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The reaction of aluminium with silicic acid in acidic solution: an important mechanism in controlling the biological availability of aluminium?

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Contents

Abstract

The reaction of aluminium (Al) with monomeric silicic acid ($Si(OH)_4$) to form an hydroxyaluminosilicate (HAS) has been well documented over the past 40 or so years. The formation of an aluminium hydroxide template, upon which $Si(OH)_4$ will condense in competition with Al, was demonstrated to be a prerequisite to HAS formation. This initial reaction results in the formation of a slowly aggregating HAS, with a Si:Al ratio of 0.5, in which silicon tetrahedra are bonded to Al octahedra through three Si–O–Al linkages. We have called this HAS_A. In solutions in which the concentration of $Si(OH)_4 \geq Al$ HAS_A acts as a template for the incorporation of further silicon tetrahedra to give a rapidly precipitating HAS (that we have called HAS_B), with a Si:Al ratio of 1.0, in which up to 50% of the constituent Al has adopted tetrahedral geometry. There are, at present, no reliable constants to describe either the formation or the solubility of these HAS. They are extremely insoluble and are likely to play an important role in the control of the release of Al from the edaphic to the aquatic environment. They may also have an important role in Al homeostasis in biota though the evidence to support this is more tentative. © 2002 Elsevier Science B.V. All rights reserved.

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1. Preface

The primary objective of this review was to critically evaluate scientific literature that has reported the interaction of aluminium (Al) with monomeric silicic acid ($Si(OH)_4$) in acidic solution. (A comprehensive and authoritative review of all silicate complexes of Al has recently been published [1].) A secondary objective was to update the significance of this chemistry to the biological availability of Al. A particular bone of contention in this field is the definition of what constitutes $Si(OH)_4$. We have attempted to reduce the ambiguity that surrounds this definition by only reviewing research in which every attempt had been made to ensure that the only reactive form of silicon in experimental solutions was the neutral monomer and was not charged or polymeric forms of this weak acid. Our interpretation of 'every attempt' has excluded any research in which: (i) the concentration of $Si(OH)_4$ in either stock or experimental solutions exceeded 2.00 mmol l^{-1} ($Si(OH)_4$ will autocondense at concentrations

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greater than 2.00 mmol l^{-1}[2]); (ii) $Si(OH)_4$ was derived from the slow dissolution of inorganic silica (polysilicates are found in equilibrium with slowly dissolving silica [3,4]); (iii) $Si(OH)_4$ was derived from the hydrolysis of an organosilane and the success of the hydrolysis was not confirmed using the rapid formation of the molybdosilicic acid complex; (iv) the literature contained insufficient detail of the provenance of the $Si(OH)_4$ used in experiments. We have also limited the scope of this review to acidic solutions (pH < 7.00) to reduce the possibility of significant contributions from deprotonated $Si(OH)_4$. Our interpretation of $Si(OH)_4$ will not be accepted universally. It has resulted in many more exclusions than inclusions. However, until we have definitive data concerning the forms of silicon in undersaturated solutions of $Si(OH)_4$, perhaps using ^{29}Si-enriched solutions and NMR, we shall continue to define solutions by using these criteria.

2. Historical perspective

It is our opinion that the most appropriate technique for the preparation of solutions of $Si(OH)_4$ is the cation exchange of undersaturated solutions of sodium silicate. When, in the mid-60s, Polzer et al., used this method to prepare acidic (pH ca. 5.00) solutions of constant ionic strength containing $Si(OH)_4$ (0–1.63 mmol l^{-1}) and Al (ca. 0.30 mmol l^{-1}) they were able to demonstrate the formation of amorphous precipitates of hydroxyaluminosilicate (HAS) with Si:Al molar ratios of between 0.5 and 1.0 [5]. The precipitates were separated by filtration (0.10 μm membrane filters) and their compositions were obtained from the differences in concentration of Al and $Si(OH)_4$ before and after filtration. The Si:Al molar ratio of one precipitate was measured directly by an unspecified wet chemical method. A later study by the same group using the same methods showed that all precipitates that were isolated from solutions in which $Si(OH)_4$ was present to considerable excess had Si:Al molar ratios of about 1.0 [6]. Using data for the concentrations of Al and $Si(OH)_4$ that had passed through the 0.10 μm filter as estimates of Al^{3+} and $Si(OH)_4$ in equilibrium with the solid phase and the postulated synthesis reaction shown below (assumption that HAS was kaolinite or halloysite);

$$2Al^{3+} + 2Si(OH)_4 + H_2O \leftrightarrow Al_2Si_2O_5(OH)_{4(s)} + 6H^+$$

an equilibrium constant of $10^{11.3}$ was estimated.

One of the most complete studies of the interaction of Al with $Si(OH)_4$ was carried out in the mid-70s by Luciuk and Huang [7]. They investigated the influence of solution age and OH/Al ratio on the precipitation of HAS from solutions containing $Si(OH)_4$ and Al (0.15 and 1.52 mmol l^{-1}) at a ratio of either 0.5 or 1.0. They made a number of important observations which included; (i) the reaction between Al and $Si(OH)_4$ at the OH/Al ratio of 3 did not result in the significant release of H^+ or H_3O^+; (ii) at the same OH/Al ratio and at the higher initial concentration of Al, the reaction of $Si(OH)_4$ with Al was proceeded by further reactions between $Si(OH)_4$ and the preformed HAS; (iii) at OH/Al ratios of 1 and 2 the presence of $Si(OH)_4$ both reduced the amount of precipitate that could be removed by filtration (0.025 μm filter) and increased the proportion of Al that had been experimentally classified as non-extractable; (iv) all precipitated HAS were amorphous to X-ray diffraction; (v) analyses of precipitates by IR showed that the formation of HAS at OH/Al of 3 resulted in the disappearance of peaks attributable to Al–OH vibrations and the appearance of peaks attributable to Si–OH vibrations; (vi) HAS precipitates formed after 100 days aging in solutions in which the Si:Al molar ratio was either 0.5 or 1.0 were composed of Si and Al in molar ratios of 0.45 and 0.67, respectively. These observations helped Luciuk and Huang to conclude that the HAS precipitates identified in their experiments had been formed by the condensation of $Si(OH)_4$ at hydroxyl bridges and/or Al–OH on aluminium hydroxide lattices.

The early work from the groups of JD Hem and PM Huang was supported and extended in its scope by Wada [8,9]. In particular, cation exchange was used to retain HAS and to identify their composition in solutions of fixed concentration of Al and different pH, concentrations of $Si(OH)_4$ and age. It was demonstrated that for solutions of OH/Al ≥ 1 the primary determinant of the Si:Al molar ratio of the HAS was the ratio of $Si(OH)_4$ to Al in the parent solution. In solutions that had been aged for 100 days the Si:Al ratio of HAS ranged from ca. 0.40 (for parent solutions with an excess of Al) to ca. 1.0 (for solutions with an excess of $Si(OH)_4$). An increasing excess of $Si(OH)_4$ did not result in a higher content of Si in the retained HAS. Because of their composition, the HAS were likened to the soil aluminosilicates allophane and imogolite. However, unlike these structures they were amorphous to X-ray diffraction and had no distinct structure when viewed under the electron microscope [9].

Prominent in the field of the reaction of $Si(OH)_4$ with Al is Farmer's group in Aberdeen, Scotland, pioneers in the identification and structural characterisation of imogolite [10]; they also demonstrated the formation of HAS of Si:Al molar ratio of 0.50 in acidic solutions (pH 4.50–5.50) in which the concentration of $Si(OH)_4$ exceeded 0.10 mmol l^{-1} [11]. When these solutions were heated, they generated imogolite and this prompted Farmer to call the precursors to this phase, the aforementioned HAS, protoimogolite. It is unusual that Farmer's group did not observe the formation of HAS of Si:Al molar ratio of 1.0 when $Si(OH)_4$ was present to excess in their solutions. This group have continued their investigations into ‘proto-imogolite’ and they have used potentiometry [12] to determine a formation constant of $\mathrm{p}K_{110} = 2.50 \pm 0.05$ for the putative species;

$$Al^{3+} + Si(OH)_4 \leftrightarrow AlOSi(OH)_3^{2+} + H^+$$

and equilibrium dialysis and the above formation constant to obtain a solubility expression, $\log K_{so} = 7.02$, for a protoimogolite sol [13];

$$2Al(OH)_{3(s)} + Si(OH)_4 \leftrightarrow (HO)_3Al_2O_3SiOH_{(s)} + 3H_2O$$

The inability of this solubility expression to explain the formation of HAS in both synthetic and natural waters has raised some discussion in the scientific literature [14–16].

We have been investigating the reaction of Al with $Si(OH)_4$ for the last 15 years with particular emphasis on the influence of this reaction on the biological availability of Al [17–19]. Initial research served, in the main, to confirm the aforementioned earlier studies and used both membrane filtration and cation exchange to demonstrate the formation in acidic solutions of HAS of Si:Al molar ratios 0.3–0.6 [19,20]. A lack of reliable quantitative data describing both the formation and solubility of HAS in acid solution prompted an investigation into HAS formation at an environmentally (physiologically) significant concentration of Al [21,22]. Equilibrium dialysis, using tubing with a nominal pore size of ca. 1 nm, was used to confirm the formation of HAS in acidic solutions containing 0.10 mmol l^{-1} $Si(OH)_4$ and only 4.0 μmol l^{-1} Al. The dialysis experiment showed that HAS colloids were significantly smaller than hydroxyaluminium (HA) colloids formed and aged under the same solution conditions. It was proposed that the formation of HAS involved the poisoning of HA polymerisation by $Si(OH)_4$ [22]. Subsequent experiments using the same low concentration of Al used membrane filtration (40 nm nominal filter rating) to describe how $Si(OH)_4$ influenced the formation and precipitation of HAS in acidic solution [21]. In solutions in which $Si(OH)_4$ was present to considerable excess, the formation of HAS was instantaneous. The aggregation of colloidal HAS to a filterable size was significantly slower than the corresponding HA colloids. The latter showed an unchanged particle size distribution after about 3 weeks whereas HAS were still aggregating towards a filterable size after 12 weeks. In addition the pH of minimum solubility had shifted from ca. pH 6.50 for HA colloids to ca. pH 5.50 for HAS. It was interesting to note that this shift in the pH of minimum solubility corresponded closely to the base-neutralising capacity of the solutions. Solutions in which HAS were the predominant form of Al were unable to buffer base additions at pH greater than ca. 5.20 whereas in solutions of HA colloids, this buffering capacity was evident up to ca. pH 5.90. This research confirmed the formation of HAS in acidic solutions containing only 4.0 μmol l^{-1} total Al and it provided a great deal of support for the proposed mechanism of their formation. However, it was only recently that the next significant step forward towards the confirmation of this mechanism was made.

We began by using a combination of membrane filtration (0.1 μm membrane filter) and morin-Al fluorescence (estimate of the fast-reactive Al fraction) to demonstrate that HAS were only formed in solutions which were saturated with respect to amorphous aluminium hydroxide [23,24]. The next challenge was to understand the structure and stoichiometry of HAS that were formed under various solution conditions. This was achieved by collecting HAS formed in synthetic solutions in sufficient quantities to enable their structures to be probed by solid state NMR [24]. After 3 months aging at ca. pH 6.20 HAS were collected by filtration from solutions in which the $Si(OH)_4$ to Al ratio varied from 8:1 (2.0 mmol l^{-1} $Si(OH)_4$) to 1:4 (0.5 mmol l^{-1} $Si(OH)_4$). HAS that were formed in parent solutions in which the concentration of $Si(OH)_4 \geq Al$ had aggregated sufficiently to be removed using a 2.0 μm membrane filter whereas those HAS that were formed in parent solutions in which Al was present to excess were collected using a 0.2 μm membrane filter. This was our first indication that we should expect to find more than one form of HAS in the parent solutions. Solid state ^{29}Si- and ^{27}Al-NMR combined with elemental composition by SEM-EDX revealed two distinct forms of HAS (Fig. 1). HAS_A had an ideal Si:Al ratio of 0.5 and its structure was dominated by Si coordinated through three Si–O–Al linkages (Q^3(3Al)) to Al in an octahedral geometry. HAS_B had an ideal Si:Al ratio of 1.0 and whilst it retained some of the structure of HAS_A its structure now included a significant framework of Si (Q^4(1–2Al) and Q^3(1–2Al)) and Al tetrahedra. HAS_B had no Al-associated protons and a maximum of one silanol group per Si. HAS_A was the predominant HAS formed in parent solutions in which Al was present to excess whereas HAS_B predominated in parent solutions in which $Si(OH)_4$ was present to excess. We used atomic force microscopy (AFM) to confirm that the precipitates that we had isolated using filtration and analysed by NMR were representative of the colloidal HAS in the parent solutions (Fig. 2). We identified two distinct forms of colloidal HAS, rectangular (up to 170 nm in length) and discoid (up to 43 nm in diameter), and the occurrence of these forms in the parent solutions matched the occurrence of HAS_A (rectangular) and HAS_B (discoid) in the precipitates that had been filtered from the same solutions. It was of note that HAS_B was not found in those solutions in which Al was present to excess whereas HAS_A was found in solutions in which Si was present to excess [23]. We have proposed structures for HAS_A and HAS_B and have suggested how HAS_B

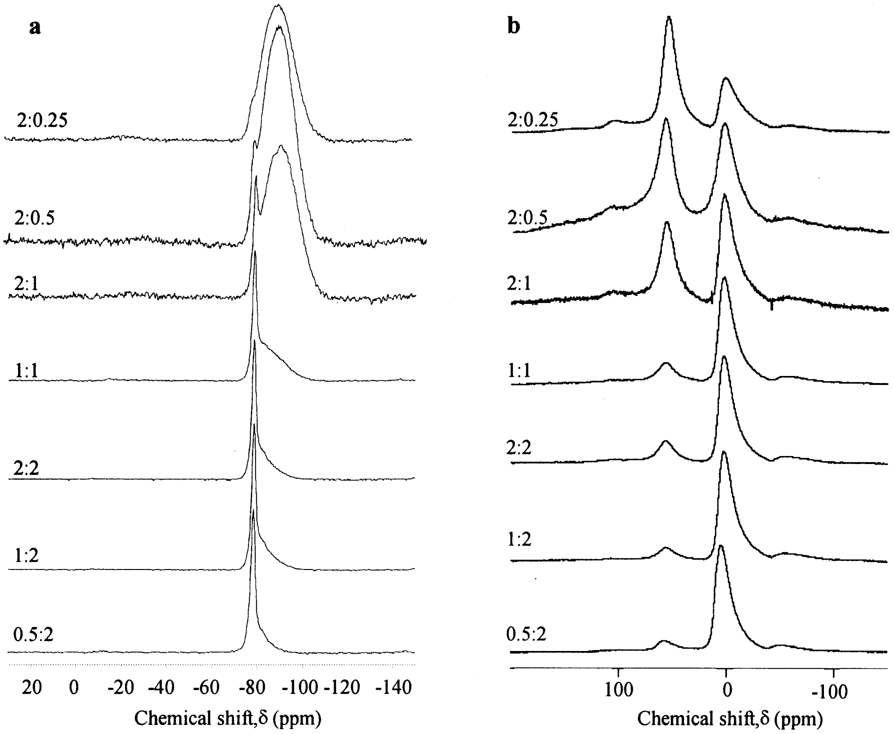

Fig. 1. The influence of different combinations of $Si(OH)_4$ and Al (units are mmol dm^{-1}) in treatment solutions on the structure of precipitated HAS. Representative spectra of two to three replicate samples are shown. (a) ^{29}Si- CP-MAS NMR. Field strength: 9.4 Tesla. Contact time: 5 ms. Sample spinning speed close to 5 kHz. Acquisition time: 129 ms. Pulse delay: 5 s. Chemical shifts referenced to Q8M8. Each spectrum was collected from 3500 to 5000 scans. (b) ^{27}Al- HD-MAS NMR. Field strength: 9.4 Tesla. Sample spinning speed close to 4 kHz. Acquisition time: 30 ms. Pulse delay: 1 s. Chemical shifts referenced to 1 M $Al(H_2O)_6^{3+}$ solution. Each spectrum was collected from 5000 scans. (Reproduced with permission from [24].)

was formed from the interaction of HAS_A with excess $Si(OH)_4$ [24].

3. The mechanism of formation of HAS

It has proven to be an easier task to identify the formation of HAS than to elucidate their mechanism of formation. In the early 1990s we proposed that the formation of HAS involved the inhibition of the growth of aluminium hydroxide by the substitution of hydroxylated Al by $Si(OH)_4$ [22]. Luciuk and Huang had come to the same conclusion almost 20 years earlier [7]! Both groups, and others [5,6,8,9], had observed that the presence of $Si(OH)_4$ in a saturated solution of Al acted to both increase the proportion of Al that passed through a membrane filter and reduce the fraction of Al that was experimentally defined as being in a monomeric form. The consensus of opinion was that $Si(OH)_4$ had reacted with a HA template to form HAS which had subsequently grown at a very much reduced rate to that of aluminium hydroxide in equivalent solutions in which $Si(OH)_4$ was absent. Other consistent observations have been the reduced base-neutralising capacities of Al solutions containing $Si(OH)_4$ [7,21] and the dependence of the Si:Al ratio of HAS precipitates on the ratio of $Si(OH)_4$ to Al in parent solutions [9,24].

The recent elucidation of the structures and stoichiometries of two distinct HAS, HAS_A and HAS_B [24], which are probably identical to the HAS that have been identified by other means in earlier work will now help in elucidating their mechanisms of formation. For example, it would now seem very likely that the HAS of Si:Al molar ratio of 1.0 identified by Hem and coworkers [5,6] were neither kaolinite nor halloysite but rather an HAS (HAS_B) in which Al was present as a 50:50 mixture of octahedral and tetrahedral geometries. We also know that this HAS was formed as the result of the continued incorporation of $Si(OH)_4$ into another HAS (HAS_A) [24], a reaction that had been alluded to in an earlier publication [7]. A summary of proposed reaction schemes for the formation of the simplest precursors to HAS_A colloids is presented in Fig. 3. It is interesting that Schemes 1–3 show $Si(OH)_4$ condensing with hydroxyl or water groups on an aluminium hydroxide framework in which the adjacent Al atoms are joined by two hydroxy bridges. These double-hydroxy bridges are the main repetitive units in the hydrated structures of the crystalline forms of both aluminium hydroxide, such as gibbsite, bayerite and nordstrandite, and a number of aluminosilicates, includ-

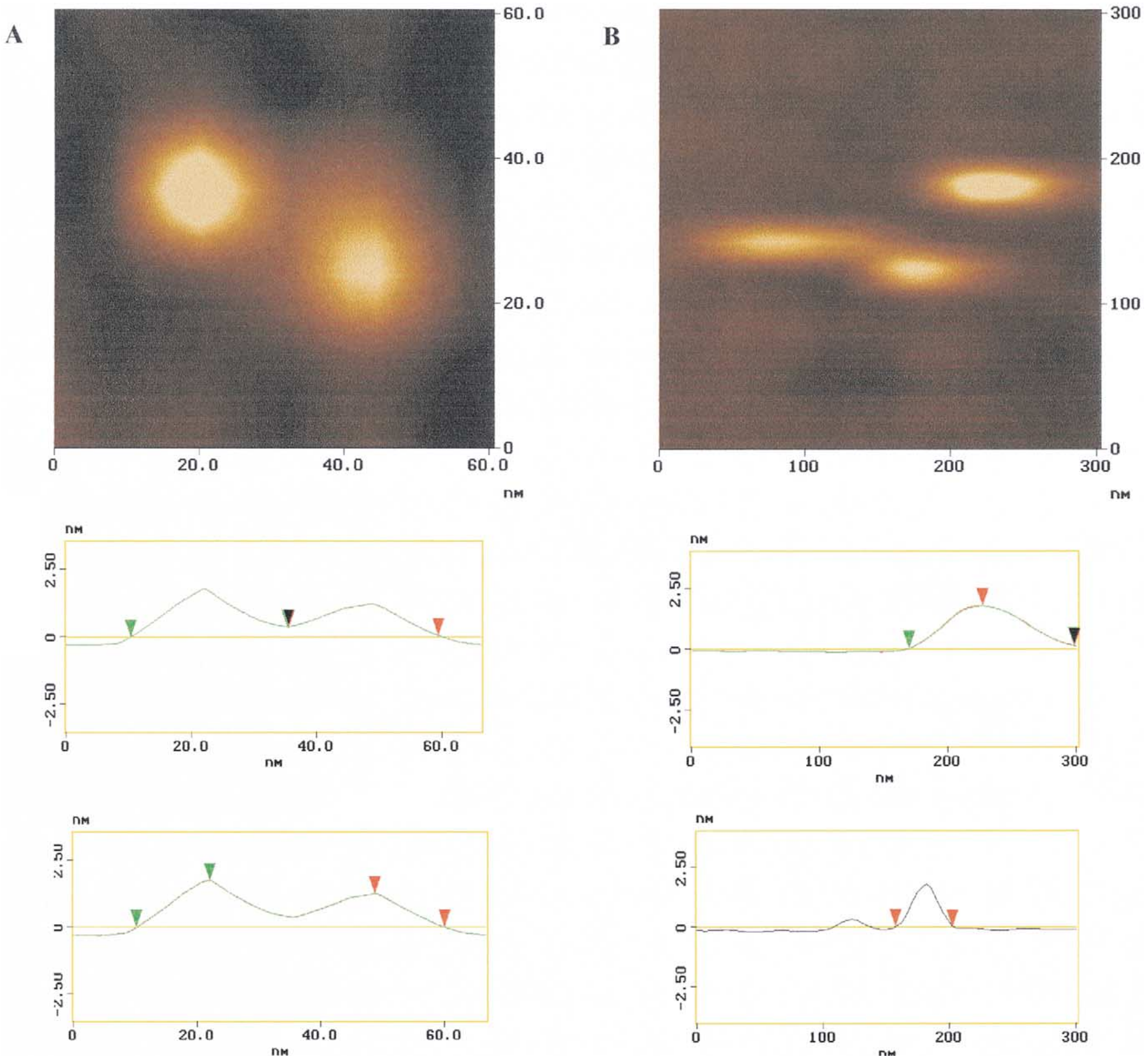

Fig. 2. Close up AFM images of representative individual HAS structures and line profiles representing the section analysis of these two structures: (A) discoid HAS, depth 1–2 nm, diameter 23–25 nm; (B) rectangular HAS, depth 1–2 nm, width 40–45 nm, length 87–170 nm. (Reproduced with permission from [23].)

ing imogolite, kaolinite and halloysite. The HAS that are formed from the interaction of $Si(OH)_4$ with Al are amorphous to both wide angle and small angle X-ray diffraction spectrometry [5–7,24] and do not show any distinct structural features under the electron microscope [24]. The amorphous nature of HAS has been one of the most consistent observations made by researchers in the field over the years and this must bring into question the appropriateness of reaction schemes which suggest that $Si(OH)_4$ will condense at or across groups which are supported by a double-hydroxy bridge structure? For example, whilst the crystalline aluminosilicate imogolite will apparently satisfy much of the structural and stoichiometric data available for HAS_A, (Si:Al ratio = 0.50; Si coordinated through three Si–O–Al linkages to octahedral Al), HAS_A is an amorphous mineral with no gross structural similarity to imogolite. It is also easy to imagine how $Si(OH)_4$ could be trapped within the hexagonal framework of individual gibbsite units through condensation across alternate hydroxy bridges, these units then coalescing to build a structure with a Si:Al ratio of 0.5 (Fig. 4). However, it is difficult to see how the incorporation of $Si(OH)_4$ in such a structure would lead to a significant reduction in the

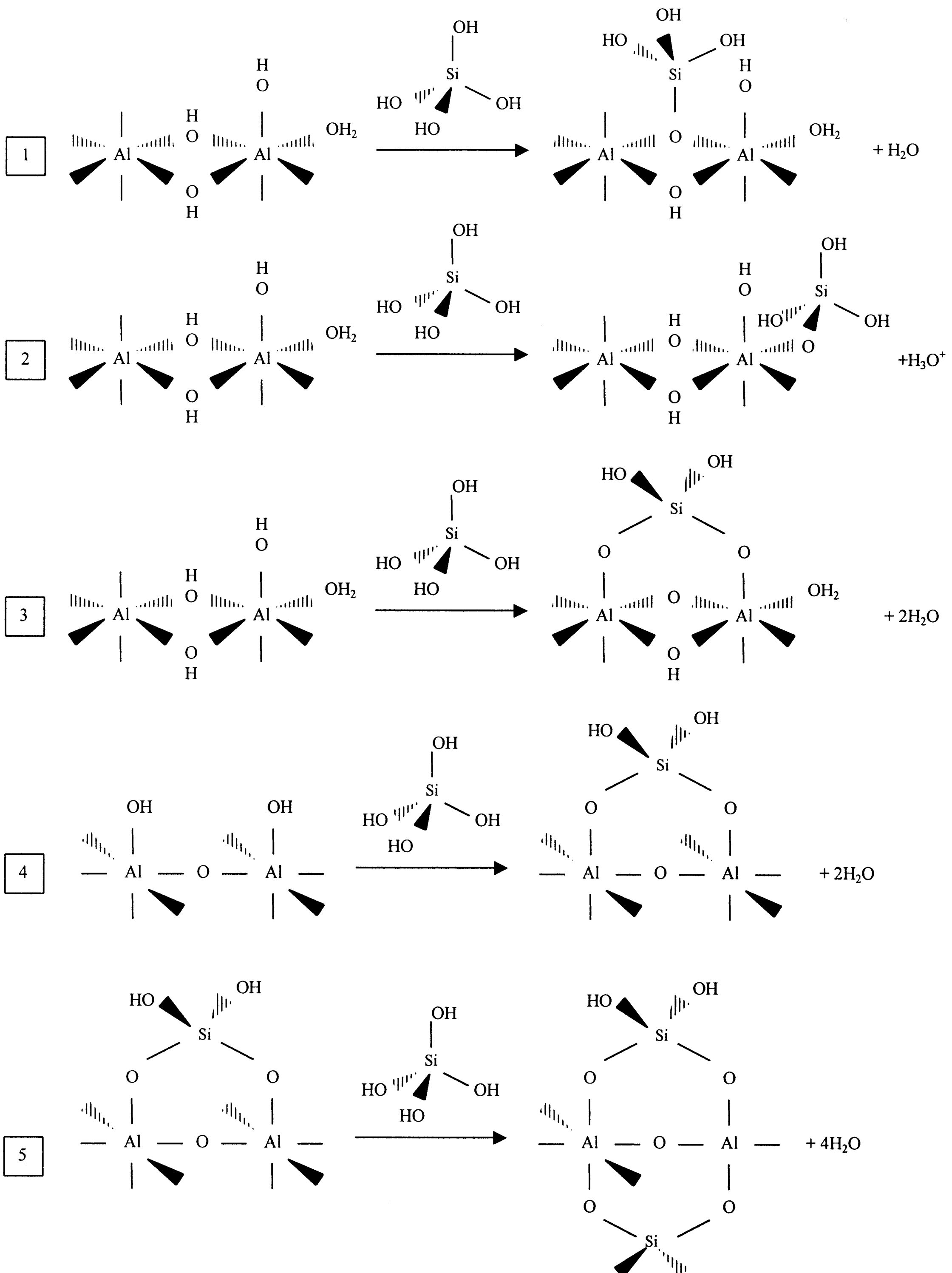

Fig. 3. Schematic showing possible reaction schemes for the formation of the precursors to HAS_A (Scheme 1–4) and HAS_B (Scheme 5).

growth of the gibbsite (aluminium hydroxide) sheet since the growth sites have not been blocked by the inclusion of $Si(OH)_4$. The growth sites would be blocked if the imogolite sheet curled to form tubes. However, these structures or even fragments of these structures are not formed in HAS prepared at room temperature. Whilst it is has been shown that boiling a solution of an HAS prepared in a similar manner to HAS_A will result

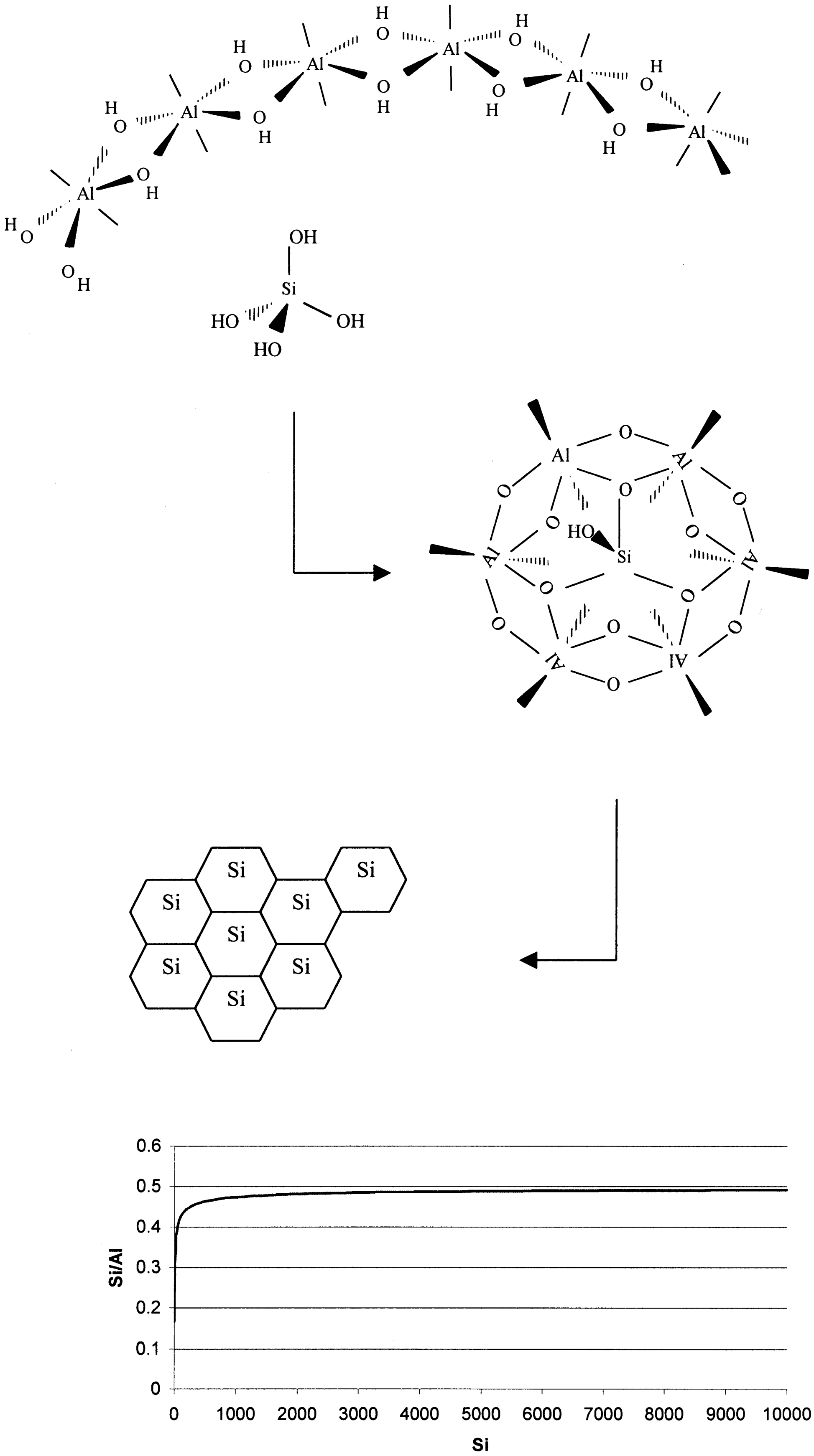

Fig. 4. Schematic showing a possible chain of events leading to the formation of protoimogolite.

in the formation of imogolite [25] this is not direct evidence that HAS_A has either the structure of imogolite or that it would, in time, form imogolite in the natural environment. It is very likely that the act of boiling will bring with it its own influences on the arrangement and rearrangement of the Si tetrahedra and Al octahedra in producing the extremely stable crystalline phase of imogolite.

It is clear from experiments that the condensation of $Si(OH)_4$ at growth sites on aluminium hydroxide is competitive with further condensation reactions with HA units. To be competitive the reaction with $Si(OH)_4$ must be kinetically and thermodynamically preferable. Single replacements of Al–OH or Al–OH_2 with Al–$OSi(OH)_3$ are unlikely to be competitive. The instability of the putative $AlSiO(OH)_3^{2+}$ species in competition with OH^- is testimony to the unfavoured nature of this reaction in solutions which are saturated with respect to an amorphous aluminium hydroxide phase [12,26]. We have speculated that the initial condensation reaction will involve $Si(OH)_4$ bridging Al–OH on adjacent Al atoms (Fig. 3; Scheme 4) and that the interaction with $Si(OH)_4$ will be stabilised further by a third Si–O–Al linkage upon the aggregation of these HAS units [24]. This interaction would favour growth in one particular direction and this is in fact what we have observed for HAS_A using AFM (Fig. 2). Such a reaction scheme is also supported by titration data which together suggest that the interaction with $Si(OH)_4$ does not involve any proton release [7,21].

In much of the earlier research on the formation of HAS $Si(OH)_4$ was present in solutions to excess and we now know that under these conditions the predominant form of HAS would be HAS_B [24]. The structure of HAS_B was a surprise and not least because of the high proportion of tetrahedrally coordinated Al but also because of the room temperature dehydroxylation reactions which allowed the further incorporation of $Si(OH)_4$ into the HAS_A structure. HAS_B must have a smaller unit structure than HAS_A since its growth sites are severely limited by the inclusion of further $Si(OH)_4$ and the switch in geometry of up to 50% of the coordinated Al. The smaller unit size of HAS_B was supported by AFM (Fig. 2). However, HAS_B is likely to be uncharged, at least in acidic solution, and will aggregate much more rapidly than HAS_A. This explains the ease with which it can be filtered from solution in comparison to both HAS_A and aluminium hydroxide [24].

There has been up until now only one valid attempt to determine the solubility of HAS formed from the interaction of $Si(OH)_4$ with Al and this was only applied to HAS equivalent to what has now been identified as HAS_A [13]. It is likely that this has significantly underestimated the solubility of this HAS and it may turn out that HAS_B is an even more insoluble HAS. We have been following the dissolution of both of these HAS for over 18 months now and we have yet to record any measurable release of Al. We are in the process of quantifying the formation and solubility of HAS_A and HAS_B and we hope to be able to report on the progress of this research in the near future.

4. HAS and the biological availability of Al

It is not yet clear at which level $Si(OH)_4$ will have a significant impact upon the biological availability, and hence toxicity of Al. There has been much speculation about the amelioration of Al toxicity by $Si(OH)_4$ though we have found very few experiments which have investigated, indirectly or directly, the toxicity of HAS in biota. We found that this was particularly the case when we applied our criteria for excluding studies in which there was some ambiguity about the reactive form of silicon. Even our own ‘seminal’ study [27] has failed these criteria as we were unable to guarantee that $Si(OH)_4$ was the only form of reactive silicon in the stock solutions used in these experiments!

The research which has shown a protective effect of $Si(OH)_4$ in Alzheimer's disease [28–30] and Al-related renal disease [31] was circumstantial in that it did not demonstrate a direct involvement of HAS. However, it was interesting that each of these studies demonstrated that $Si(OH)_4$ was only protective at concentrations in excess of 150–200 μmol l^{-1}. The question as to the mechanism of these protective effects has not been answered though it may have involved both non-systemic (e.g. reduced absorption of Al [32]) and systemic (e.g. accelerated excretion of Al [33]) formation of HAS.

Al toxicity in plants was ameliorated by $Si(OH)_4$ acting, apparently, both ex planta [34] and in planta [35]. In the former study the authors demonstrated a reduced concentration of monomeric Al (total [Al] of 60 and 120 μmol l^{-1}) in the presence of 4.0 μmol l^{-1} $Si(OH)_4$ at pH 4.0. However, the low pH of the solution would make it difficult to ascribe the protective effect of $Si(OH)_4$ to the ex planta formation of HAS. In another study $Si(OH)_4$ both increased and decreased the toxicity of Al in barley. Again, the low solution pH used in this study (pH 4.2) would probably have prevented any ex planta formation of HAS. The ability of $Si(OH)_4$ to increase the biological availability of inorganic phosphate in algae in the presence of Al was attributed to the formation of HAS [36]. Al limited the biological availability of phosphate in both a diatom, *Navicula pelliculosa*, and a green alga, *Chlorella vulgaris*, and this effect was abolished in the presence of $Si(OH)_4$ in excess of 100 μmol l^{-1}. This prompted the suggestion that a mechanism of silicon essentiality in biology was to maintain the biological availability of phosphate in the presence of Al.

The only experiment to have prepared HAS, identified their presence in solution and, thereafter, tested their toxicity was carried out in fish in acidic water [37]. HAS prepared from stock solutions which included 2.0 mmol l^{-1} $Si(OH)_4$ and 1.0 mmol l^{-1} Al (most probably a mixture of what we now know as HAS_A and HAS_B) were, upon being diluted into a fish assay at pH 5.5 to give a total concentration of Al of ca. 13.0 μmol l^{-1}, completely non-toxic. The same concentration of Al added from a stock solution in which there was not any $Si(OH)_4$ resulted in 100% death of fish within 48 h exposure. Clearly preformed HAS which have been allowed to aggregate to a filterable size (ca. >100 nm) were stable when they were diluted into the fish assay system. What is not yet known is the degree of aggregation that would be required to result in biologically inert HAS.

The formation of HAS is an important control of the biological availability of Al. However, it would seem that this control is mainly geochemical in nature with HAS contributing to Al solubility control in the natural environment [21]. There is some in vitro evidence that the formation of HAS might act directly in limiting the biological availability of Al (for example, in preventing Al being bound by biomolecules [38,39]) though we do not yet have a mechanism to explain how stable HAS might be formed in vivo. The ubiquity of Al in the earth's crust is slowly being matched by the ubiquitous number of applications of Al in modern life. If we are to sustain this 'Al Age' we must ensure that Al will be used safely and its unique inorganic chemistry with $Si(OH)_4$ may be important in achieving this aim.

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