

SCIENTIFIC REPORTS

OPEN

What is the mechanism of formation of hydroxyaluminosilicates?

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Received: 26 May 2016

Accepted: 08 July 2016

Published: 01 Aug 2016

The formation of hydroxyaluminosilicates is integral to the biogeochemical cycles of aluminium and silicon. The unique inorganic chemistry which underlies their formation explains the non-essentiality in biota of both of these elements. However, the first steps in the formation of hydroxyaluminosilicates were hitherto only theoretical and plausibly only accessible *in silico*. Herein we have used computational chemistry to identify and define for the first time these unique and ultimately critically important reaction steps. We have used density-functional theory combined with solvent continuum models to confirm first, the nature of the reactants, an aluminium hydroxide dimer and silicic acid, second, the reaction products, two distinct hydroxyaluminosilicates A and B and finally, how these are the precursors to highly insoluble hydroxyaluminosilicates the role of which has been and continues to be to keep inimical aluminium out of biota.

Silicon and aluminium are the second and third most abundant elements of the Earth's crust¹. Paradoxically neither element is essential to life and aluminium is inimical to biota. Silicon's non-essentiality is reflected both in its non-existent biochemistry, there are no known Si-C, Si-N, Si-O-C...etc. bonds in biota, and its limited inorganic chemistry under physiological conditions². The latter only consists of (i) the autocondensation of silicic acid ($\text{Si}(\text{OH})_4$) in forming silica ($n\text{SiO}_2 \cdot m\text{H}_2\text{O}$), (ii) the reaction of $\text{Si}(\text{OH})_4$ with ammonium molybdate to form molybdosilicic acid complexes (the basis for the spectrophotometric determination of $\text{Si}(\text{OH})_4$) and (iii) the reaction of $\text{Si}(\text{OH})_4$ with aluminium hydroxide ($\text{Al}(\text{OH})_{3(s)}$) to form hydroxyaluminosilicates (HAS). The formation of HAS is suggested as a basis for the essentiality of silicon in keeping aluminium out of biota^{3,4}. Therefore the unique inorganic chemistry of the formation of HAS has been critical in the non-selection of aluminium in biochemical evolution and it continues to be important in combating the ecotoxicity of aluminium including human exposure to aluminium⁵.

The mechanism of formation of HAS proceeds via the competitive condensation of $\text{Si}(\text{OH})_4$ across hydroxyl groups on a template of $\text{Al}(\text{OH})_{3(s)}$ ⁶. The reaction is competitive because $\text{Si}(\text{OH})_4$ competes with the further hydroxylation or autocondensation of $\text{Al}(\text{OH})_{3(s)}$ and its eventual precipitation as gibbsite^{6,7}. Two discrete forms of HAS, known as HAS_A and HAS_B, have been identified⁷. HAS_A is the predominant HAS formed in solutions in which the initial concentration of $\text{Si}(\text{OH})_4$ is less than or equal to the total aluminium while HAS_B predominates where the initial concentration of $\text{Si}(\text{OH})_4$ is at least twice that of aluminium. $\text{Al}(\text{OH})_{3(s)}$ is a prerequisite to the formation of HAS_A which is itself required for the formation of HAS_B. Filterable solids of HAS_A have an elemental Si:Al ratio of 0.50 and their structure is dominated by Si coordinated through three Si-O-Al linkages ($\text{Q}^3\text{3Al}$) to Al(III) in octahedral geometry (Al^{VI}). The solid phase of HAS_B has an elemental Si:Al ratio of 1.0 and Al(III) is found in tetrahedral (Al^{IV}) and octahedral (Al^{VI}) geometries in equal amounts⁷. This shift from octahedral to tetrahedral geometry is supported by changes in Si coordination from $\text{Q}^3(3\text{Al})$, the signature for HAS_A, to $\text{Q}^3(1-2\text{Al})$ ⁷. Atomic force microscopy was used to show that HAS solids adopt discrete morphologies with HAS_A forming flat (1–2 nm) rectangular (up to 170 nm in length) particles while HAS_B are also flat (1–2 nm) but discoid (up to 40 nm in diameter) particles⁸.

Present understanding of the formation and structures of HAS_A and HAS_B has, in the main, been obtained from solid state measurements of air-dried, filterable solids⁹. These data have allowed the formulation of potential reaction pathways beginning with monomeric and soluble reaction moieties, $\text{Al}^{3+}_{(\text{aq})}$ and $\text{Si}(\text{OH})_4$, and finishing

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with precipitates of HAS_A and HAS_B. The intermediates in this series of reactions are potentially myriad and their identities are certainly inaccessible through conventional bench-top analytical chemistry. Herein we have, for the first time, applied density-functional methods of computational chemistry to elucidate reaction intermediates in the formation of HAS_A and HAS_B and thereby support current solution and solid state data on these critical phases in the biogeochemistry of both aluminium¹ and silicon².

Methods

Density functional theory calculations. All geometrical optimisations were carried out in aqueous-phase using the Gaussian 09 suite of programmes¹⁰, B3LYP functional^{11–14} and the 6–31++G(d,p) basis set^{15,16}. The B3LYP functional has previously been shown to be effective for modelling interactions involving aluminium¹⁷. To confirm that optimised structures were real minima on the potential energy surfaces, frequency calculations were carried out at the same level of theory. All structures showed positive force constants for all the normal modes of vibration. The frequencies were then used to evaluate the zero-point vibrational energy (ZPVE) and the thermal ($T = 298\text{ K}$) vibrational corrections to the enthalpies and Gibbs free energies within the harmonic oscillator approximation. To calculate the entropy, the different contributions to the partition function were evaluated using the standard statistical mechanics expressions in the canonical ensemble and the harmonic oscillator and rigid rotor approximation. The solvent effect was introduced by using the self-consistent reaction field (SCRF) method with the polarised continuum model (PCM), using the integral equation formalism variant (IEFPCM)¹⁸. The electronic energies were refined by single-point energy calculations at the B3LYP/6–311++G(3df,2p) level of theory^{19,20}. For the most important structures and to validate our results, we recalculated the energies with PBE0^{21,22} and M062-X²³ functionals.

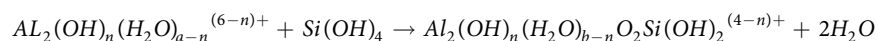
Preparation of structures. Based on the work of Bogatko and co-workers, aluminium hydroxide dimer templates (Al_2 hereafter) were studied with aluminium atoms linked by double and single hydroxy bridges¹⁷ (e.g. structures a and b, Fig. 1), and at three charge states: dication, monocation and neutral. The first coordination shell was completed with water molecules and hydroxyl groups to produce the desired charge for each particular structure, with Al coordinated octahedrally. Several hydroxyaluminosilicate structures in both HAS_A and HAS_B forms (e.g. structures c and d, Fig. 1) were also investigated. Potential HAS_A particles in the same charge range were investigated by constructing an aluminium hydroxide dimer with either a double or single hydroxy bridge, and incorporating silicic acid ($\text{Si}(\text{OH})_4$) into the structure by using one coordination site on each Al atom to form an additional bridge between the two Al atoms, in the form of Al–O–Si–O–Al (structure a, Fig. 2; structure c, Fig. 1). The two remaining coordination sites on the incorporated Si were occupied with hydroxyl groups, as found on $\text{Si}(\text{OH})_4$ (structure a, Fig. 2; structure c, Fig. 1). Potential HAS_B structures were tested by incorporating a second Si into the structures, in the same manner (structure b, Fig. 2; structure d, Fig. 1).

Conformational changes occurred in some structures during geometry optimisation, for instance rearrangement of water and hydroxyl groups. This resulted in some conformations collapsing to identical ones already being investigated (*i.e.* some of the stable structures, as presented in the Supplementary material, could be reached from more than one different starting geometry). Some structures were found to be unstable, breaking apart during the geometry optimisation stage, releasing one or more water molecules from the structure.

Geometries were also investigated where the aluminium atoms were linked by oxygen, rather than hydroxy bridges; however in almost all cases, geometry optimisation resulted in protons migrating from elsewhere to change the bridge to the hydroxy type. The exceptions to these were HAS_B and the AlSi monomer. As a result of this consistent conformational search, a set of 33 stable structures were obtained. For the sake of clarity, we only show the lowest-energy structures of each kind (Fig. 3), whereas all identified stable structures may be found in the Supplementary material (Tables S2–S6). The corresponding enthalpy (ΔH_{aq}) and Gibbs free energy (ΔG_{aq}) differences in the aqueous phase, for the formation of all these structures, can be found in several figures and tables in the Supplementary material: We show $\Delta H_{aq}/\Delta G_{aq}$ for the formation of single-bridge Al hydroxide dimer structures (Al_2^{SB}) in Table S2, and double-bridge ones (Al_2^{DB}) in Table S3; formation of HAS_A structures departing from aluminium hydroxide dimers in Tables S4 (single-bridge, HAS_A^{SB}) and S5 (double-bridge, HAS_A^{DB}), and finally, formation of HAS_B from HAS_A in Table S6.

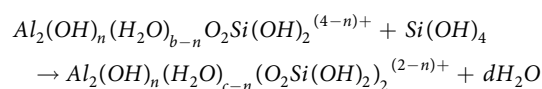
Condensation reactions. For the condensation reactions of $\text{Si}(\text{OH})_4$ on to Al_2 hydroxide dimers to form HAS_A and subsequently HAS_B, the condensation of a $\text{Si}(\text{OH})_4$ on to an Al_2 or HAS_A unit was assumed to involve the interaction between two silanol groups on the $\text{Si}(\text{OH})_4$ and two suitably-distanced adjacent hydroxyl groups on the Al_2 or HAS_A. Each OH pair that interacts in this way must release one OH^- and one H^+ into the bulk solution to form each Al–O–Si bond, *i.e.* the condensation of $\text{Si}(\text{OH})_4$ on to the structure releases two water molecules.

For the formation of HAS_A, we consider



where $a = 11$ for single-bridge Al_2 or $a = 10$ for double-bridge Al_2 ; and $b = 9$ for single-bridge HAS_A or $b = 8$ for double-bridge HAS_A.

For the formation of HAS_B, we consider



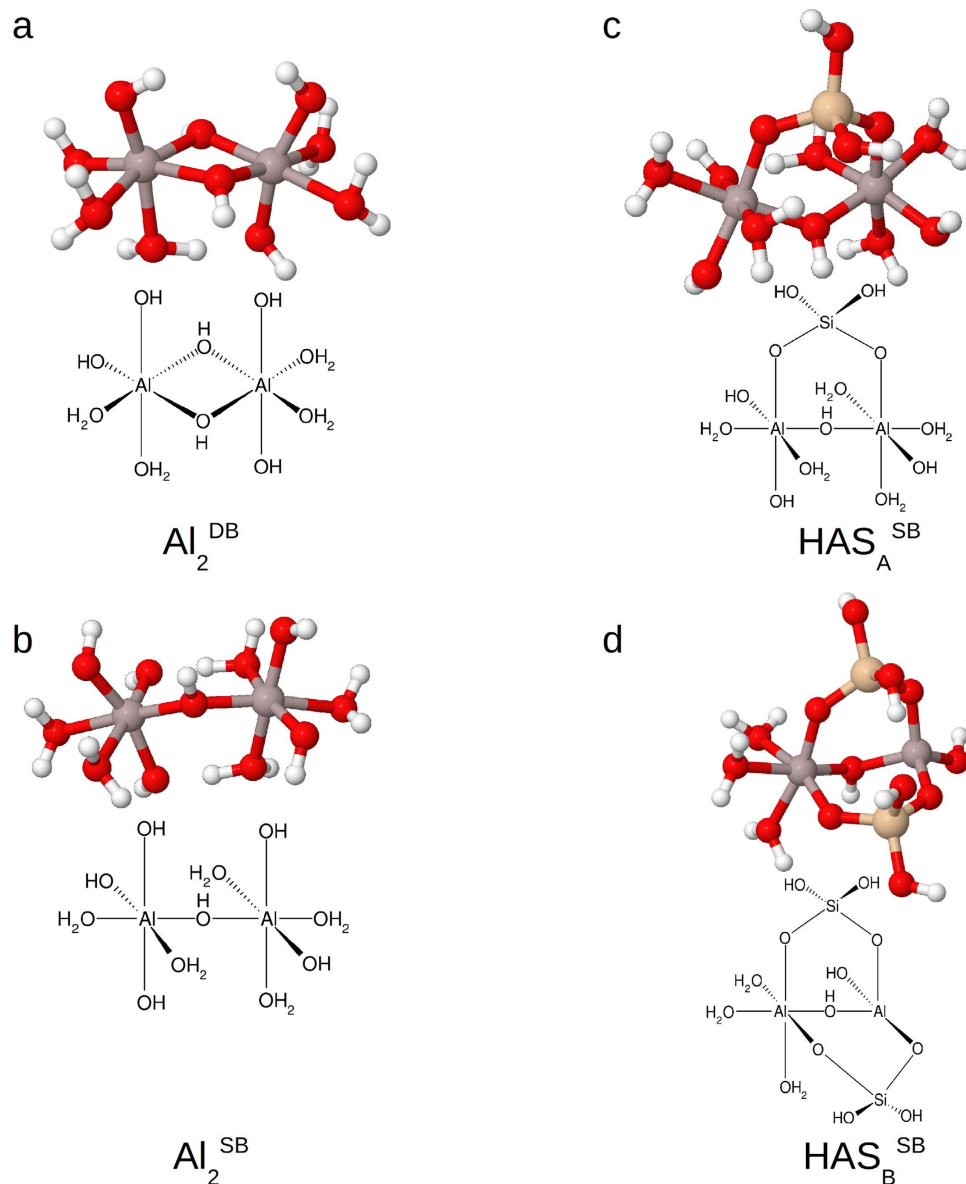


Figure 1. Example aluminium hydroxide and hydroxyaluminosilicate structures tested. (a) Double-bridge Al dimer, (b) Single-bridge Al dimer, (c) Single-bridge dimer b with $Si(OH)_4$ bound at OH groups to form HAS_A , (d) HAS_A structure comparable to c, with second $Si(OH)_4$ bound to form HAS_B , and $2H_2O$ removed from the rightmost Al, leaving it with tetrahedral coordination.

where $b = 9$ for single-bridge HAS_A or $b = 8$ for double-bridge HAS_A ; c is 7 for single-bridge HAS_B with octahedrally-coordinated Al, 6 for double-bridge HAS_B with octahedrally-coordinated Al, 5 for single-bridge HAS_B that has 50% tetrahedrally-coordinated Al, and 4 for double-bridge HAS_B that has 50% tetrahedrally-coordinated Al. $d = 2$ for HAS_B that has octahedrally-coordinated Al, and $d = 4$ for HAS_B that has 50% tetrahedrally-coordinated Al.

Thus, based on the experimental information^{6,7}, we consider that the formation of each Al-O-Si bridge implies the release of a water molecule formed by the hydroxy group of the aluminium hydroxide and a proton of the incoming silanol group, as shown schematically in Fig. 2. Other condensation mechanisms, in which the silanol group would displace a water molecule from the first solvation layer of aluminium to release a H_3O^+ , would alter the solution pH, a behaviour discarded based upon experimental evidence⁶.

Results and Discussion

Formation of Al_2 dimer is more favourable than formation of AlSi monomer. First we analysed competition between the formation of aluminium hydroxide dimers and the condensation reaction between aluminium monomer and $Si(OH)_4$ to form an AlSi monomer, as proposed by Browne and Driscoll²⁴. Formation of an AlSi monomer required the release of one water molecule into the bulk solvent. We considered three aluminium monomers which differed in their charge states: $Al(OH)(H_2O)_5^{2+}$, $Al(OH)_2(OH_2)_4^+$ and $Al(OH)_3(H_2O)_3$.

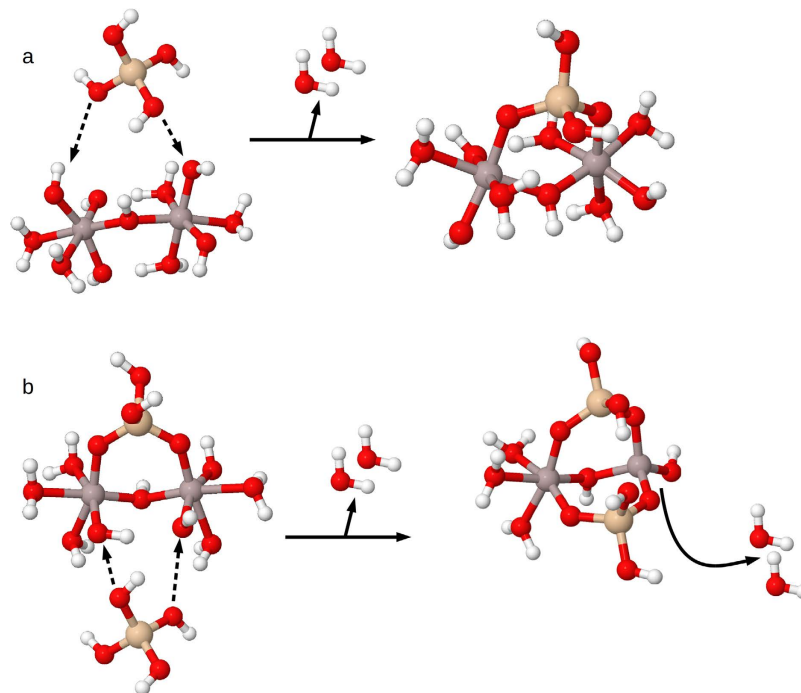


Figure 2. Binding of silicic acid molecule to (a) an aluminium hydroxide dimer to form HAS_A , and (b) a HAS_A unit to form HAS_B .

Both the condensation reaction of two aluminium monomer units to form an aluminium hydroxide dimer (Al_2), and the condensation of aluminium hydroxide monomer and $Si(OH)_4$ to form an AlSi hydroxide unit were exothermic and therefore possible in aqueous solution; however, the exothermicity of Al_2 formation was much higher than the exothermicity of AlSi formation for any charge state. For example, the most favourable 1:1 interaction between an Al monomer and $Si(OH)_4$ was between $Al(OH)^{2+}$ and $Si(OH)_4$ to form a $AlSi^{2+}$ with Al bound to Si via an oxygen rather than hydroxy bridge. The enthalpy/entropy of reaction was $-90.2/-84.6$ kcal/mol. The most stable identified Al hydroxide dimer had a formation enthalpy/entropy of $-199.1/-193.19$ kcal/mol, when formed from two neutral $Al(OH)_3$ monomers. The formation enthalpies of other Al dimers were of comparable values to the most favourable dimer (Table S1). Therefore, in solutions shown experimentally to result in HAS the formation of aluminium hydroxide dimers was always preferred to the reaction of Al monomer with $Si(OH)_4$.

HAS_A formation from Al_2 hydroxide dimers is favourable, especially for neutral structures.

Several stable aluminium hydroxide dimers were identified (Tables S2 and S3). We were also able to characterise several structures in which $Si(OH)_4$ was incorporated into aluminium hydroxide dimers (Tables S4 and S5). Here we will only discuss the lowest-energy structures for each type (Fig. 3). There is a competitive situation between single-bridge and double-bridge aluminium dimer structures at the three different charge states. If we look at the enthalpies, both dicationic and monocationic Al_2 show a preference for single-bridge structures, although when entropic corrections are introduced, double-bridge structures are preferred. For neutral structures, both enthalpic and free energies point to the double-bridge structure as the preferential form for Al_2 . However, the difference in ΔH_{aq} is only 1.1 kcal/mol at the B3LYP level of theory indicating that single-bridge structures are also accessible in aqueous solution. This is consistent with the results of Bogatko *et al.*¹⁷, who pointed to the coexistence of single-bridge and double-bridge Al_2 structures in aqueous solution. Next, we analysed the reaction energy for the incorporation of $Si(OH)_4$ into Al_2 hydroxide dimers. The formation of HAS_A structures by the condensation of $Si(OH)_4$ on to the Al dimer, and release of two water molecules, was favourable in several instances. Thus, according to ΔG_{aq} values, the formation of HAS_A structures was found to be an overall exothermic process in all cases. On the other hand, it was found that ΔH_{aq} was negative in four cases and only slightly positive (within the error of the calculation) in two cases: condensation of $Si(OH)_4$ on to Al_2^{SB1+} and neutral Al_2^{DB} . In general, therefore, there is a propensity to form HAS_A structures, with a preference for the addition of $Si(OH)_4$ into neutral single-bridge Al_2 hydroxide to form neutral single-bridge HAS_A structures, with values of $-5.6/-12.0$ kcal/mol for $\Delta H_{aq}/\Delta G_{aq}$.

HAS_B formation from HAS_A is highly favourable from neutral single-bridge structures.

For charged HAS_A , taking into account the number of hydroxyl groups, there is only the possibility to condense a second $Si(OH)_4$ on to an Al_2^{SB1+} structure. When we do so, we observe a change in the coordination shell of one of the aluminium atoms to four-coordination and the release of two waters. Therefore, the overall reaction corresponds to the addition of a $Si(OH)_4$ molecule, with the formation of two Al-O-Si bridges and release of four water molecules. The reaction ΔH_{aq} is positive with a value of 5.8 kcal/mol, however, the release of four water molecules increases the reaction entropy, and therefore, ΔG_{aq} is now quite negative, -21.6 kcal/mol. In the case of

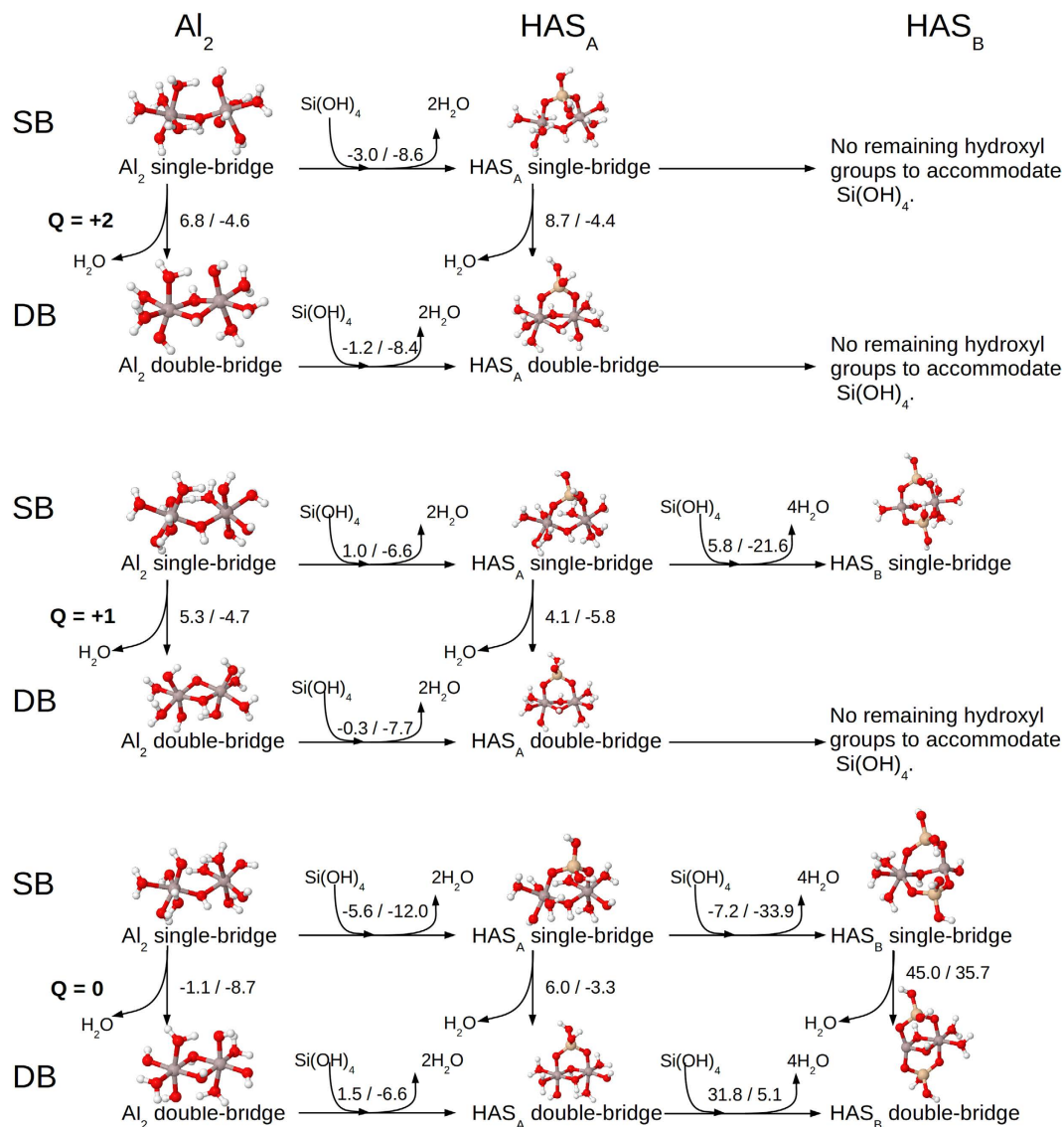


Figure 3. Enthalpies and free energy changes ($\Delta H_{aq}/\Delta G_{aq}$) for transitions between the most stable Al hydroxide dimer, HAS_A unit, and HAS_B unit of each charge and bridge-type. Units are in kcal/mol.

neutral HAS_A , we were able to find HAS_B structures originating from both single-bridge and double-bridge HAS_A species. In both cases, one of the aluminium atoms changes its coordination from six to four, but only one case, the condensation of $Si(OH)_4$ on to a neutral single-bridge HAS_A structure, is exothermic, with $\Delta H_{aq}/\Delta G_{aq}$ values of $-7.2/-33.2$ kcal/mol. Attempting to produce a HAS_B structure with Al linked via an oxygen atom, rather than a hydroxy bridge, by shifting the proton from the bridge to a hydroxyl group elsewhere on the structure, resulted in a $\Delta H_{aq}/\Delta G_{aq}$ energy penalty of $24.6/23.5$ kcal/mol.

In all cases where HAS_B was formed, we observed a tendency for $Si(OH)_4$ groups to orient adjacent to each other, rather than on opposite sides of the structure. However, neutral double-bridge HAS_B implied opposing $Si(OH)_4$ groups, and this consistently lead to a structure with a high degree of strain and unfavourable energy. In summary, the formation of HAS_B via HAS_A is favourable from neutral single-bridge structures, leading to a dramatic change in the coordination shell of one Al atom (Fig. 3). We note that this is the exact behaviour that has been observed experimentally by NMR⁷.

The formation of HAS_B is exothermic and requires specific orientation of hydroxyl groups.

Experimental data^{6–8}, and supported by the *in silico* measurements herein, suggest that neutral structures are the precursors to the formation of HAS (Fig. 4). Formation of aluminum hydroxide is a prerequisite for HAS formation. Our results for aluminum hydroxide dimer templates suggest that there is a competition between single-bridge and double-bridge structures in the case of charged species. Neutral Al hydroxides however tend to favour double-bridge species (although the energy differences are not as large as to prevent the formation of single-bridged structures at room-temperature) and are more favourable to aggregate. Repulsion between positively-charged molecules in solution may make the aggregation and growth of neutral Al hydroxide more

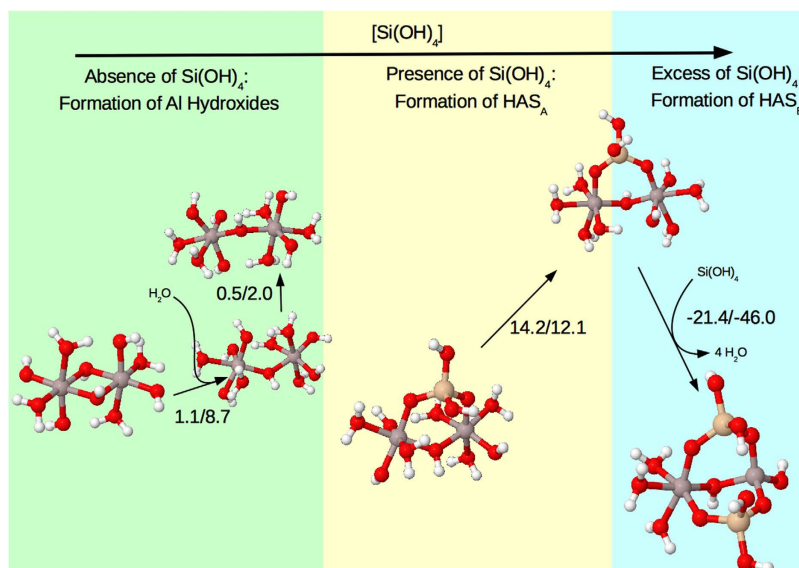


Figure 4. Most favourable reaction pathway for neutral structures as a function of $\text{Si}(\text{OH})_4$ concentration. Data extracted from Fig. 3, showing the most favourable Al hydroxide dimer, HAS_A and HAS_B structures, and the intermediates connecting these species. The figure shows schematically the influence of $\text{Si}(\text{OH})_4$ concentration in the formation of HAS_A and HAS_B species. Reaction-enthalpies and free energies in the aqueous phase are given in kcal/mol.

Reaction	B3LYP		PBE0		M062X	
	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
$\text{Al}_2^{\text{DB}} + \text{H}_2\text{O} \rightarrow \text{Al}_2^{\text{SB}}$	1.1	8.7	0.6	10.3	0.6	9.3
$\text{Al}_2^{\text{SB}} \rightarrow \text{Al}_2^{\text{SF}}$	0.5	2.0	1.0	0.6	0.4	0.4
$\text{Al}_2^{\text{SF}} + \text{Si}(\text{OH})_4 \rightarrow \text{HAS}_A^{\text{SB}} + 2\text{H}_2\text{O}$	-6.1	-14.0	-6.7	-14.9	-8.2	-15.4
$\text{HAS}_A^{\text{SB}} \rightarrow \text{HAS}_A^{\text{SF}}$	14.2	12.1	15.7	13.7	17.1	15.9
$\text{HAS}_A^{\text{SF}} + \text{Si}(\text{OH})_4 \rightarrow \text{HAS}_B^{\text{SB}} + 4\text{H}_2\text{O}$	-21.4	-46.0	-16.3	-43.6	-11.1	-38.5

Table 1. Enthalpy and Free Energy changes for each stage of the reaction pathway in kcal/mol depicted in Fig. 4, calculated with three different functionals: B3LYP, PBE0 and M062X.

competitive than that of positively-charged Al hydroxide, which would be consistent with existing experimental data. In order to form HAS_A , a single-bridge Al hydroxide configuration is needed, structures that are easily accessible, implying small energy requirements. In addition, in order for $\text{Si}(\text{OH})_4$ to condense, the structure must shift its conformation, to provide two adjacent hydroxyl groups (spaced approximately 0.3 nm apart) for incorporation of $\text{Si}(\text{OH})_4$. This provides an additional $\Delta G/\Delta H$ energy penalty of 0.5/2.0 kcal/mol (Fig. 4, Table 1). Thus, only moderate energy requirements were identified in the stages of HAS formation. The small barrier to HAS_A formation is consistent with laboratory observations that its formation is comparatively quick. The incorporation of $\text{Si}(\text{OH})_4$ into this structure with the release of two water molecules results in an enthalpy/entropic-change of -6.1/-14.0 kcal/mol, making the formation of HAS_A from Al hydroxide favourable over-all. To analyse the consistency of this theoretical picture, we have recalculated the energies of the structures of Fig. 4 and reevaluated the corresponding $\Delta H_{\text{aq}}/\Delta G_{\text{aq}}$ with two other functionals, PBE0 and M062-X (see Table 1), finding the same behaviour.

Laboratory observations point to relatively slow HAS_B formation and its high stability. Our results show that incorporation of a second $\text{Si}(\text{OH})_4$ into the structure requires a second pair of suitably-spaced hydroxyl groups, however, this requirement implies an important increase in energy, 14.2/12.1 kcal/mol. In addition, the incorporation of a second $\text{Si}(\text{OH})_4$ into the structure and release of four water molecules, results in a reaction energy $\Delta H_{\text{aq}}/\Delta G_{\text{aq}}$ of -21.4/-46.0 kcal/mol, making the formation of HAS_B from HAS_A very stable thermodynamically, and therefore, almost irreversible, in agreement with experimental data. It is important to note that the energy penalty for reorientation of the corresponding hydroxyl groups in HAS_A is much higher than for Al_2 dimer structures, and is consistent with the experimentally known slow formation of HAS_B with respect to HAS_A ⁷. Notice that the spacing of the hydroxyl groups on the $\text{Si}(\text{OH})_4$ molecule is 0.3 nm, and the spacing remains constant when two of the groups participate in condensation on to the aluminium hydroxide dimer. The spacing of one out of each set of opposing functional groups on the aluminium hydroxide dimer is always approximately 0.3 nm. The opposing group may be spaced more widely occasionally, due to the angle formed at the hydroxyl group(s) bridging the aluminium atoms. On aluminium hydroxide dimers with two adjacent hydroxyl groups capable of

accepting a single $\text{Si}(\text{OH})_4$, it is possible for these hydroxyl groups to be spaced slightly wider than 0.3 nm, however upon introduction of $\text{Si}(\text{OH})_4$ to the structure, the hydroxy bridge between the aluminium atoms rotates, altering the angle, thus reducing the gap to the favoured 0.3 nm. The slight angle at the hydroxy bridge between the aluminium atoms is also a likely factor in the second $\text{Si}(\text{OH})_4$ favouring hydroxyl groups that are adjacent (perpendicular) to the first $\text{Si}(\text{OH})_4$, rather than the opposing groups. Perpendicular silanol groups allow for less strain and torsion of the HAS_B molecule than opposing ones, due to the ability of the Al-OH-Al bridge to rotate to a position that allows both silanol groups to maintain their optimal 0.3 nm spacing. The favourability of single-bridge HAS structures over double-bridge variants may be in part due to the relative flexibility of a single hydroxy bridge compared to a double-bridge, with the single-bridge acting as a means of reducing strain across the rest of the structure. A more complete picture of the reaction mechanisms shown here would require calculation of corresponding transition states for all possible condensation reactions. Due to the high variety of structures calculated in this work, this task is beyond the scope of the present work and is the subject of future work. However, the agreement with experimental data supports our initial assumption that the formation of HAS_A and HAS_B can be understood in a simplified way by the thermodynamic requirements of the formation of ideal precursors for condensation of SiOH_4 onto aluminium hydroxides (HAS_A formation) and HAS_A templates (HAS_B formation).

Conclusions

The first, initial steps in the mechanism of formation of HAS have hitherto not been confirmed by experiment. One reason for this is the nature of the initial reactants. HAS are not true solution species which upon reaching saturation precipitate to give the now well characterised solid phases⁷. Herein we have confirmed previous suggestions that soluble aluminosilicates²⁴ are formed in acidic solutions, specifically $\text{Al}(\text{H}_2\text{O})_5\text{OSi}(\text{OH})_3^{2+}$, and we have similarly been able to demonstrate that such soluble forms of aluminosilicates are not precursors to HAS as their formation is not favoured under conditions where $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_{3(\text{aq})}$ spontaneously condenses to give $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_{3(\text{s})}$. These are the conditions which support the formation of HAS and the simplest example of such is the reaction of a dimer of $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_{3(\text{s})}$ with $\text{Si}(\text{OH})_{4(\text{aq})}$, the reaction of a solute with a solid phase and not the reaction of two solutes to form a soluble HAS. There is no such thing as a soluble HAS. What is intriguing about this reaction is that a highly insoluble solid phase, amorphous aluminium hydroxide, is the prerequisite to the even more insoluble solid phases of HAS_A and HAS_B . It was this novel form of non-solution chemistry which made the attribution of a solubility product to HAS_B a non-trivial task²⁵. When two $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_{3(\text{s})}$ react to form a dimer the Al atoms are initially linked by a single oxy/hydroxyl bridge which spontaneously rearranges to give the double oxy/hydroxyl bridge characteristic of aluminium hydroxide and eventually gibbsite. The answer as to which of these forms of the dimer was the precursor to HAS_A was answered previously in part by electron probe analyses⁷ of HAS_A which did not identify enough elemental oxygen to support a double-bridge in HAS_A . This suggested that when an aluminium hydroxide dimer formed in the presence of $\text{Si}(\text{OH})_4$ the formation of HAS_A 'stabilised' the single oxy/hydroxyl bridge and such is fully supported by our computational analyses. The formation of HAS_A is competitive with respect to its precursor, an aluminium hydroxide dimer, and it will be the only reaction product where $[\text{Al}_T]$ in solution equals the $[\text{Si}(\text{OH})_4]$ at which point half of the original $[\text{Si}(\text{OH})_4]$ remains in solution effectively preventing the dissolution of HAS_A . Evidence suggests that HAS_A can carry a slight positive charge, slowing its subsequent aggregation, and that remaining hydroxyl (Al-OH) linkages may be either opposite to or at right angles to Al-O-Si linkages. The latter is important because when the residual $[\text{Si}(\text{OH})_4]$ exceeds the concentration of the HAS_A dimer by a factor of two or more (when the original $[\text{Si}(\text{OH})_4]$ is more than twice the original $[\text{Al}_T]$) HAS_A becomes the precursor for the formation of HAS_B . The energy barrier for the condensation of a second molecule of $\text{Si}(\text{OH})_4$ coming from its significant excess in solution. The subsequent high stability of HAS_B being then achieved by the spontaneous loss of two water molecules and a shift in the geometry of one of the aluminium atoms from octahedral to tetrahedral. This is equivalent to a room temperature dehydroxylation reaction and as we have shown herein its success depends upon the availability of hydroxyl groups on HAS_A which are approximately 0.3 nm apart and at right angles to the Al-O-Si linkages. The dehydroxylation and subsequent shift in geometry also ensures neutrality of the resultant HAS_B and its rapid subsequent aggregation towards filterable solids.

The reactions described herein and confirmed for the first time by computational methods have wider significance than simply their unique inorganic chemistry. These reactions are fundamental to the geochemical cycling of aluminium¹ and integral to the biological availability of the non-essential but potentially toxic free metal cation, $\text{Al}^{3+}_{(\text{aq})}$. In particular humans are experiencing a burgeoning exposure to aluminium in everyday life²⁶ and such is implicated in a number of chronic diseases including neurological conditions such as Alzheimer's disease²⁷. The formation of HAS has been shown to protect against the toxicity of aluminium^{3,28} and is believed to underlie the mechanism whereby silicon-rich mineral waters facilitate the removal of aluminium from the human body²⁵. The therapeutic potential of $\text{Si}(\text{OH})_4$ was recently reviewed⁹ but it was Louis Pasteur (June 13th 1878) who is attributed as saying that “*effects of silicic acid are destined to play a great and major role in therapy*” and the formation of HAS may well be the mechanism.

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Acknowledgements

Technical and human support was provided by SGI/IZO (SGIker) of UPV/EHU. EPSRC are thanked for funding this research (EP/J004146/1). Santander are thanked for supporting travel for this project. J.I.M. and X.L. would like to thank the Spanish Ministerio de Ciencia e Innovación (CTQ2015-67608-P) and Eusko Jaurlaritz for funding.

Author Contributions

C.E. designed the study and wrote the manuscript. X.L. designed the study, performed calculations and wrote the manuscript. J.B. performed the bulk of the calculations and wrote the manuscript. J.I.M. performed calculations. All authors read and contributed towards the final manuscript.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Beardmore, J. *et al.* What is the mechanism of formation of hydroxyaluminosilicates? *Sci. Rep.* **6**, 30913; doi: 10.1038/srep30913 (2016).



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