silicate glasses are interconnected on a nearest tetrahedral neighbor level, whereas the four and six coordinate silicate sites present in a sodium phospho-silicate glass are not.

2. Experimental

2.1. Chemistry

The glasses were prepared by fusing the required amounts of 95.3% ^{29}Si enriched SiO_2, natural abundance SiO_2, Na_2CO_3 and $(NH_4)_2HPO_4$ for about 30 min at about 50 °C above the liquidus temperatures, in a crimp sealed Pt tube, and then quenching in water. This process was repeated twice, with the sample being ground with an agate mortar and pestle between fusions. The glasses were checked for crystallinity with an optical microscope. The crimp sealed Pt tube prevented Na volatilization. To allow recovery of the ^{29}Si, the samples were not analyzed, but the ^{29}Si MAS NMR spectra obtained are essentially identical to those of Dupree et al. [1,3] and Stebbins [2]. In order to reduce the ^{29}Si spin lattice relaxation time, T_1, 0.5 wt.% $MnCO_3$ was added to all samples except the 95% ^{29}Si, 20 : 80 ($Na_2O : SiO_2$) glass, which contained no relaxation reagent. All chemicals used were of the highest purity commercially available.

2.2. NMR spectroscopy

All spectra were recorded on a 'home built' 11.7 T NMR spectrometer operating at 99.3 MHz for the ^{29}Si nucleus. 'Magic angle' spinning (MAS) was achieved using 5 mm o/d Al_2O_3 rotors and a multinuclear probe (Doty Scientific, Columbia, SC). The spectrometer operating parameters are given in detail in the appropriate figure captions. In all cases, the sample rotor was spun using dry nitrogen as the drive gas, and the chemical shift is quoted with respect to the ^{29}Si NMR signal of an external sample of tetramethylsilane in acetone (50 : 50 by vol.). All chemical shifts are quoted in ppm, with high frequency signals denoted positive (IUPAC δ-scale).

3. Results and discussion

In fig. 1 we show the 99.3 MHz ^{29}Si MAS NMR spectra of three representative silicate glasses, all prepared with silica isotopically enriched to 95.3% in ^{29}Si. The compositions were chosen by comparison with previous work [1–3] to give glasses containing two chemically distinct types of silicate site in approximately equivalent amounts. Thus in fig. 1(A) we show the spectrum of a sodium silicate glass with a $Na_2O : SiO_2$ ratio of 49 : 51. The glass contains Q^2 and Q^3 units, which give rise to two broad (~ 10 ppm at half height) signals centered around −75 and −85 ppm, respectively. In fig. 1(B) we show the spectrum of a 20 : 80 ($Na_2O : SiO_2$) sodium silicate glass. The two signals, at −92 and −105 ppm, arise from Q^3 and Q^4 sites, respectively. In fig. 1(C) the spectrum of a sodium phosphosilicate glass of composition 60 : 20 : 20 ($P_2O_5 : Na_2O : SiO_2$) is shown. In this case, approximately half the silicon is in sixfold coordination by oxygen [3], giving rise to the signal at −212 ppm. The remaining sites are four coordinate Q^4 units, as witnessed by the peak at −116 ppm.

In fig. 2, we show the ^{29}Si COSY MAS NMR spectrum of the 20 : 80 ($Na_2O : SiO_2$) glass in the form of a contour plot, obtained under conditions similar to those for the spectrum shown in fig. 1(B). In the COSY contour plot, the conventional

NMR signals appear on the diagonal, and any off diagonal peaks ("cross peaks") indicate connectivity between the appropriate diagonal peaks [5]. In the contour plot shown in fig. 2, there is a cross peak between the two Q sites, indicating that at least some of the Q^3 and Q^4 sites in this glass occur as interconnected nearest neighbor tetrahedra. Scalar coupling between *next* nearest neighbor silicate tetrahedral sites is not expected to give rise to a cross peak, since such long range coupling has been shown to be negligible for the structures found in isotopically enriched silicate solutions [7] ($^4J_{Si-O-Si-O-Si} = 0$). Consequently a

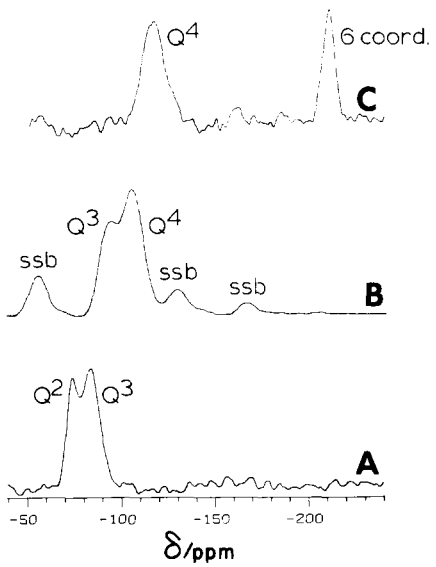

Fig. 1. The 99.32 MHz (11.75 T) ^{29}Si 'Magic Angle Spinning' (MAS) NMR spectrum of three ^{29}Si isotopically enriched glasses of various compositions. (A) The spectrum is that of a sodium silicate glass with a $Na_2O:SiO_2$ ratio of 49:51. The spectrum was recorded over a sweepwidth of 30.3 kHz, using eight 10 μs (90°) pulses, with an interpulse delay of 20 s. The rotor was spun at ~6.5 kHz. (B) The spectrum is that of a sodium silicate glass with a $Na_2O:SiO_2$ ratio of 20:80. The spectrum was recorded over a sweepwidth of 41.6 kHz and required 16 8.5 μs (90°) pulses, using an interpulse delay of 180 s. The rotor speed was ~5 kHz. Spinning side bands are labelled 'ssb'. (C) The spectrum is that of a sodium phosphosilicate glass of composition 60:20:20 ($P_2O_5:Na_2O:SiO_2$). The spectrum was recorded over a sweepwidth of 20.0 kHz, using 18 11.5 μs (90°) pulses and an interpulse delay of 100 s. The rotor was spun at ~6.5 kHz. All glasses except the 20:80 sample contain ~0.5% by weight $MnCO_3$, which brings the T_1 (^{29}Si) relaxation times down by approximately a factor of five, to ~8 s.

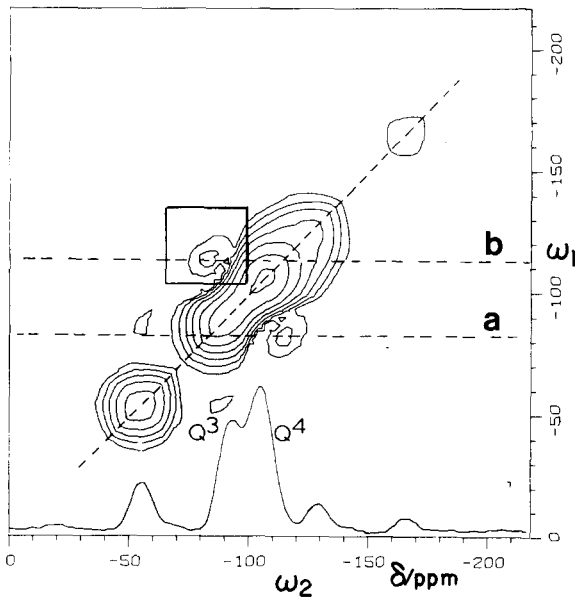

Fig. 2. The 99.32 MHz (11.75 T) ^{29}Si homonuclear shift correlated (COSY) MAS NMR spectrum of the 95% ^{29}Si 20:80 ($Na_2O:SiO_2$) sodium silicate glass, shown in the form of a contour plot. The spectrum was obtained with 16-step phase cycling and *n*-type peak selection. The spectral width in each dimension was 41.6 kHz, obtained from 32 t_1 points, zero filled to 128 t_1 points, using 16 transients per point and a recycle time of 180 s. The spectrum has been symmetrized. The conventional ^{29}Si NMR spectrum shown below the contour plot is that described in fig. 1(B).

cross peak appearing in the COSY ^{29}Si MASS NMR spectrum of a silicate glass indicates that the two sites are *directly* connected, via a siloxy linkage. The observed cross peak is, however, of relatively low intensity and does not line up with the centers of either the Q^3 or Q^4 peak. Rather, it falls to high frequency of the Q^3 resonance (it is centered around −82 ppm) and to low frequency of the Q^4 signal (at around −112 ppm), indicating that signals from interconnected sites are shifted away from their 'bulk' values.

These observations raise some doubts about the interpretation of the COSY spectrum and consequently we undertook an additional experiment to determine whether or not the cross peaks are artifacts. By preparing additional glasses with different levels of isotopic enrichment it is possible to determine whether the intensities of the cross peaks depend upon the level of isotopic enrichment of

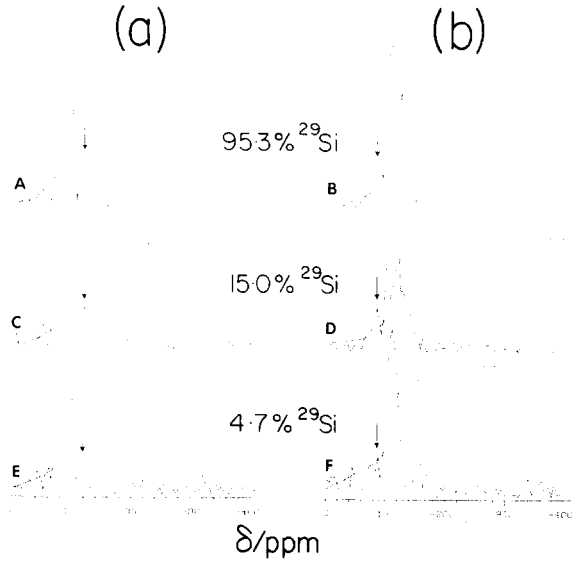

Fig. 3. Cross sections through COSY MAS NMR contour plots, for three sodium silicate glasses ($Na_2O:SiO_2 = 20:80$) prepared with silica enriched to 95% in ^{29}Si (spectra A and B), 15% in ^{29}Si (spectra C and D) and at natural isotopic abundance, 4.7% ^{29}Si (spectra E and F). The cross sections are taken at the frequency of the greatest cross peak intensity, corresponding, in the case of spectra (A, B), to slices through the COSY contour plot shown in fig. 2 at the positions (a) and (b). In these cross sections, the most intense peak is the diagonal peak, and the weaker signal is the cross peak.

the glass. Thus, two more 20 : 80 sodium silicate glasses were prepared, one enriched to 15% in ^{29}Si and the other prepared with natural abundance silica, which contains 4.7% ^{29}Si. As with the 95% enriched 20 : 80 sodium silicate glass sample, the COSY ^{29}Si MAS NMR spectrum was obtained for each glass, and the intensity of the cross peaks was measured. The results are shown in fig. 3 in the form of cross sections through the COSY contour plots. Six cross sections are shown: two for each level of enrichment, taken at the frequency corresponding to the maximum cross peak intensity (at about −82 ppm, fig. 3(A, C and E) and about −112 ppm, fig. 3(B, D and F)). These cross sections correspond to slices taken through the COSY contour plot shown in fig. 2 at the positions labelled (a) and (b), respectively. It is clear from fig. 3 that as the level of isotopic enrichment is reduced, the intensity of the cross peak falls. This correlation between the level of isotopic enrichment and the intensity of the cross peak suggests that the cross peak shown in fig 2 is not an experimental artifact, and provides the first direct evidence that some of the Q^3 and Q^4 sites exist as nearest neighbors, indicating at least a partial intimate mixing of the two sites.

Similarly, COSY MAS NMR experiments on the 41 : 59 ($Na_2O:SiO_2$) glass also reveal a cross peak, lying to high frequency of the Q^2 signal (at around −70 ppm) and to low frequency of the Q^3 peak (at around −88 ppm, data not shown). The implication is that, as with the Q^3 and Q^4 sites of the 20 : 80 sodium silicate glass discussed above, some of the Q^2 and Q^3 sites are interconnected on a nearest neighbor level; in other words they are linked by a Si–O–Si bond. These conclusions are in agreement with those of Dupree et al. [1], which are based on the decreased shielding of the ^{29}Si MAS NMR peaks observed with increasing $Na_2O:SiO_2$ ratio in the glass.

That the cross peak is observed at more shielded values than the maximum of the peak of the more polymerized site (Q^4 in the 20 : 80 glass, Q^3 in the 41 : 59 glass) and at less shielded values than the maximum of the less polymerized sites (Q^3 in the 20 : 80 glass; Q^2 in the 41 : 59 glass) may be taken to indicate that the Si–O–Si bond angle distribution is different for 'interconnected' and 'non-interconnected' sites. For the Q^4 sites, for which the correlation between Si–O–Si bond angle and ^{29}Si NMR chemical shift is best known, this observation implies that the mean Si–O–Si bond angles of the 'interconnected' sites are about 8° larger than for the 'bulk', or 'non-interconnected' sites (the exact value depending on the correlation used [8,9]). In the model of alkali silicate glass structure involving volumes (or 'icebergs') of pure SiO_2 glass surrounded by alkali silicate [6,10], such Q^4 sites would be on the outsides of the SiO_2 volumes. Of course, MAS NMR spectroscopy cannot determine the size of the volumes, since it is only sensitive to relatively short range (nearest or next nearest neighbor) interactions.

The ^{29}Si MAS NMR COSY spectrum of the isotopically enriched sodium phospho-silicate glass shows no evidence of a cross peak, even at the lowest possible contour level, and the contour plot is shown in fig. 4. This observation implies that

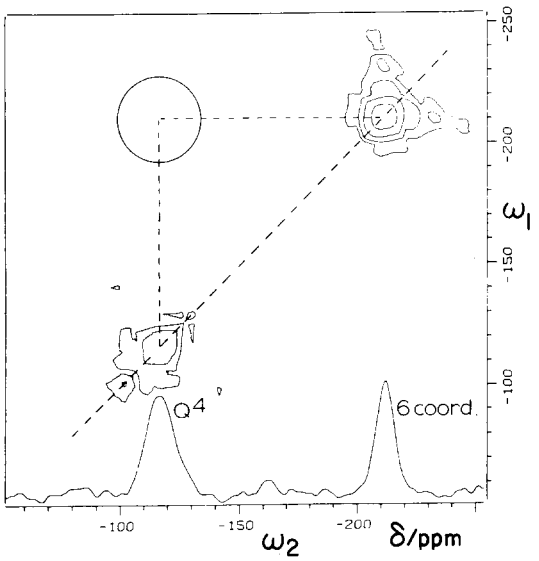

Fig. 4. The 99.32 MHz (11.75 T) ^{29}Si homonuclear shift correlated (COSY) MAS NMR spectrum of the 60:20:20 ($P_2O_5:Na_2O:SiO_2$) sodium phosphosilicate glass, shown in the form of a contour plot. The circle indicates the region of the spectrum in which a cross peak would be expected. The spectrum was obtained with 16-step phase cycling and *n*-type peak selection. The spectral width in each dimension was 20.0 kHz, obtained from 32 t_1 points, zero filled to 128 t_1 points, using 16 transients per point and a recycle time of 60 s. The plot has been symmetrized. The conventional spectrum shown below the contour plot is that shown in fig. 1(C).

these two sites are not substantially interconnected as nearest neighbor cation sites, in agreement with the ideas of Dupree et al. [3].

Based on our observations, as well as the ^{29}Si, ^{23}Na and ^{31}P chemical shifts and peak intensities reported by Dupree et al. [3], it appears that the structure of the 60:20:20 ($P_2O_5:Na_2O:SiO_2$) glass consists of Q^4 silica tetrahedra, silica octahedra and phosphorus tetrahedra, with the sodium atoms neutralizing the charge on the non-bridging oxygens of the PO_4^{3-} tetrahedra. The silica tetrahedra and octahedra are not substantially interconnected, if at all. The relatively shielded ^{29}Si chemical shift values in the sodium phospho-silicate glass studied (−116 ppm versus about −111 ppm for Q^4 units in SiO_2 glass; −212 ppm versus −191 ppm for octahedral Si in SiO_2 stishovite) are consistent with the increased shielding at the Si nucleus in P–O–Si linkages [3]. Thus it appears that the glass may be composed of silicate tetrahedra and octahedra linked by phosphorus tetrahedra.

Note. After this work was completed, a paper by Fyfe et al. [11] appeared in the literature, describing the use of similar two-dimensional ^{29}Si MAS NMR experiments in the structural elucidation of ^{29}Si isotopically enriched zeolites.

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