Structure of Ancient Glass by ^{29}Si Magic Angle Spinning NMR

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Abstract: [29]Si magic angle spinning (MAS) NMR spectroscopy is applied for the first time to the structural analysis of ancient glass samples obtained from archaeological excavations. The results show that it is possible to establish the distribution of Si environments in ancient glass by ^{29}Si MAS NMR, so long as the concentrations of magnetic impurities, such as Mn and Fe oxides, are low. In general good agreement has been obtained with compositions found using electron probe microanalysis. In addition, the ^{29}Si MAS NMR data reveal structural differences between glasses manufactured at separate ancient sites.

Introduction

Silicate glasses consist of SiO_4 tetrahedra which link via bridging oxygen atoms to form three-dimensional networks. In man-made silicates the SiO_4 network is disrupted by the introduction of alkali metal or alkaline earth oxides (mostly Na_2O and CaO) in order to lower the melting temperature and improve workability. These result in non-bridging oxygen atoms and a negatively charged silica framework which is balanced by the modifying cation. The silicate glasses produced have no long-range order because distributions of bond lengths and angles within and between the tetrahedra or variations in modifier concentration preclude the formation of any well-defined repeating unit. Therefore, the structures of silicate glasses are usually discussed in terms of quantities such as the number of non-bridging oxygens per tetrahedron, *NBO/T*. This ratio follows directly from the chemical composition, but composition alone only does not fully determine the local glass structure, since this also depends on factors such as thermal history.

Conventionally the notation Q^n with *n* between 0 and 4 is used to indicate a SiO_4 tetrahedron with n bridging oxygen atoms. [29]Si magic angle spinning (MAS) NMR spectroscopy is widely used for structural analysis of silicate glasses,[1-4] resulting in a direct measure of the relative amounts of the Q^n tetrahedra in the network. The [29]Si peak positions are determined in the first instance by the number of bridging oxygen atoms surrounding the observed nucleus, and in favourable cases a typical [29]Si spectrum contains a number of resolved lines, each corresponding to a different Q^n environment. In general, the Q^4 NMR peak occurs at a chemical shift of approximately $\delta(^{29}Si)$ = -103 ppm referenced to tetramethylsilane (TMS), while each reduction in the number of bridging oxygen atoms results in an additional deshielding of about 10 – 15 ppm. The linewidths results from the distributions of structural parameters associated with each Q^n environment and are therefore a measure of the disorder in the network. Given certain precautions ^{29}Si MAS NMR peak intensities are quantitative, and spectral deconvolution allows the relative proportions x^n of the Q^n environments in the sample to be determined.

In this contribution we apply ^{29}Si MAS NMR spectroscopy for the first time to ancient glass samples obtained from archaeological excavations. We demonstrate that ^{29}Si MAS NMR can be used to determine the structure of these glasses and establish the conditions under which this is possible. Solid-state NMR is a bulk measurement which can be carried out in a non-destructive fashion on relatively large samples and individual fragments of glass. This means that NMR results are not affected by sample heterogeneity or surface modifications resulting from processes such as leaching that are common for archaeological samples. In addition, our results suggest that additional information which is not accessible from composition alone, such as details of thermal history, can be obtained from ^{29}Si MAS NMR.

Ancient Glass Technology

Soda-lime glass is produced from three principal raw materials: a source of silica as the network former, lime (CaO) as a network stabilizer and a flux to lower the melting temperature. The main type of glass manufactured in Europe and the Middle East during the 1st millennium BC and the 1st millennium AD was produced using natron, an evaporitic mineral, rich in the flux sodium carbonate ($Na_2CO_3.10H_2O$). This was combined with beach sand, containing aragonite ($CaCO_3$) shell fragments as the source of lime. In addition the sand contained a range of minerals, including magnetite (Fe_3O_4), ilmenite ($FeTiO_3$), sodium- or potassium-rich feldspars (a source of the network former Al_2O_3) and zircons ($ZrSiO_4$). These minerals introduced chemical impurities in the glass batch, including iron which can potentially produce the "natural" green colour in particular gaseous furnace atmospheres. Large scale chemical analysis and archaeological excavation of first millennium AD natron glasses has revealed that production mainly occurred along the Levantine coast and in Egypt,[5-7] though with some exceptions.[8,9] Natron glass was used by the Phoenicians, the Greeks, the Romans and by early medieval populations such as the Anglo-Saxons in the UK.

In 800 AD natron was largely replaced as a flux by ash from halophytic plants, including of the family Chenopodiaceae. Although plant-ash glasses were manufactured and used at various times in the first millennium AD, for example sporadically by the Romans and more regularly by the Sasanians, the technology was introduced on a more global scale by the Muslims.[10,11] The manufacture of plant-ash glasses also involved the use of sand as a silica source, sometimes derived from inland quarries rather than from beaches or rivers. As a result, calcium was probably introduced in the plant ash rather than as shell fragments in sand. The halophytic plants used grew (and still grow) in semi-desert, evaporitic and maritime environments. Not all were suitable for making glass, since some did not contain sufficient sodium carbonate, and others did not contain sufficient lime. Examples of possible plant genera that may have been used include *Salsola*, *Salicornia*, *Arthrocnemum*, *Halopeplis* and *Hammada (Haloxylon)*.[12]

After the 2nd century BC the glass batches were melted in large rectangular tank furnaces producing up to 10 tons, or more, of raw glass with each batch.[13,14] Such furnaces, or their remains, have been excavated in Beirut[15,] the Lebanon, and Al-Raqqa, Syria.[16] The colours produced with each melt varied depending on a range of factors including the gaseous atmosphere of the furnace and the range of impurities. To deliberately colour the glass with mineral-rich colourants such as cobalt, chunks of raw glass would have been re-melted in crucibles in a second type of much smaller, beehive-shaped furnace and tiny amounts of colorants rich in transition metals would have been added. Glass blowing was invented in the 1st century BC in the Levant. To blow glass the raw coloured glass would have been re-melted in a crucible and extracted on a blowing iron.

Glass Samples

A total of 22 glass samples were available, excavated from two sites in Beirut and Al-Raqqa. The 14 samples from Beirut were obtained from excavations of the earliest recorded tank furnaces found there and are all natron glasses.[15] Compositions were determined previously by electron probe microanalysis (unpublished data) indicating SiO_2 contents between 67.7 and 73.7 wt%; Na_2O 15.3 and 19.5 wt%; CaO 7.2 and 8.6 wt%; K_2O 0.4 and 1.0 wt%; MgO 0.4 and 0.7 wt%, and Al_2O_3 2.2 and 2.6 wt%. The eight samples from Al-Raqqa were excavated from the early Islamic West palace complex and the industrial complex (Tell Zujaj) there. These date to the late 8th and early 9th century AD and provide part of comprehensive evidence for the primary production of raw glass in now destroyed tank furnaces. The Al-Raqqa glasses are a mixture of natron and plant-ash glasses according to electron probe microanalysis.[16] Because of the variation in plant ashes Al-Raqqa glasses have a broader range of composition than those from Beirut. SiO_2 contents range between 63.4 and 71.2% Na_2O 8.8 and 15.5 wt%; CaO 4.5 and 9.7%; K_2O 0.5 and 4.0 wt%; MgO 0.5 and 6.7 wt% and Al_2O_3 1.1 and 4.1 wt%. In addition, all glasses contain small amounts of other species, including magnetic Mn and Fe oxides. The Beirut samples contain up to 1.7 % Mn and up to 0.7% Fe oxides, but the majority have < 0.5 wt% of either. The Mn and Fe oxide content of the Al-Raqqa glasses is generally higher, especially for Mn, with extremes of 8.5% and 2.3%, while the majority contained less than 1.5% and 0.5 %, respectively.

Composition data for all the available glasses is given in the Supporting Information (Table S1), along with the *NBO/T* ratio, calculated by neglecting small amounts of other network forming oxides, in particular Al_2O_3, since the high SiO_2 content ensures that all non-bridging oxygens are located on SiO_4 tetrahedra. Usually wt% oxide compositions are calculated from elemental analysis by assuming the stoichiometries of the oxides present, and in some cases, such as Fe, mixed oxides can render this process inaccurate. One measure of the quality of the elemental analysis is whether compositions obtained in this way sum to 100% as expected, and for all the samples used here the range for this sum was between 99 and 103%. Finally, to test for sample homogeneity the average of two separate

elemental analyses was taken, and for all the samples used here the difference between the sum of the compositions was less than 0.5%.

The Mn and Fe oxide content proved to be the main determinant of whether quantitative analysis by ^{29}Si MAS NMR was possible. This is because of spectral broadening which prevents resolution of the [29]Si lines from different Q species and was observed in samples containing higher amounts of magnetic Fe and Mn oxides. An example ^{29}Si MAS NMR spectrum of this type of sample (BEI87) is included in the Supporting Information (Figure S1). As a rule of thumb, quantitative analysis was found to be generally impossible if the Mn or Fe oxide composition exceeded 0.5 wt%, although there were some exceptions. Quantitative analysis by ^{29}Si MAS NMR proved possible for 50% of the available glasses. However, the plant-ash glasses from Al-Raqqa with high Mn and Fe oxide content were mostly impossible to analyse in his way. The eight Beirut glasses for which quantitative analysis was possible are green (BEI73, BEI79, BEI94 and BEI96), purple (BEI75), yellow (BEI93), brown (BEI97) and blue (BEI98). Of the three analysable Of the three possible Al-Raqqa glasses RAQ29 is a pale green bowl fragment, RAQ35 a colourless bowl fragment, and RAQ43 a green window fragment. RAQ29 and RAQ43 are natron glasses, while RAQ35 is a plant-ash glass.

Results and Discussion

^{29}Si MAS NMR Spectra

Magnetic impurities (mainly Mn and Fe oxides) present in small amounts have the beneficial effect of reducing the spin-lattice relaxation time T_1 without significantly broadening the lines. It should be noted that silicate glasses synthesized for NMR studies are sometimes doped with a small (< 0.2%) of Fe_2O_3 to achieve this effect.[16] For the ancient glass samples studied here quantitative ^{29}Si MAS NMR spectra with good signal-to-noise could be recorded in a reasonable time, typically 12 hours for the data presented here. As a result of magnetic impurities in the ancient glass the measured T_1 relaxation times were significantly shorter than most silicate glasses synthesized without doping, ranging from 0.6 to 7 s. Typical ^{29}Si MAS NMR spectra for a few representative samples are shown in Figure 1, and these consist of two overlapping resonances corresponding to Q^3 and Q^4 environments at about -92 ppm and -103 ppm, respectively. The spectra show little evidence for any significant amount of [29]Si in the Q^2 environment which is expected to result in a peak at approximately -80 ppm. Even without fitting any spectra Figure 1 suggests that the glasses from Al-Raqqa contain more Q^4 sites that those from Beirut. This is despite the fact that RAQ29, for example, has a very similar composition to both the Beirut samples shown (see Supporting Information Table S1). This observation holds for all the glasses studied here (see Supporting Information Figure S2).
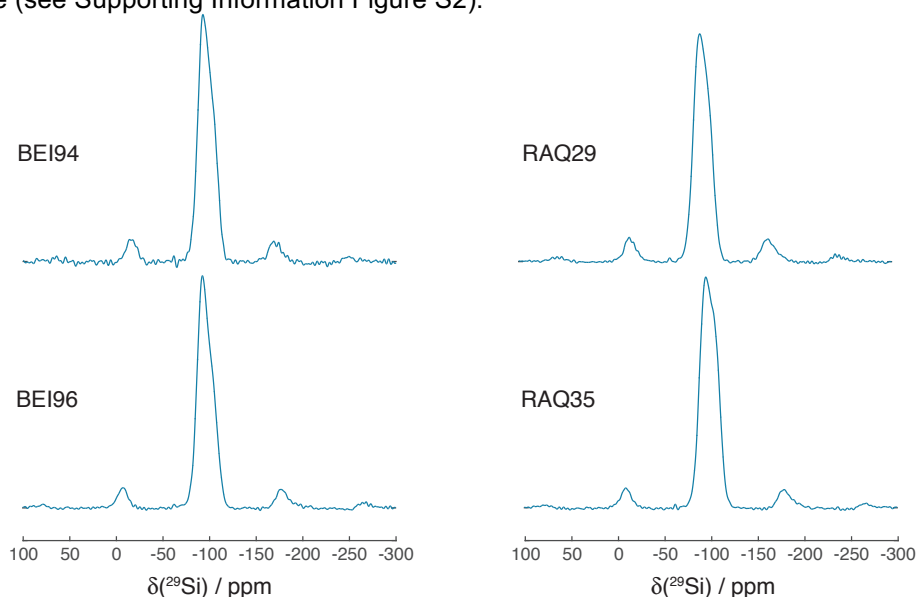

Figure 1. Typical experimental ^{29}Si MAS NMR spectra of ancient glass samples recorded in the fashion described in the text.
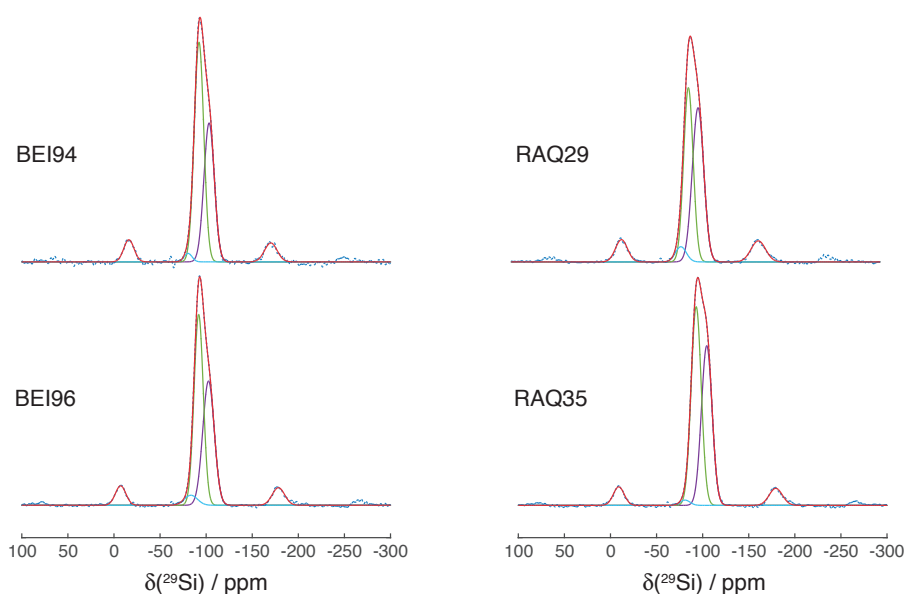
Figure 2. As Figure 1 with experimental spectra (dotted blue lines) and fits to Gaussian lines corresponding to Q2, Q3 and Q4 sites with the overall fitted spectrum (red lines) For clarity individual Gaussian components are shown for the centerbands only (cyan: Q2, green: Q3, violet: Q4), but first-order spinning sidebands were included in the fitting, as described in the Experimental Section.

Fitting

The fitting (see Table 2 and Figure 2) confirms that there is a structural difference between Al-Raqqa and Beirut glasses. Figure 2 shows the experimental spectra from Figure 1 (dotted blue lines) overlaid by fitted spectra (red lines) resulting from a fit to five Gaussians (as described above), together with the individual Gaussian components for the three centerbands (cyan: Q^2 green: Q^3, violet: Q^4). Note that, although the first-order sidebands are included in the fit (see Experimental Section), for clarity the individual Gaussians have been omitted from Figure 2. The results in Figure 2 and Table 1 confirm that there is a substantially larger proportion of Q^4 sites in all glasses obtained from Al-Raqqa than in all those obtained from Beirut. Fits for the other samples are shown in the Supporting Information (Figure S3). Introducing a Q^2 contribution increases the $Q^4:Q^3$ ratio in all cases, although the resulting uncertainty in both position and integral for the low intensity Q^2 line is substantial. Note, however, that omitting the Q^2 peak does not alter the observation that Al-Raqqa glasses show substantially more Q^4 sites than those from Beirut, as shown in the Supporting Information (Figure S4).

Comparison with Composition

It is interesting to compare the Q^n site distribution in the ancient glass measured directly from the ^{29}Si MAS NMR spectra to those calculated from the composition. As described above the latter requires the assumption of a model, and limiting binary and random approaches have both been used here. Figure 3 shows experimental values of x^3 (left) and x^4 (right), the proportions of Q^3 and Q^4 sites, respectively, obtained by fitting ^{29}Si MAS NMR spectra of ancient glass samples from Beirut (filled symbols) and Al-Raqqa (open symbols). These data are plotted as a function of the *NBO/T* ratio and compared with x^3 (left) and x^4 (right) calculated from the glass compositions using the random (solid lines) and binary (dashed lines) limiting models. With the exception of RAQ35 all the NMR-derived x^3 and x^4 lie between the two composition limits, suggesting that the Q^n distributions obtained by the fitting are consistent with the composition data. However, all Al-Raqqa samples show structures which correspond more closely to the random model than their Beirut counterparts. It has been shown previously that neither the binary nor the random extreme is followed by the experimental Q^n distribution for alkaline-earth silicate glasses.[20-25] Glasses with modifier cations with low field strength (the charge to radius ratio), such as Na^+ and K^+, conform more closely to the binary model, while those containing high field strength cations, such as Mg^{2+} and Ca^{2+}, have a more random distribution.
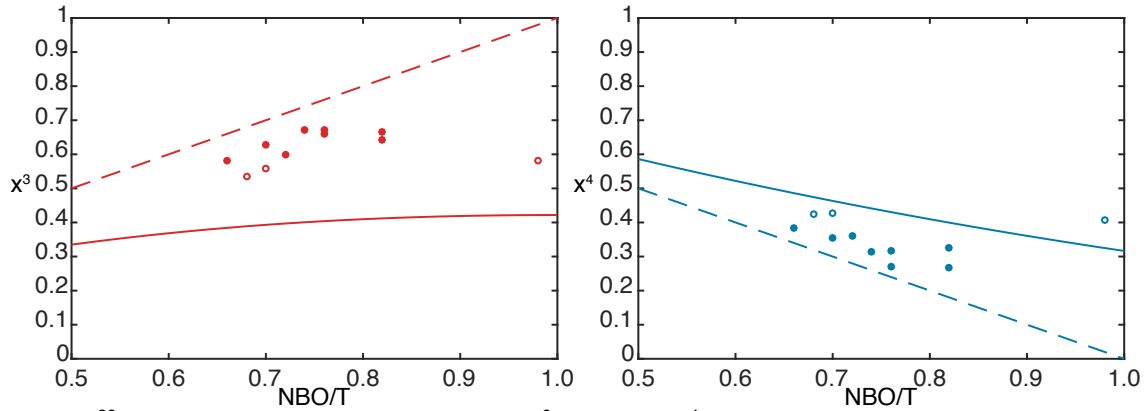
Figure 3. ^{29}Si MAS NMR-based experimental x^3 (left) and x^4 (right) for Beirut (filled symbols) and Al-Raqqa (open symbols) glasses plotted as a function of *NBO/T* and compared with values calculated from glass composition using the binary (dashed lines) and random (solid lines) models.

The similarity in composition between, for example, RAQ43 and BEI94 suggests an alternative contribution to the observed differences between the Al-Raqqa and Beirut glasses. Brandriss and Stebbins[26] have showed that structural differences for modern synthetic glasses with the same composition resulting from different quenching rates could be detected by ^{29}Si wideline NMR. They showed that for soda-lime glasses faster quenching during glass manufacture results an increase in the Q^4/Q^3 ratio due to the freezing of more disorder into the structure. Of course, the effect of heat treatment on the Q^n distribution can be obscured by composition effects. Stebbins[18] has estimated that when comparing $Li_2Si_2O_5$ with $Na_2Si_2O_5$ the effect on the proportion of Q^4 of substituting Li for Na would be equivalent to an increase in glass fictive temperature of as much as 200 K where high quenching rates lead to high fictive temperatures.

Table 1. Fitting ^{29}Si MAS NMR spectra to five Gaussian lines

Sample/ Site	Position/ppm[a]	Proportion[b]	Sample/ Site	Position/ppm[a]	Proportion[b]
BEI73/Q^2	-77.8	0.01	**BEI75**/Q^2	-76.0	0.05
Q^3	-90.7	0.67	Q^3	-90.8	0.69
Q^4	-101.3	0.31	Q^4	-102.9	0.26
BEI79/Q^2	-79.3	0.02	**BEI93**/Q^2	-80.1	0.02
Q^3	-89.8	0.65	Q^3	-90.9	0.66
Q^4	-99.8	0.33	Q^4	-101.0	0.32
BEI94/Q^2	-80.4	0.02	**BEI96**/Q^2	-83.4	0.04
Q^3	-92.2	0.63	Q^3	-91.9	0.58
Q^4	-103.2	0.35	Q^4	-102.5	0.38
BEI97/Q^2	-81.0	0.07	**BEI98**/Q^2	-76.2	0.04
Q^3	-90.5	0.67	Q^3	-90.6	0.61
Q^4	-101.5	0.27	Q^4	-100.6	0.35
RAQ29/Q^2	-84.0	0.04	**RAQ35**/Q^2	-80.9	0.01
Q^3	-92.1	0.53	Q^3	-93.0	0.58
Q^4	-102.6	0.43	Q^4	-104.4	0.41
RAQ43/Q^2	-78.9	0.02			
Q^3	-91.6	0.56			
Q^4	-102.3	0.43			

[a] error ±0.3 ppm (±5 ppm for Q^2).
[b] Sideband intensities counted towards Q^3 site; error ±0.03 (± 0.01 for Q^2).

Conclusions

In summary this paper describes the first analysis of ancient glass by ^{29}Si MAS NMR. The results demonstrate somewhat unexpectedly that it is possible to establish the distribution of Si environments in ancient glass by ^{29}Si MAS NMR, despite their complex compositions. This paper shows that quantitative analysis is possible, so long as the concentrations of magnetic impurities such as Mn and Fe oxides are sufficiently low (generally less than 0.5 wt%). In fact, one half of all the ancient glass samples available for measurement fell into this category, suggesting that analysis is possible for a range of glass types and provenances. In general good agreement was obtained with compositions derived from electron probe microanalysis with x^3 and x^4 for the ancient glass samples falling between limits expected from random and binary structural models. In some cases the composition analysis predicted similar limiting structures for Al-Raqqa and Beirut glasses, but the ^{29}Si MAS NMR measured showed a significant increase in randomness the former. Given the small number of samples studied here, the data are not sufficient to prove that these structural differences originate from the different provenance of the glasses. However, they do suggest that ^{29}Si MAS NMR is sensitive to aspects of ancient glass manufacture, such as different quench rates employed at different sites. Further research is necessary to determine the extent to which this is in fact possible and this is ongoing in our laboratory.

Experimental Section

^{29}Si MAS NMR measurements were carried out using a small number of glass fragments packed into a 7.5 mm MAS rotor with potassium bromide powder to ensure stable spinning. This procedure avoids the need to grind the sample into a powder, and potassium bromide, which has a similar density to glass, can easily be separated from the glass by dissolution and filtration after measurements. ^{29}Si MAS NMR spectra of samples prepared in this way were recorded at room temperature on a Varian Chemagnetics Infinityplus spectrometer operating at a Larmor frequency of 59.608 MHz using a 7.5 mm MAS probe spinning at 5 kHz. Relatively low spinning rates were used to allow large sample volumes, and at the low magnetic field employed here these were sufficient to separate the first order spinning sidebands from the isotropic lines. A spin-echo sequence with a short echo delay of 20 µs was used in order to suppress probe background signals. The [29]Si $\pi/2$ pulse duration was 4.5 µs, the spectral width was 500 kHz and the acquisition time was 4.906 ms. The resulting free induction decays were decimated by a factor five giving a final spectral width of 100 kHz, equivalent to 1678 ppm. No weighting functions were applied prior to Fourier transformation. Chemical shifts are quoted relative to TMS using kaolinite as an external secondary reference. Prior to acquiring [29]Si spectra spin-lattice relaxation times T_1 were determined for each sample by saturation recovery. Saturation was achieved by 100 [29]Si $\pi/2$ pulses spaced by delays of 5 ms with recovery delays of between 1 ms and 50 s. Quantitative ^{29}Si MAS NMR spectra required relaxation delays (5 T_1) of between 3 s and 35 s.

The resulting spectra were fitted to a set of Gaussian lineshapes which were integrated in order to quantify the proportions x^n of the different Q^n environments in the sample. Given the complexity of the compositions, the constrained iterative fitting procedure suggested by Edén et al.[17] for split-network soda-lime glasses containing small amounts of Al_2O_3 and B_2O_3 was adopted. Initially the fitting involved four Gaussian lines, corresponding to the Q^3 and Q^4 centerbands, as well as two first-order Q^3 spinning sidebands. Sidebands from the symmetric Q^4 environment are expected to have negligible intensity under these experimental conditions.[18] The peak positions were constrained to fall within ±3 ppm of the expected δ([29]Si), but the fits never resulted in values outside this range. The minor amounts (< 3 wt%) of other glass forming species such as Al_2O_3 in the ancient glass studied here are assumed to make only marginal differences to the [29]Si resonance positions.[17] Subsequently, other constraints were applied, for example applying a maximum linewidth, but these made only small differences to the fitted values. Finally, a fifth Gaussian line was added at the Q^2 centerband position. Since the integral of the Q^2 line was always less than 7% of the total, the first-order sidebands for this site were assumed to make a negligible contribution to the spectrum. It should be noted that typically linewidths are comparable with the peak separation, so that the reliability is low and the results should be interpreted in a semi-quantitative fashion, especially for the low intensity Q^2 line. The reproducibility of the quantification was investigated by recording several separate spectra for selected samples and comparing the results of fitting. An example is given in the Supporting Information (Table S2) for four separate measurements of BEI96. In order to predict x^n from the compositional analysis for comparison with NMR a structural model must be assumed. In this work the limiting random and binary models[17]

were employed. Minor amounts of additional network forming species, in particular Al_2O_3 (< 3 wt%), have been neglected.

Keywords: Magic Angle Spinning, Nuclear Magnetic Resonance, Glass, Structure, Archaeology

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