Aqueous Aluminates, Silicates, and Aluminosilicates

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1 Introduction

By far the most abundant elements in the Earth's crust are oxygen, silicon, and aluminium (62 6, 21 2, and 6 5 atom %, respectively) In this article, we present an overview of the aqueous solution chemistry of these elements in the context of some applications of current interest, with emphasis on the generally neglected topic of *aluminosilicates as aqueous solutes*

This relative neglect is due partly to experimental difficulties noted below, but chiefly to the perception that the solubility of aluminosilicate rocks, soils, *etc* , in water is very low under ordinary conditions of temperature and pH Dent Glasser and Harvey,[1] however, have shown that it is possible to create metastable solutions containing dissolved aluminosilicate ions at concentrations up to several tenths molar by mixing solutions of aluminates and silicates such that the onset of deposition of gels may be delayed for hours, days, or even weeks, depending on the concentrations of the reactants, the identity of the counter-ion(s), and the pH The gels eventually crystallize to form zeolites – aluminosilicates of the type $M_m[(AlO_2)_m(SiO_2)_n]\cdot pH_2O$ with open structures consisting of cages and channels (*e g* , Figure 1, $m \leq n$, from Loewenstein's rule – see below) and exchangeable cations M^+ to balance the charge-deficit of the Al^{3+} An understanding of these processes is required in connection with the synthesis of zeolites for use as heterogeneous catalysts, molecular sieves, cation exchangers, *etc* [2 4] Furthermore, aqueous aluminosilicates are important, even at low concentrations, in fields as diverse as environmental geochemistry, steam injection oil recovery, bauxite refining for aluminium production, kraft pulp mill operation, and the toxicology of aluminium,[5 7] and we give first a brief outline of some of these applications to place the chemistry in context

Soluble silicates ('waterglass') and/or aluminates are used in water clarification, textile treatment, adhesives, cements, and as detergent builders

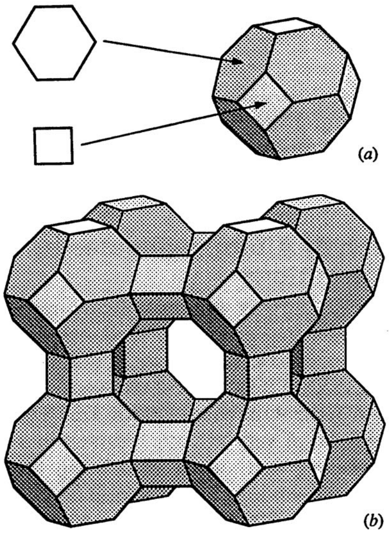

Figure 1 Schematic representation of the structure of (a) the sodalite cage, showing how this may be assembled in principle by corner-linking four-Si/Al rings or fusion of six-Si/Al rings, and (b) zeolite-A formed by corner-sharing of sodalite cages Each corner represents an Al or Si atom tetrahedrally surrounded by four oxygens, and each straight line includes a bridging oxygen
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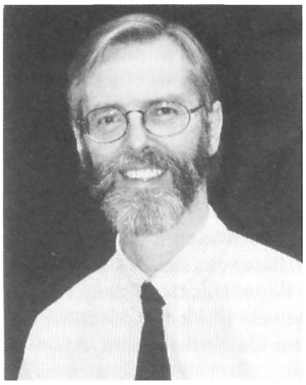

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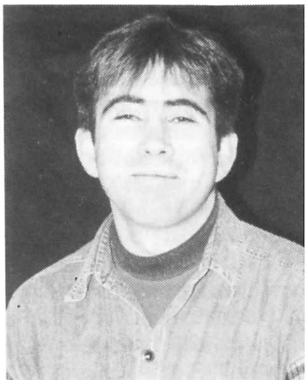
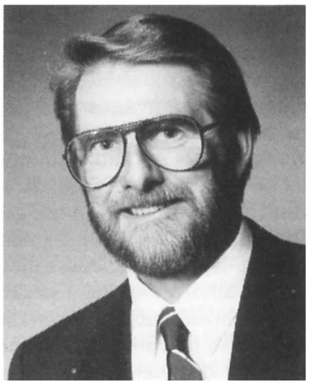


Julian Salerno

Julian Salerno was born in Melbourne, Australia in 1965 He obtained his B Sc (Hons) from the University of Melbourne where he is currently undertaking a multinuclear NMR investigation of speciation and dynamics in alkaline solutions of aluminates, silicates, and aluminosilicates The study is a joint Industry/University collaboration with the support of the Australian Research Council and Comalco Research and Technology

Tom Swaddle, a native of Newcastle upon Tyne, read chemistry at University College London (B Sc , 1958) and did research under Colin Eaborn at the University of Leicester (Ph D 1961) In 1964, following postdoctoral studies with John P Hunt and Edward L King in the U S A , he joined the academic staff of the University of Calgary where he is now professor of chemistry He has held visiting appointments at the Universities of Adelaide, Lausanne and Melbourne, and at the Tokyo Institute of Technology



Tom Swaddle

2 Aluminosilicates in Aluminium Production

Aluminium metal is generally produced by electrolytic reduction of alumina (α-Al_2O_3) in molten cryolite (Na_3AlF_6) with graphite electrodes – the Hall-Heroult process. Alumina of the requisite purity is usually obtained by the Bayer process, *i.e.*, by leaching bauxite ore with aqueous NaOH (initially some 10—15 mol l^{-1}), typically at about 165 °C and 600 kPa, whereupon the gibbsite, γ-$Al(OH)_3$, in the ore goes into solution as sodium aluminate while most of the silica or silicates present precipitate as insoluble aluminosilicates and are removed along with TiO_2 and iron(III) oxide/hydroxides as 'red mud'. Pure gibbsite then crystallizes from the filtered solution as it cools below about 70 °C, following seeding, and is calcined to give alumina. Not all of the silica, however, is precipitated as aluminosilicates at the 'red mud' stage, some continues to deposit slowly, usually as the zeolite-like solids sodalite or cancrinite (M = Na, $m = n = 6$, $p = 8$) or, below *ca.* 70 °C, zeolite-A (Figure 1), so fouling the equipment and possibly contaminating the alumina product. Similar problems arise from the use of alkaline pulping liquors in kraft paper mills. It would appear, then, either that some long-lived soluble aluminosilicate species exist in the Bayer solutions, or that the formation of sodalite or cancrinite precursors from aluminate and silicate species can be slow, even at *ca.* 165 °C.

3 Formation of Aluminosilicates by Water–Rock Interactions

Many naturally-occurring aluminosilicate minerals form by geological hydrothermal processes,[3] and, not surprisingly, similar solids may form as a consequence of industrial activity such as (for example) steam injection oil recovery. Major reserves of petroleum exist in the Athabasca Oil (or Tar) Sands of northern Alberta in the form of very viscous bitumen in a sandy matrix. The most promising method of recovering the more deeply buried reserves involves injection of steam or superheated water at temperatures up to 300 °C and pressures up to 5 MPa, and collecting the produced petroleum. The sandy matrix, however, is significantly soluble in hot water, especially if the pH is high, and hydrothermal reactions occur between the small amounts of clay minerals, dolomite, *etc.*, and the predominant quartz. Thus, in addition to silica reprecipitated in the cooler regions of the water flow path, deposits of voluminous aluminosilicates such as montmorillonite and zeolites (notably analcime, formation of which is associated with hot water-silica systems low in Al^{III}) may form, blocking the communication path and impeding production. This process is not necessarily disadvantageous – it may close off a depleted section of the geological formation – but clearly, if it is to be controlled, knowledge of the solution chemistry of silicates and aluminosilicates is required.

4 Synthesis of Zeolites

Synthetic zeolites are generally made by mixing solutions of aluminates and silicates, often with formation of a gel, and maintaining the mixture at temperatures of 100 °C or more for selected periods.[2–4] The identity of the crystalline product depends upon the reaction time and temperature, the solid surfaces present, and the specific solution conditions – particularly the nature of the cation(s) and any organic solutes. Thus, zeolite A, sodalite and cancrinite tend to form in aqueous Na^+ media (as in the Bayer process), while zeolites with low Al content are favoured by large cations such as tetraalkylammonium (R_4N^+). In his seminal study of the kinetics of formation of zeolites A, B, and X, Kerr[8] found that nucleation in the gel was slow, but both spontaneous nucleation and the subsequent OH^--accelerated growth of the zeolite crystal were controlled by some solute species derived from the amorphous gel. Indeed, if the findings of Bell *et al.*[9] can be generalized, such gels contain little Al, and form through destabilization of a silica sol by the added aluminate, so that the formation of aluminosilicates is solution-mediated. Furthermore, analcime (for example) can be grown from clear, non-colloidal silicate solutions very low in Al.[2] Thus, the consensus[2] is that the formation of zeolites in general involves redissolution of any precipitated gel (or metastable zeolite intermediates), rather than internal reordering of the gel itself.

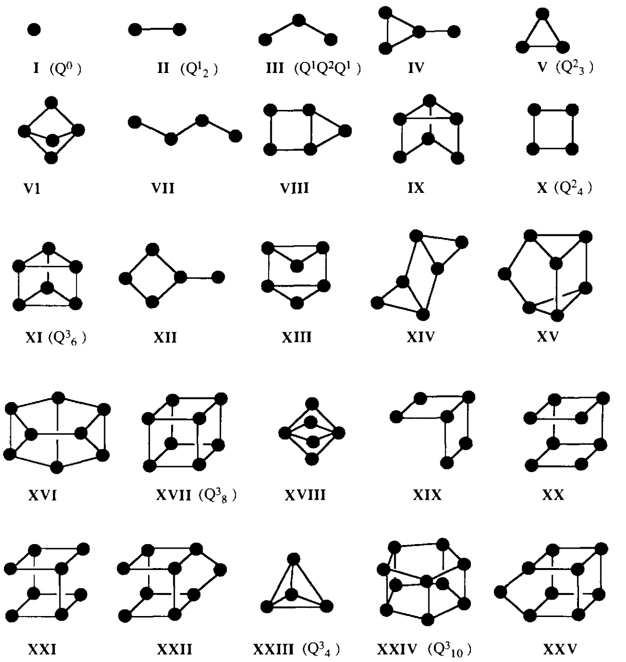


Figure 2 Silicate structures that have been detected by ^{29}Si-NMR in alkaline aqueous media. Filled circles represent Si atoms tetrahedrally coordinated by O atoms; lines represent links through O atoms. Structures I—XIX and XXIII are numbered according to Harris and Knight (reference 20). From references 9, 12 and 20.

Water is important as a guest molecule in zeolite structures with relatively high Al contents, and consequently aqueous media favour their formation, while salts have a parallel role in the stabilization of sodalite and cancrinite. Highly siliceous zeolites such as silicalite and ZSM-5, which have zeolitic structures but contain very little Al^{III} and M^{m+}, are less hydrophilic than aluminous zeolites, and their structures can be stabilized by certain organic guest molecules – notably amines, alcohols, and amino-alcohols. There is, however, no obvious general correlation between the geometries of the organic molecules and the structures they promote. Similarly, although cations such as R_4N^+ are commonly said to direct the structure of the zeolitic product by acting as a template, this should not be construed to mean that the ions act simply as objects of the right geometry around which Al- and Si-containing units assemble themselves. Thus, we need to understand, not only the speciation and properties of aqueous Al- and Si-containing anions, but also how these are affected by cations and organic molecules.[10,11]

Direct correlations between the structures of precursor solutes and zeolite products, however, may be difficult to establish. For example, although the structure of ZSM-5 is based on pairs of rings containing five silicon atoms (linked by oxygens), there is no definite proof that the 'double-five-ring' aqueous silicate anion (Q^3_{10}, in which Q^x represents an SiO_4 centre of connectivity x – species XXIV of Figure 2) is a precursor of ZSM-5, even though ZSM-5 certainly forms in solutions in which XXIV is known to be the predominant silicate species.[2] Furthermore, the smaller silicate[12] and especially the aluminosilicate[13] species that have been identified in alkaline aqueous solutions are very *labile* in the exchange of silicate and/or aluminate units, although some larger silicate oligomers such as the cubic octamer (Q^3_8) are relatively inert.[14] Consequently, the structure of aluminosilicate solids grown from aqueous solutions or gels need not necessarily reflect the structures of the predominant solute species, as these, with the exception of the larger oligomers, might rearrange 'on demand' at the growing crystal surface For example, Figure 1 shows that the zeolite A structure can, in principle, be assembled by the corner-linking of Q_4^2 (cyclic tetramer, species X) units, but these are in labile equilibrium with other small species such as I—V and VII [12] Conversely, if the larger oligomers are building-blocks for growth of the solid phase, the rate of crystallization could be controlled by the rate of formation of these in solution One source of difficulty is that the mechanisms of nucleation and of subsequent crystal growth might well be different – small, labile oligomers may add rapidly to a nuclear structure that formed only slowly In any event, it is clear that knowledge of the *kinetics* of aluminate, silicate, and aluminosilicate exchange reactions at various pH and temperatures is a prerequisite for understanding hydrothermal zeolite formation

5 Toxicology of Aluminium and the Biological Role of Silicon

Several excellent articles on the role of aluminium in medicine and biology have recently appeared [7,15–17] Debate has tended to centre upon the highly controversial question of the apparent association of Al$^{\text{III}}$ with Alzheimer's disease (AD) – a form of senile dementia characterized by the development of neurofibrillary tangles and β-amyloid protein plaques and loss of neurons in the patient's brain Since 1973, several research groups have reported (though some have denied) that *post mortem* examinations of brain tissue from victims of AD showed aluminosilicate material within the β-amyloid plaques by conventional microscopy This seemed to vindicate inferences of the involvement of Al in AD made from epidemiology (there are correlations between the incidence of AD and the Al content of water supplies), observations of Al-induced dementia amongst renal dialysis patients, retardation of the progress of the disease by administration of the Al^{3+}-chelating agent desferrioxamine, and so forth, but in late 1992 Landsberg *et al* [18] used *nuclear* microscopy to study neuritic plaques and found no evidence for the presence of increased levels of Al in them They pointed out that aluminium is so widespread in the environment (*e g* , in dust) that it is extremely difficult to eliminate it from experimental materials – in this case, from the staining solutions necessary in conventional microscopy This echoes a familiar problem in the analytical chemistry of low levels of Al, in which samples often appear, embarrassingly, to have negative Al contents relative to controls

Medical interest in Al from the standpoint of AD research has therefore waned in recent months (perhaps wrongly), but the broader issue of the toxicology of Al^{3+} remains – for toxic it most certainly is, being unequivocally implicated in bone deterioration (osteomalacia) and dementia (dialysis encephalopathy) in dialysis patients Because Al^{3+} is strongly bound by transferrin in the blood, a few tens of μmol l^{-1} of Al$^{\text{III}}$ in the dialysis fluid (as when the fluid is made up with tapwater, in some locations) will prevent Al excretion and, in fact, cause Al$^{\text{III}}$ to pass in reverse into the bloodstream, leading to toxic effects The symptoms of Al intoxication generally disappear when 'Al free' dialysis fluid is used Fish are very susceptible to gill damage by Al^{3+} (aq), and massive fish kills through acidification of lakes to pH < 5 by acid precipitation reflect the dissolution of the normally poorly-soluble $Al(OH)_3$ Root growth in acid-sensitive plants is suppressed by Al$^{\text{III}}$ The toxic action of Al^{3+} at the cellular level is incompletely understood,[17,19] but probably it displaces Mg^{2+} in several processes and binds strongly to phosphate functions in ADP, ATP, and phosphorylated proteins

Our daily intake of Al in food and water is typically 2—25 mg,[15] but can be much more [*e g* , if $Al(OH)_3$-based antacids are taken] Why, then, is Al poisoning rare? First, the toxic form of Al$^{\text{III}}$ is Al^{3+}(aq),[17b] whereas Martin[7,16,19] has shown (Figure 3) that at physiological pH the only important form of aqueous Al$^{\text{III}}$ is $Al(OH)_4$ and the saturated concentration of Al^{3+}(aq) becomes sub-nanomolar Second, ingested Al^{3+} becomes firmly bound to the intestinal mucosal cells and is excreted through the lumen as these die, so that only some 2 μg Al normally gets past the gastrointestinal barrier per day, while up to 20 μg per day can be excreted in the urine Third, the concentration of free Al^{3+}(aq) can be still further depressed by complexation with chelating agents such as citrates or maltol, which are common constituents of foods (there is, however, a risk of enhanced Al absorption with citrate, since the chargeless citratoaluminium complex can pass relatively easily through biological barriers), or with *dissolved silica* Silica is beneficial to many living things – *e g* , it is essential for normal development of bones in rats and chickens – and Birchall[7,17] has argued convincingly that, in many cases, this property derives from complexation of Al$^{\text{III}}$ by aqueous $Si(OH)_4$ to give *soluble aluminosilicate species* such as $(HO)_3SiOAl(OH)_3$, so depressing the free Al^{3+}(aq) level still further Thus, the apparent correlation of the incidence of dementia with the Al content of drinking water may actually reflect an *inverse* correlation with dissolved silica (and so explain the absence of a dose–effect relationship in the Al intake, most of which comes from food, not water) [17] Similarly, dissolved silica can protect fish from acute Al poisoning in acidic ground waters [17d] The characterization of these postulated soluble aluminosilicates is therefore important in biomedical contexts

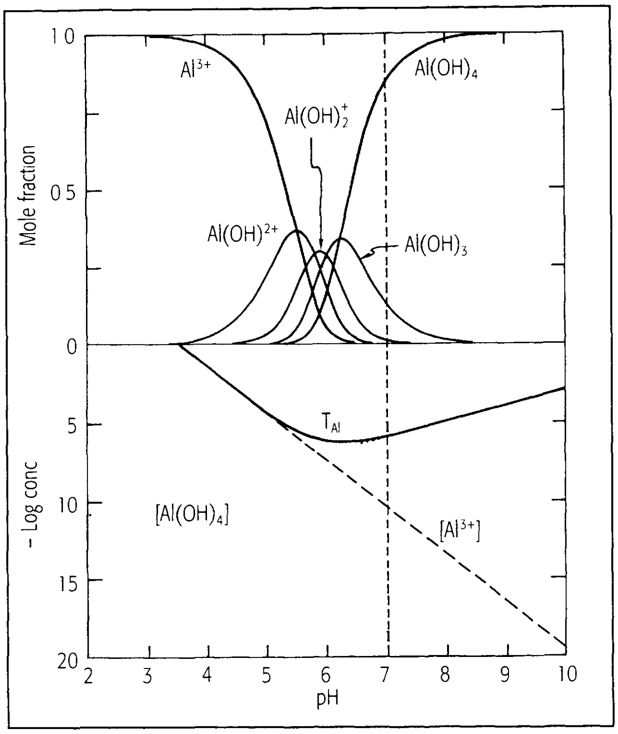


Figure 3 Distribution of monomeric species as a function of pH in hydrolysis of Al$^{\text{III}}$ Upper frame mol fraction of soluble species Lower frame molar concentrations of Al^{3+} (dashed line), $Al(OH)_4$ (dotted line) and total dissolved Al (T_{Al} solid curve)
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6 Experimental Methods

Until relatively recently, it was difficult to learn much about aluminium and silicate solutes because of the lack of characteristic Al or Si features in UV/VIS spectra (the weak UV bands sometimes reported for aluminates at high pH are probably artefacts due to traces of transition metal ions), redox electrochemistry, *etc* , while pH measurements, conductiometry, and vibrational spectra give ambiguous results Trimethylsilylation of silicate solute species gives volatile products that can be separated and identified by gas chromatographic methods[4] – for example, the cubic octamer $Si_8O_{20}^{8-}$ gives rise to $Si_8O_{12}(OSiMe_3)_8$ – but, since many of the smaller silicate oligomers are very labile,[12,14] trimethylsilylation is likely to perturb the equilibria among them, and the yields of the trimethylsilylated product may not represent the original distribution of silicate solute species.

Nowadays, however, with the routine availability of Fourier transform multinuclear magnetic resonance spectroscopy at magnetic fields of 4.7 T and higher, structural, thermodynamic, and kinetic information *specific to* ^{29}Si, ^{27}Al, and ^{17}O can be obtained 'non-invasively', *i.e.*, without perturbing the solution chemically. Furthermore, NMR spectra (chemical shifts) of species in solution can be compared with those of relevant solids of known structure.[4] Silicon-29 is the most useful nucleus,[10,12,14,20–23] as it gives sharp-line spectra (spin quantum number $I = \frac{1}{2}$) and hence detailed structural information, in the absence of chemical exchange. Its natural abundance (4.7%) and receptivity (about twice that of ^{13}C), however, are not high. Additional structural information (from $^{29}Si-^{29}Si$ coupling) as well as increased sensitivity is obtainable with highly enriched ^{29}Si, but this currently costs around $(US)8000 for 100 mg of 94% ^{29}Si as SiO_2. Kinetic information on Si site exchange can be extracted from ^{29}Si line broadening,[12,21] 2D-NMR,[14] or selective inversion recovery methods.[12,22] The longitudinal relaxation time T_1 of ^{29}Si in aqueous silicates is fortunately much shorter than in solids or organosilicon compounds, but is dependent in a perplexing way on the nature of the cation; ion pairing is presumably involved.[23] Aluminium-27 has good receptivity and 100% abundance, but is quadrupolar ($I = \frac{5}{2}$) and so gives rather broad lines.[24] Oxygen-17 also has $I = \frac{5}{2}$ but its receptivity is low [0.061 that of ^{13}C, natural abundance 0.037%, 20% enriched water costs about $(US)320 per g] and it has been little used in this field.[25]

7 Silicate Solutions

The solubility of silica in water is not simply stated, as it depends markedly on the particle size and form of the solid (quartz, cristobalite, tridymite, vitreous, *etc.*) and the degree of polymerization of the solute, and increases with increasing alkalinity, temperature, and pressure.[26] As working numbers, however, the solubility of quartz in pure water at 25 °C and 0.1 MPa may be taken to be 11 mg kg^{-1}, and that of amorphous silica to be 60—200 mg kg^{-1}. Sjoberg and co-workers[27] found the pK_1's for acid ionization of monomeric silicic acid $Si(OH)_4$ and $(HO)_3SiO^-$ to be 9.47 and 12.65, respectively, at 25 °C and ionic strength 0.6 mol l^{-1}, with various values for silicate oligomers [*e.g.*, for $(HO)_3SiOSi(OH)_2O^-$, 10.25], so that the average charge *per* Si is essentially -1 at pH $\approx$ 10—12 with correspondingly high solubilities.

The definitive work of Harris and Knight[20] used high-field (11.75 T) ^{29}Si NMR of enriched samples with homonuclear $^{29}Si-\{^{29}Si\}$ decoupling to identify unambiguously 18 silicate oligomers in KOH/SiO_2 solutions with $K^+:Si = 1:1$ to $2:1$, $[Si] = 0.6$ mol l^{-1}; these are the species denoted by I—XVIII in Figure 2. Silicate centres with four-way connectivity (Q^4) are generally not observed in solution,[9,12] evidently because their formation would nucleate gelation. Knight *et al.*[28] have subsequently used multiple quantum filtered NMR to confirm the presence of six (but *only* six) single-Si-site silicate species in solutions with $K^+:Si = 1:1$, $[Si] \approx 1.5$ mol l^{-1}; these are species I, II, V, X, XI, and, with less certainty, the P_4O_{10} analogue XXIII.[12] In particular, the cubic (Q^3_8, species XVII) and pentagonal prismatic (Q^3_{10}, species XXIV) structures identified in aqueous Me_4N^+ and Pr_4N^+/aqueous dimethylsulfoxide media, respectively,[4,14] and the hexagonal prism (Q^3_{12}) characteristic of many zeolite structures were not detected (< 3% of [monomer]). This illustrates the strong influence of cations on the distribution of silicate species in solution. Similarly, Kinrade and Pole[11] found that complexation of Na^+ in sodium silicate solutions by cryptand 2.2.2 led to large increases in the (albeit still small) fractions of the single-Si-site cage structures XXIII (Q^3_4), XVII (Q^3_8) and, less markedly, XI (Q^3_6). Undoubtedly, anion–cation pairing is one of several influences acting on the species distribution,[9,10,23] with the smaller cations (hydrated alkali metal ions) expected to pair more strongly than the larger. On this basis, the observations suggest that pairing of the smaller, more labile silicate units with cations *deactivates* them towards condensation to the cage structures.

Lowered Si concentrations or increases in temperature or pH favour the monomer and small oligomers,[12] so that the ^{29}Si spectra become simpler as the alkali to Si ratio is increased. Increased temperature and [Si], however, also cause line broadening attributable largely, if not entirely, to the increased rate of Si site exchange between silicate units, mediated mainly by the attack of $Si(OH)_4$ or possibly $(HO)_3SiO^-$ on $O-Si\equiv$ in the case of intermolecular exchange or by intramolecular ring opening and closure (*e.g.*, interconversion of species III and V, or of VII and the less labile X), the intramolecular processes being the more rapid.[12,14] The dependence of the line-broadening on [Si] reflects the intermolecular site exchange pathways, but no simple rate equation can be derived because of the plethora of known and hypothetical[12] silicate species that are likely to be simultaneously involved. The doubly deprotonated monomer $(HO)_2SiO_2^{2-}$ and presumably other Si centres with more than one local negative charge are relatively inert towards exchange,[12] with the result that Si site exchange is slower, and ^{29}Si spectra sharper with fewer lines, at high pH.

Caution must be exercised when interpreting NMR line broadening in terms of chemical exchange, since field inhomogeneities, ion pairing, relaxation by paramagnetic impurities, and other factors might mimic chemical exchange in causing line broadening that increases with rising temperature, but the *selective inversion recovery* technique introduced by Creswell *et al.*[22] shows clearly that magnetization is transferred between Si sites at measurable rates that can only be due to chemical exchange. It should be noted that the ^{29}Si selective inversion recovery experiments described to date[12,22] have been conducted at higher pH than most line-broadening studies, for the sake of simplified spectra, and so show slower site exchange rates (*e.g.* site exchange time constants decrease by about 100-fold when the $KOH:SiO_2$ ratio is increased from 1:1 to 4.5:1).

Because of the complexity of the exchanging systems, it is difficult to extract reliable rate constants for specific reactions, but for hydrolysis of $^-O(HO)_2SiOSi(OH)_2O^-$ the first order rate constant is 14 s^{-1} at 25 °C and $\Delta H^\ddagger$ is 51 ± 2 kJ mol^{-1}.[12] Thus, substitution in this small oligomer is rapid on the preparative timescale. In contrast, in Me_4N^+ silicate solutions that have been quenched from boiling (where the monomer and small oligomers are the most abundant species), the prismatic hexamer XI 'grows in' over a period of several hours at room temperature, while the ultimately dominant cubic octamer XVII continues to grow at the expense of all other silicate species over several days.[14] Rigid Q^3 cage species such as XI and XVII will be sterically very resistant to the S_N2-type reaction mechanism that is typical of Si^{IV} centres, so, once formed, they may become 'black holes' into which smaller oligomers disappear. From the standpoint of zeolite formation mechanisms, however, it would seem that the predominant aqueous silicate species at synthesis temperatures (usually ≥ 100 °C) are the smaller, labile oligomers, so that rapid reorganization of these, rather than the presence of specific preformed cage structures in solution at equilibrium, may provide the primary route to crystal growth, although nucleation may still require the formation of a cage.

8 Aluminate Solutions

Figure 3 summarizes the speciation of dilute Al^{III} solutions as a function of pH. A striking feature is the very narrow pH range (compared with, say, Fe^{III}) between the predominance of $Al(H_2O)_6^{3+}$ and that of $Al(OH)_4^-$, with only minor roles for $AlOH^{2+}$, $Al(OH)_2^+$, and dissolved $Al(OH)_3^0$; this reflects the facility with which Al^{III} can change from 6- to 5- to 4-coordination.[16,19] By contrast, SiO_6 centres form only at pressures of several GPa.

The ^{27}Al-NMR-based work of Akitt's laboratory[24] has done much to clarify the chemistry of Al^{III} hydrolysis. In acidic solutions, partially hydrolysed Al^{3+}(aq) can dimerize to $(H_2O)_4Al(\mu\text{-}OH)_2Al(OH_2)_4^{4+}$, but this is not normally found in significant concentrations[19] Indeed, solid salts of this ion disproportionate in water to the monomer and polymers, showing once again that solid phases need not show any direct structural relation to their progenitors in solution If, however, the temperature, basicity, and [Al] are kept low during hydrolysis to avoid the formation of higher polymers,[29] the remarkably stable tridecamer $(AlO_4)Al_{12}(OH)_{24}(OH_2)_{12}^{7+}$ can form[24] This ion contains a central Al^{3+} in a highly symmetrical *tetrahedral* O environment, surrounded by four blocks of three *octahedrally* coordinated edge-sharing AlO_6 units (an isomer of the familiar Keggin structure) The quadrupolar ^{27}Al nucleus gives relatively narrow NMR lines only when the electric field gradient at the nucleus is small or zero, so that the single central Al gives a well-defined NMR line but the 12 peripheral Al nuclei are hard to detect because the comparatively low symmetry of their environments causes excessive line broadening[24] This problem of 'missing Al' is widespread and plagues efforts to use ^{27}Al NMR quantitatively, particularly at low magnetic field strengths and temperatures

Early work on Al^{III} speciation at $pH \geq 7$ – that is, the pH range relevant to the Bayer and kraft processes – has been summarized by Eremin *et al*[30] From infrared/Raman and NMR spectra and other information, it was recognized that the solutions were not colloidal and that the only important Al species at $7 \leq pH \leq 13$ is tetrahedral $Al(OH)_4^-$, whether or not the solutions are allowed to 'age' (which results in some drift in pH, if this is initially in the 8—10 range) Linear AlO_2^-, square planar $Al(OH)_4^-$, $Al(OH)_4(OH_2)_2^-$, and significant concentrations of polymeric aluminates were specifically ruled out At pH > 13, however, it might be anticipated that Al^{III} might expand its coordination number to six to form $Al(OH)_6^{3}$, which is known as the solid calcium salt, while at high [Al] and low water activities $Al(OH)_4$ does appear to condense to $(HO)_3AlOAl(OH)_3^{2}$, the potassium salt of which is of known structure and has infrared and Raman spectral features that correspond to those that appear in aluminate liquors as [Al] is raised above 1 5 mol l^{-1} Measurements of pH at high alkalinities are impractical because the electrodes are attacked Even liquid-phase ^{27}Al NMR is not very helpful in concentrated solutions,[24] as anion–cation pairing, the higher viscosity, and rapid Al–Al site exchange may broaden the lines, while the reduced site symmetry in any oligomeric species present may lead to a 'missing Al' problem Indeed, the presence of polymeric aluminates may be revealed by the reduction in intensity of the $Al(OH)_4$ line Nevertheless, Akitt *et al*[24] found ^{27}Al-NMR evidence for $Al(OH)_6^{3-}$ in addition to $Al(OH)_4^-$ in extremely alkaline solutions (23 mol l ^{1} NaOH, 0 95 mol l ^{1} Al^{III}), while a recent *solid state* ^{27}Al NMR study[31] of Na aluminates precipitated by acid hydrolysis from solutions of high pH (OH Al = 3 9—5 3, [Al] ≈ 1 mol l ^{1}) suggests that some polyoxoanion(s) containing six-coordinate Al^{III} are present in the solution phase

A critical piece of missing information in aqueous aluminate chemistry is the rate of substitution at Al centres If chemical exchange in aluminate species were rapid on the NMR timeframe, little or no structural information could be gleaned from ^{27}Al NMR spectra Kinetic information on aqueous aluminosilicates (see below) suggests that this may indeed be the case at room temperature and above, and preliminary ^{17}O NMR line-broadening studies in our Melbourne laboratory on the aqueous $Al(OH)_4^-$/OH exchange rate seem to confirm this rapid exchange process

9 Aluminosilicate Solutions

Engelhardt and Michel[4] reviewed the NMR literature on aqueous aluminosilicates up to 1987, at which time the existence of aluminosilicate species in *alkali metal* hydroxide solutions had not been proven because of low solubility in typical preparations, two Raman studies, for example, had led to opposite conclusions Experience with the ^{29}Si NMR of solid aluminosilicates, however, enabled them[4] to predict the likely chemical shift ranges of Si atoms in a Q^x(y Al) environment (where x is the total connectivity through oxygens to Si *and* Al atoms, and y is the number of those atoms that are Al) Thus, it was expected that a Q^x(1Al) resonance would generally lie about 5 ppm downfield from an analogous Q^x line It was recognized that such features would be most likely to be observable in metastable solutions such as were described by Dent Glasser and Harvey,[1,2] but no lineshifts or new ^{29}Si NMR lines were found, only some broadening of the Q^0 and Q^1 lines We suggest that this broadening was due to rapid formation and hydrolysis of Al–O–Si links, this would imply that the already weak aluminosilicate Si lines would be broadened too much to be observed, and also that Al–O–Si links are *more labile* than their Si–O–Si analogues, since the latter gave sharp ^{29}Si lines under the same conditions

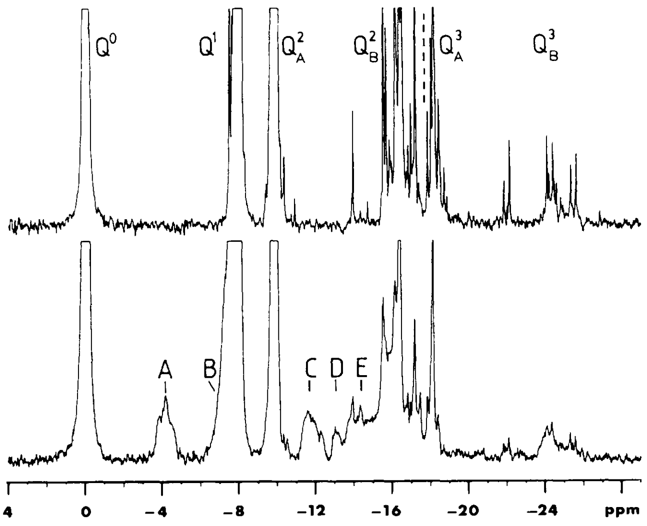

Figure 4 Vertically expanded ^{29}Si NMR spectra (79 49 MHz) of solutions containing 1 1 mol kg ^{1} SiO_2 and 2 4 mol kg ^{1} aqueous NaOH at 5 °C the lower spectrum is of a solution that also contained 0 07 mol kg ^{1} Al^{III} The spectra are normalized to give equal areas of the Q^0 resonance, and include 2 4 Hz artificial line-broadening
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Thus, Kinrade and Swaddle,[13] again using Dent Glasser–Harvey supersaturated solutions, were able to demonstrate the existence of Al–O–Si species with ^{29}Si NMR on a 9 4 T spectrometer by cooling the solutions to 5 °C to slow down this inferred aluminate–silicate exchange Figure 4 shows that the addition of a small quanity of sodium aluminate solution to an excess of aqueous silicate produced new ^{29}Si resonances due to aluminosilicate solute species, 4—5 ppm downfield from silicate lines of known origin, and also broadened the silicate line to an extent consistent with Si site lifetimes in the aluminosilicate environments of some 60—120 ms, implying exchange rates some 10^2—10^3 times faster than for comparable silicate sites[13] Because of some overlapping of the new aluminosilicate bands A—E in Figure 4, the identification of the individual aluminosilicate solute species (Figure 5) remains to some degree tentative

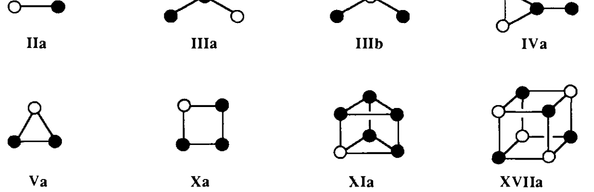

Figure 5 Structures of aqueous aluminosilicate species assigned tentatively from ^{29}Si and ^{27}Al NMR spectra Code and numbering follow Figure 2 open circles represent Al atoms From references 4 13 23 and 34

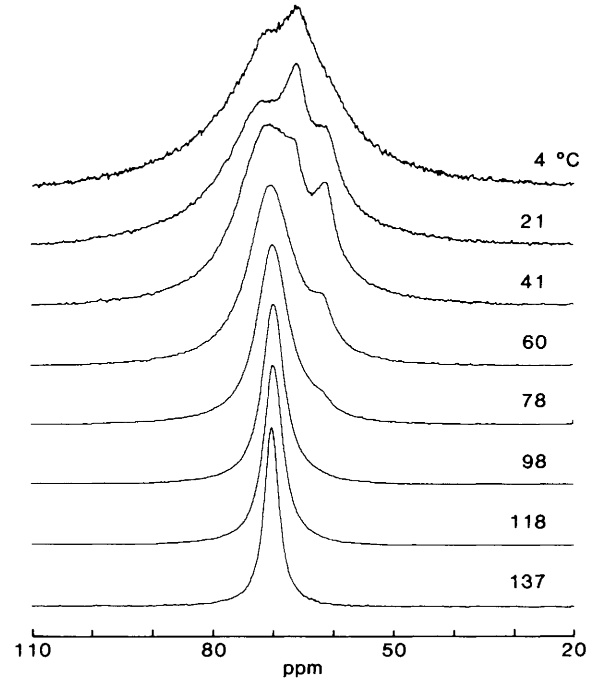

Figure 6 ^{27}Al NMR spectra (52 12 MHz) for the sodium aluminate/silicate solution of Figure 4 Spectra are not normalized, and include 2 Hz artifical line broadening
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Figure 6 shows the ^{27}Al NMR spectrum of the aluminate/silicate solution of Figure 4, three distinct ^{27}Al resonances emerge as the temperature is raised from 4 °C, in accordance with the expected sharpening of quadrupolar resonance lines with rising temperature, but above 41 °C this structure is lost because of chemical exchange line broadening Figure 6 confirms that the aluminosilicates present are 2—3 orders of magnitude more labile than the analogous silicate species Again, the limitations placed on NMR-based structural studies by chemical exchange kinetics are emphasized

Bell and co-workers,[23] using high-field (11 7 T) ^{29}Si, ^{27}Al, ^{23}Na, and ^{133}Cs NMR techniques including DANTE 'hole-burning', found that the extent of aluminosilicate formation in Na or Cs aluminate/silicate (Al Si = 1 0) solutions increased with the ratio of silica to alkali, *i e* , as the solutions became less alkaline, and that aluminate ions reacted more extensively with the more acidic silicate species such as the cyclic trimer (Q_3^2) – in accordance with quantum mechanical calculations[32] that predict that the substitution of Si by Al in an aluminosilicate framework should be favoured by the presence of a proton The ions $(HO)_3AlOSi(OH)_2OSiO_3H_{3-q}^{(q+1)-}$ and $(HO)_3AlOSiO_3H_{3-q}^{(q+1)-}$ were also detected, but the formation constants of these (particularly the latter) seemed to be small under the experimental conditions Increased cation size (reduced ion pairing) also favoured aluminosilicate formation, and this is precisely as would be expected if, as proposed above, pairing of the smaller oligomers with cations deactivates them toward reaction with further silicate or aluminate units

The solubility limitations of alkali-metal aluminosilicate solutions can be avoided by going to R_4N^+ solutions, but in these media specific silicate cage structures such as XI and XVII of Figure 3 tend to predominate Engelhardt and Michel[4] summarize trimethylsilylation and ^{29}Si NMR evidence for the presence of $Q^3(3Al)$ centres (presumably substituted into structure XVII) and, less certainly, some $Q^2(2Al)$ species in Me_4N^+ aluminate/silicate solutions that have first been heated to 90 °C and then cooled to room temperature Interestingly, little or no substitution of Si in cages by Al seems to occur in unheated solutions, showing once again that silicate cage anions are much less labile than the smaller oligomers In tetraethylammonium (Et_4N^+) solutions with Si Al = 4, three new ^{29}Si NMR peaks show up clearly in addition to the singlet due to the Q_6^3 of silicate XI ($Si_6O_{15}^{6}$), the new peaks arise from the three distinct Si sites relative to the single Al in the monosubstituted trigonal prismatic cage $Si_5AlO_{15}^{7}$ Ziemens *et al* [33] found ^{29}Si NMR and trimethylsilylation evidence for the cubic $Si_7AlO_{20}^{9}$ coexisting with $Si_8O_{20}^{8}$ (silicate species XVII) in triethyl(hydroxyethyl)ammonium aluminate/silicate solutions, while a more detailed ^{29}Si NMR study of aqueous and methanolic Me_4N^+ aluminate/silicate solutions by Bell's group[34] found these same species in high concentrations Aluminium-27 NMR of Me_4N^+ aluminate/silicate solutions has similarly provided evidence for Al centres $Al(OSi)_n(O\ \ )_{4-n}$ with Si connectivity *n* [4 24] Fahlke *et al* [35] noted that ^{27}Al NMR features attributed to aluminosilicate solute species in the synthesis mixtures of zeolites X and Y were broad, and interpreted this breadth as reflecting the presence of many such species, but we suggest that it could also indicate rapid chemical exchange of aluminate units in these species, as noted above Finally, Bell *et al* [34] have used both ^{29}Si and ^{27}Al NMR spectra of dilute but highly alkaline tetrapropylammonium aluminate/silicate solutions to identify Si centres with $Q^1(1Al)$, $Q^{2\Delta}(1Al)$, $\{Q^{2\Delta}(1Al) + Q^{3\Delta}(1Al)\}$, and $Q^3(1Al)$ connectivity (Δ signifies a 3-Al/Si ring), and Al with Si connectivity 0, 1, 2, and 3 (Figure 5) Interestingly, the trigonal prismatic hexameric silicate (Q_6^3, species XI) appeared not to react with $Al(OH)_4$ in these solutions, which is consistent with Engelhardt and Michel's observation[4] on Et_4N^+ solutions that the hexamer is unreactive unless broken up at high temperatures Additions of 20% or more dimethylsulfoxide to the solutions increased the abundances of silicate species XI and XVII, whereupon new features in the ^{29}Si and ^{27}Al NMR spectra, corresponding to Al substitution into these, were observed

The readiness with which Al^{III} becomes incorporated into tetrahedral sites in aluminosilicates contrasts with the reluctance of $Al(OH)_4$ units in solution to join together to form aluminate oligomers In aluminate solutions in aqueous alkali, even the dimer $(HO)_3AlOAl(OH)_3^2$ forms (if at all) only under forcing conditions of low water activity Such polymers of Al^{III} as are known to exist in water (including the tridecamer, which has one tetrahedral Al surrounded by linked octahedral AlO_6 units) are formed at pH < 7 from *octahedral* AlO_6 units, as are also found in the gibbsite that precipitates from (alkaline) Bayer process liquors In aluminosilicate mineralogy, this avoidance of direct links between AlO_4 tetrahedra is known as Loewenstein's rule, and may be thought of in terms of minimizing electrostatic repulsions between the excess negative charges associated with the AlO_4 centres [3] Recent theoretical studies[36] show that extended aluminosilicate structures with Al–O–Al links would be some 120 kJ mol^{-1} higher in energy per Al pair than equivalent structures with Al–O–Si–O–Al links The experimental evidence available to date suggests that Al^{III} in aqueous aluminosilicates avoids Al–O–Al links, and prefers coordination by two Si tetrahedra over single connectivity [13]

The stability of aqueous aluminosilicates is difficult to express quantitatively At pH up to 12, solutions contain a large number of silicate oligomers into which one or more aluminate units could be incorporated At higher pH the stabilities of aluminosilicates are reduced and there are uncertainties over the possible occurrence of oligomeric aluminates or six-coordinate Al centres as in $Al(OH)_6^3$, as well as over the degree of secondary deprotonation of the (less numerous) silicate species Thus, in a study of the solubility of sodalite at 95 °C (ionic strength 4 0 mol kg^{-1}, NaOH/NaCl) with $[OH^-] = 0\ 1$ to 4 0 mol kg ^{1}, Gasteiger *et al* [6] found that the apparent [Al][Si] product rose strongly with increasing [OH], but this reflects the deprotonation of $(HO)_3SiO$ and $(HO)_2SiO_2^2$ rather than any increase in the stability of soluble aluminosilicates Yokayama *et al* ,[37] using ^{27}Al NMR, found a formation constant of 22 8 l mol ^{1} for $H_{3\ \ q}O_3SiOAl(OH)_3^{(q+1)}$ from monosilicate and $Al(OH)_4$ in 0 1 mol l ^{1} NaOH at 25 °C, but no detectable reaction in 1 0 mol l^{-1} NaOH At physiological pH (7 4) and 25 °C, Martin[38] estimates $K = [AlOSi(OH)_3^{2+}]/[Al^{3+}][Si(OH)_4] = 3 \times 10^4$

l mol ^{1} (the actual species present would be $(HO)_3SiOAl(OH)_3^-$ and $Al(OH)_4$), which, given that [Si] in blood plasma ≈ 20 μmol l ^{1}, means that some 60% of the Al^{III} burden of the bloodstream is probably bound to silicic acid Exley and Birchall[39] have confirmed the importance of soluble aluminosilicates under physiological conditions, and show that complexation of $Al(OH)_4$ by silicic acid inhibits the nucleation of $Al(OH)_3$ precipitates At the still lower pH range (4 0—5 5) of acidic natural waters, $Al^{III}-Si(OH)_4$ binding is complicated by the acid ionization of $Al^{3+}(aq)$ and its silicic acid complexes, but Browne and Driscoll[5] estimate from fluorimetric measurements using morin complexation of free Al^{III} that up to 95% of the total inorganic mononuclear Al^{III} is present as soluble aluminosilicates, so that these may be controlling factors in the weathering of rocks or soils leading to new mineral deposition

10 Summary

Aqueous Al^{III} and Si^{IV} readily form aluminosilicate complexes that can have significant solubilities, particularly if gelation of aluminate/silicate mixtures is not prompt Their thermodynamic stabilities are lower at high pH The structures of these aluminosilicate species are much like those of the numerous silicate oligomers that have been characterized in alkaline aqueous solution by NMR methods, and stand in contrast to the very limited range of structures known for aqueous aluminate species The effects of temperature, pH, and cations on the speciation and thermodynamic stability of Al, Si, and aluminosilicate oligomers are profound and need further clarification The larger, cage-like silicate anions are kinetically rather inert at room temperature, but the small silicate and especially aluminosilicate species are very labile These dynamic and thermodynamic aspects have far-reaching industrial, biomedical, environmental, and scientific implications, and further data are urgently needed, particularly for aluminates

Acknowledgement We thank the Natural Sciences and Engineering Research Council of Canada (TWS) and Comalco Aluminium Ltd (JS, PAT) for financial support TWS thanks the University of Melbourne for a visiting fellowship

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