Oxygen-17 Nuclear Magnetic Resonance Spectroscopic Studies of Aqueous Alkaline Silicate Solutions

Christopher T. G. Knight, Arthur R. Thompson, Ajit C. Kunwar, Herbert S. Gutowsky, and Eric Oldfield *
School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, IL 61801, U.S.A.
R. James Kirkpatrick
Department of Geology, University of Illinois at Urbana-Champaign, 1301 W. Green Street, Urbana, IL 61801, U.S.A.

High-field (11.75 T) oxygen-17 n.m.r. spectra have been obtained for a variety of aqueous silicate solutions isotopically enriched in the oxygen-17 nuclide. Oxygen-17 n.m.r. linewidths of the silicate anions are broad ($\Delta\nu_{\frac{1}{2}}$ *ca.* 3 to 20 p.p.m.) and the chemical shift range is relatively small (about 50 p.p.m.), often resulting in considerable spectral overlaps. Assignment of the observed resonances to known silicate structures is nevertheless possible in some cases by using suitable 'model' solutions containing silicate structures which have been previously characterized by ^{29}Si n.m.r. spectroscopy and by making use of spectral simulations. In this manner, two overlapping spectral regions may be distinguished: a 35—55 p.p.m. range (from water) typical of non-bridging, or 'terminal' oxygen groups (Si–O$^-$ or Si–O–H, or both), and a 45—85 p.p.m. range, assigned to bridging groups (Si–O–Si). Contrary to recent Raman spectroscopic studies, ^{17}O n.m.r. spectroscopy shows no evidence for any silicate species other than the monomeric silicate anion in very dilute solution (0.01 mol dm^{-3} in SiO_2). Preliminary kinetic investigations indicate that in tetramethylammonium silicate solutions very different bulk water exchange rates exist for the two types of oxygen site present, with that for the non-bridging oxygen being much greater than that of the bridging oxygen. Concentrated alkali-metal silicate solutions yield complex ^{17}O n.m.r. spectra with many overlapping signals.

Aqueous alkaline silicate solutions are of fundamental importance to the chemical industry, and have numerous applications. As a result, they have been the subject of extensive and prolonged research.[1] It is, however, only with the recent advent of sophisticated, non-invasive spectroscopic techniques that their time-dependent compositions are becoming apparent.[2–6] It has been found that concentrated ($\geqslant 1$ mol dm^{-3} in SiO_2) alkali-metal silicate solutions often contain a great many cage-like silicate anions in dynamic equilibrium,[6,7] while in equivalent tetramethylammonium silicate solutions the equilibrium is often dominated by a single silicate species,[8] the cubic octamer or double four-membered ring. Silicon-29 n.m.r. spectroscopy has played an invaluable role in determining the structures of the anions present in solution, since chemical exchange between the silicate anions is slow on the n.m.r. time-scale, and the chemical shift range is large, relative to the ^{29}Si n.m.r. linewidth. Moreover, isotopic enrichment in silicon-29 provides structural information, due to Si–O–Si scalar coupling, and consequently this technique has been particularly widely used.[6,7] On the other hand, oxygen-17 n.m.r. spectroscopy of such solutions has received little attention, and no ^{17}O n.m.r. spectra of aqueous alkaline silicate solutions have been published to date (although ^{17}O n.m.r. has been used to monitor the early stages of the hydrolysis and condensation of tetraethoxysilane in acidic solution[9]). This paucity of data is not surprising, since at first sight the oxygen-17 nucleus, with its low natural abundance (0.04%) and moderate quadrupole moment ($Q = -2.6 \times 10^{-26}$ cm^2), has few commendable n.m.r. properties. Enrichment in the ^{17}O nucleus increases the sensitivity of the technique, but cannot provide similar structural information to that of ^{29}Si, because of large ^{17}O linewidths, resulting from efficient quadrupolar relaxation, and the lack of observable J coupling. Furthermore, the aqueous nature of the samples presents dynamic range problems associated with the intense bulk water resonance.

Use of the ^{17}O nucleus to study silicate solutions offers, however, four intrinsic advantages over similar studies using the silicon-29 nucleus. First, all silicate species other than the orthosilicate, or monomeric, anion contain two types of oxygen site, bridging and non-bridging, but often only a single silicon site. Thus the dimer, silicate rings, and regular cages yield only a single silicon-29 n.m.r. signal even after isotopic enrichment, but should give rise to two distinct ^{17}O n.m.r. signals. The intensity ratio of the two oxygen signals can provide a unique assignment tool, since it is a characteristic of a given set of silicate structures. Secondly, observation of the ^{17}O nucleus affords insight into solution kinetics, since chemical exchange between bulk water and both oxygen sites in silicate anions may be directly monitored by ^{17}O n.m.r. spectroscopy. Thirdly, acceptable ^{17}O n.m.r. spectra of ^{17}O-enriched silicate solutions may be obtained very rapidly, usually in less than a minute, since quadrupolar relaxation of the ^{17}O nucleus is highly efficient. Silicon-29 n.m.r. spectra of similar solutions generally require several hours of spectrometer time to achieve an equivalent signal-to-noise ratio, even when using (very expensive) ^{29}Si-enriched materials. Fourthly, ^{17}O n.m.r. spectroscopy yields information about other solution species which may be of fundamental importance to the properties of the silicate solution, but which are not observable by ^{29}Si n.m.r. spectroscopy. In this category we include H_2O, OH^-, HCO_3^-, and various organic additives that may also be present, such as CH_3OH, CH_3CH_2OH, $(CH_3)_2CO$, and $(CH_3)_2SO$.

In this article we describe the results of preliminary ^{17}O n.m.r. studies of several 'model' aqueous silicate solutions, prepared using materials enriched in ^{17}O. Solutions whose constituents have been well defined by ^{29}Si n.m.r. spectroscopy were chosen in order to provide a basis for assigning the ^{17}O n.m.r. spectra. Our results to date show that there are two, somewhat overlapping, spectral regions, assigned to non-bridging oxygen sites (*ca.* 35—55 p.p.m.) and bridging oxygen sites (*ca.* 45—85 p.p.m.). Although overlapping, these ranges are, in favourable cases, sufficiently large to allow resolution of all signals from individual silicate anions. In all solutions studied, the resonance signal of the monomer appears to low frequency of the signals of all other silicate species, although chemical shifts are markedly dependent upon sample composition, presumably as a result of changes in protonation equilbria. In general, non-bridging oxygens give rise to sharper signals than do bridging oxygens, typical room-temperature values being *ca.* 4 and *ca.* 20 p.p.m., respectively, a result consistent with the larger quadrupole coupling constants observed previously for non-bridging oxygens.[10] In solutions in which many silicate species exist, resolution of the ^{17}O n.m.r. signals of individual species is no longer possible, at currently available magnetic field strengths and at ambient temperatures, and the resulting spectra consist of a series of overlapping resonances. Nevertheless, a pattern of characteristic signals is observed, which may be of use for 'fingerprint' analysis of silicate solutions, and, with further work, may be amenable to spectral simulation.

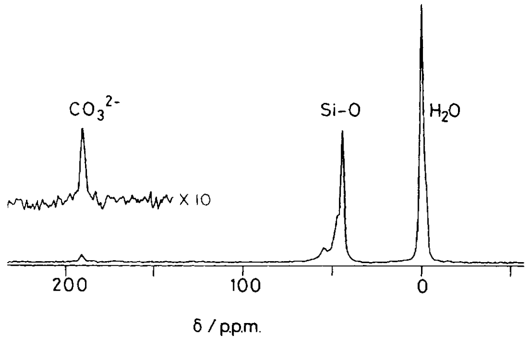


Figure 1. The 67.8-MHz ^{17}O n.m.r. spectrum of an aqueous sodium silicate solution 0.1 mol dm^{-3} in SiO_2 and 0.2 mol dm^{-3} in NaOH, prepared with water enriched to 10% in ^{17}O. The spectrum was recorded at 295 K over a 32-kHz sweep width. An interpulse delay of 1 s was used, and the water peak has been attenuated by a factor of *ca.* 100 by preacquisition saturation

Experimental

Silicate Chemistry.—Aqueous silicate solutions were isotopically enriched in ^{17}O by either dissolving the constituents in ^{17}O-enriched water (Cambridge Isotopes, Woburn, MA), directly adding aliquots of $H_2{}^{17}O$ to silicate solutions containing naturally abundant ^{17}O, or by using ^{17}O-enriched silica ($Si^{17}O_2$). This was prepared by hydrolyzing doubly distilled $SiCl_4$ with water enriched to 56.4% in ^{17}O, washing in natural abundance water, then drying overnight at *ca.* 60 °C under vacuum. Individual samples were prepared by dissolving the appropriate quantity of SiO_2 in either a sodium or potassium hydroxide solution, made using 'Ultrapure' sodium or potassium hydroxide (Alfa Chemicals, Danvers, MA) and triply distilled or ^{17}O-enriched water. The tetramethylammonium hydroxide solutions were made from 97% tetramethylammonium hydroxide pentahydrate crystals (Aldrich Chemicals, Milwaukee, WI) and triply distilled or ^{17}O-enriched water. Generally, all samples were heated to boiling in polyethylene bottles until dissolution of the SiO_2 was complete. Because paramagnetic contamination of alkaline silicate solutions may result from prolonged contact with glass surfaces, samples were mixed, heated, and stored in polyethylene bottles, under nitrogen, whenever possible. Glassware used in sample preparation was soaked in an alkaline silicate solution, and then in an ethylenediaminetetra-acetate (edta) solution, for several days prior to use. Solution viscosities were measured at 298 K using a Ostwald viscometer, with solution densities being calculated using a pycnometer. Several consecutive measurements were performed, and the values reported are average ones. Errors are estimated to be less than 5%.

N.M.R. Spectroscopy.—All ^{17}O and ^{29}Si n.m.r. spectra were recorded on a 'home-built' 11.7-T n.m.r. spectrometer (at 67.78 and 99.32 MHz, respectively), which consists of an 11.7-T 52-mm bore superconducting solenoid (Oxford Instruments, Osney Mead, U.K.), a model 1280 data acquisition system (Nicolet, Madison, WI), a model 200L amplifier (Amplifier Research, Souderton, PA), and a 5-mm multinuclear probe (Cryomagnet Systems, Indianapolis, IN). Spectra were simulated using the Nicolet program NMRCAP. Chemical shifts are reported relative to the ^{17}O resonance of an external sample of tap-water, for the ^{17}O n.m.r. spectra, and to the ^{29}Si resonance of an external sample of $Si(CH_3)_4$ (50:50 v/v in [$^2H_6$]acetone), in the case of the ^{29}Si n.m.r. spectra, both at 295 K. High-frequency (low-field, deshielded or paramagnetic) shifts are reported as positive (IUPAC δ scale). In the ^{17}O n.m.r. spectra, the water resonance was attenuated by either continuous-wave saturation of the signal prior to data acquisition, or by choosing the observe pulse length to correspond exactly to a 180° pulse at the water resonance frequency.

Results and Discussion

To illustrate some general aspects of the ^{17}O n.m.r. spectra of silicate solutions, we show in Figure 1 a typical ^{17}O n.m.r. spectrum of an aqueous silicate solution, 0.1 mol dm^{-3} in silica and 0.2 mol dm^{-3} in sodium hydroxide, at 295 K, prepared using 10% ^{17}O-enriched water. The sample was allowed to stand open to the atmosphere for several weeks prior to recording the spectrum. Silicate solutions readily absorb CO_2 from the atmosphere and the weak, high-frequency signal at δ 190 p.p.m. is assigned to carbonate in the sample. (The ^{17}O n.m.r. signal of $CO_3{}^{2-}$ in water has been previously reported[11] at 192 p.p.m.) The intense, low-frequency signal at 0 p.p.m. is that of water, attenuated by a factor of *ca.* 100 by continuous-wave saturation prior to data acquisition. The signals around 50 p.p.m. arise from silicate anions in solution, and strategies for their assignment are dealt with in detail below.

Model Silicate Solutions.—Silicate solutions containing a single, well characterized silicate species provide good model systems for investigating the ^{17}O n.m.r. signals of the oxygen sites in silicate anions, and are invaluable in structural assignment. To our knowledge, only two such solutions exist: very dilute (< 0.01 mol dm^{-3} in SiO_2) solutions, in which only the monomer is present, within the limits of detection;[12] or concentrated, methanolic tetramethylammonium silicate solutions, which contain only the cubic octameric silicate cage.[8] The following discussion is based upon the results obtained from these two types of system.

Previous ^{29}Si n.m.r. studies[12] of dilute silicate solutions prepared using material enriched to 95% in ^{29}Si have shown that only the monomeric silicate anion exists in alkaline solution with total silica concentrations of less than 0.01 mol dm^{-3} (within the limits of detection, estimated at less than 8% of the silicon atom concentration[12]). However, more recent ^{29}Si n.m.r. investigations[13] of the structure of silicate species at equilibrium in *neutral* aqueous solution (at concentrations below the solubility limit of amorphous silica, in this case 97 p.p.m.) indicate that about 6% of the total silicon atoms are present in the form of the dimer, $H_6Si_2O_7$. This observation has since been supported by results from Raman spectroscopic studies.[14] In Figure 2(*a*) we show the ^{29}Si n.m.r. spectrum of a potassium silicate solution, 0.01 mol dm^{-3} in SiO_2 and 0.02 mol

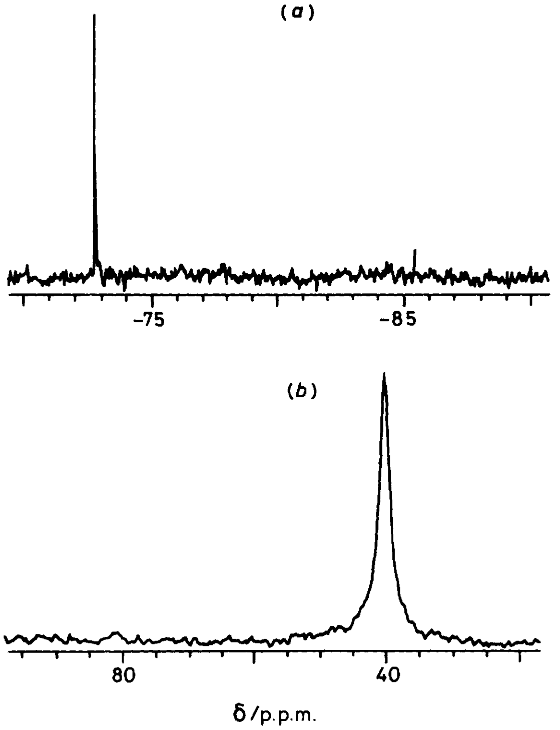


Figure 2. (*a*) The 99.3-MHz ^{29}Si n.m.r. spectrum of an aqueous potassium silicate solution, 0.01 mol dm^{-3} in SiO_2 and 0.02 mol dm^{-3} in KOH, prepared with water enriched to 10% in ^{17}O. The spectrum was recorded at 295 K over a 6-kHz sweep width, using 2 241 15-μs (67°) pulses, and a recycle delay of 20 s. (*b*) The 67.8-MHz ^{17}O n.m.r. spectrum of the same solution, using 2 348 73-μs (180° at the water resonance) pulses recorded over a 26-kHz sweep width. A recycle delay of 0.1 s was used

dm^{-3} in KOH, prepared using water enriched to 20% in ^{17}O. It is clear that the major species present is the monomeric silicate anion, Q^0. (In accord with other authors, we use the now standard 'Q' notation to denote a quadrifunctional, tetrahedral SiO_4^{4-} unit. The superscript indicates the number of other directly attached Q units, and the degree of protonation is ignored.) Figure 2(*b*) illustrates the ^{17}O n.m.r. spectrum of the same solution. The peak at 39.9 p.p.m. can immediately be assigned to the non-bridging $Si-O^-$ or Si–O–H groups of the monomer. We find no evidence in either the ^{29}Si or the ^{17}O n.m.r. spectra for any other silicate structures in solution at greater than the 5% level, and conclude from the ^{17}O n.m.r. spectrum that if any are present they must either contain less than 5% of the Si–O units present in solution, or else must have the same chemical shift as that of the monomer. This seems unlikely, since all other silicate species must contain two oxygen sites, bridging and non-bridging. Our results are not contrary to the findings of Cary *et al.*,[13] since their study concerned neutral aqueous solutions, and it is well established[15] that the silicate equilibrium shifts in favour of the monomer as the pH of the solution increases. They are, however, in conflict with the results obtained from Raman spectroscopy, in which dilute *alkaline* solutions were investigated, although it is possible that in this case the concentration of polymeric silicates was less than the detection limit of our experiments.

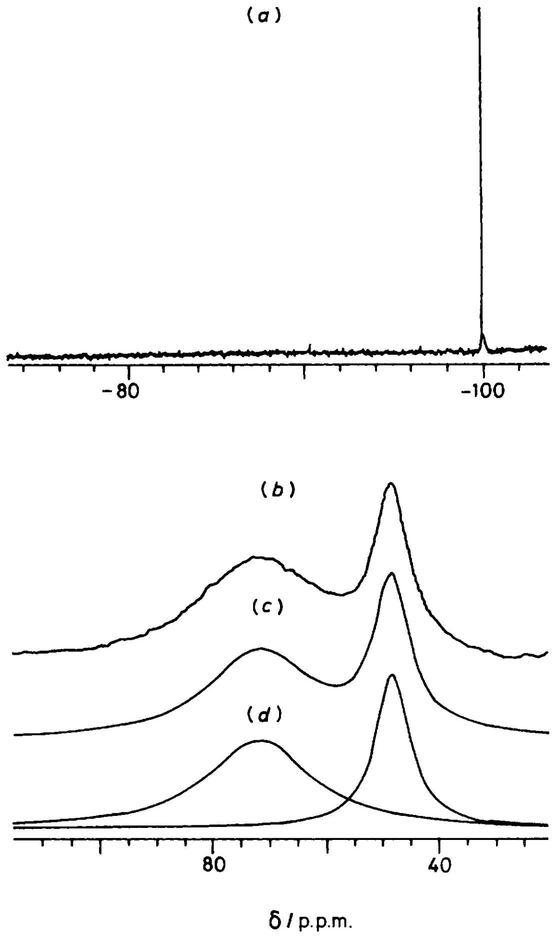
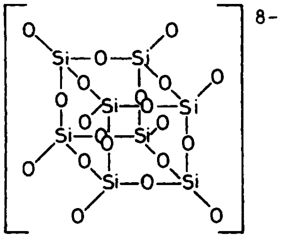


Figure 3. (*a*) The 99.3-MHz ^{29}Si n.m.r. spectrum of a tetramethylammonium silicate solution, 1 mol dm^{-3} in SiO_2 and 2 mol dm^{-3} in tetramethylammonium hydroxide, prepared using 56% ^{17}O-enriched SiO_2 and 56% ^{17}O-enriched water. The solution contains *ca.* 30% (v/v) [$^2H_4$]methanol. The spectrum is the result of 100 18-μs (90°) pulses, with a sweep width of 4 kHz. A 25-s recycle delay was used. (*b*) The 67.8-MHz ^{17}O n.m.r. spectrum of the same solution, from the accumulation of 3 612 25-μs (50°) pulses over a 76-kHz sweep width, using a 1 s recycle delay. (*c*), (*d*) Computer simulations of this spectrum, generated by two Lorentzian signals with an area ratio of 1 : 1.78 (after correcting for differential T_2 effects)

The second model system we investigated was a concentrated, methanolic tetramethylammonium silicate solution. It is now well established that concentrated tetramethylammonium silicate solutions, at equilibrium, contain primarily a single silicate anion, the cubic octameric cage, $[Si_8O_{20}]^{8-}$, or Q_8^3, together with minor amounts of the monomer, dimer, and other small species.[8] Boxhoorn *et al.*[16] demonstrated that addition of an organic solvent to a tetrapropylammonium silicate solution displaced the equilibrium in favour of cage compounds, and it has recently been shown[17] that a silicate solution containing the cubic octameric cage alone may be produced by the addition of dimethyl sulphoxide to a tetramethylammonium silicate solution. Similarly, we have found that the addition of methanol to tetramethylammonium silicate solutions also yields a solution containing *only* the cubic octameric cage (within the limits of detection, estimated at 2% of the silicon atom concentration). In Figure 3(*a*) we give an example of this. The figure illustrates the ^{29}Si n.m.r. spectrum of a tetramethylammonium silicate solution, 1 mol dm^{-3} in SiO_2 and 2 mol dm^{-3} in tetramethylammonium hydroxide, prepared with both silica and water enriched to 56.4% in ^{17}O. The solution contains 30% (v/v) [$^2H_4$]methanol, and was prepared several weeks prior to data acquisition, to allow equilibration.[8] The sharp peak at −100 p.p.m. arises from the cubic octameric cage.[8,17,18] In this species, eight equivalent silicon atoms occupy the apices of a cube [structure (**I**)]. They are linked by twelve bridging oxygens, and each is bound to a non-bridging oxygen, as shown in the diagram (the extent of protonation has been ignored). The ^{17}O n.m.r. spectrum of this species, Figure 3(*b*), is expected to show two signals, having an area ratio of three to two (bridging to non-bridging). Computer simulation of the ^{17}O n.m.r. spectrum, Figure 3(*c*) and (*d*), indicates that this is indeed the case, the experimental bridging to non-bridging ratio of 1.8:1 being in good agreement with the theoretical value of 1.5:1, providing an unambiguous assignment of the ^{17}O n.m.r. signals. Thus, the broad, high-frequency peak in Figure 3(*b*), at δ 72.0 p.p.m., arises from the twelve bridging oxygen sites in the cage, and the narrower, low frequency peak, at δ 47.5 p.p.m., is assigned to the eight terminal oxygen sites.



(**I**)

The bridging oxygen chemical shift is close to both the average bridging oxygen chemical shift of 74 p.p.m. observed in a series of alkaline-earth-metal metasilicates[10] and the value of 73 p.p.m. noted by us for an ^{17}O-labelled poly(dimethylsiloxane) gum.[19]

In general, ^{17}O n.m.r. signals arising from silicate species present in tetramethylammonium silicate solutions are broader than the signals of the anions occurring in equivalent alkali-metal hydroxide solutions, a phenomenon that may be partially explained by both the water structuring properties attributed to the organic base, which may cause a decrease in the correlation time of the silicate anions in tetramethylammonium silicate solutions, and the increased viscosity of the organic base solutions. (At 298 K, we find that the bulk viscosity of a 1 mol dm^{-3}, 1:1 potassium silicate solution is 1.08 cP, 1.08 × 10^{-3} Pa s^{-1}, while an equivalent tetramethylammonium silicate solution has a bulk viscosity of 1.28 cP, 1.28 × 10^{-3} Pa s^{-1}.) Spectral resolution may, of course, be improved by the use of higher temperatures, but heating tetramethylammonium silicate solutions is known to cause the cubic octameric cage to break down into smaller silicate species,[8,17,20] resulting in a poorly defined system. Consequently, work in this area has not been pursued.

Selective Isotopic Enrichment.—The methanolic tetramethylammonium silicate solution described above provides a good model system for investigating the bulk-water exchange kinetics of the oxygen sites in silicate anions, since it contains both bridging and terminal oxygen sites in a known ratio. By adding a few drops of ^{17}O-enriched water to a methanolic tetramethylammonium silicate solution prepared with natural ^{17}O abundance materials, mixing thoroughly, and immediately recording the ^{17}O n.m.r. spectrum, it is in principle possible to monitor the bulk water ⟷ non-bridging oxygen and bulk water ⟷ bridging oxygen-exchange rates. The ^{17}O n.m.r. spectrum of an unenriched tetramethylammonium silicate solution, 1 mol dm^{-3} in silica and with a base-to-silicon ratio of 2, recorded 120 s after the addition of 0.12 cm^3 of 20% ^{17}O-enriched water shows a single peak, at δ 49.0 p.p.m., Figure 4(*a*). This peak is assigned to the non-bridging oxygen groups of the cubic octamer. Recording successive ^{17}O n.m.r. spectra as a function of time reveals no change in the spectrum over a period of several days, and it is only after several weeks (at 295 K) that the signal of the bridging oxygen sites starts to appear [Figure 4(*b*)]. Even after a year [Figure 4(*c*)] the bridging to non-bridging intensity ratio has not returned to the equilibrium value of three to two [Figure 3(*b*)]. This indicates that the bulk water ⟷ non-bridging oxygen-exchange rate is very much greater than that of the bulk water ⟷ bridging oxygen exchange. It is unlikely that bulk water ⟷ bridging oxygen exchange can proceed any faster than the rate of interconversion of the silicate anions themselves, and, indeed, it seems plausible that all bridging oxygen labelling probably occurs *via* non-bridging oxygen ⟷ bridging oxygen-exchange pathways.

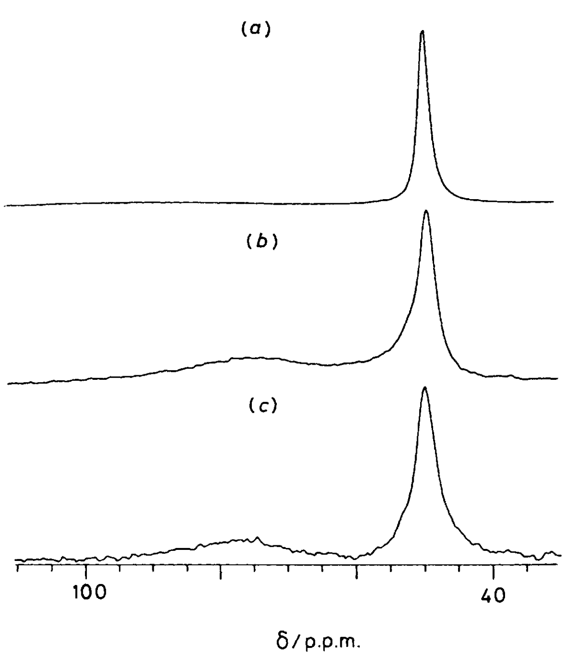


Figure 4. (*a*) The 67.8-MHz ^{17}O n.m.r. spectrum of a 2 mol dm^{-3}, 2:1 (N:Si) tetramethylammonium silicate solution, prepared with natural abundance materials, 120 s after adding 0.12 cm^3 of 20% ^{17}O-enriched water. The spectrum is recorded over a sweep width of 20 kHz and required 7 156 22-μs (90°) pulses, using a 0.2-s recycle delay. (*b*) The spectrum of the same solution recorded 2 months later, over a sweep width of 32 kHz, using 1 143 10-μs (40°) pulses, with a recycle delay of 1 s. (*c*) The spectrum of the same solution recorded after 1 year, over a sweep width of 20 kHz, using 8 328 46-μs (180° at the water signal) pulses and a recycle delay of 0.5 s

An upper limit to the bulk water ⟷ non-bridging oxygen-exchange rate is provided by ^{17}O n.m.r. magnetization-transfer experiments. Our results (data not shown) indicate that there is no magnetization transfer occurring during the time taken for the ^{17}O n.m.r. signal of water to relax, and therefore the exchange rate must be less than the water relaxation rate, $1/T_1$ (^{17}O). This gives a limiting value of 3.3 × 10^2 s^{-1} at 335 K, the temperature at which the experiment was performed. Conversely, non-bridging oxygens appear to have fully exchanged before an ^{17}O n.m.r. spectrum can be recorded (approximately 10 s after mixing), giving a lower exchange-rate limit of 0.1 s^{-1}. Establishing limiting exchange rates is impossible for bridging oxygens in this system, since the exchange is so slow, even at high temperatures.

More Complicated Systems.—Increasing the concentration of SiO_2 in alkali-metal silicate solutions is known to increase the average degree of polymerization of the silicate anions,

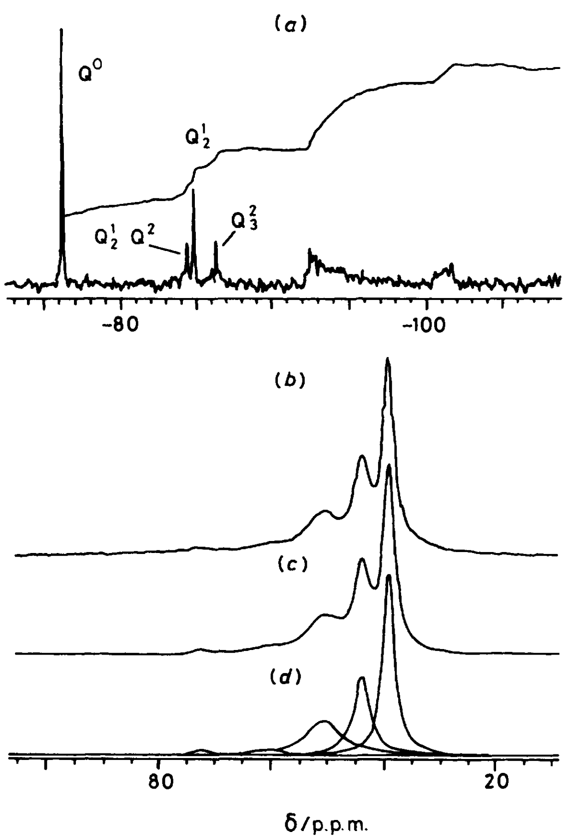


Figure 5. (*a*) The 99.3-MHz ^{29}Si n.m.r. spectrum of a potassium silicate solution, 0.1 mol dm^{-3} in SiO_2 and 0.2 mol dm^{-3} in KOH, prepared using deuterium oxide–water (50:50, v/v) containing 20% $H_2{}^{17}O$, at 295 K. The spectrum required 1 220 20-μs (45°) pulses over a 6-kHz sweep width, with an interpulse delay of 60 s. (*b*) The 67.8-MHz ^{17}O n.m.r. spectrum of the same solution. This required 5 004 73-μs (180° at the water resonance) pulses, with a sweep width of 26 kHz and a recycle delay of 0.1 s. (*c*), (*d*) Computer simulations of (*b*), generated by five Lorentzian signals with area ratios of 44:26:25:3:2, in order of increasing frequency

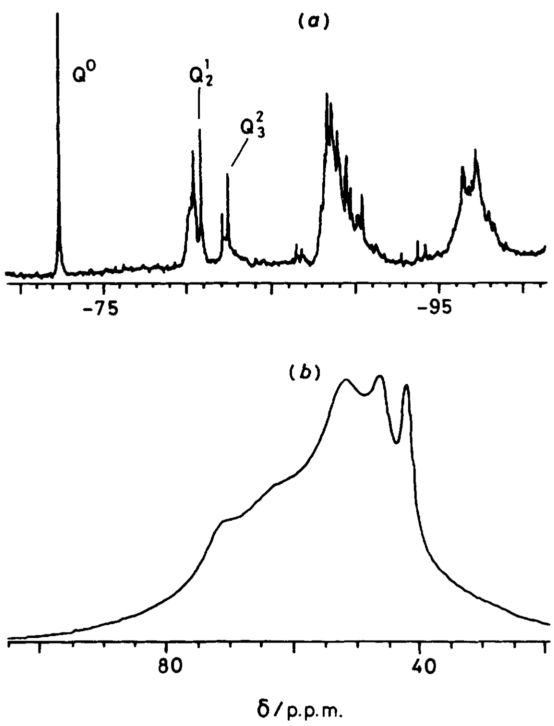


Figure 6. (*a*) The 99.3-MHz ^{29}Si n.m.r. spectrum of a 1.4 mol dm^{-3}, 1:1 (K:Si) potassium silicate solution at 295 K, prepared using 10% ^{17}O-enriched water. The spectrum was recorded over a sweep width of 6 kHz, and required 5 088 15-μs (67°) pulses with an interpulse delay of 10 s. (*b*) The 67.8-MHz ^{17}O n.m.r. spectrum of the same sample, from the accumulation of 800 75-μs (180° at the water resonance) pulses over a 26.3-kHz sweep width and a 0.1-s interpulse delay

resulting in an increase in the complexity of the n.m.r. spectra. We find that even at moderately low silica concentrations (0.1 mol dm^{-3}) the ^{29}Si n.m.r. spectrum indicates the presence of several anions, and the ^{17}O n.m.r. spectrum is already too complicated to furnish any unambiguous information. This is illustrated in Figure 5. Here the solution studied was 0.1 mol dm^{-3} in SiO_2 and 0.2 mol dm^{-3} in KOH, and was prepared using water enriched to 20% in ^{17}O. Similar solutions prepared with ^{29}Si isotopically enriched materials have been well characterized by ^{29}Si n.m.r. spectroscopy.[6,7,12] Accordingly, signals from the monomer (Q^0), dimer (Q^1_2), cyclic trimer (Q^2_3), and linear trimer ($Q^1_2Q^2$) may be recognized in Figure 5(*a*). The corresponding ^{17}O n.m.r. spectrum is shown in Figure 5(*b*), together with its computer simulation, Figure 5(*c*) and (*d*). From Figure 5(*d*) it is clear that the ^{17}O n.m.r. spectrum may be adequately simulated with five component signals. The most intense, low-frequency peak, at δ 39.0 p.p.m., may be assigned on both chemical shift and intensity grounds to the (non-bridging) oxygens of the monomer. Comparison with the intensities of the signals noted in the ^{29}Si n.m.r. spectrum [Figure 5(*a*)] indicates that the next most intense resonance, at δ 43.5 p.p.m., probably arises from the non-bridging oxygen groups of both the dimer and the linear trimer. The broader signal, at δ 51.5 p.p.m., is more difficult to assign. The non-bridging oxygens of the cyclic trimer are insufficient to account fully for the intensity of this peak, and there are no other obvious signals visible in the ^{29}Si n.m.r. spectrum. Integration of the ^{29}Si n.m.r. spectrum, Figure 5(*a*), shows that, aside from the monomer and dimer, the highest proportion of the signal appears in broad, low-intensity bands centred around −90 and −99 p.p.m. The structures responsible for these peaks have not been well characterized in such dilute solutions, and may possibly be large silicate species, perhaps of colloidal dimensions, containing a variety of similar silicon chemical environments, or else they may be a series of smaller silicate cages of unknown structure.[15] In neither case is it possible at present to correlate definitively the ^{17}O n.m.r. spectrum with the ^{29}Si n.m.r. spectrum. These are, however, the only features of sufficient intensity to account for the signal at δ 51.5 p.p.m. in the ^{17}O n.m.r. spectrum, and so it is likely that this peak arises, at least in part, from the oxygen sites of these poorly defined silicate structures. The width of the ^{17}O n.m.r. signal at 51.5 p.p.m. suggests that bridging oxygens may be responsible, and this, together with the absence of any other intense peaks in the ^{17}O n.m.r. spectrum, implies that these structures may be highly condensed, comprised primarily of Q^3 silicate units.

At least two broad, low-intensity signals occur to high frequency in the ^{17}O n.m.r. spectrum. On intensity grounds alone the highest-frequency signal, at δ 73 p.p.m., is tentatively assigned to the bridging oxygen sites of the dimer and linear trimer, while bridging oxygens of the cyclic trimer may be responsible for the lower-frequency signal, at δ 61 p.p.m. It should be noted that coincident or overlapping signals must already be invoked in the ^{17}O n.m.r. spectrum in order to rationalize the species identified by ^{29}Si n.m.r. spectroscopy, even in relatively dilute solutions such as this, in which few major silicate species occur. Further work aimed at correlating

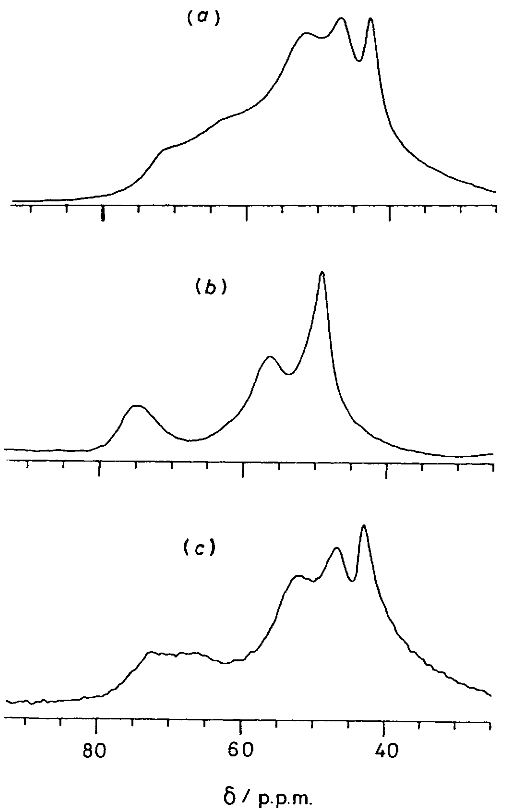


Figure 7. (*a*) The 67.8-MHz ^{17}O n.m.r. spectrum of a 1.5 mol dm^{-3}, 1:1 potassium silicate solution, prepared with ^{17}O-enriched water (20% ^{17}O). The spectrum is the result of 600 75.8-μs (180° at the water resonance) pulses, recorded over a sweep width of 26.3 kHz. An interpulse delay of 0.1 s was used. (*b*) The 67.8-MHz ^{17}O n.m.r. spectrum of a 2 mol dm^{-3}, 1:1 potassium silicate solution to which 0.125 cm^3 of 56% ^{17}O-enriched water had been added, bringing the total concentration of both K and Si to 1.5 mol dm^{-3}. The beginning of data acquisition occurred 30 s after mixing, and the spectrum required 300 76-μs (180° at the water resonance) pulses, over a sweep width of 26.3 kHz, with an interpulse delay of 0.1 s. (*c*) The spectrum of the same solution, 1 year after mixing, with 3 815 91-μs (180° at the water resonance) pulses, over a sweep width of 20.0 kHz, and an interpulse delay of 0.1 s

the ^{17}O and ^{29}Si n.m.r. spectra in such complex silicate systems is clearly warranted.

We show in Figure 6(*a*) the ^{29}Si n.m.r. spectrum of a more concentrated potassium silicate solution, 1.4 mol dm^{-3} in both SiO_2 and KOH, prepared with 10% ^{17}O-enriched water. This is closer to the concentration of solutions of industrial importance, and many silicate species coexist, as witnessed by the complexity of the ^{29}Si n.m.r. spectrum. Once again, many of the structures present have been characterized by ^{29}Si n.m.r. spectroscopy of ^{29}Si isotopically enriched solutions.[6,7] The ^{17}O n.m.r. spectrum is shown in Figure 6(*b*). It consists of numerous broad, overlapping resonances. By comparison with the more dilute systems, the sharper, low-frequency signal may be tentatively attributed to the monomer. However, a more detailed analysis is difficult.

In Figure 7 we show the effects of a selective isotopic enrichment experiment performed on a similar solution, in order to facilitate assignments. Figure 7(*a*) is the ^{17}O n.m.r. spectrum of a freshly prepared, 1.5 mol dm^{-3} 1:1 potassium silicate solution made up in 20% ^{17}O-enriched water, and is essentially the same as that shown in Figure 6(*b*). Figure 7(*b*) is the ^{17}O n.m.r. spectrum of a potassium silicate solution, originally 2 mol dm^{-3} in both K and Si, to which sufficient ^{17}O-enriched water (56% in ^{17}O) has been added to bring the concentration of both K and Si down to 1.5 mol dm^{-3}. The spectrum was obtained immediately after mixing, and shows only three signals, two of which fall in the region ascribed to non-bridging oxygens, at δ 48 and 56 p.p.m., while the third lies at δ 76 p.p.m., within the region assigned to bridging oxygen sites. These chemical shifts are novel, and do not correlate with any of those of the 'equilibrium' spectrum, Figure 7(*a*). The spectrum does not change rapidly with time, and the sample gives an 'equilibrium' ^{29}Si n.m.r. spectrum, similar to that shown in Figure 6(*a*). It is only after several months at room temperature that the ^{17}O n.m.r. spectrum starts to return to the equilibrium situation, as shown in Figure 7(*c*), which illustrates the ^{17}O n.m.r. spectrum of the same sample recorded after 1 year.

Although it is difficult to interpret these observations in terms of individual silicate structures, it seems clear that the labelled oxygen atoms are not being incorporated into all the sites in the silicate anions at the same rate. There appear to be two, very different, bulk water exchange rates, some sites having fully exchanged in a matter of seconds, and others requiring many months. Although it is tempting to assign the former to non-bridging and the latter to bridging sites, as in the case of the tetramethylammonium silicate solution described above, this is not borne out by the chemical shift or linewidth of the high-frequency signal, both of which suggest that it arises from a bridging oxygen. Furthermore, ^{29}Si two-dimensional n.m.r. exchange experiments show a relatively rapid exchange between the linear and cyclic trimer in these solutions,[21] thereby providing a convenient pathway for rapidly incorporating the oxygen label into a bridging site. It is therefore possible that the high-frequency signal in Figure 7(*b*) arises from bridging oxygen sites in such labile cyclic structures. Further assignments are, however, impossible, and it must be concluded that, at present, ^{17}O n.m.r. spectra of such complex solutions may be more useful in providing 'fingerprint analysis,' rather than in the structural elucidation of the individual components. Additional experiments involving selective isotopic enrichment in ^{17}O, variable temperatures, and organic additives are in progress in order to help clarify the situation.

Acknowledgements

This work was supported in part by the United States National Science Foundation (grants DMR 86-15206 and EAR 84-08421), and in part by the Mobil Foundation.

References

1 See, for example, R. K. Iler, 'The Chemistry of Silica,' Wiley, New York, 1979; D. Barby, T. Griffiths, A. R. Jacques, and D. Pawson, in 'The Modern Inorganic Chemicals Industry,' ed. R. Thompson, The Chemical Society, London, 1977.
2 E. Freunde, *Bull. Soc. Chim. Fr.*, 1973, 2238, 2244.
3 H. C. Marsmann, *Z. Naturforsch., Teil B*, 1974, **29**, 495.
4 G. Engelhardt, D. Ziegan, H. Jancke, D. Hoebbel, and W. Wieker, *Z. Anorg. Allg. Chem.*, 1975, **418**, 17.
5 R. K. Harris and R. H. Newman, *J. Chem. Soc., Faraday Trans. 2*, 1977, 1204.
6 R. K. Harris, C. T. G. Knight, and W. E. Hull, *ACS Symp. Ser.*, 1982, **194**, 79.
7 R. K. Harris and C. T. G. Knight, *J. Chem. Soc., Faraday Trans. 2*, 1983, 1525, 1539.
8 R. K. Harris and C. T. G. Knight, *J. Mol. Struct.*, 1982, **78**, 273; C. T. G. Knight, R. J. Kirkpatrick, and E. Oldfield, *J. Chem. Soc., Chem. Commun.*, 1986, 66.
9 C. W. Turner and K. J. Franklin, *J. Non-Cryst. Solids*, 1987, **91**, 402.
10 H. K. C. Timken, S. Schramm, R. J. Kirkpatrick, and E. Oldfield, *J. Phys. Chem.*, 1987, **91**, 1054.

11 B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Proc. R. Soc. London, Ser. A*, 1962, **269**, 469.
12 R. K. Harris, J. Jones, C. T. G. Knight, and D. Pawson, *J. Mol. Struct.*, 1980, **69**, 95.
13 L. W. Cary, B. H. W. S. de Jong, and W. E. Dibble, *Geochim. Cosmochim. Acta*, 1982, **46**, 1317.
14 R. Alvarez and D. L. Sparks, *Nature (London)*, 1985, **318**, 649.
15 L. S. Dent-Glasser and E. E. Lachowski, *J. Chem. Soc., Dalton Trans.*, 1980, 393, 399.
16 G. Boxhoorn, O. Sudmeijer, and P. H. G. van Kasteren, *J. Chem. Soc., Chem. Commun.*, 1983, 1416.
17 E. J. J. Groenen, A. G. T. G. Kortbeek, M. Mackay, and O. Sudmeijer, *Zeolites*, 1986, **6**, 403.
18 C. T. G. Knight, R. J. Kirkpatrick, and E. Oldfield, *J. Am. Chem. Soc.*, 1986, **108**, 30.
19 C. T. G. Knight, L. Reven, R. J. Kirkpatrick, and E. Oldfield, unpublished work.
20 G. Engelhardt and D. Hoebbel, *Z. Chem.*, 1983, **23**, 33.
21 C. T. G. Knight, R. J. Kirkpatrick, and E. Oldfield, *J. Magn. Reson.*, 1988, **78**, 31.

Received 1*st February* 1988; *Paper* 8/00369F