



Innovations in Inorganic and Materials Chemistry

# Silicic Acid: Nature's 'Detox' for Aluminium

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## Silicic acid: The omniscient molecule

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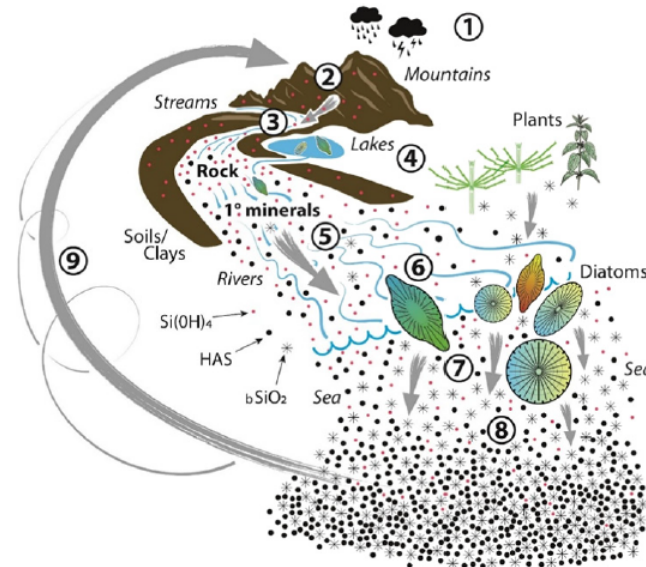


### HIGHLIGHTS

- Silicic acid plays a fundamental role in planetary health.
- Silicic acid is a small neutral molecule.
- Silicic acid keeps aluminium out of biota.
- Silicic acid is deposited as biogenic silica.
- The silicic acid cycle is Earth's thermostat and contributes towards climate change.

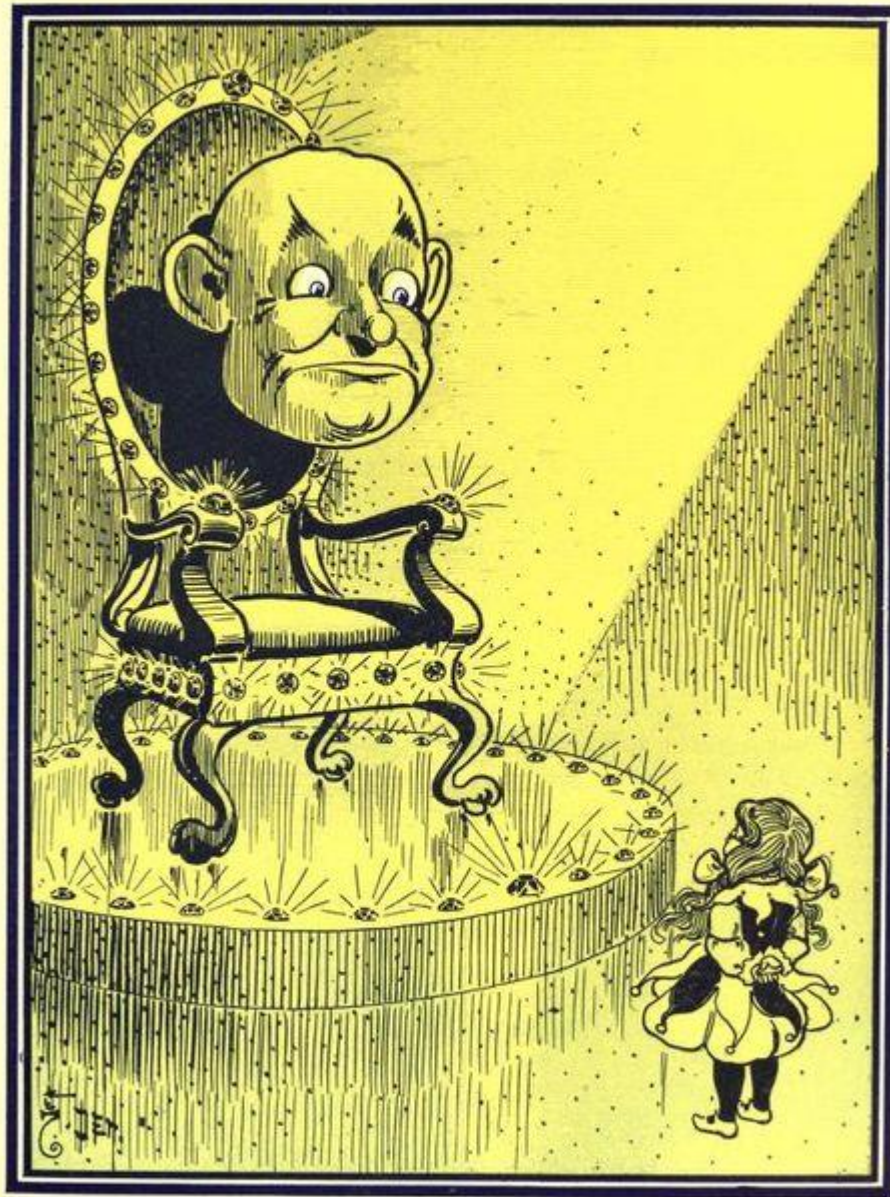
### GRAPHICAL ABSTRACT

The Silicic Acid Cycle is Earth's Thermostat.



Omniscient – adjective ‘all knowing’





*"The Eyes looked at her thoughtfully."*





Silicic Acid Keeps Aluminium Out of Biota

## Acute toxicity of aluminium to fish eliminated in silicon-rich acid waters

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AN increased level of aluminium in acidified natural waters is a primary cause of fish death from damage to gill epithelia and loss of osmoregulatory capacity<sup>1-4</sup>. Aluminium toxicity depends on the species of aluminium present (cationic, neutral or anionic) and hence is affected by pH and the presence of complexing ligands, such as fluoride, and organic material, such as humic acid, which may ameliorate aluminium toxicity<sup>5,6</sup>. But silicic acid,  $\text{Si}(\text{OH})_4$ , present in natural waters as a consequence of the weathering of the aluminosilicates of rocks and soil minerals, has a strong and unique affinity for aluminium<sup>7</sup>, although its influence on toxicity has not been investigated. Here we show that, with an excess of Si over Al and with the formation of hydroxy-aluminosilicate species, the bioavailability of aluminium at pH 5 is reduced and acute toxicity is eliminated. Silicic acid concentration should therefore be considered as a key parameter in toxicity studies and could be important for the treatment of vulnerable waters.

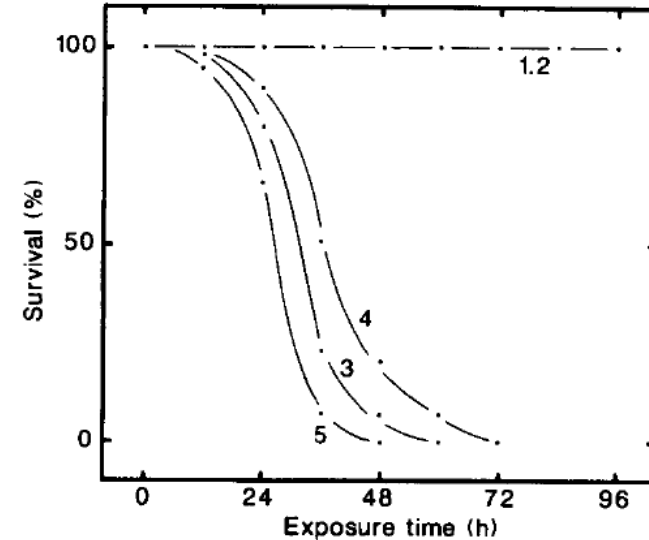


FIG. 1 Per cent survival of Atlantic salmon fry (1 g mass, post-first feeding) as a function of exposure time for the different treatment tanks (120 fish per tank). The curves are labelled for the respective tanks. All fish were kept under the control conditions for seven days before exposure and counts were made at 12-h intervals.

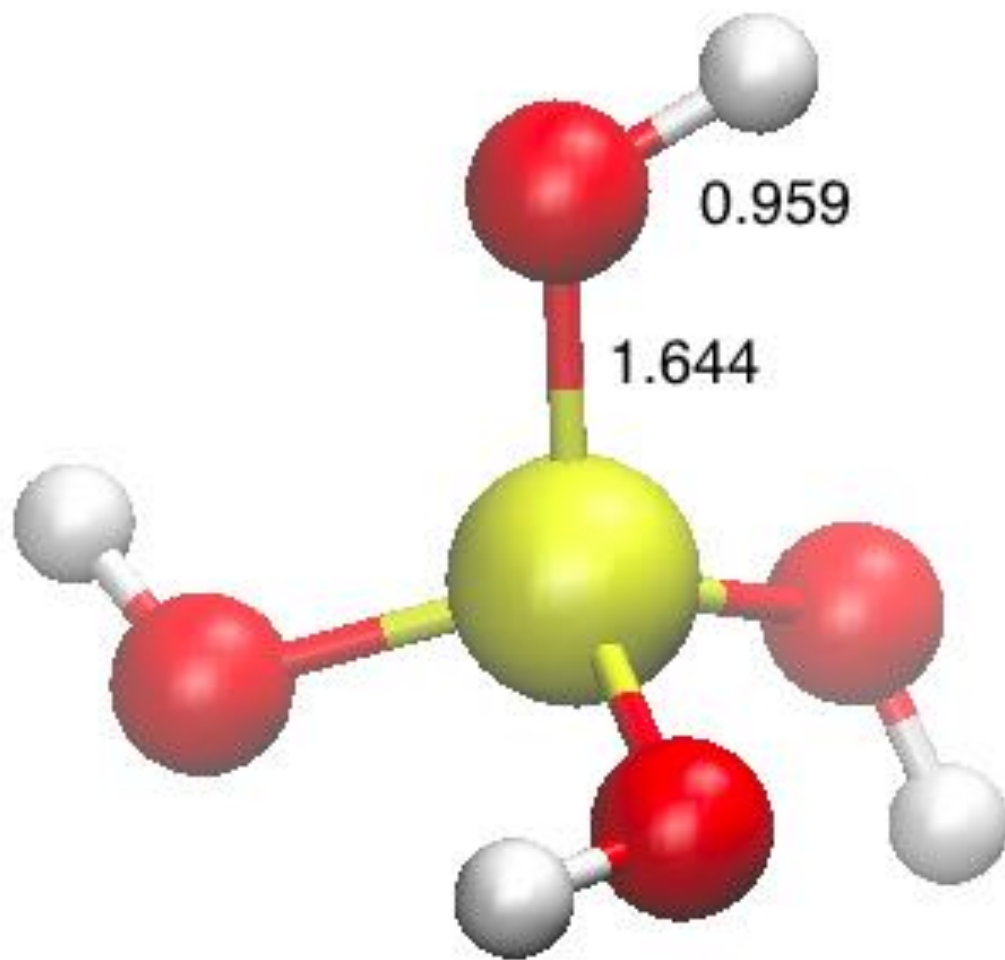
was eliminated and gill structures of the fish were normal when examined in the light microscope, in spite of the fact that this water contained the highest level of exchangeable aluminium. Whole fish were collected at intervals of 12 hours and analysed for accumulated Al and Si. Table 2 shows the mean levels of aluminium and silicon recorded in fish from each of the experimental tanks. The fraction of the total aluminium that is

Silicic Acid is a Small Neutral Molecule



# Silicic Acid; $\text{Si(OH)}_4$

Vol. = 45.939  $\text{cm}^3/\text{mol}$



## A MECHANISM OF HYDROXYALUMINOSILICATE FORMATION

C. EXLEY\* and J. D. BIRCHALL

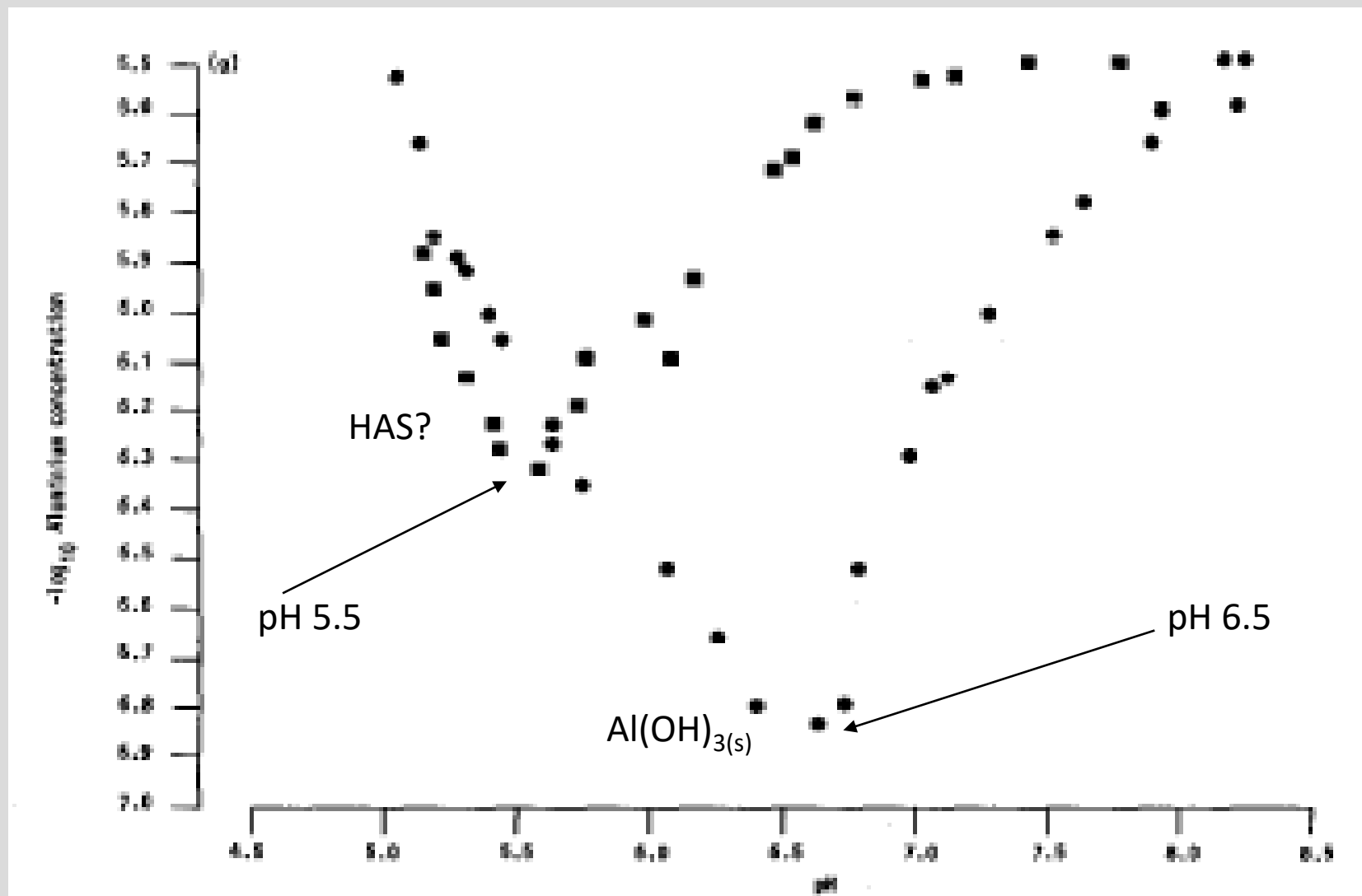
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*(Received 17 November 1992; accepted 26 January 1993)*

**Abstract**—The simple fractionation procedure membrane filtration was successfully applied to the identification of the formation of hydroxyaluminosilicates. The mechanism of formation was shown to proceed through the inhibition of the nucleation of aluminium hydroxide. The inhibition was the result of silicic acid replacing hydroxylated aluminium at growth sites on aluminium hydroxide lattices. The ability of silicic acid to poison the growth of aluminium hydroxide lattices was dependent upon solution pH and the silicic acid concentration. This may be the first fully supported observation of a reaction of this ilk involving the neutral silicic acid molecule.

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A mechanism to describe the unique inorganic chemistry of the formation of HAS



t = 12 weeks



Pergamon

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## The formation of hydroxyaluminosilicates of geochemical and biological significance

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(Received August 14, 2000; accepted in revised form December 19, 2000)

**Abstract**—Hydroxyaluminosilicates (HAS) are critical intermediates in the biogeochemical cycles of aluminium and silicon. To understand the extent of their role in controlling the solubility of Al in soil and surface waters, we need to know how they are formed and why they are formed in preference to other more soluble aluminous mineral phases. We have used a number of complementary analytical techniques to demonstrate the hitherto unproven mechanism of HAS formation of varying structure and stoichiometry. HAS were formed via the competitive condensation of silicic acid,  $\text{Si}(\text{OH})_4$ , at a hydroxyaluminium template ( $\text{HAS}_A$ ). Where  $\text{Si}(\text{OH})_4$  was present in excess,  $\text{HAS}_A$  acted as a template for further reactions with  $\text{Si}(\text{OH})_4$  ( $\text{HAS}_B$ ).  $\text{HAS}_A$  and  $\text{HAS}_B$  had idealised Si : Al ratios of 0.5 and 1.0, respectively, and were representative of HAS found in soil horizons. This mechanism of formation of HAS could be used to both explain and predict the role of  $\text{Si}(\text{OH})_4$  in Al solubility control in the natural environment. Copyright © 2001 Elsevier Science Ltd

A BREAKTHROUGH!!



THERE ARE TWO DISCRETE FORMS OF HAS!

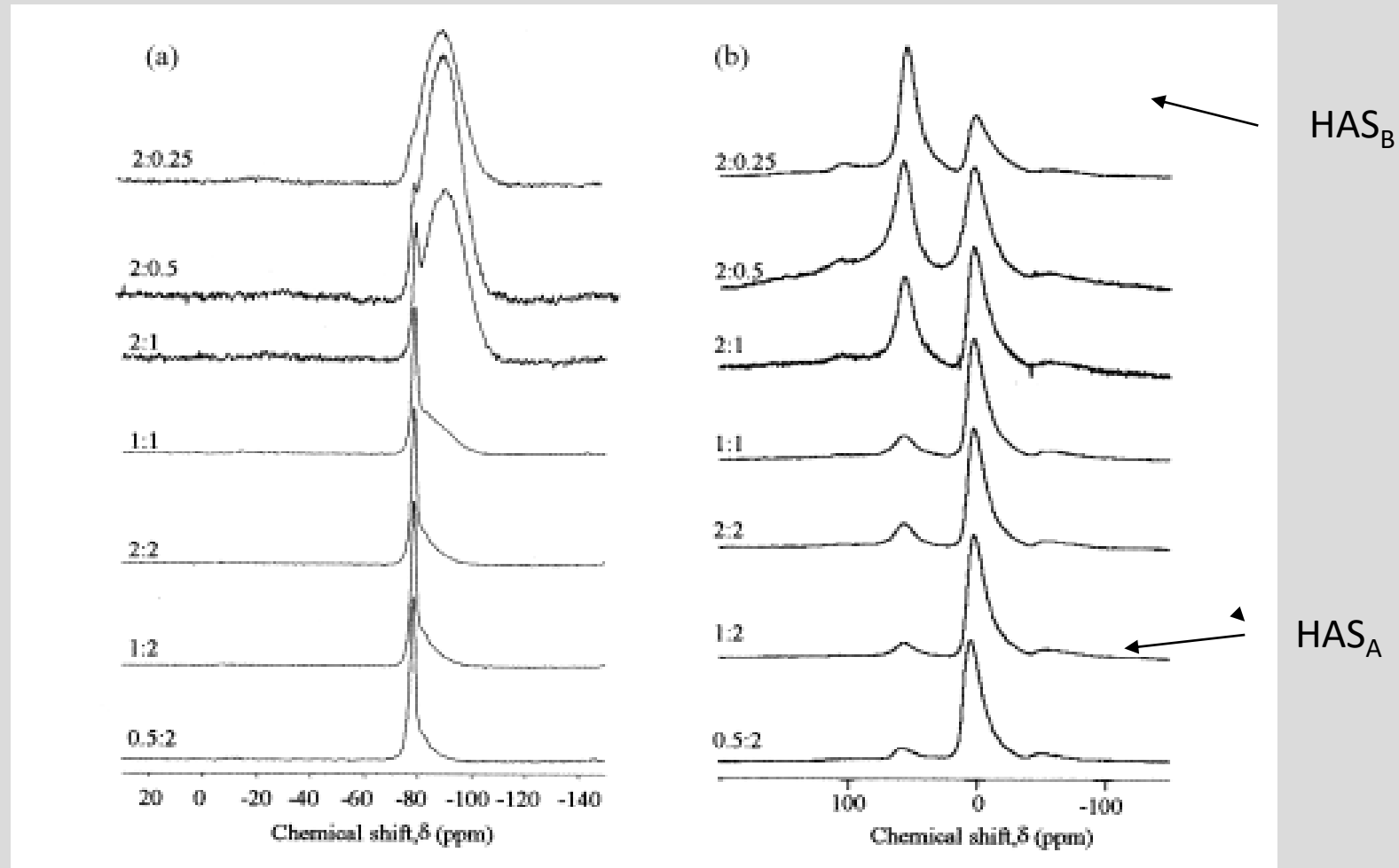


Fig. 3. The influence of different combinations of  $\text{Si}(\text{OH})_4$  and Al (units are mmol/L) on the structure of precipitated HAS.

(a)  $^{29}\text{Si}$  CP-MAS NMR. (b)  $^{27}\text{Al}$  HD-MAS NMR.

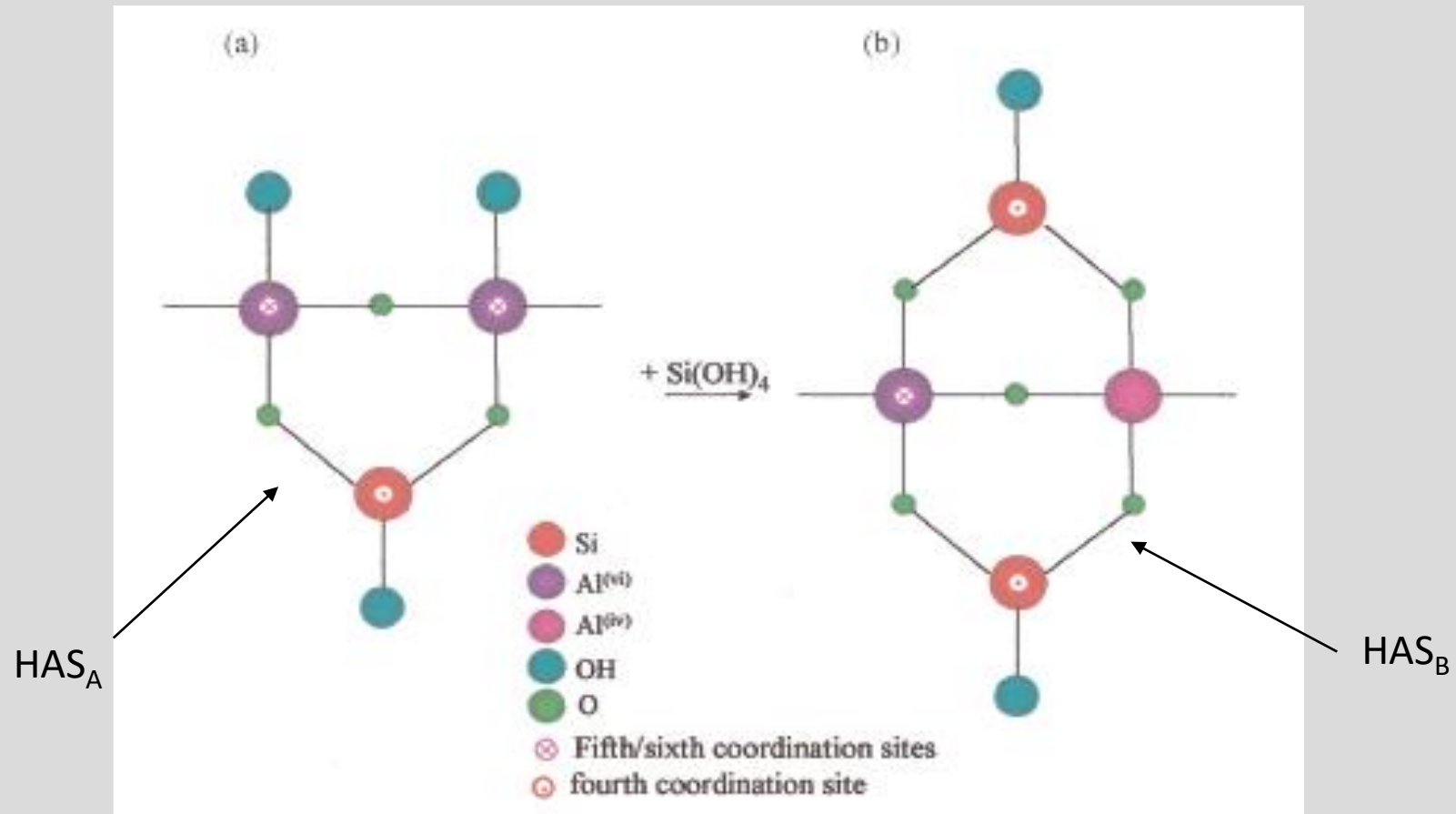


Fig. 5. Proposed unit structures of (a)  $HAS_A$  and, in the presence of an excess of  $Si(OH)_4$ , (b)  $HAS_B$ . In  $HAS_A$  the fourth coordination site on Si will be  $-O-Al$  whereas for  $HAS_B$  both  $-O-Al$  and  $-O-Si$  are predicted by NMR.



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## Direct and indirect identification of the formation of hydroxyaluminosilicates in acidic solutions

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Received 31 March 2001; accepted 9 May 2001

### Abstract

Morin–aluminium fluorescence and membrane filtration were successfully applied to the indirect identification of the formation of hydroxyaluminosilicates (HAS) in acidic solutions of varying pH and of known concentrations of aluminium (Al) and silicic acid ( $\text{Si}(\text{OH})_4$ ). It was proven to be especially useful in providing evidence of the strong competition between  $\text{Si}(\text{OH})_4$  and  $\text{Al}(\text{OH})_3$  to condense with hydroxyaluminium templates to form HAS in preference to  $\text{Al}(\text{OH})_{300}$ . The aggregation and stability of HAS and  $\text{Al}(\text{OH})_{300}$  were dependent upon both the pH and the [Al] of the solution. The applicability of these indirect techniques was confirmed using the direct observation of HAS in solution by atomic force microscopy (AFM). AFM was also a powerful tool in providing valuable information on the morphology of colloidal HAS of various structures and stoichiometries. The results have provided further confirmation of both the mechanism of HAS formation and the form and stability of HAS in solution. This information is essential to our understanding of the biological availability and hence toxicity of Al in biota, including man. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydroxyaluminosilicates; Silicon; Aluminium; Atomic force microscopy; Morin fluorescence

ATOMIC FORCE MICROSCOPY IDENTIFIES TWO DIFFERENT STRUCTURAL MOTIFS FOR HAS<sub>A</sub> AND HAS<sub>B</sub>

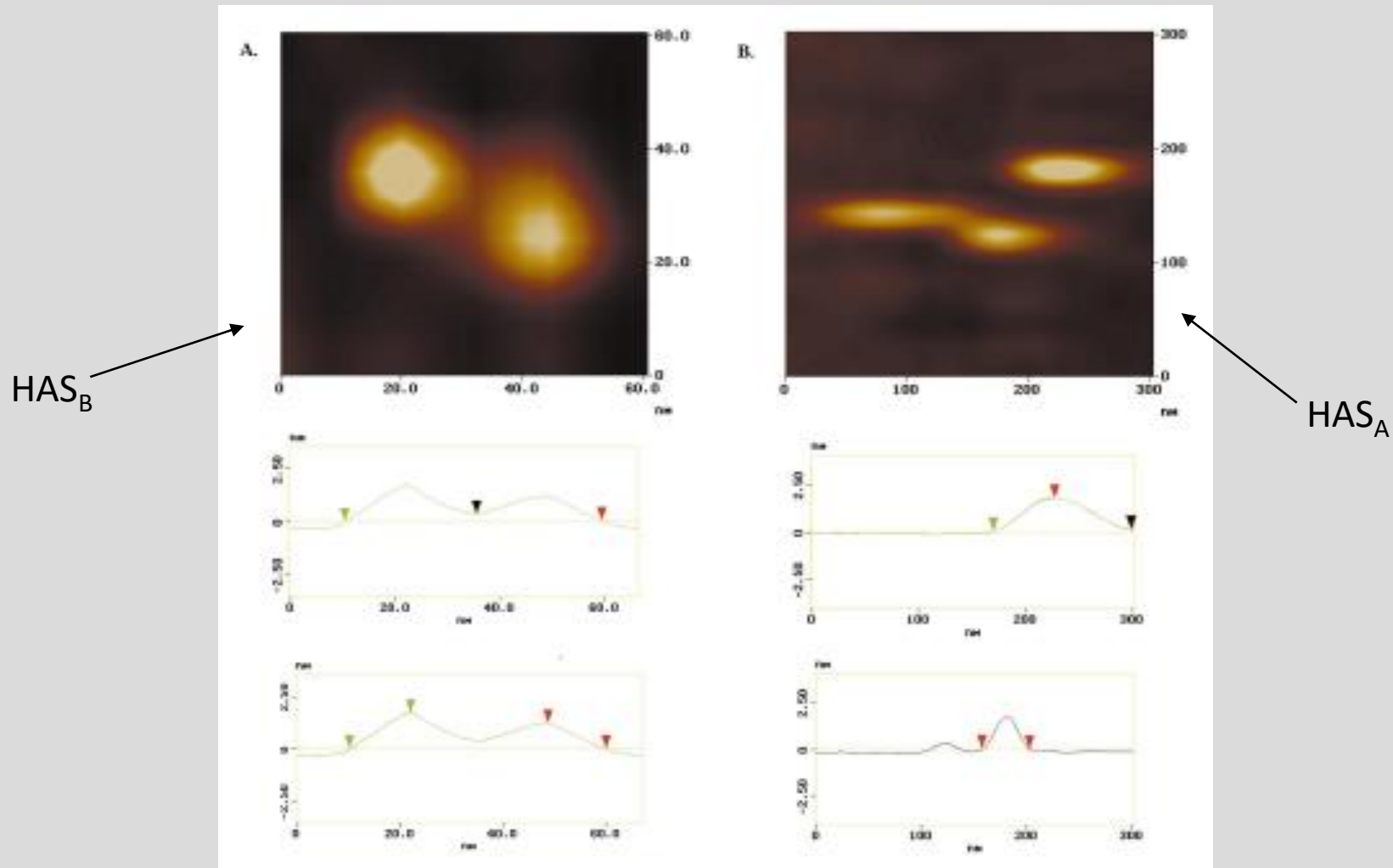


Fig. 3. Close up AFM images of representative individual HAS structures and line profiles representing the section analysis of these two structures: (A) discoid HAS, depth 1–2 nm, diameter 23–25 nm; (B) rectangular HAS, depth 1–2 nm, width 40–45 nm, length 87–170 nm.





## The solubility of an hydroxyaluminosilicate

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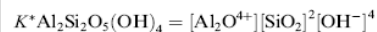
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### Abstract

Hydroxyaluminosilicates (HAS) are critical secondary mineral phases in the biogeochemical cycle of aluminium. They are formed from the reaction of silicic acid (Si(OH)<sub>4</sub>) with an aluminium hydroxide template and act as a geochemical control of the biological availability of Al. There are two main forms of HAS which we have called HAS<sub>A</sub> and HAS<sub>B</sub> and which of these will predominate will depend upon the Si(OH)<sub>4</sub> to Al ratio in any one environment. In all but the most heavily weathered environments or those undergoing a progressive acidification Si(OH)<sub>4</sub> will be present in significant excess to Al and HAS<sub>B</sub> will be the dominant secondary mineral phase. We have tried to determine the solubility of HAS<sub>B(s)</sub> so that its contribution to Al solubility control might be compared with other secondary minerals such as Al(OH)<sub>3(gibbsite)</sub>. In preliminary experiments, the dissolution of HAS<sub>B(s)</sub> was found to be non-congruent with almost no Al being released during 18 months ageing. We then demonstrated that HAS<sub>B(s)</sub> was significantly less soluble than Al(OH)<sub>3(s)</sub> prepared under identical experimental conditions. We have used this information to describe a solubility expression for HAS<sub>B(s)</sub> at a predefined quasi-equilibrium and to calculate a solubility constant.

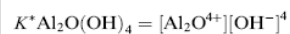


This unconventional solubility expression was derived to take account of the non-stoichiometric dissolution of HAS<sub>B(s)</sub> and included theoretical dissolution products which could then be substituted for the dissolution products which were measured experimentally.



$$K^* \text{HAS}_B = 10^{-40.6 \pm 0.15} \quad (n = 17) \quad (20 \text{ }^\circ\text{C}/I = 0.1 \text{ mol/L})$$

The derivation of the solubility expression, though non-standard in approach, was validated by its application to Al(OH)<sub>3(s)</sub> and the calculation of a realistic solubility constant.



$$K^* \text{Al}(\text{OH})_{3(s)} = [\text{Al}_i][\text{OH}^-]^4 = 10^{-30.8 \pm 0.27} \quad (n = 7) \quad (20 \text{ }^\circ\text{C}/I = 0.1 \text{ mol/L})$$

$K^* \text{HAS}_{B(s)}$  was found to be independent of [Si(OH)<sub>4</sub>] and predicted that HAS<sub>B(s)</sub> could be the predominant secondary mineral phase controlling the solubility of Al in environments in which the pH > 4.00 and [Si(OH)<sub>4</sub>] > 100 μmol/L.

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**Keywords:** Hydroxyaluminosilicate; Aluminium; Silicic acid; Aluminium solubility; Aluminium biological availability

Fast-reacting Al

HAS<sub>B</sub> is considered as the  
hydroxide of an aluminosilicate



$$K^* \text{HAS}_B = 10^{-40.6 \pm 0.15} \quad (n = 17) \quad (20 \text{ }^\circ\text{C}/I = 0.1 \text{ mol/L})$$

The expression predicts that HAS<sub>B(s)</sub> could be the predominant secondary mineral phase controlling the solubility of Al in environments in which the pH > 4.00 and [Si(OH)<sub>4</sub>] > 100 μmol/L.

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# The formation, precipitation and structural characterisation of hydroxyaluminosilicates formed in the presence of fluoride and phosphate

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Received 8 March 2005; accepted 27 April 2005

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## Abstract

Hydroxyaluminosilicates (HAS) are important secondary mineral phases formed by the reaction of silicic acid ( $\text{Si}(\text{OH})_4$ ) with aluminium. Two discrete forms of HAS have been identified ( $\text{HAS}_A$  and  $\text{HAS}_B$ ) and their structures and composition determined. Herein we have investigated the formation of HAS in the presence of equimolar  $\text{Si}(\text{OH})_4$  and fluoride ( $\text{F}^-$ ) or phosphate ( $\text{HPO}_4^{2-}$ ). The latter resulted in the precipitation of aluminium hydroxyphosphate and inhibited the formation of HAS except where the concentration of Al was significantly in excess of  $\text{HPO}_4^{2-}$  where  $\text{HAS}_A$  was co-precipitated. There was no evidence of the formation of HAS which included phosphate in the structure. Fluoride did not prevent the formation of HAS, except, possibly, when it was present at four times the concentration of Al, and the inclusion of F in precipitated HAS was confirmed using electron microprobe and solid state NMR. Both  $\text{HAS}_A$  and  $\text{HAS}_B$  were found to incorporate F though evidence from NMR, in particular, suggested that F substituted for OH on Al but not on Si. In addition F was bound to octahedrally and not tetrahedrally co-ordinated Al and this preference appeared to inhibit or delay the dehydroxylation reaction which is involved in the transition between  $\text{HAS}_A$  and  $\text{HAS}_B$ . This is the first report of F-substituted HAS and further research will be required to determine if they are of environmental significance or, indeed, if these inorganic fluorinated polymers are of any value to materials science.

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*Keywords:* Aluminium; Silicic acid; Hydroxyaluminosilicate; Biogeochemistry

## THE FIRST EXAMPLES OF FLUORIDE-SUBSTITUTED HAS

Table 1

Concentrations of silicic acid, aluminium, fluoride and phosphate in parent solutions at the beginning of the experiment and after collection of solid phases and elemental composition of the solid phases

Stoichiometry of solution (mmol/L)				Si(OH) <sub>4</sub> -dialysis (μmol/L)		Al-dialysis (μmol/L)		F-filtration (μmol/L)		P-filtration (μmol/L)		Solid phase
Si	Al	F	P	Mean	SD <sup>a</sup>	Mean	SD	Mean	SD	Mean	SD	
0.5	2.0			4	0.7	<1						SiAl <sub>3.7</sub>
0.5	2.0	0.5		7	2.1	17	4.1	110	9.7			SiAl <sub>4.0</sub> F <sub>0.47</sub>
0.5	2.0		0.5	181 <sup>b</sup>	2.0	<1				<1		SiAl <sub>6.8</sub> P <sub>1.9</sub>
1.0	2.0			73	4.0	<1						SiAl <sub>2.3</sub>
1.0	2.0	1.0		141	6.0	66	12	404	9.0			SiAl <sub>2.45</sub> F <sub>0.44</sub>
1.0	2.0		1.0	798 <sup>b</sup>	14	<1				10	0.3	SiAl <sub>9.6</sub> P <sub>6.8</sub>
1.0	1.0			255	17	<1						SiAl <sub>1.6</sub>
1.0	1.0	1.0		451	4.0	199	11	621	45			SiAl <sub>2.0</sub> F <sub>0.37</sub>
1.0	1.0		1.0	980 <sup>b</sup>	8.0	<1				165	2.0	SiAl <sub>33</sub> P <sub>7.8</sub>
2.0	1.0			563	72	<1						SiAl <sub>1.06</sub>
2.0	1.0	2.0		937	43	324	27	1349	94			SiAl <sub>1.03</sub> F <sub>0.24</sub>
2.0	1.0		2.0	1857 <sup>b</sup>	8.0	<1				268	4.1	SiAl <sub>44</sub> P <sub>14</sub>
2.0	0.5			824	45	<1						SiAl <sub>0.87</sub>
2.0	0.5	2.0		1420	61	223	45	1492	80			<sup>c</sup>
2.0	0.5		2.0	1768 <sup>b</sup>	13	<1				1209	29	SiAl <sub>25</sub> P <sub>8</sub>

<sup>a</sup> Standard deviation,  $n = 9$ .

<sup>b</sup> Filtration through 0.1 μm Durapore membrane filters.

<sup>c</sup> No solid phase collected.

Fluoride-substituted HAS



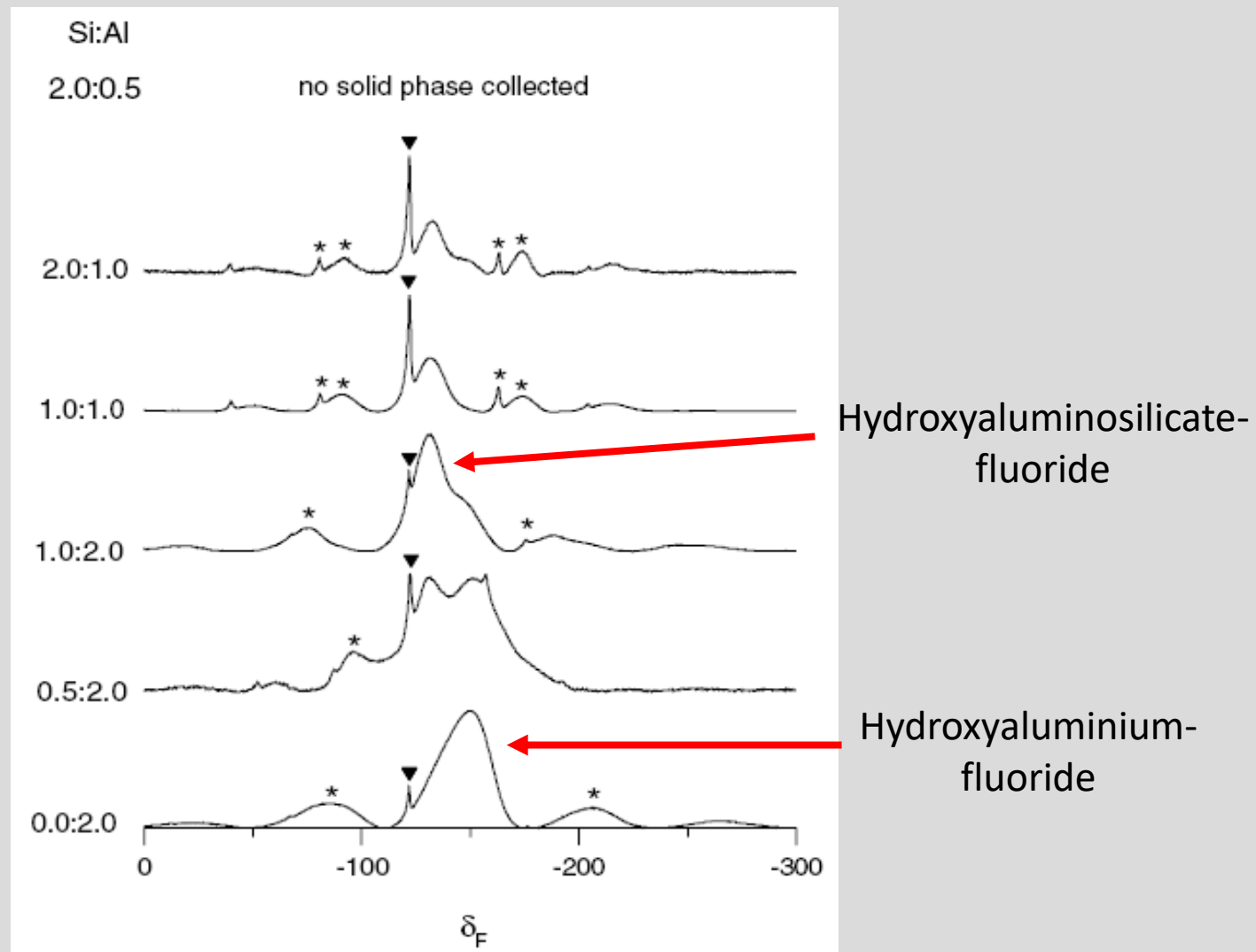


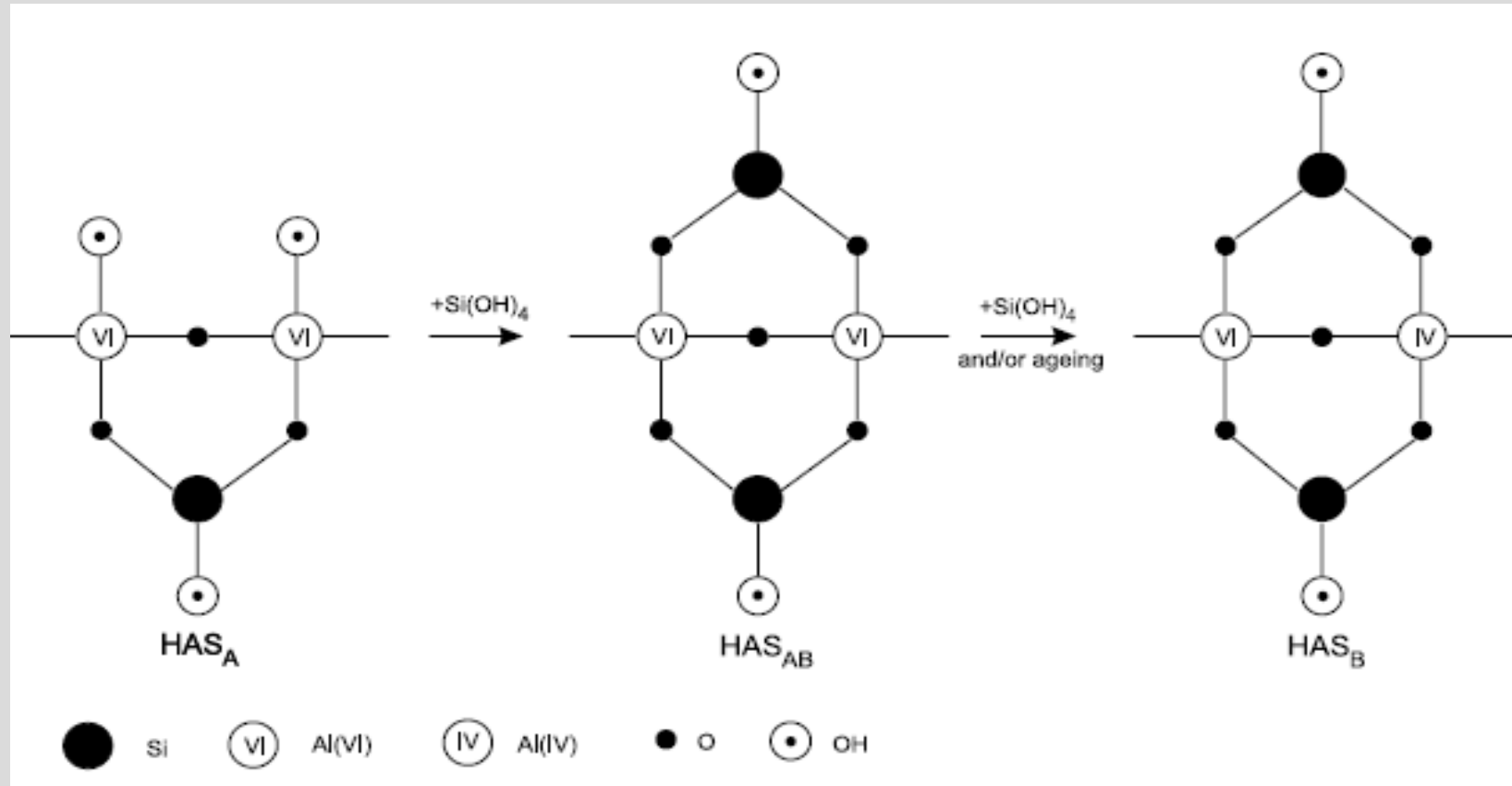
Fig. 4.  $^{19}\text{F}$  MAS NMR spectra of solid phases prepared in the presence of F.

Si:Al – indicates the concentrations of  $\text{Si}(\text{OH})_4$  and Al in parent solutions.

$[\text{F}] = [\text{Si}(\text{OH})_4]$  except, if  $[\text{Si}(\text{OH})_4] = 0$ , then  $[\text{F}] = 0.5 \text{ mmol/L}$ .

Asterisks mark positions of sidebands and inverted triangles mark the position of chemical shift corresponding to contaminating PTFE.

## A Transitional Form of HAS?



Suggested scheme for the formation of HAS<sub>B</sub> from HAS<sub>A</sub> involving a transitional form, HAS<sub>AB</sub>, which undergoes a dehydroxylation fuelled by either ageing or a significant excess of Si(OH)<sub>4</sub>.



# Thermal analyses of aluminium hydroxide and hydroxyaluminosilicates

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## Abstract

Hydroxyaluminosilicates (HAS<sub>A</sub> and HAS<sub>B</sub>) are important secondary mineral phases in the biogeochemical cycle of aluminium. HAS<sub>A</sub> is formed by the reaction of silicic acid (Si(OH)<sub>4</sub>) with an aluminium hydroxide (Al(OH)<sub>3(s)</sub>) template with further substitution of Si(OH)<sub>4</sub> into HAS<sub>A</sub> resulting in HAS<sub>B</sub>. Recently, fluoride and phosphate-substituted forms of HAS have been synthesised and characterised. Thermogravimetric analysis incorporating differential scanning calorimetry (TGA–DSC) is an effective method for studying the structure of mineral phases and was used herein as a possible tool to discriminate between different forms of HAS as well as to elucidate further upon their mechanism of formation. All of the HAS studied exhibited distinctive thermal behaviour dependent upon their Si:Al ratio and the inclusion of fluoride or phosphate in their structure. The observed thermal characteristics were sufficient to allow different HAS to be identified though they did not offer any structural information in addition to that which was obtained previously by solid-state NMR and microprobe analysis. We have identified an hitherto unrecognised form of a purely amorphous Al(OH)<sub>3(s)</sub> the thermal signature of which was a sharp exothermic peak (ca. 282 °C) which though present in HAS<sub>A</sub>-like structures (260–275 °C) was absent from HAS<sub>B</sub>-like structures. Solid-state NMR of heated HAS and Al(OH)<sub>3(s)</sub> could not identify any significant changes in the coordination of aluminium which might be associated with this characteristic exotherm. However, NMR was successful in identifying Al<sup>(V)</sup> as a potential intermediate in the transformation of HAS<sub>A</sub> to HAS<sub>B</sub>.

The identification of a novel form of purely amorphous Al(OH)<sub>3(s)</sub> may be of interest to chemists and materials scientists alike.

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*Keywords:* Aluminium; Silicic acid; Hydroxyaluminosilicate; Aluminium hydroxide; Amorphous; Thermogravimetric analysis; Differential scanning calorimetry



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## Further insight into the mechanism of formation of hydroxyaluminosilicates

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### Abstract

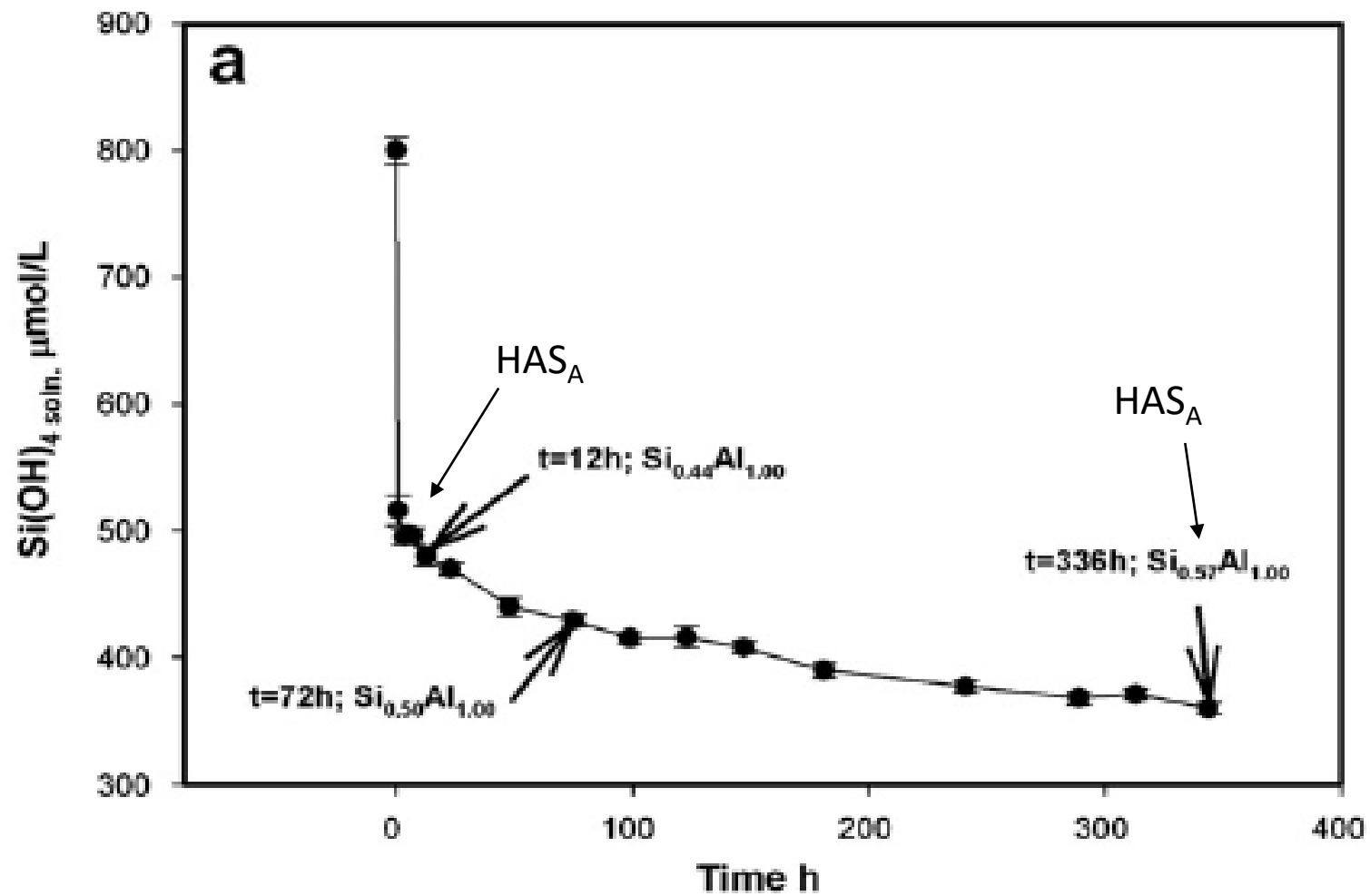
Hydroxyaluminosilicates (HAS) are formed by the reaction of silicic acid ( $\text{Si}(\text{OH})_4$ ) with adjacent hydroxyl groups on an aluminium hydroxide ( $\text{Al}(\text{OH})_{3(s)}$ ) framework or template. They are important secondary mineral phases in the biogeochemical cycling of aluminium and are extremely insoluble. Two discrete forms of HAS have been identified.  $\text{HAS}_A$  which is formed when  $[\text{Si}(\text{OH})_4] \leq [\text{Al}]$  and  $\text{HAS}_B$  which is formed when  $[\text{Si}(\text{OH})_4] \gg [\text{Al}]$ . The formation of  $\text{HAS}_B$  has been suggested to involve the further reaction of  $\text{Si}(\text{OH})_4$  with  $\text{HAS}_A$  and it is this contention that, in the main, we have tested herein. Applying a number of analytical and structural tools we have demonstrated the critical importance of both absolute concentrations and relative ratios of  $\text{Si}(\text{OH})_4$  and Al in solution in determining which form of HAS will be precipitated from solution. In addition, by collecting HAS both almost immediately upon their precipitation from solutions (ca 0.5 h) and after ageing in solutions for up to 336 h and analysing their stoichiometries and structural configurations we have shown that the formation of  $\text{HAS}_A$  was the first step in the formation of HAS including in those solutions in which  $[\text{Si}(\text{OH})_4] \gg [\text{Al}]$  and ultimately ( $\geq 72$  h ageing) only  $\text{HAS}_B$  was identified. These are the first experimental results which support the long held belief that  $\text{Al}(\text{OH})_{3(s)}$  is a prerequisite to the formation of  $\text{HAS}_A$  which, in turn, is the precursor to the formation of  $\text{HAS}_B$ . The insight we have gained should enable a better understanding of the role of HAS both in their control of the biological availability of aluminium and in their potential future applications in materials science.

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*Keywords:* Aluminium; Silicic acid; Hydroxyaluminosilicate; Biogeochemistry; Bioinorganic chemistry

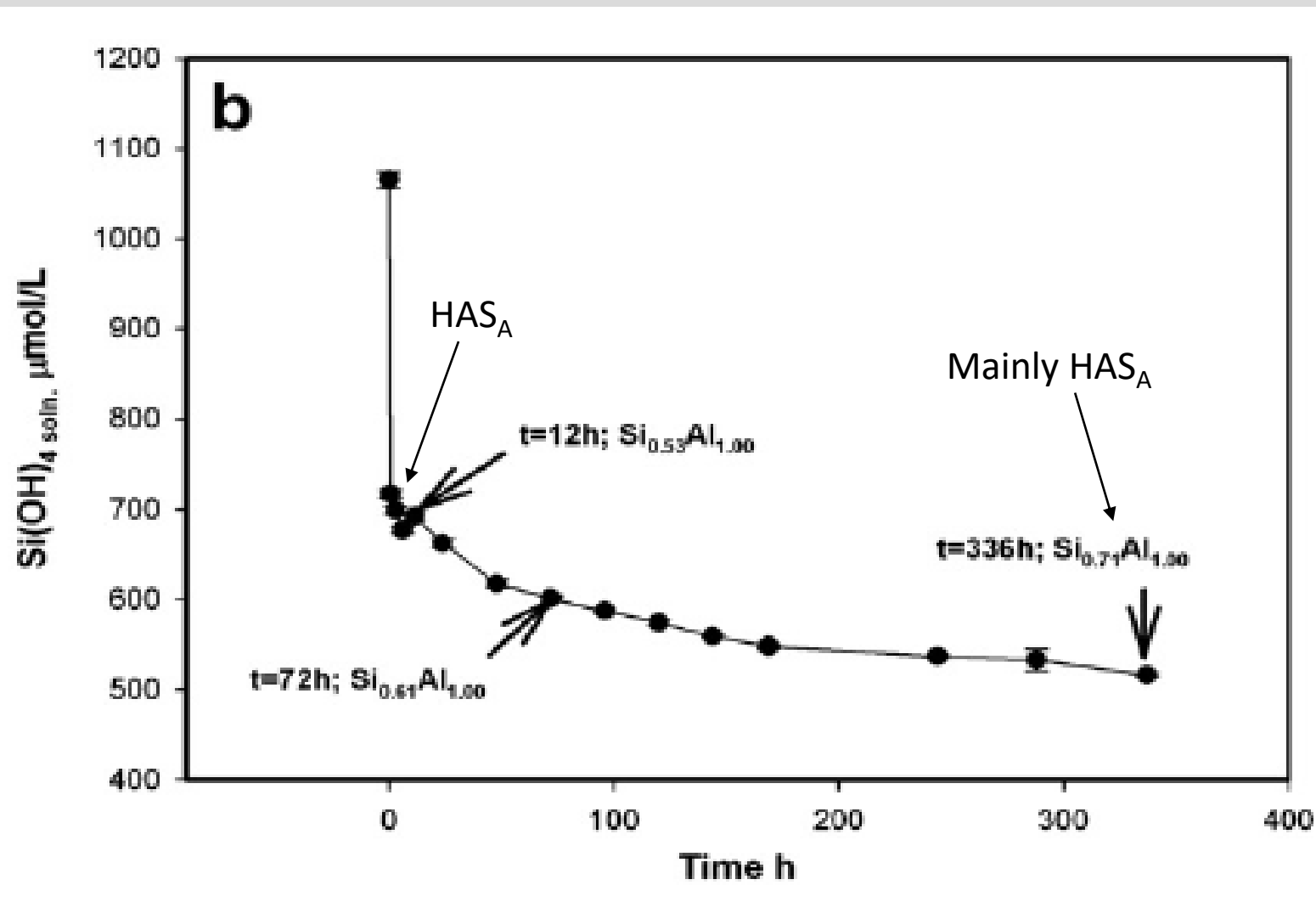
$\text{Al}(\text{OH})_{3(s)}$  is a prerequisite to  $\text{HAS}_{A(s)}$  which is a prerequisite to  $\text{HAS}_{B(s)}$

0.8 mM Al + 0.8 mM Si(OH)<sub>4</sub>

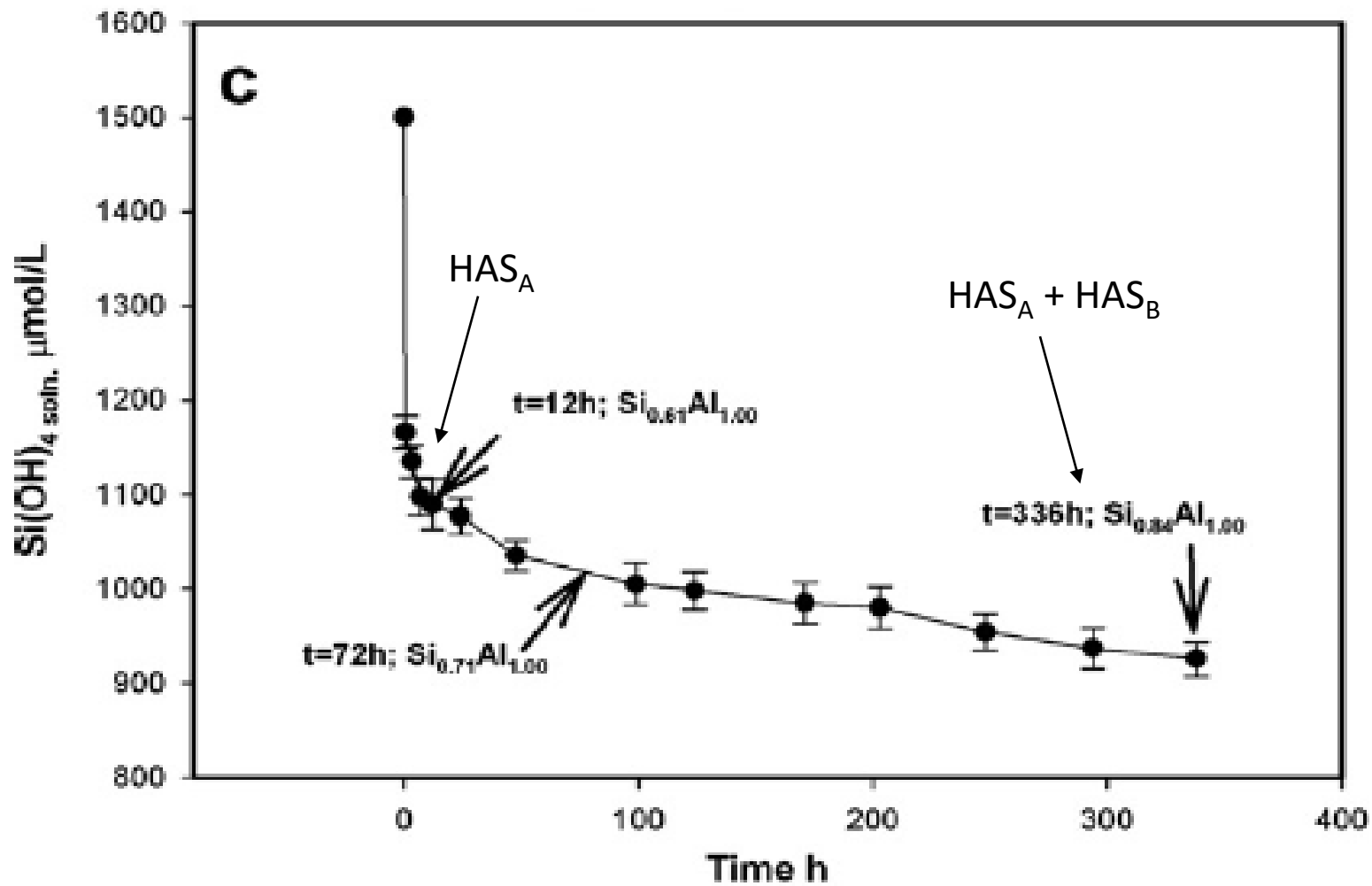


Which HAS is predicted/formed?

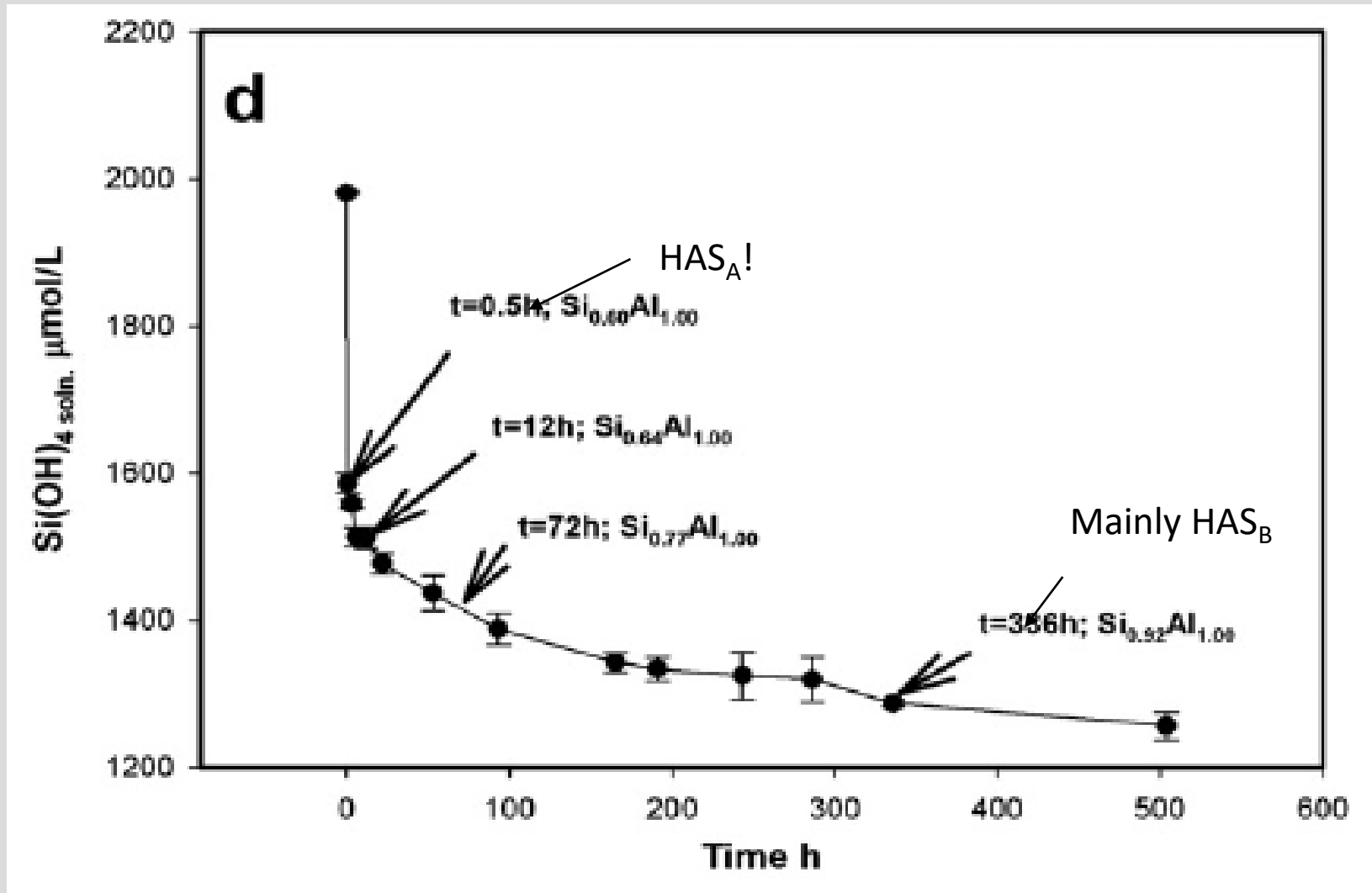
0.8 mM Al + 1.1 mM Si(OH)<sub>4</sub>



0.8 mM Al + 1.5 mM Si(OH)<sub>4</sub>



0.8 mM Al + 2.0 mM Si(OH)<sub>4</sub>



The earliest solid phase that can be collected from these solutions has the stoichiometry of 2 Al to 1 Si....HAS<sub>A</sub>!!

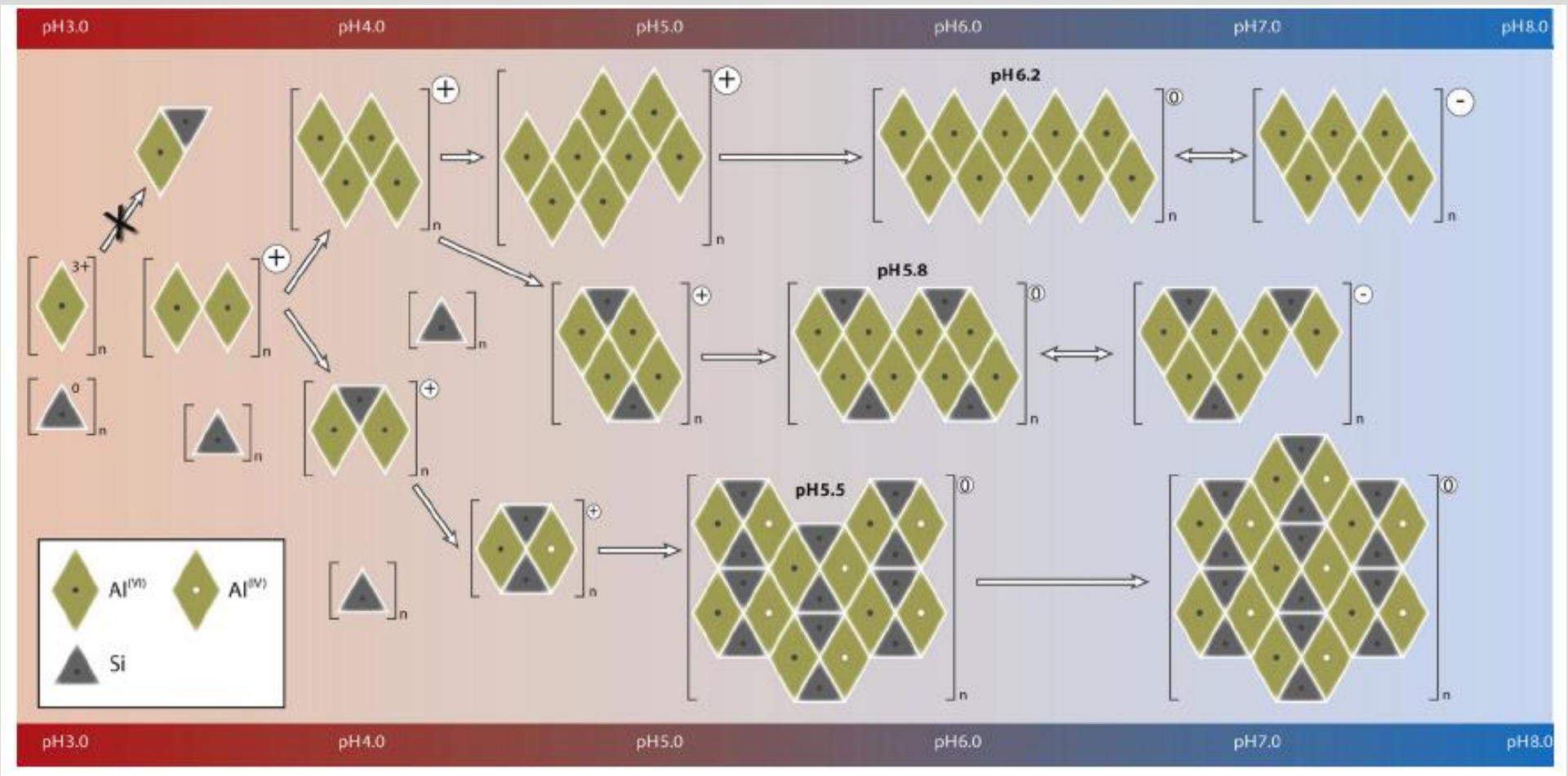


# SUMMARY OF WHAT WE NOW KNOW ABOUT HAS

- (i)  $\text{HAS}_{(s)}$  are only formed in solutions which are saturated with respect to  $\text{Al}(\text{OH})_{3(s)\text{amorphous}}$ .
- (ii)  $\text{HAS}_{(s)}$  are formed in solutions in which the precipitation of  $\text{Al}(\text{OH})_{3(s)}$  is approached from either acidic or basic conditions or where  $\text{Si}(\text{OH})_{4(aq)}$  is mixed with preformed  $\text{Al}(\text{OH})_{3(s)}$ .
- (iii) The initial step in the formation of  $\text{HAS}_{(s)}$  is the 'competitive' condensation of  $\text{Si}(\text{OH})_{4(aq)}$  across adjacent hydroxyl groups on a framework of  $\text{Al}(\text{OH})_{3(s)}$ .
- (iv) There are two discrete and structurally distinct forms of  $\text{HAS}_{(s)}$ . They are not simply an amorphous 'mixture' of  $\text{Al}(\text{OH})_{3(s)}$  and  $\text{Si}(\text{OH})_{4(aq)}$ .
- (v)  $\text{HAS}_{A(s)}$  is composed of aluminium and silicon in the ratio of 2:1 and is the predominant form of  $\text{HAS}_{(s)}$  in solutions in which the initial  $[\text{Si}(\text{OH})_{4(aq)}]$  is less than or equal to  $[\text{Al}_T]$ .

## SUMMARY cont.

- (vi)  $\text{HAS}_{\text{B(s)}}$  is composed of aluminium and silicon in the ratio of 1:1 and is the predominant form of  $\text{HAS}_{\text{(s)}}$  in solutions in which the initial  $[\text{Si}(\text{OH})_{4(\text{aq})}]$  is significantly in excess (more than twice) of  $[\text{Al}_{\text{T}}]$ .
- (vii) The formation of  $\text{HAS}_{\text{A(s)}}$  is a prerequisite to the formation of  $\text{HAS}_{\text{B(s)}}$  and this is irrespective of the initial solution ratio of  $\text{Si}(\text{OH})_{4(\text{aq})}$  and  $\text{Al}_{\text{T}}$ . Thus,  $\text{HAS}_{\text{B(s)}}$  is formed via the further condensation of  $\text{Si}(\text{OH})_{4(\text{aq})}$  across adjacent hydroxyl groups on a framework of  $\text{HAS}_{\text{A(s)}}$ .



Reflections upon and recent insight into the mechanism of formation of **hydroxyaluminosilicates** and the therapeutic potential of **silicic acid**.

OPEN

## What is the mechanism of formation of hydroxyaluminosilicates?

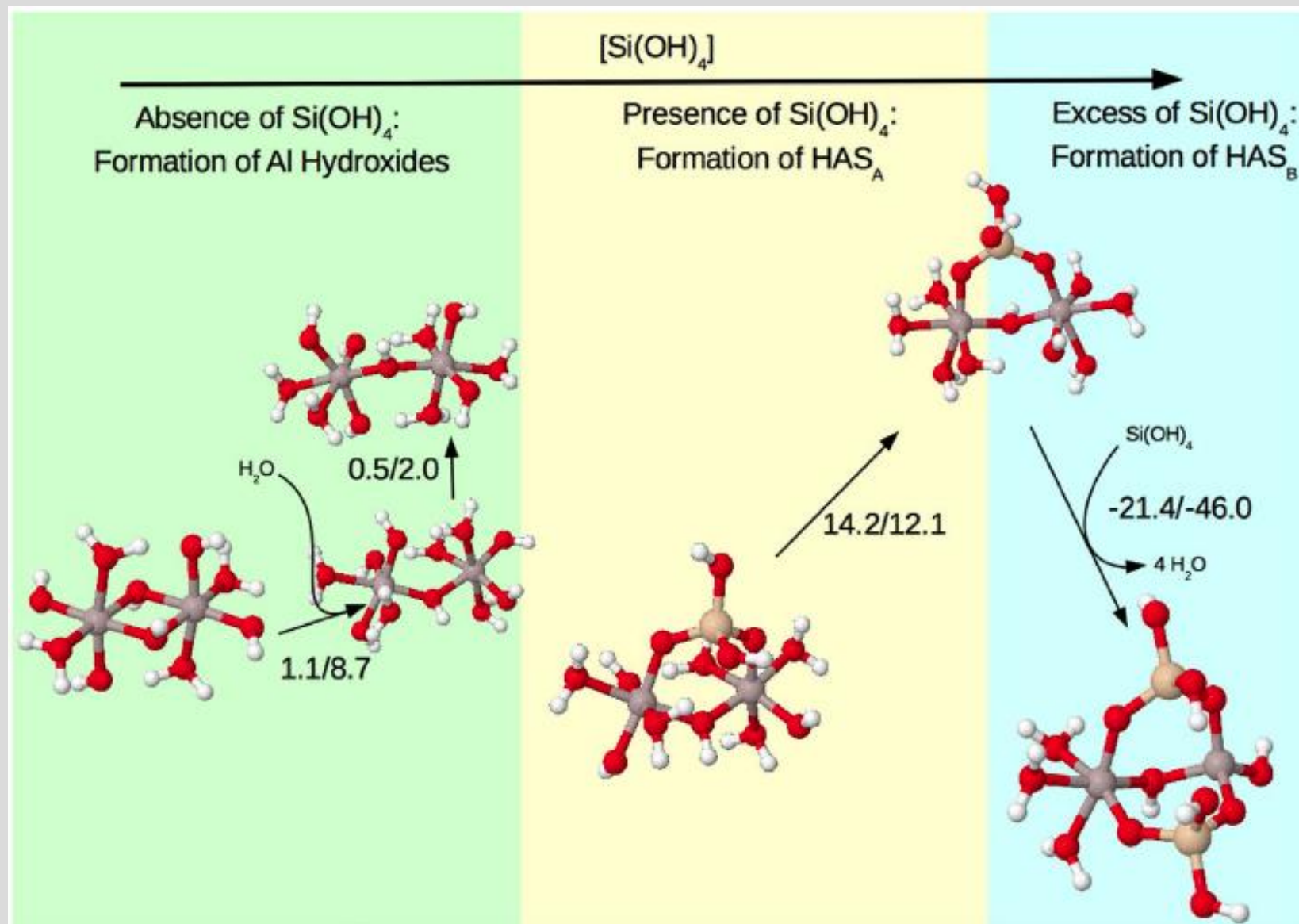
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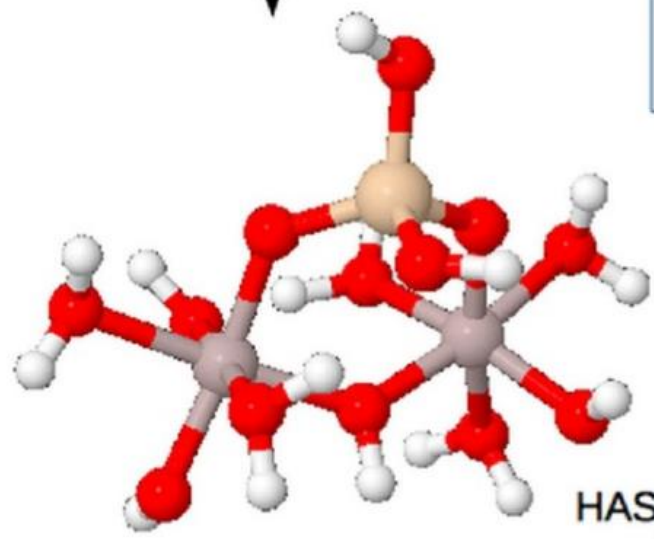
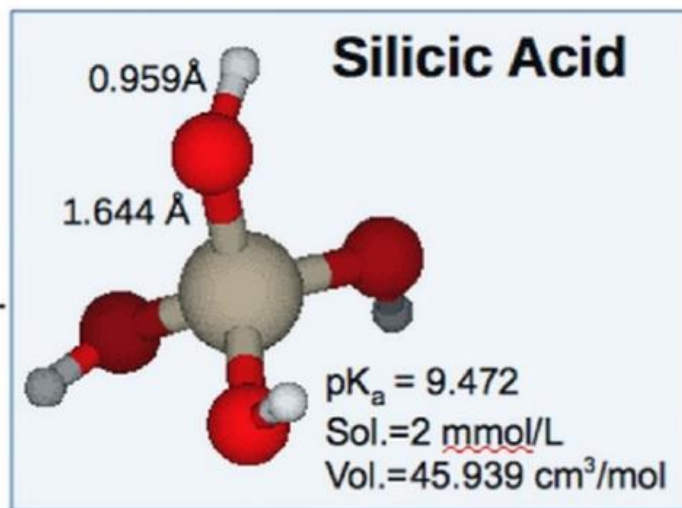
James Beardmore<sup>1</sup>, Xabier Lopez<sup>2</sup>, Jon I. Mujika<sup>2</sup> & Christopher Exley<sup>1</sup>

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.

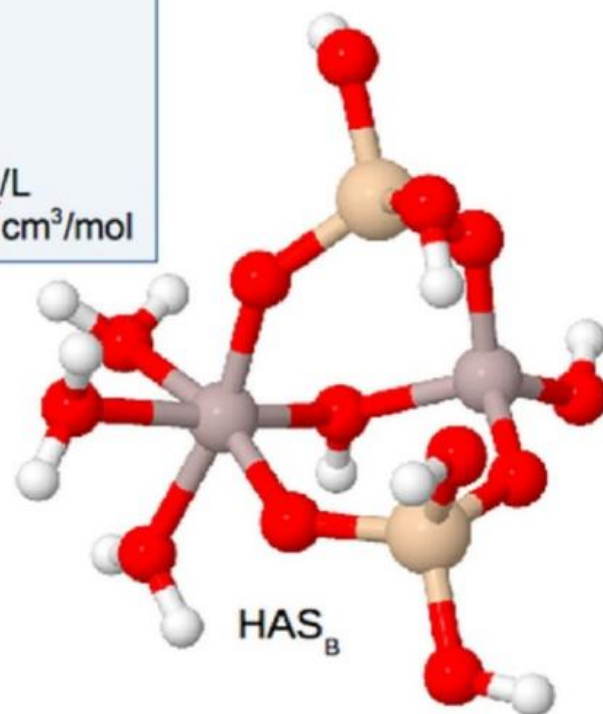




Aluminium Hydroxide

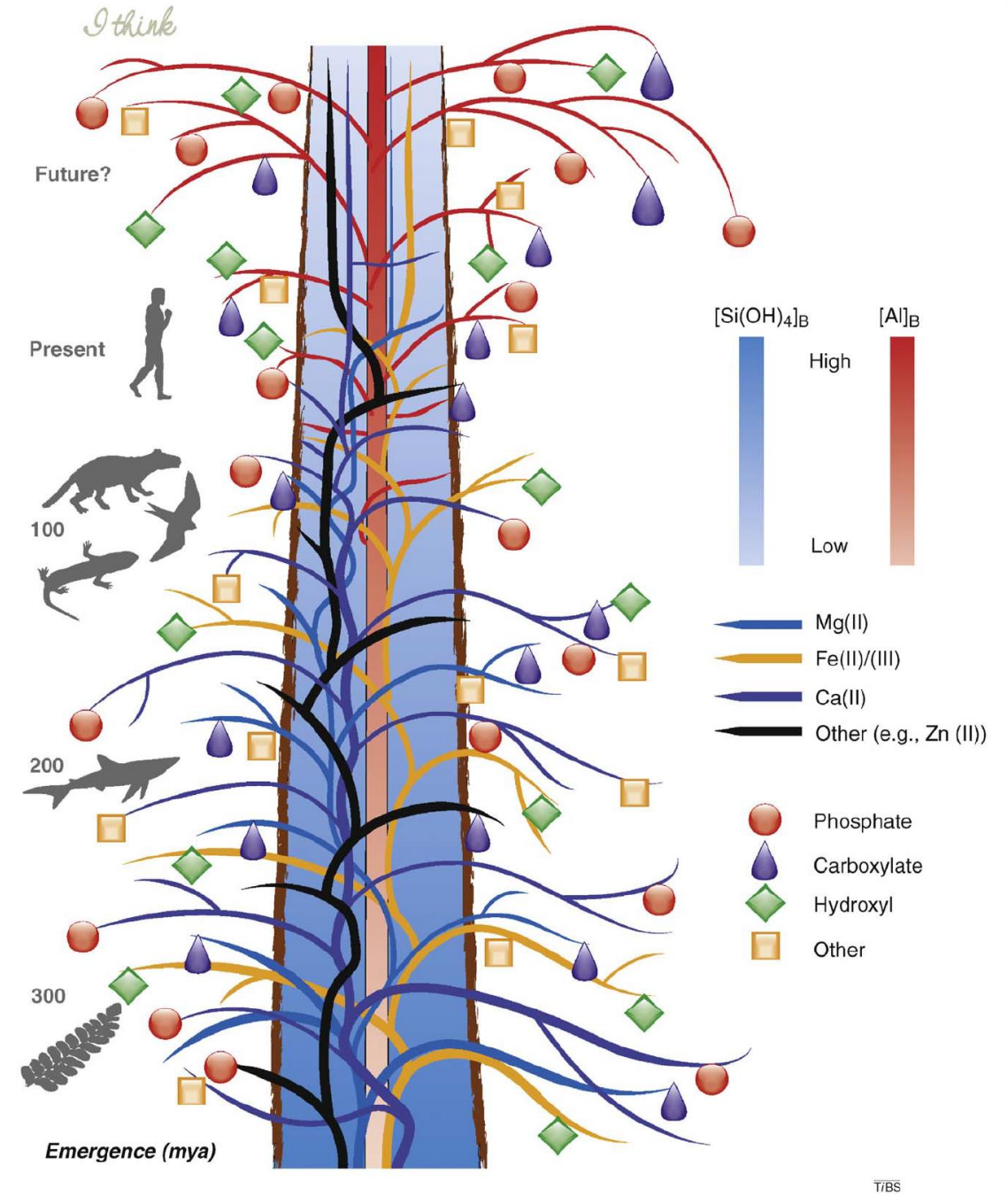


HAS<sub>A</sub>



HAS<sub>B</sub>





TIBS

# Silicic Acid, The Beneficent Molecule

Coordination Chemistry Reviews 256 (2012) 82–88



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Review

Reflections upon and recent insight into the mechanism of formation of hydroxyaluminosilicates and the therapeutic potential of silicic acid

Christopher Exley\*



# Silicon-Rich Mineral Water as a Non-Invasive Test of the ‘Aluminum Hypothesis’ in Alzheimer’s Disease

Samantha Davenward<sup>a</sup>, Peter Bentham<sup>b</sup>, Jan Wright<sup>b</sup>, Peter Crome<sup>c</sup>, Deborah Job<sup>c</sup>, Anthony Polwart<sup>d</sup> and Christopher Exley<sup>a,\*</sup>

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Accepted 4 August 2012

**Abstract.** There has been a plausible link between human exposure to aluminum and Alzheimer’s disease for several decades. We contend that the only direct and ethically acceptable experimental test of the ‘aluminum hypothesis’, which would provide unequivocal data specific to the link, is to test the null hypothesis that a reduction in the body burden of aluminum to its lowest practical limit would have no influence upon the incidence, progression, or severity of Alzheimer’s disease. Herein we are testing the hypothesis that silicon-rich mineral waters can be used as non-invasive methods to reduce the body burden of aluminum in individuals with Alzheimer’s disease and a control group consisting of their carers and partners. We have shown that drinking up to 1 L of a silicon-rich mineral water each day for 12 weeks facilitated the removal of aluminum via the urine in both patient and control groups without any concomitant affect upon the urinary excretion of the essential metals, iron and copper. We have provided preliminary evidence that over 12 weeks of silicon-rich mineral water therapy the body burden of aluminum fell in individuals with Alzheimer’s disease and, concomitantly, cognitive performance showed clinically relevant improvements in at least 3 out of 15 individuals. This is a first step in a much needed rigorous test of the ‘aluminum hypothesis of Alzheimer’s disease’ and a longer term study involving many more individuals is now warranted.

We have provided preliminary evidence that over 12 weeks of silicon-rich mineral water therapy the body burden of aluminum fell in individuals with Alzheimer's disease and, concomitantly, cognitive performance showed clinically relevant improvements in at least 3 out of 15 individuals. This is a first step in a much needed rigorous test of the 'aluminum hypothesis of Alzheimer's disease' and a longer term study involving many more individuals is now warranted.



## Research Paper

# Urinary Excretion of Aluminium and Silicon in Secondary Progressive Multiple Sclerosis



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## ABSTRACT

**Background:** Progressive multiple sclerosis is a chronic autoimmune condition of unknown aetiology and few therapeutic options. Human exposure to aluminium has been linked with multiple sclerosis and affected individuals are known to excrete unusually high amounts of aluminium in their urine. Silicon-rich mineral waters facilitate the removal of aluminium from the body in urine and herein we have tested their efficacy in affecting urinary excretion of aluminium in individuals diagnosed with secondary progressive multiple sclerosis (SPMS). **Methods:** Urinary excretion of aluminium and silicon, measured using transversely-heated graphite furnace atomic absorption spectrometry, was determined in 15 individuals diagnosed with SPMS over 24 weeks, a 12 week baseline period (control) followed by a 12 week treatment period, during which individuals consumed up to 1.5 L of a silicon-rich mineral water every day.

**Findings:** Individuals with SPMS excreted high amounts of aluminium during the baseline period (135.2 nmol/mmol Cr<sub>t</sub> (70.3–222.2, n = 180) and females excreted significantly more aluminium than males. Regular drinking of a silicon-rich mineral water increased the urinary excretion of aluminium significantly (349.0 nmol/mmol Cr<sub>t</sub> (231.7–524.7, n = 180; three-way ANOVA,  $F_{1,13} = 59.17$ , p-value = 0.000003) relative to the baseline period. The majority of individuals, 14 out of 15, excreted more aluminium ( $\mu\text{mol}/24\text{ h}$ ) following drinking of a silicon-rich mineral water (independent-test,  $p < 0.05$ ). Silicon-rich mineral waters may be an effective and non-invasive therapy for the removal of aluminium from the body of individuals with SPMS.

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# Myriad Anecdotes a Clinical Trial Doth Not Make

“A little over 2 months ago we started Fiji water. I thought it was silly so I drank 1.5 liters very quickly and my 5 year old (who has asd and spd) had 16 oz. My son got a headache a few hours later and had some wild behaviors in the following days. I continued to drink 1.5 and I lowered my son quite a bit. I then started to get super dizzy so I lowered my consumption as well. That first week was pretty dramatic! My brain fog lifted and the feeling of a heavy chest vanished. My son was much calmer, more focused, less sensory sensitive, and generally more happy. Fast forward 2 months. My sons eye contact has increased dramatically, he sings every once and awhile, he is playing more with kids, and he now begs for Fiji water. My own symptoms have improved quite a bit, I have POTS, MCAS, and EDS”.