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Direct Detection of Aluminosilicate Species in Aqueous Solution by Silicon-29 and Aluminum-27 NMR Spectroscopy

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Silicon-29 NMR spectra of solutions containing 1 mol kg^{-1} SiO_2 and 0.07 mol kg^{-1} Al in 2.4 mol kg^{-1} aqueous NaOH at 5 °C show five bands which are attributable to dissolved species containing Si–O–Al links. The major aluminosilicate species in solution appear to be Al-substituted derivatives of the silicate dimer, cyclic trimer, cyclic tetramer, and acyclic trimer. ^{29}Si spectra suggest and ^{27}Al NMR spectra confirm that little or no free $Al(OH)_4^-$ is present and that a major fraction of the bound Al is connected to more than one SiO_4 unit. The time constant for Al exchange is on the order of 60–120 ms for the most of these aluminosilicate species. In solutions containing only 0.01 mol kg^{-1} of each of Si and Al in 0.03 mol kg^{-1} NaOH, ^{27}Al NMR spectroscopy shows that free $Al(OH)_4^-$ predominates but some aluminosilicate species are present. The behavior of Al in alkaline silicate solutions reflects Loewenstein's rule.

Introduction

The question of whether dissolved aluminosilicate species are involved as precursors in the hydrothermal formation of natural or synthetic solid aluminosilicates (and, if so, what these species might be) has been debated by the geochemical community[1] and inorganic chemists[2] for some years. In principle, NMR spectroscopy is uniquely capable of detecting and characterizing ^{27}Al and ^{29}Si centers in aqueous solution,[3,4] but its application is hindered by the low solubility of aluminosilicates. To date most of the evidence offered for the existence of Si–O–Al links in solution has come from ^{27}Al NMR spectroscopy,[1,5-7] which gives only limited information because of quadrupolar line broadening, or from subtle effects (such as shifting or broadening) on ^{29}Si NMR lines,[1,6,8] the significance of which is unclear but could be pH related. Engelhardt and co-workers[9] published a ^{29}Si NMR spectrum, backed by trimethylsilylation studies,[10] of an aqueous tetramethylammonium aluminate/silicate solution which showed features attributable to Si–O–Al units different from the $Si_xAl_{8-x}O_{20}^{(16-x)-}$ anions present in the solid phase that separated from the solution on cooling; tetramethylammonium silicate solutions, however, represent a special case in view of the anomalously slow equilibration of the anions[11] and are unlikely to occur as such in geochemical systems.

We report here observations of weak but distinctive ^{29}Si resonances, in metastable aqueous sodium silicate solutions containing excess NaOH and small amounts of aluminate, which are assignable to dissolved species of low molar mass containing Si–O–Al links that undergo aluminate exchange with a site residence time τ on the order of 100 ms at 5 °C under the conditions of our experiments. This exchange becomes rapid on the NMR time scale at 25–40 °C, at which the characteristic ^{29}Si–O–Al resonances broaden excessively and become lost in the background noise. The keys to successful observation of these features in alkali-metal aluminate/silicate solutions at natural ^{29}Si abundance are therefore as follows: (1) to work within the composition ranges in which the gelling times of metastable solutions, as mapped out by Dent Glasser and Harvey,[6] are sufficiently long; (2) to use NMR instrumentation with sufficient sensitivity to record small amounts of ^{29}Si–O–Al units in presence of large excesses of Al-free silicate species; (3) to cool the solution to 5 °C or below during spectrum measurement to suppress line broadening due to silicate[12] and particularly aluminate group exchange; (4) to eschew the use of glass NMR tubes,[12-14] which give a troublesome ^{29}Si background and also may contaminate the alkaline solutions through etching (as may glass laboratory ware).

Table I. Relative Chemical Shifts (δ) and Integrated Band Intensities for ^{29}Si Resonances Shown in Figure 1

band	$-\delta(^{29}Si)$/ppm	integrated intens/% Si Al absent	 Al present
Q^0	0	37.8	35.6
A	3.9, 4.2, 4.5		2.4
B + Q^1	6.8–8.6	21.4	24.5
$Q^2{}_A$	9.2–10.5	21.0	14.9
C	11.6, 11.9, 12.3		2.0
D	13.0	16.8	17.4
E	14.3		
$Q^2{}_B$	15.2–17.5		
$Q^3{}_A$	17.5–19.0		
$Q^3{}_B$	21–27	3.1	3.1

Experimental Section

Polyethylene or Teflon FEP laboratory ware was used exclusively. Stock sodium silicate and aluminate solutions were prepared separately by dissolving amorphous silica (from hydrolysis of redistilled $SiCl_4$[12]) and high-purity aluminum metal (Spex), respectively, in standardized aqueous NaOH enriched in ^{2}H for NMR locking. The aluminosilicate solutions were prepared by carefully adding the aluminate solution, a few droplets at a time, from a syringe down the sides of a FEP tube liner containing the silicate solution and immediately shaking the solution vigorously for about 5 min before the next addition. A silky white precipitate often formed as the droplets were added but would disappear during the shaking; this silky material was qualitatively different from the dense precipitate that formed irreversibly after extended periods or on heating, in solutions with $[OH^-]:([Si] + [Al]) < 20:1$ and aluminum concentrations more than a few mmoles per kilogram (solutions with higher $[OH^-]:(Si + Al)$ or lower [Al] than this were stable indefinitely at 20 °C). The requirement for long metastable solution lifetimes[6] at Si concentrations high enough for NMR purposes restricted the choice of [Si], [Al], and $[Na^+]$ to about 0.5–1.0, < 0.1, and 1–3 mol kg^{-1} respectively. Such solutions were stable indefinitely at 5 °C, but threw a precipitate after 2 weeks at 20 °C or immediately on heating to about

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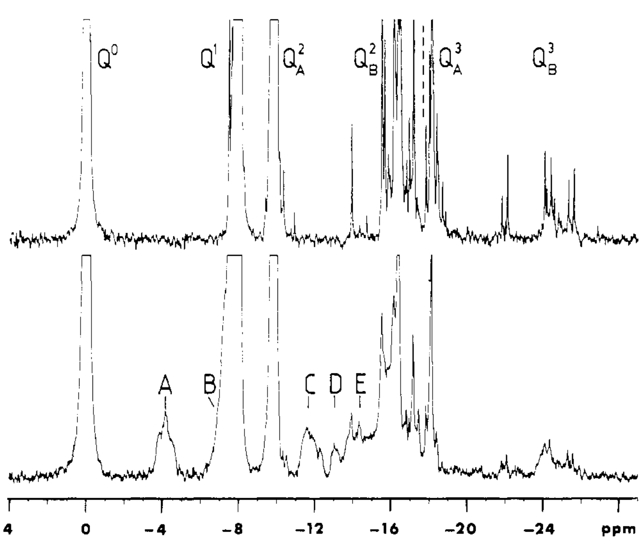

Figure 1. Vertically expanded ^{29}Si NMR spectra (79.49 MHz) of solutions containing 1.1 mol kg^{-1} SiO_2 in 2.4 mol kg^{-1} aqueous NaOH at 5 °C; the lower spectrum is of a solution containing 0.07 mol kg^{-1} Al in addition. The spectra are normalized to give equal areas of the orthosilicate (Q^0) resonance, and include 2.4-Hz artificial line broadening. Spectra generated with 6200 (upper) and 9300 (lower spectrum) 90° pulses of 11 μs with a 10-s repetition time.

50 °C. Where precipitation did occur, the *distribution* of aqueous species seen in the NMR spectra remained the same—i.e., the silicate and aluminosilicate systems were at equilibrium in solution.

Results and Discussion

Silicon-29 Spectra. Figure 1 typifies the reproducible ^{29}Si spectra obtained at 79.49 MHz on a Bruker AM 400 spectrometer for pairs of sodium silicate solutions, with and without added sodium aluminate but otherwise identical. It is known from the ^{29}Si NMR spectra of solid aluminosilicates[9,15] that if a silicate unit attached to a resonating ^{29}Si is replaced by an aluminate tetrahedron, the ^{29}Si resonance frequency increases by 4–5 ppm. It is to be expected, on the basis of the experience of Knight, Kirkpatrick, and Oldfield[16] with the effects on ^{29}Si NMR spectra of partially replacing Si by Ge in the cubic octamer $Si_8O_{20}^{8-}$ (Q^3_8),[17] that small but significant second-order shifts on more distant Si atoms will complicate the spectra (see below). Nevertheless, the primary 4 ppm effect allows one to make the following assignments of the main aluminate-related ^{29}Si features A–E, which appear in the lower spectrum of Figure 1 and are quantified in Table I, in terms of the established[3] polysilicate structures represented by the bands designated Q^1, Q^2_A, etc.,[17] in the upper (Al-free) spectrum.

Band A. This is assigned to terminal Si centers (Q^1) attached to one AlO_4 unit. The most important contributor is almost certainly the unique mono-Al-substituted Q^1_2 dimer $O_3SiOAlO_3^{7-}$, but the band shows some structure—in nearly all spectra, three components of this band were discernable. This structure is unlikely to be due to the spin–spin splitting of the Si resonance by the Al nucleus ($I = {}^5/_2$), as six resonances of equal area would then result. Probably, the main, central feature at $\delta = -4.2$ ppm is due to the mono-Al-substituted dimer, the peak at −3.9 ppm comes from $O_3SiO(AlO_2)OSiO_3^{9-}$, and the balance of the band derives from Si side groups attached to Al centers in strained structures, e.g., to an Al substituting for the Q^3 Si in the tetrameric species IV (three-Si ring with one Si side group) of Harris and Knight.[3]

Band A comprises roughly 30% of the integrated ^{29}Si intensity associated with Al–O–Si links (Table I); a precise fraction cannot be calculated because the proportions of the integrated areas of bands (B + Q^1), (D + E + Q^2_B + Q^3_A) and the region downfrequency of −19 ppm that are due to Al–O–Si species cannot be determined. It should be noted that the Al-substituted dimer has only one Si juxtaposed to Al, whereas other aluminosilicate species may have two or three. Consequently, the area of band A underestimates the importance of the substituted dimer, and the integrated intensity of peaks A–E is a greater fraction of the total ^{29}Si intensity than the atom fraction of Al.

Band B. This feature, which is more obvious in spectra without vertical expansion than in Figure 1, appears as a shoulder on the upfrequency limb of the Q^1 silicate band at about −7 ppm, so that the apparent integrated intensity of the Q^1 band is increased (Table I) rather than decreased as expected on the basis of loss of Si intensity to bands A–E (cf. the reduced contributions of the Q^0 and Q^2_A bands to the total Si intensity in the Al-containing solution). Band B accounts for some 40% of the total Al–O–Si intensity and is probably derived from Q^2_A (strained[3,12]) Si centers in Al-substituted derivatives of species such as the cyclic trimer (Q^2_3) or Harris and Knight's[3] structures VIII (pentamer with fused three- and four-Si rings) or IV.

Band C. This evidently arises from Q^2_B-type (i.e., relatively strain-free[3,12]) ^{29}Si resonances in Al-substituted derivatives of such silicate structures as the important cyclic tetramer (Q^2_4). Its integrated area is about one-fourth of the total for bands A–E.

Band D. This relatively weak feature is 4 ppm upfrequency from the silicate line due to the Q^2 center in the acyclic trimer $Q^1Q^2Q^1$, and is probably due primarily to the central Si in $O_3SiO(SiO_2)OAlO_3^{9-}$. In this part of the spectrum and at still lower frequencies, however, the possibility of additional spectral complexity due to second-order Al effects on the ^{29}Si NMR of nonvicinal Si atoms[16] must be borne in mind.

Band E. This minor peak correlates with the prominent resonance due to the strained double-three-ring cage silicate structure (Q^3_6) and is probably associated with Al-substituted derivatives of this anion.

Bands D and E together account for less than 10% of the total integrated intensity of bands A–E. Some definite spectral changes, notably peak height reductions, associated with the introduction of Al are discernible at $\delta < -19$ ppm, yet the decrease in the integrated ^{29}Si intensity for this area which would result (cf. the Q^2_A band) on adding Al if there were no ^{29}Si–O–Al resonances in this region does not occur. Thus, some Al insertion next to Q^3_B Si atoms must take place, although spectral complexity (perhaps due in part to second-order effects) prevents the identification of particular species. In any event, Table I shows that these Al–O–Si(Q^3_B) species are of minor importance.

It may therefore be concluded that the principal aluminosilicate species in solutions of the composition regime considered here are the Al-substituted derivatives of the silicate dimer (Q^1_2), cyclic trimer (Q^2_3), cyclic tetramer (Q^2_4), and (less importantly) the acyclic trimer ($Q^1Q^2Q^1$). At the low Al to Si concentration ratios used here, it is statistically unlikely that more than one Al would be present in a given aluminosilicate anion. Consideration of the foregoing assignments and integrated ^{29}Si intensities of the aluminosilicate species relative to the total amount of Si suggests that little or no free aluminate ion remains and that a large fraction of the bound Al is connected to more than one SiO_4 tetrahedron under the conditions specified for Figure 1.

The spectra of Figure 1 show that the addition of Al results in broadenings of 4.2, 5.7, 2.7, and 3.8 Hz for the Q^0, Q^1_2, Q^2_3, and Q^3_6 ^{29}Si peaks, respectively, and the broadening increases with temperature in the manner characteristic of control by chemical exchange[12,13] with site lifetimes τ in the range 60–120 ms at 5 °C. These are 10^2–10^3 times faster than Si–Si exchange in labile Al-free silicates under the same conditions,[12] so that these τ values reflect the Al exchange rates in aqueous aluminosilicates.

Aluminum-27 Spectra. Aluminum-27 spectra of sodium silicate/aluminate solutions were obtained on a Varian XL-200 spectrometer at 52.12 MHz with a pressurizable sample tube[14]

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(17) A silicate center of connectivity *y* in an all-silicate polymer is customarily designated Q^y. Thus, the acyclic trimer $O_3SiO(SiO_2)OSiO_3^{8-}$ can be represented by $Q^1Q^2Q^1$, and the cyclic trimer by Q^2_3. Except at very high pH, most silicate anions are protonated to variable degrees in water (ref 12 and 13); this is ignored here for convenience.

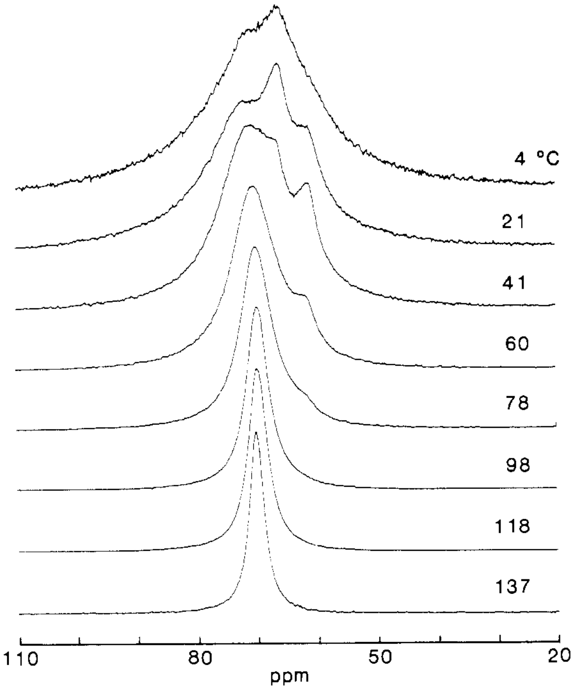

Figure 2. ^{27}Al NMR spectra (52.12 MHz) for the sodium aluminate/silicate solution of Figure 1. Chemical shifts are relative to an external aqueous $AlCl_3$ standard. All spectra were generated with 12 000–15 000 90° pulses of 70 μs with a 0.4 s repetition time, and include 2 Hz artificial line broadening. Peak areas are not normalized.

and a rebuilt probehead free of internal Al. Chemical shifts δ are referred to external aqueous $AlCl_3$.

Figure 2 shows ^{27}Al NMR spectra of the same solution as in Figure 1. At 4 °C, quadrupolar line broadening obscures spectral detail; this effect diminishes with rising temperature, but the features seen at about 70 and 66 ppm, representing Al coordinated to two and three silicate centers respectively,[5] coalesce at higher temperatures, indicating that Al site exchange is becoming rapid in the ^{27}Al NMR time frame just as in ^{29}Si NMR. Line-shape analysis of the ^{27}Al spectra for kinetic information, however, is impractical in this complex system.

A resonance corresponding to Al coordinated to a single Si center seems to contribute to the high-frequency tail of the band around 75 ppm. The feature at 61 ppm, which resists coalescence until relatively high temperatures are reached, seems to be due to a small, nonlabile fraction of the Al that is coordinated to *four* silicate units; the line is relatively narrow and is not removed by filtration of the solution or induction of precipitation, so it is evidently due to a dissolved species. A greatly retarded exchange rate would indeed be expected for such a species on mechanistic grounds, but no corresponding Q^4 silicate species seem to exist in aqueous solution.[12] In general, Figure 2 confirms the inferences, made above from the ^{29}Si spectra, that little or no free $Al(OH)_4^-$ (resonance frequency ca. 80 ppm[4,5]) is present and that most of the Al is connected to more than one SiO_4 unit, under the pertinent experimental conditions.

Figure 3 shows 52.12-MHz ^{27}Al NMR spectra of a solution containing 100-fold lower [Si] and 7-fold lower [Al] than that of Figures 1 and 2 ([Si] and [Al] are now equimolar). Spectral lines are sharper than in Figure 2 because chemical exchange is slower (greater dilution) and quadrupolar broadening is reduced (lowered viscosity). Although the strong resonance at 80.6 ppm shows that most of the Al content exists as free $Al(OH)_4^-$[4] at this dilution, peaks at 75, 70, and 66 ppm show that Al centers connected to one, two, and three Si units are present. Furthermore, there seems to be a preference for coordination of Al by two Si units, at least at elevated temperatures, as is also suggested by the above analyses of Figures 1 and 2.

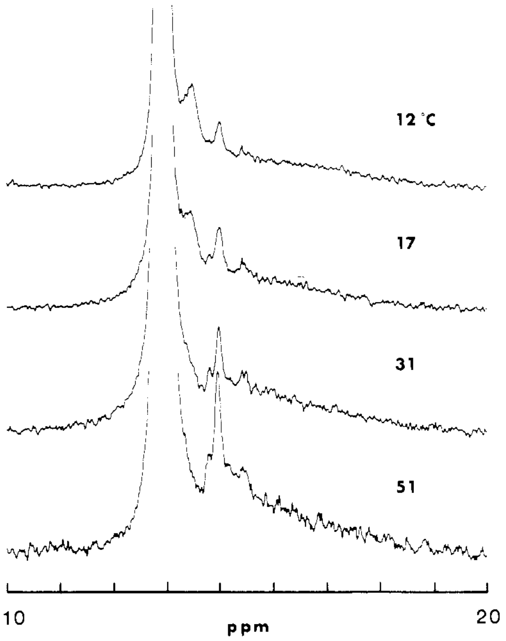

Figure 3. ^{27}Al NMR spectra (52.12 MHz) of a solution containing 0.010 mol kg^{-1} Si, 0.010 mol kg^{-1} Al, and 0.029 mol kg^{-1} NaOH. Peak areas are normalized on the area of the main resonance at 80.6 ppm. At 51 °C, some aluminosilicate was lost by precipitation.

The presence of some detail in Figure 3, such as the small peak on the upfrequency side of the 70 ppm band (best seen in the 31 °C spectrum), suggests that informative fine structure might be seen at higher field. Unfortunately, there was excessive background noise in ^{27}Al spectra obtained on the Bruker AM-400 instrument at 104.2 MHz, apparently arising from Al in the unmodified commercial probehead.

The contrast between the reluctance of aqueous $Al(OH)_4^-$ ion to polymerize and its ability to insert between Si atoms in silicate structures may be viewed as a manifestation, this time for solutions, of Loewenstein's rule[18] for solid aluminosilicates (i.e., that two Al atoms cannot occupy adjacent tetrahedral sites).

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Registry No. $O_3SiOAlO_3^{7-}$, 39357-31-8; $O_3SiO(AlO_2)OSiO_3^{9-}$, 120204-72-0; $O_3SiO(SiO_2)OAlO_3^{9-}$, 120204-73-1; $O(SiO_2)O(SiO_2)$-$OAlO_2^{8-}$, 120204-74-2; sodium silicate, 1344-09-8; sodium aluminate, 1302-42-7.

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