Aqueous Silicates

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The Structure of Silicate Anions in Aqueous Alkaline Solutions**

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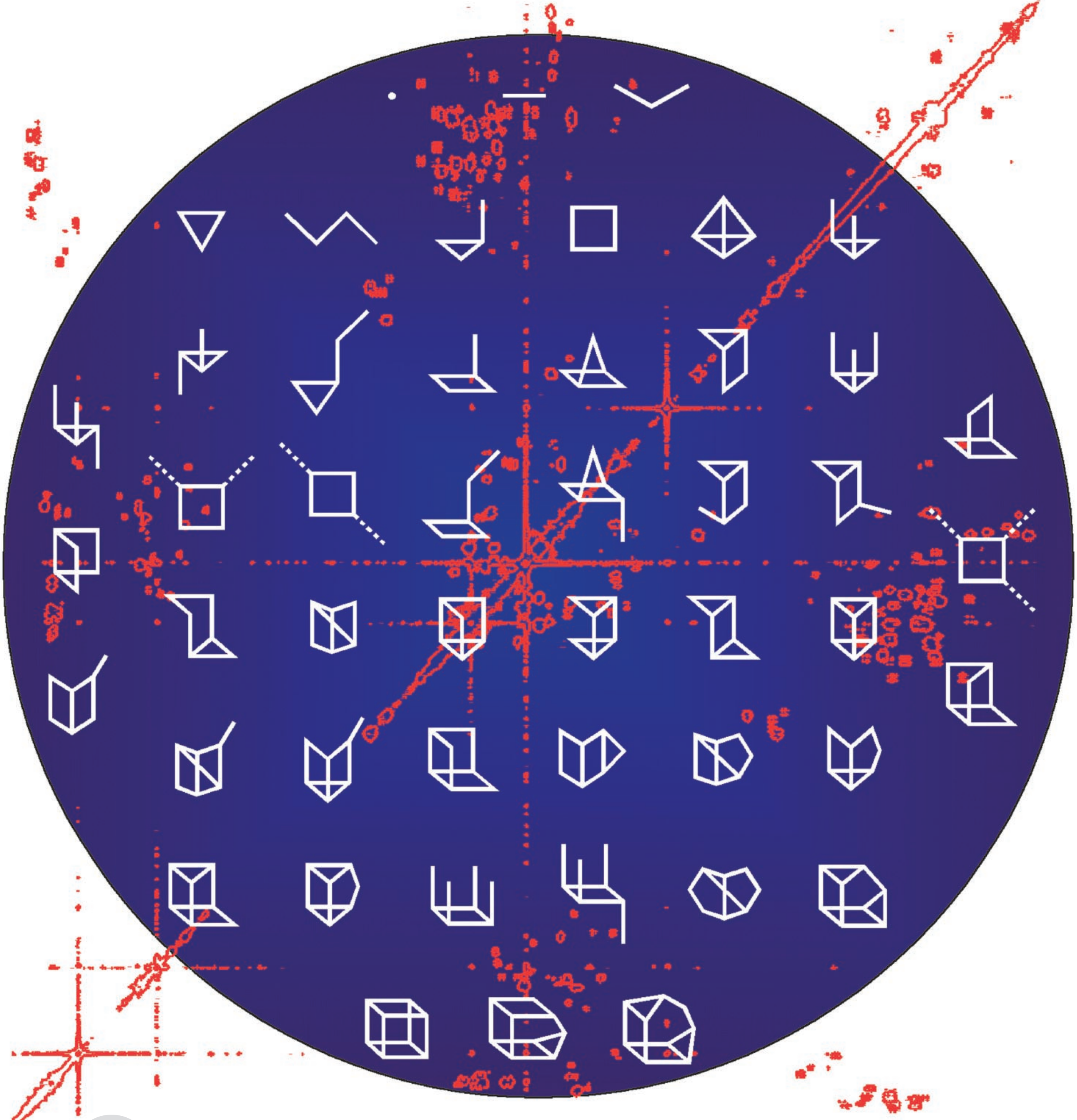

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Although aqueous silicates rank among the world's major chemical commodities—they are fundamental to applications as diverse as coatings, detergents, paper manufacturing, and water treatment—relatively few of the polyanions that they contain have been identified. Unmasking the structure of aqueous silicates is crucial to the debate over whether or not zeolite molecular sieves grow from solution by addition of prefabricated molecular building blocks ("precursor species").[1] Direct evidence of oligomeric silicate structures was initially obtained from analysis of their trimethylsilyl-substituted derivatives.[2] However, this wet-chemical technique was later found to induce structural rearrangement.[3] Harris and Knight reported the first unambiguous identification of aqueous silicate species in 1983.[4] By conducting ^{29}Si NMR spectroscopic analysis of ^{29}Si-enriched solutions, they determined the structure of twelve multisite oligomers and provided clues to the identity of seven single-site species.[4,5a] No other structures have been identified with certainty in the intervening years, with the exception of organoclathrated species found only in low alkalinity tetraalkyl ammonium solutions.[6] Herein we show the results of a high-field (17.6 T) ^{29}Si NMR COSY analysis of an isotopically enriched potassium silicate solution. We identify 48 different structures (including those of Harris and Knight), thus providing the most complete picture of silicate speciation to date. The anions are all compact, containing fewer than ten Si sites, and obvious zeolite precursor structures are conspicuous by their absence.

It is well known that concentrated silicate solutions contain many structurally similar species in dynamic equilibrium.[5b] This situation gives rise to crowded ^{29}Si NMR spectra with signals that are notoriously difficult to assign. Because ^{29}Si is a "rare spin" (4.7% natural abundance), no ^{29}Si–^{29}Si coupling is visible, and each chemically distinguishable silicon site gives rise to a single peak, making it impossible even to determine which resonances belong to sites in the same anion. Moreover, ^{1}H–^{1}H chemical exchange between silicate anions and water molecules is rapid on the NMR timescale, ensuring that no ^{29}Si–^{1}H scalar coupling is apparent. These difficulties can be partially overcome by the use of ^{29}Si-enriched solutions in conjunction with standard NMR spectroscopic structure elucidation techniques, such as COSY.

Indeed, Cho et al.[7] recently used phase-sensitive and double-quantum-filtered ^{29}Si NMR COSY analysis to characterize an isotopically enriched sodium silicate solution. In addition to confirming Harris and Knight's initial assignments,[4] they proposed nine further structures. Haouas and Taulelle[8] reported ^{29}Si–^{29}Si connectivity data from a ^{29}Si INADEQUATE NMR spectroscopy study, while suggesting other hypothetical species. Neither study provided definitive evidence for any new structures, however, owing to the insufficient sensitivity and resolution of the spectrometers involved.

An obvious remedy is to obtain the NMR spectrum at the highest possible external magnetic field, since this approach increases both sensitivity and spectral dispersion. We therefore acquired spectra at 17.6 T (750 MHz for ^{1}H) and maximized resolution by careful choice of sample and operating temperature, as detailed in the Experimental Section. Our sample contained over 99 atom% ^{29}Si, thereby reducing signals from isotopomers. The resulting ^{29}Si NMR spectra show over 200 sharp signals, most of which appear as spin multiplets arising from $^{2}J(^{29}\text{Si-O-}^{29}\text{Si})$ scalar coupling. Seven singlet peaks are also apparent. These peaks arise from the silicate monomer (species **1** in Figure 1), dimer (**2**), cyclic trimer (**3B**), cyclic tetramer (**4C**), tetrahedral tetramer (**4D**), prismatic hexamer (**6M**), and cubic octamer (**8D**). Since these species contain only a single silicon chemical environment, ^{29}Si enrichment yields no further information. The structures responsible can only be inferred by comparing their chemical shifts and relaxation parameters to those of multisite silicate species for which assignments are definitive.[4,5] Signals from the prismatic hexamer (**6M**) and cubic octamer (**8D**) have been confirmed using heteroatom substitution.[9]

We show in Figure 2 the full ^{29}Si NMR COSY spectrum with the corresponding one-dimensional spectrum along each axis. None of the spectra we acquired showed more than the seven singlets noted above, down to a silicon site concentration of 4 μmol kg^{-1}, and we can thus rule out the presence of rings larger than the cyclic tetramer and symmetric cages greater than the cubic octamer. Figure 1 illustrates all 41 multisite silicate anion structures that could be derived from the data of Figure 2. The systematic name, concentration, formation constant, ^{29}Si NMR spectroscopic chemical shifts and $^{2}J(^{29}\text{Si-O-}^{29}\text{Si})$ coupling constants for each species are listed in Table S1 in the Supporting Information.

The first step in determining individual anion structures is to identify a set of connected signals in the COSY spectrum. The chemical environment of the site corresponding to each signal is then inferred by comparing its chemical shift to those of previously assigned peaks. Signal areas are taken into account and, finally, tentative structures are proposed. The observed coupling constants can be used to simulate the expected NMR spectrum. Only structures whose simulated spectrum matches the experimental spectrum are listed in Figure 1 and in Table S1 in the Supporting Information.

We illustrate this procedure in detail for the most abundant of the newly identified anions, species **7J** (tetracyclo[7.5.1.1^{3,7}.1^{5,11}] heptasilicic acid) in Figure S1 in the Supporting Information. Figure 3 shows simulated and experimental spectra for **7J** and two additional species, **6E** and **6G**. Cho et al.[7] also suggested species **6G**, proposing that two isomeric forms exist simultaneously in solution; we find no

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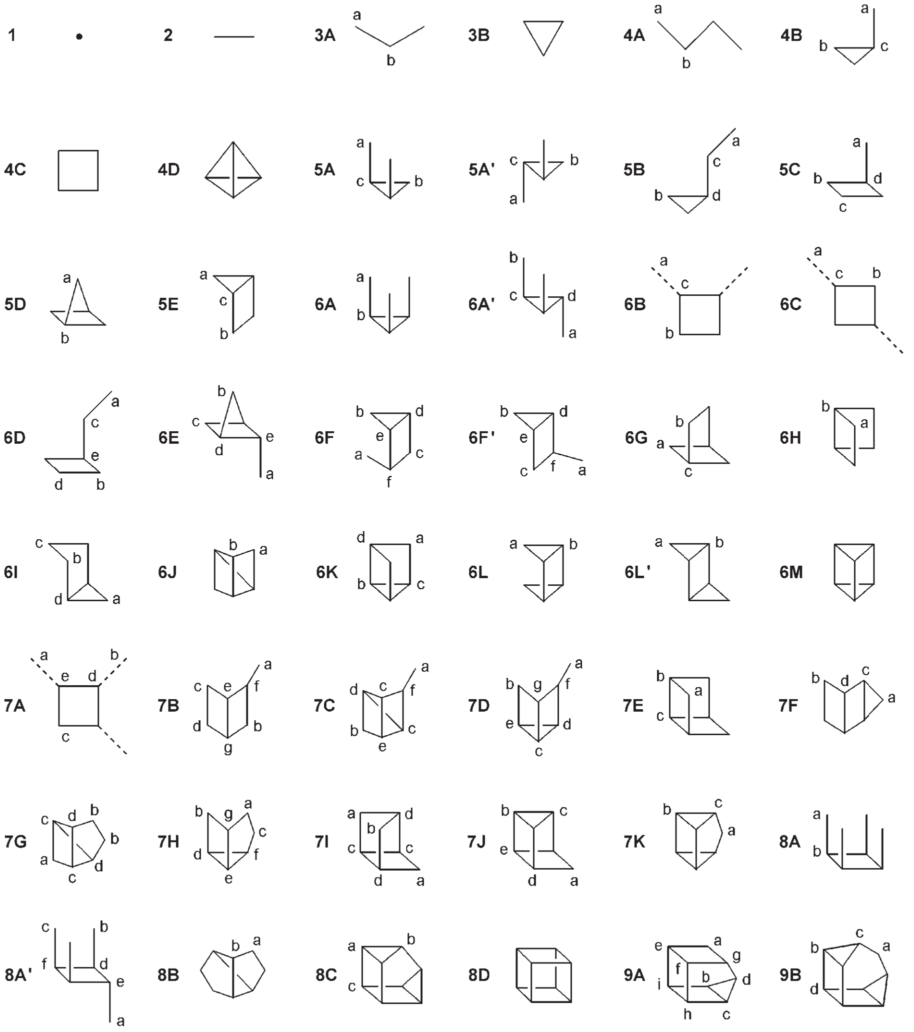

Figure 1. Aqueous silicate structures identified in concentrated alkaline solution. Each line in the stick figures represents a Si-O-Si (siloxane) linkage. Of these 48 structures, 41 contain multiple chemically distinct Si sites, making them amenable to characterization by ^{29}Si–^{29}Si COSY NMR spectroscopy (Figure 2). All the structural assignments are definitive except for species **6B**, **6C**, and **7A**, for which we were unable to resolve the various isomeric forms.

evidence for this. The *cis,trans,trans* and *trans,cis,trans* isomers of species **8A** are similarly absent, presumably because of steric hindrance between the trihydroxysilyl groups.

The superior dispersion and sensitivity afforded by our experimental method is evident in the end-group region ($\delta = -7.6$ to -8.7 ppm) shown in Figure 4. We resolve 25 individual cross-peaks for these signals, as opposed to the four observed by Knight[10] and the seven detected by Cho et al.[7] The region is unique in that each site is coupled to only one other, giving a series of doublets for which only one cross-peak can exist. Therefore, at least 25 different end-group environments exist in this solution. We can assign 21 of these resonances to 18 different anions. (Species **6A′** and **8A′** contain two and three inequivalent end-groups, respectively.) Figure S2 in the Supporting Information shows the end-group cross-peaks corresponding to the structurally related species **4B**, **5A**, **5A′**, **6A** and **6A′**.

The remaining end-group cross-peaks are partially obscured by other spectral features. Nevertheless, their location in the COSY spectrum is diagnostic of end groups attached to four-membered rings, being close to those of species **5C**, **6F**, **6F′**, and **7B**. Given the existence of both monosubstituted and tetrasubstituted four-membered rings (species **5C**, **8A**, and **8A′**), the most logical candidates are the disubstituted and trisubstituted analogues (**6B**, **6C**, and **7A**), although it is impossible to assign signals with certainty to any of the seven individual isomers.

Thus, even at 17.6 T, NMR spectral overlap and sensitivity still limit structural determination. Indeed, hundreds of weak signals are visible throughout the spectrum, suggesting the presence of myriad minor structures, although the 48 we present herein account for 85 % of the silicon in solution. We cannot, however, find evidence for some species tentatively claimed in earlier studies using ^{29}Si-enriched materials, such as species **15** and **16** in reference [10] and species **1–4** in reference [7]. It is clear, though, that advances in NMR spectroscopy will further extend the array of structures found in this inorganic chemical staple.

Experimental Section

An aqueous solution containing $^{29}SiO_2$ (1.00 mol kg^{-1}) and KOH (1.00 mol kg^{-1}) was made by heating amorphous silica (0.1860 g) containing 99.35 atom % ^{29}Si (Isonics), with aqueous KOH (3.2400 g, 1.000 mol kg^{-1}, prepared from Sigma Aldrich KOH (99.99 %) and deionized water deuterated to 22 atom % to provide a field-frequency lock) in a teflon-lined pressure vessel at 140 °C for 48 h. Potassium silicates exhibit the slowest translational ^{29}Si NMR relaxation of all alkali-metal silicate solutions and, thus, the narrowest ^{29}Si resonances.[11] The high level of ^{29}Si enrichment is crucial to ensuring that the spectra were completely devoid of complex spin-multiplet patterns from isotopomers.

All ^{29}Si NMR spectra were acquired on a Varian Inova 750 spectrometer (operating at 149 MHz for ^{29}Si) using a 10-mm broadband probe (signal-to-noise (S/N) = 1300:1 for 40 % dioxane/C_6D_6 using single $\pi/2$ ^{13}C pulse and 3.5 Hz exponential line-broadening), 9 mm inner diameter Kel-F NMR tubes, and an operating temperature between 270 and 280 K to prevent ^{29}Si–^{29}Si chemical-exchange line-broadening.[11] The resulting peak widths were 0.5–1.0 Hz. The one-dimensional spectra were acquired with 2000–3000 $\pi/2$ pulses recycled over a period of 25 s, that is, greater than three times the longest measured longitudinal relaxation time (T_1) to ensure quantitative peak measurements.[11] The recycle period was shortened to 4.3 s for the COSY experiments, which ran for 67 h. Computer

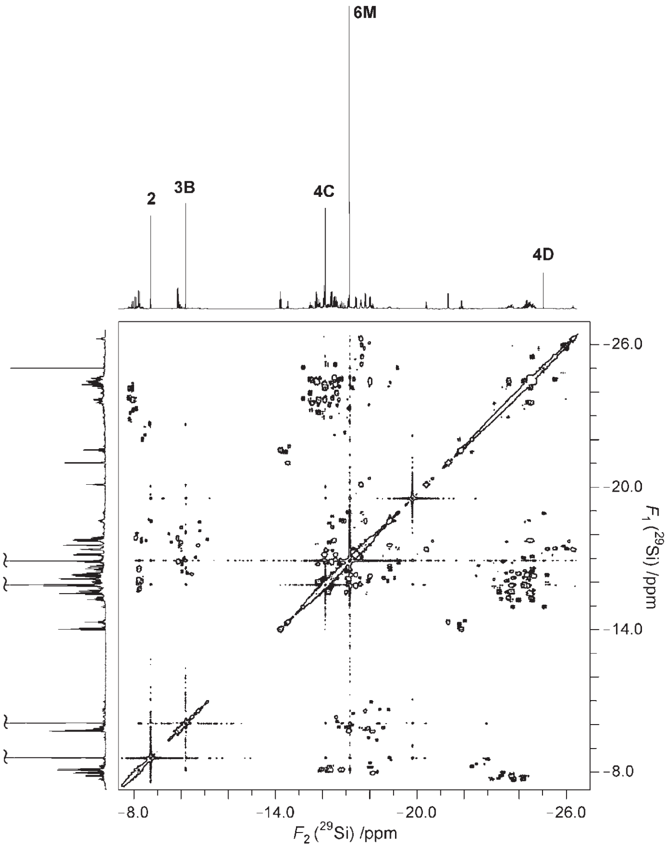

Figure 2. ^{29}Si NMR one-dimensional and COSY spectra (149 MHz) at 280 K of an aqueous potassium silicate solution containing 1.0 mol kg^{-1} SiO$_2$ (enriched 99.35 atom% in ^{29}Si) and 1.0 mol kg^{-1} KOH. The entire spectrum is shown except for the orthosilicic acid resonance at 0 ppm, for which there is no cross-peak. Resonances corresponding to single-site silicate species are labeled in accordance with Figure 1.

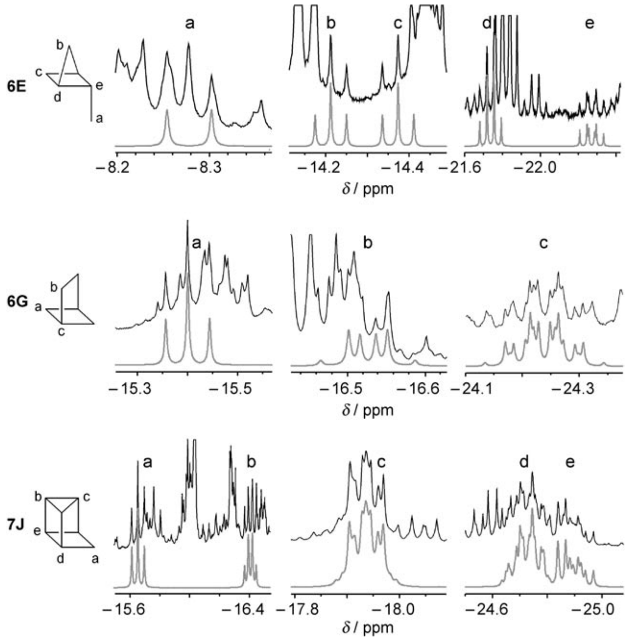

Figure 3. Expanded 1D ^{29}Si NMR spectrum from Figure 2. The resonances corresponding to species **6E** (3-trihydroxysilylbicyclo-[3.3.3]pentasilicic acid), **6G** (bicyclo[5.3.3]hexasilicic acid), and **7J** (tetracyclo-[7.5.1.1^{3,7}.1^{5,11}]heptasilicic acid) are displayed, along with their computer-modeled simulations (shown in gray).

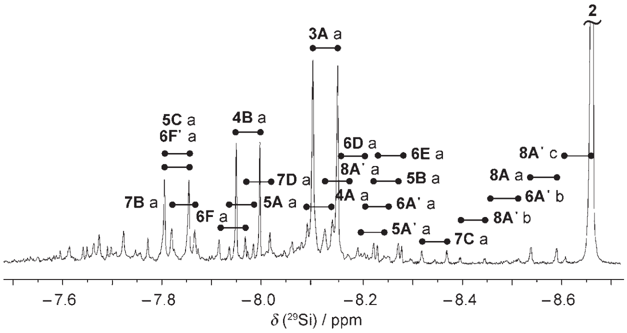

Figure 4. Expanded ^{29}Si NMR one-dimensional spectrum of the potassium silicate solution from Figure 2 at 272 K, showing the end-group spectral region.

simulations were conducted using NUTS (NMR Utility Transform Software, Acorn NMR).

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