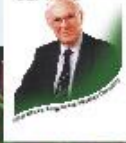


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Innovations in Inorganic and Materials Chemistry

Silicic acid, a molecule for all seasons (and climates)

Christopher Exley PhD FRSB

The Birchall Centre, Lennard-Jones Laboratories, Keele University, Keele, Staffordshire, ST5 5BG, UK.

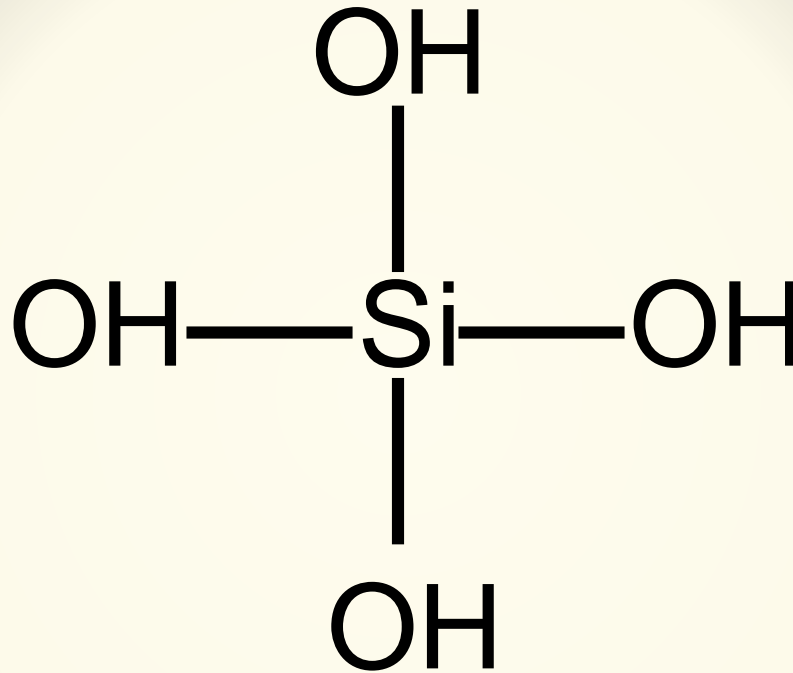
c.exley@keele.ac.uk

<http://www.keele.ac.uk/aluminium/>

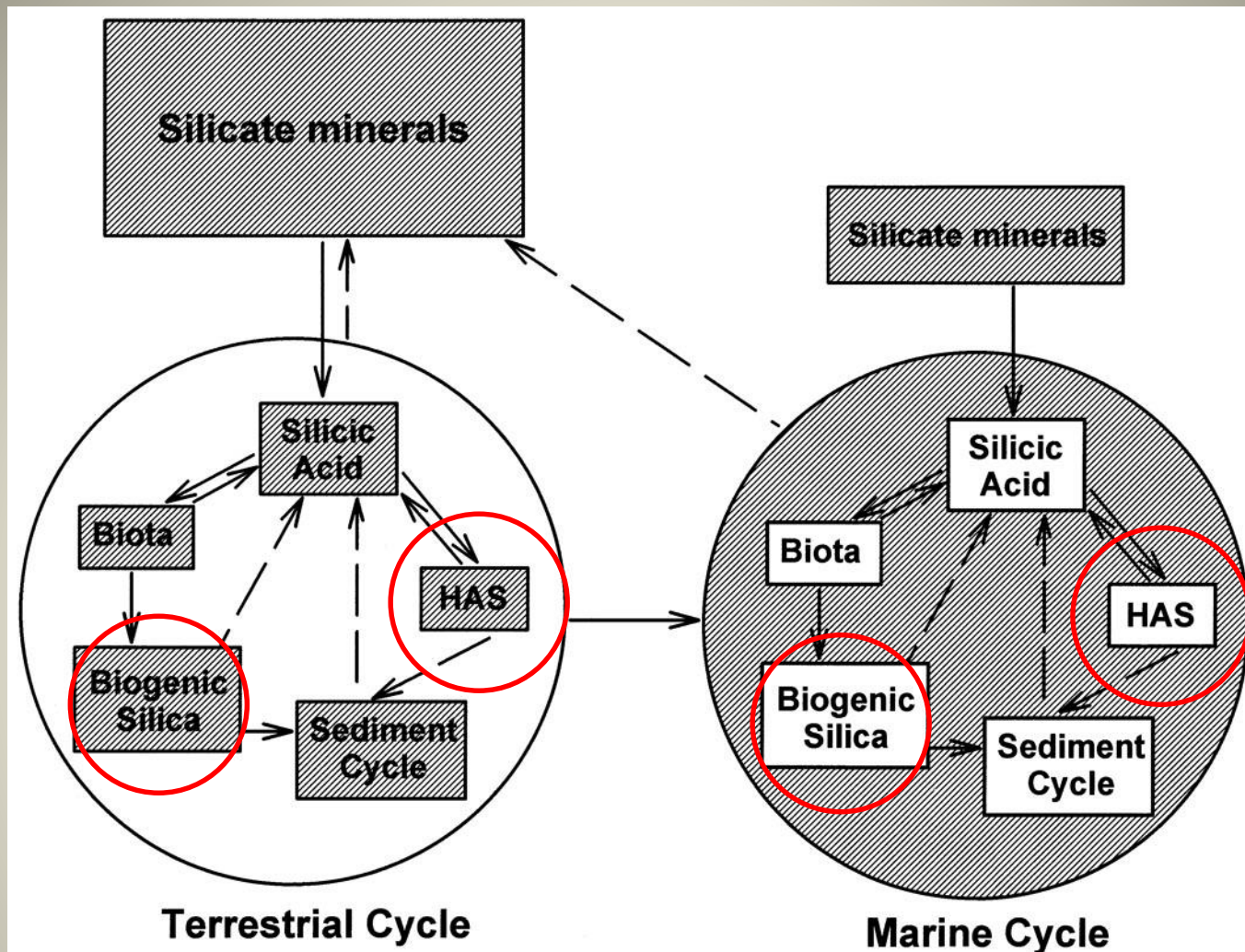
Si Silicon

Atomic Number: 14

Atomic Mass: 28.09



The (Only) Biologically Available Form of Silicon is Silicic Acid
(neutral monomer, pka ~ 9.6, Ksp ~ 2 mmol/L)

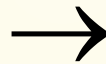
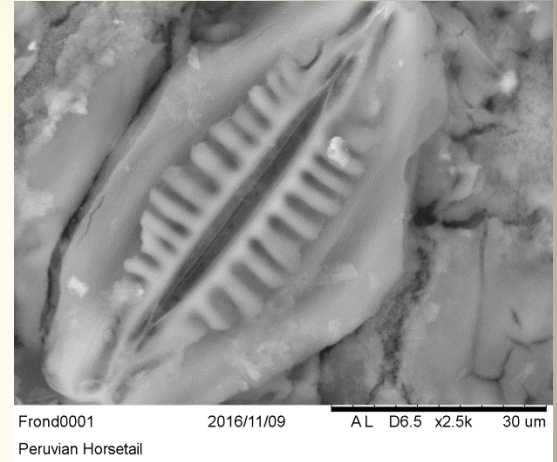
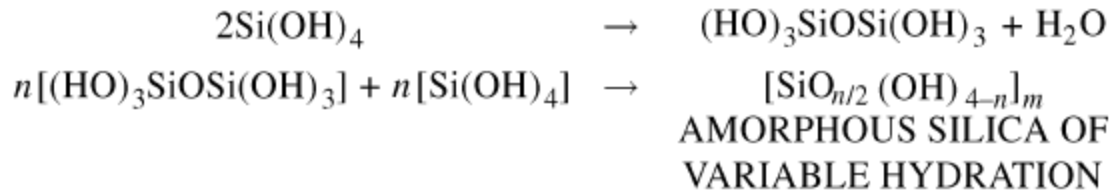


The Biogeochemical Bi-Cycle of Silicon

Exley (1998) J Inorg Biochem 69, 139-144.

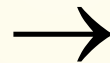
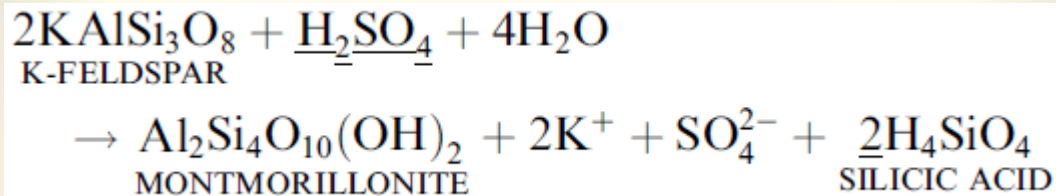
Silicic Acid Chemistry

The Advent of Biosilicification



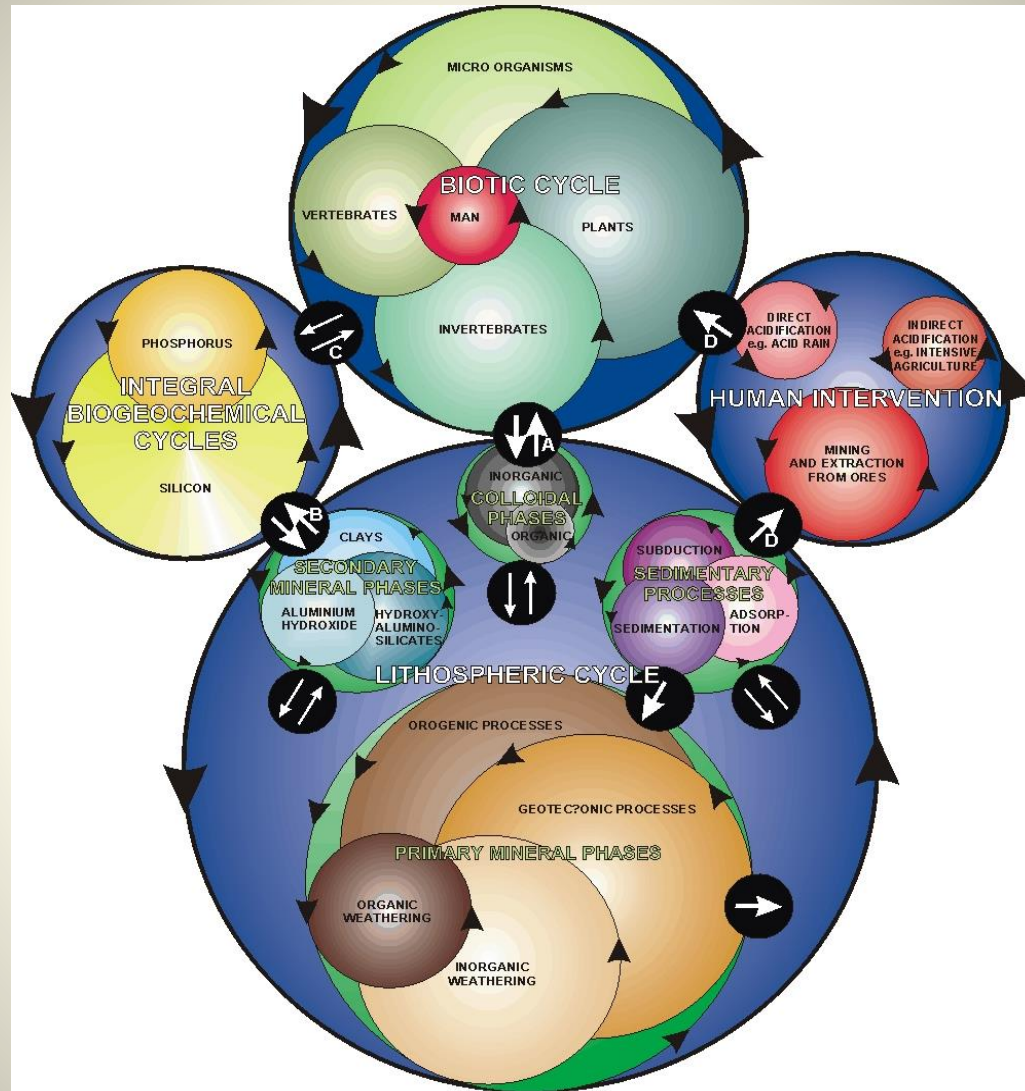
Removal of silicic acid as biogenic silica,
accelerated mineral weathering,
consumed more carbon dioxide,
cooled the Earth

Switch in Major Acidic Anion in Rain From Carbon Dioxide to Sulphate Due To Anthropogenic Emissions



Accelerated rate of mineral weathering,
produced less silicic acid,
consumed less carbon dioxide,
warmed the Earth!

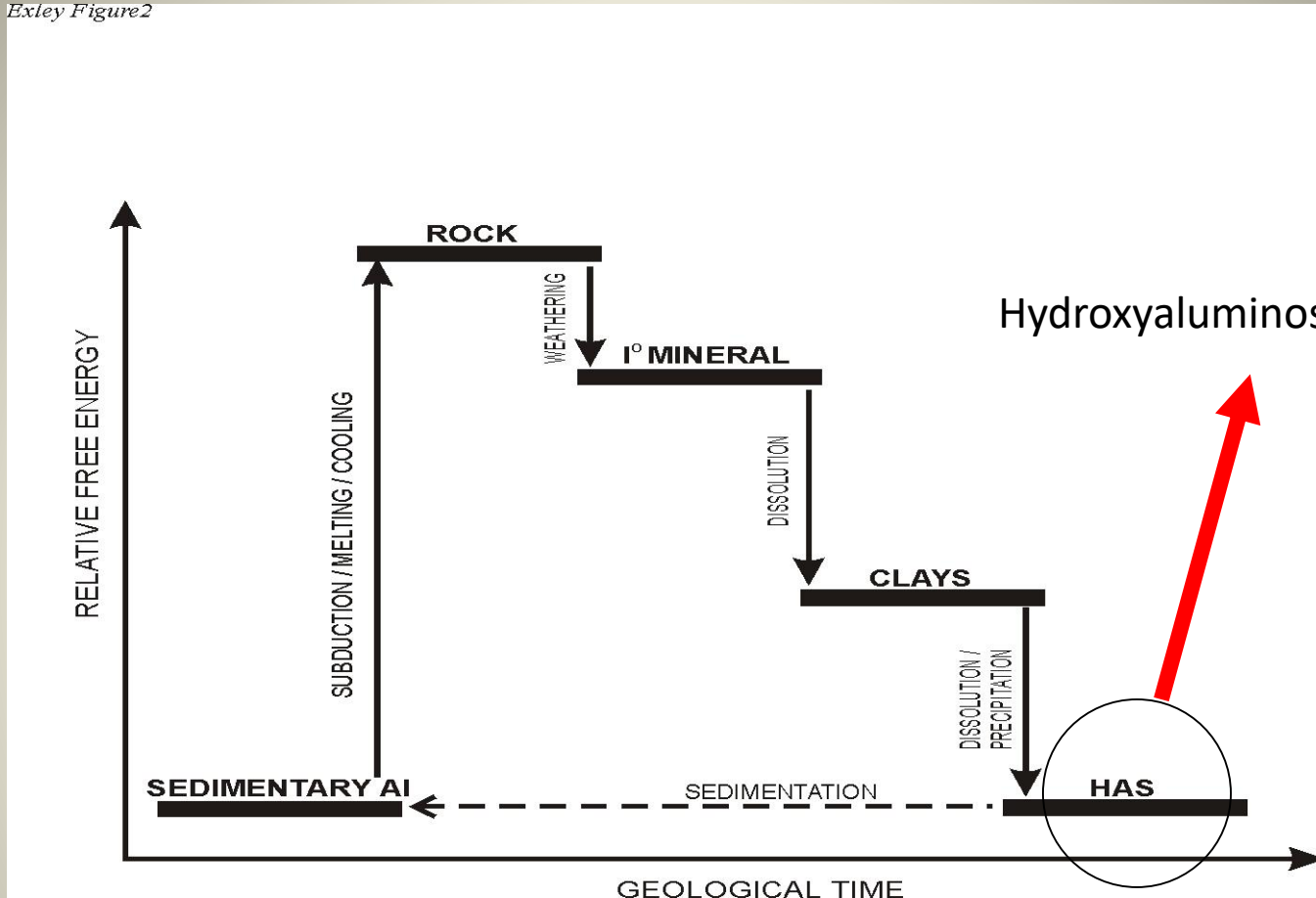
More Silicic Acid Chemistry



THE BIOGEOCHEMICAL CYCLE OF ALUMINIUM

Exley C (2003) A biogeochemical cycle for aluminium? J. Inorg. Biochem. 97, 1-7.

Exley Figure 2



Aluminium is 'cycled' through a series of sparingly soluble mineral phases: from its dissolution from (old) mountains to its incorporation into (new) mountains.

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

J. D. Birchall*, C. Exley†, J. S. Chappell*
& M. J. Phillips†

* ICI plc, PO Box 11, Runcorn, Cheshire WA7 4QE, UK

† Institute of Aquaculture, University of Stirling, Stirling FK9 4LA, UK

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 capacity¹⁻⁴. 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^{5,6}. 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 aluminium⁷, 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.

cf. silicic acid

A MECHANISM OF HYDROXYALUMINOSILICATE FORMATION

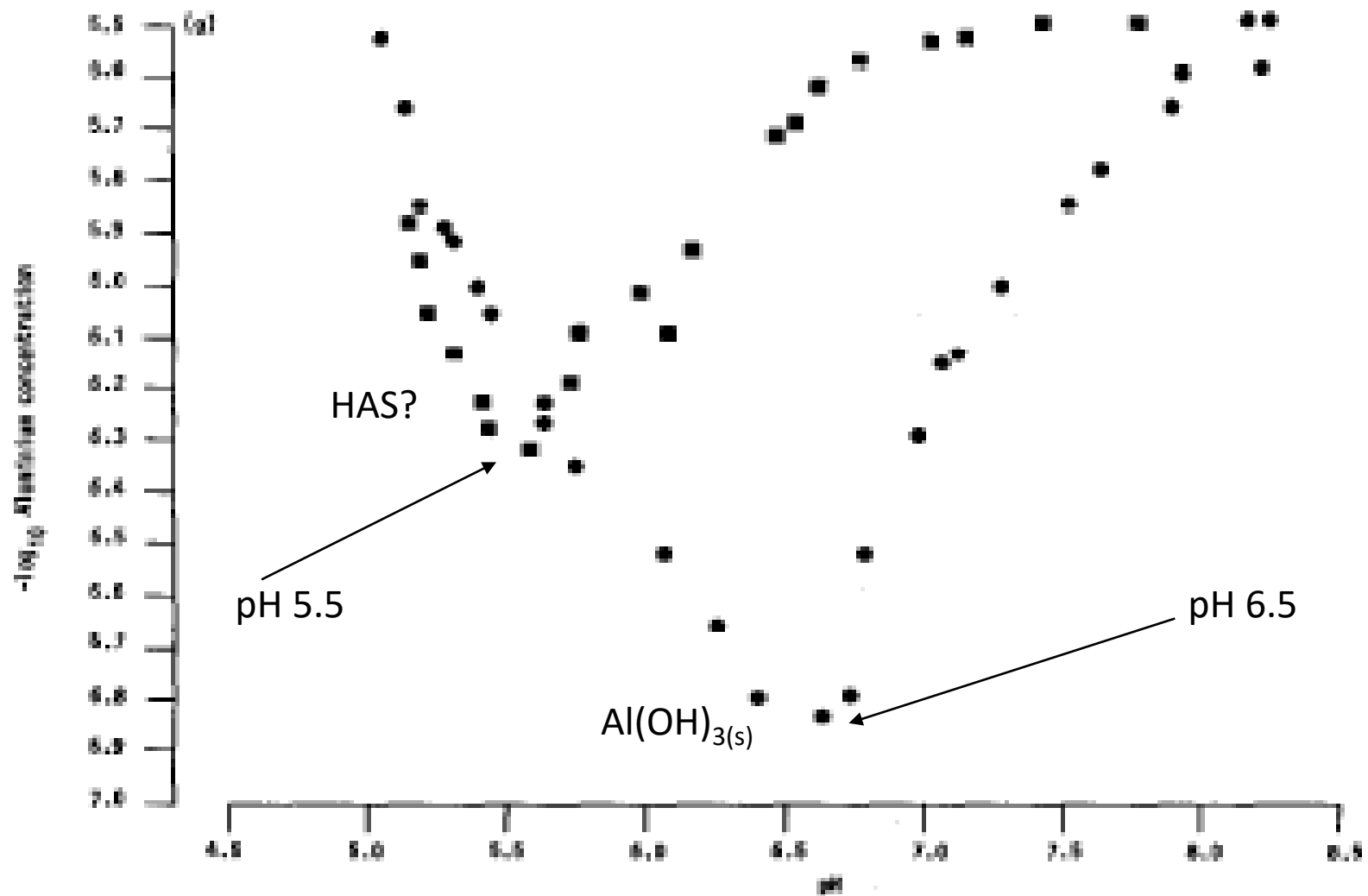
C. EXLEY* and J. D. BIRCHALL

Unit for Inorganic Chemistry and Materials Science, Department of Chemistry,
Keele University, Staffordshire ST5 5BG, U.K.

(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.

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



t = 12 weeks



Pergamon

Geochimica et Cosmochimica Acta, Vol. 65, No. 15, pp. 2461–2467, 2001
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0016-7037/01 \$20.00 + .00

PII S0016-7037(01)00571-3

The formation of hydroxyaluminosilicates of geochemical and biological significance

FRÉDÉRIC J. DOUCHI,¹ CÉLINE SCHNEIDER,¹ SIMEON J. BONES,² AXEL KRETCHMER,² IAN MOSS,² PIOTR TEKELY,³ and
CHRISTOPHER EXLEY^{1,*}

¹Birchall Centre for Inorganic Chemistry and Materials Science, School of Chemistry and Physics, Keele University, Staffordshire ST5 5BG, UK

²Dow Corning Limited, Barry, S. Glamorgan CF6 2YL, UK

³Laboratoire de Méthodologie RMN, UPRESA CNRS 7042, Université de Nancy 1, Vandœuvre-les-Nancy 54506, France

(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 (HAS_A). Where $\text{Si}(\text{OH})_4$ was present in excess, HAS_A acted as a template for further reactions with $\text{Si}(\text{OH})_4$ (HAS_B). HAS_A and 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!

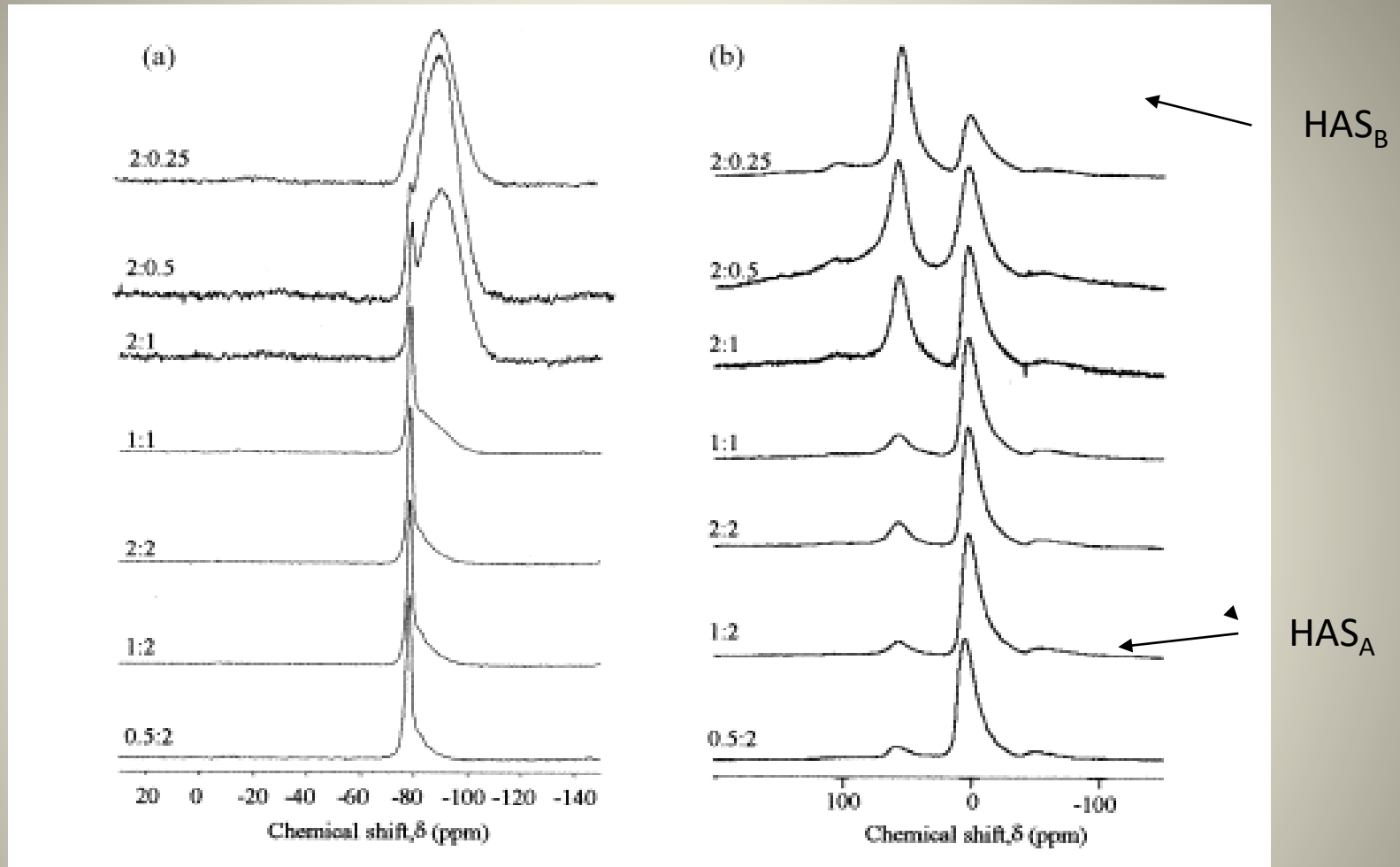


Fig. 3. The influence of different combinations of $\text{Si}(\text{OH})_4$ and Al (units are mmol/L) on the structure of precipitated HAS.

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

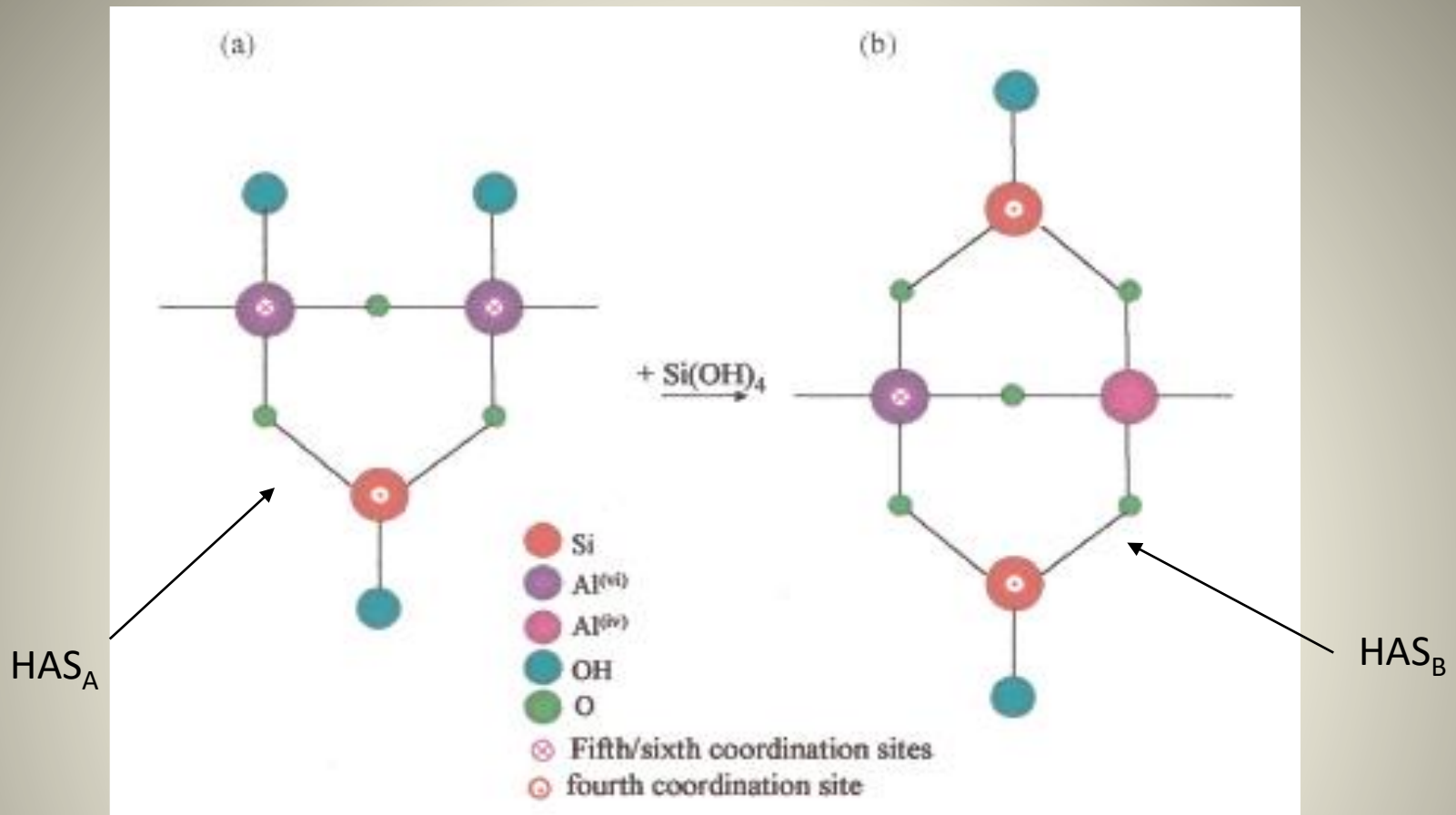


Fig. 5. Proposed unit structures of (a) HAS_A and, in the presence of an excess of $Si(OH)_4$, (b) HAS_B . In HAS_A the fourth coordination site on Si will be $-O-Al$ whereas for HAS_B both $-O-Al$ and $-O-Si$ are predicted by NMR.



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Journal of Inorganic Biochemistry 87 (2001) 71–79

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

Frédéric J. Doucet^{1,a}, Mikhail E. Rotov^b, Christopher Exley^{a,*}

^a*Birchall Centre for Inorganic Chemistry and Materials Science, School of Chemistry and Physics, Keele University, Keele, Staffordshire ST5 5BG, UK*

^b*School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

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_A AND HAS_B

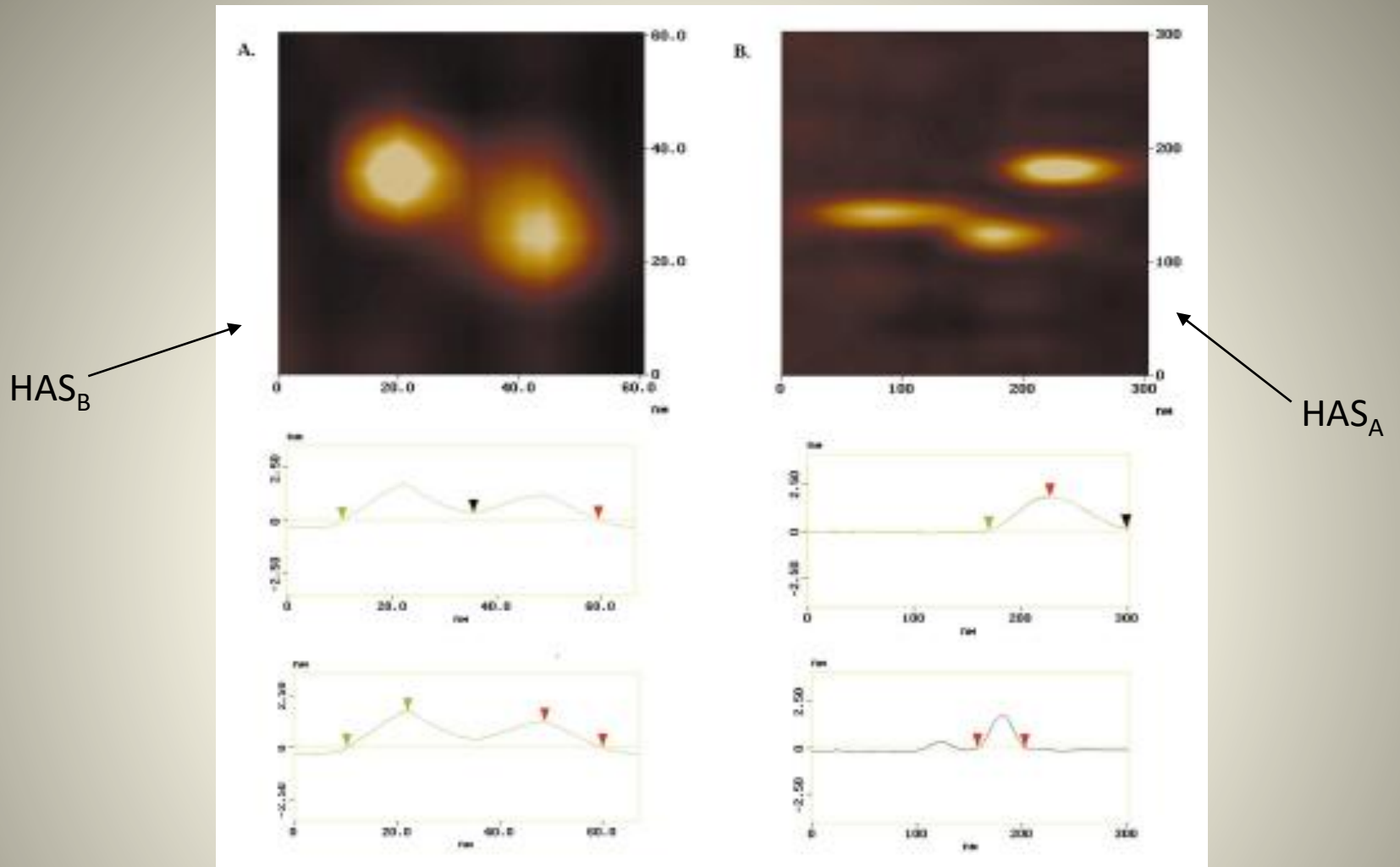


Fig. 3. Close up AFM images of representative individual HAS structures and line profiles representing the section analysis of these two structures: (A) discoid HAS, depth 1–2 nm, diameter 23–25 nm; (B) rectangular HAS, depth 1–2 nm, width 40–45 nm, length 87–170 nm.



The solubility of an hydroxylaluminosilicate

Céline Schneider ^a, Frédéric Doucet ^b, Stanislav Strekopytov ^c, Christopher Exley ^{c,*}

^a Chemistry Department, University of British Columbia, 2036 Main Mall, Vancouver, Canada BC V6T 1Y6

^b Division of Food Sciences, School of Biosciences, University of Nottingham, Sutton Bonington Campus, Loughborough, Leicestershire LE12 5RD, UK

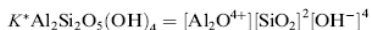
^c Birchall Centre for Inorganic Chemistry and Materials Science, Lennard-Jones Laboratories, School of Chemistry and Physics, Keele University, Staffordshire ST5 5BG, UK

Received 28 June 2004; accepted 6 October 2004

Available online 11 November 2004

Abstract

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

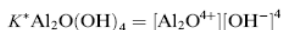


This unconventional solubility expression was derived to take account of the non-stoichiometric dissolution of HAS_{B(s)} and included theoretical dissolution products which could then be substituted for the dissolution products which were measured experimentally.



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

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



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

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

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Keywords: Hydroxylaluminosilicate; Aluminium; Silicic acid; Aluminium solubility; Aluminium biological availability

Fast-reacting Al

HAS_B 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_{B(s)} could be the predominant secondary mineral phase controlling the solubility of Al in environments in which the pH > 4.00 and [Si(OH)₄] > 100 μmol/L.

AN UNCONVENTIONAL APPROACH TO A SOLUBILITY EXPRESSION



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Polyhedron 24 (2005) 1585–1592



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

Stanislav Strekopytov, Christopher Exley *

Birchall Centre for Inorganic Chemistry and Materials Science, Lennard-Jones Laboratories, Keele University, Staffordshire ST5 5BG, UK

Received 8 March 2005; accepted 27 April 2005

Available online 4 June 2005

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 (HAS_A and 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 (F^-) or phosphate (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 HPO_4^{2-} where 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 HAS_A and 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 HAS_A and 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) ₄ -dialysis (μmol/L)		Al-dialysis (μmol/L)		F-filtration (μmol/L)		P-filtration (μmol/L)		Solid phase
Si	Al	F	P	Mean	SD ^a	Mean	SD	Mean	SD	Mean	SD	
0.5	2.0			4	0.7	<1						SiAl _{3.7}
0.5	2.0	0.5		7	2.1	17	4.1	110	9.7			SiAl _{4.0} F _{0.47}
0.5	2.0		0.5	181 ^b	2.0	<1				<1		SiAl _{6.8} P _{1.9}
1.0	2.0			73	4.0	<1						SiAl _{2.3}
1.0	2.0	1.0		141	6.0	66	12	404	9.0			SiAl _{2.45} F _{0.44}
1.0	2.0		1.0	798 ^b	14	<1				10	0.3	SiAl _{9.6} P _{6.8}
1.0	1.0			255	17	<1						SiAl _{1.6}
1.0	1.0	1.0		451	4.0	199	11	621	45			SiAl _{2.0} F _{0.37}
1.0	1.0		1.0	980 ^b	8.0	<1				165	2.0	SiAl ₃₃ P _{7.8}
2.0	1.0			563	72	<1						SiAl _{1.06}
2.0	1.0	2.0		937	43	324	27	1349	94			SiAl _{1.03} F _{0.24}
2.0	1.0		2.0	1857 ^b	8.0	<1				268	4.1	SiAl ₄₄ P ₁₄
2.0	0.5			824	45	<1						SiAl _{0.87}
2.0	0.5	2.0		1420	61	223	45	1492	80			^c
2.0	0.5		2.0	1768 ^b	13	<1				1209	29	SiAl ₂₅ P ₈

^a Standard deviation, *n* = 9.

^b Filtration through 0.1 μm Durapore membrane filters.

^c No solid phase collected.

Fluoride-substituted HAS

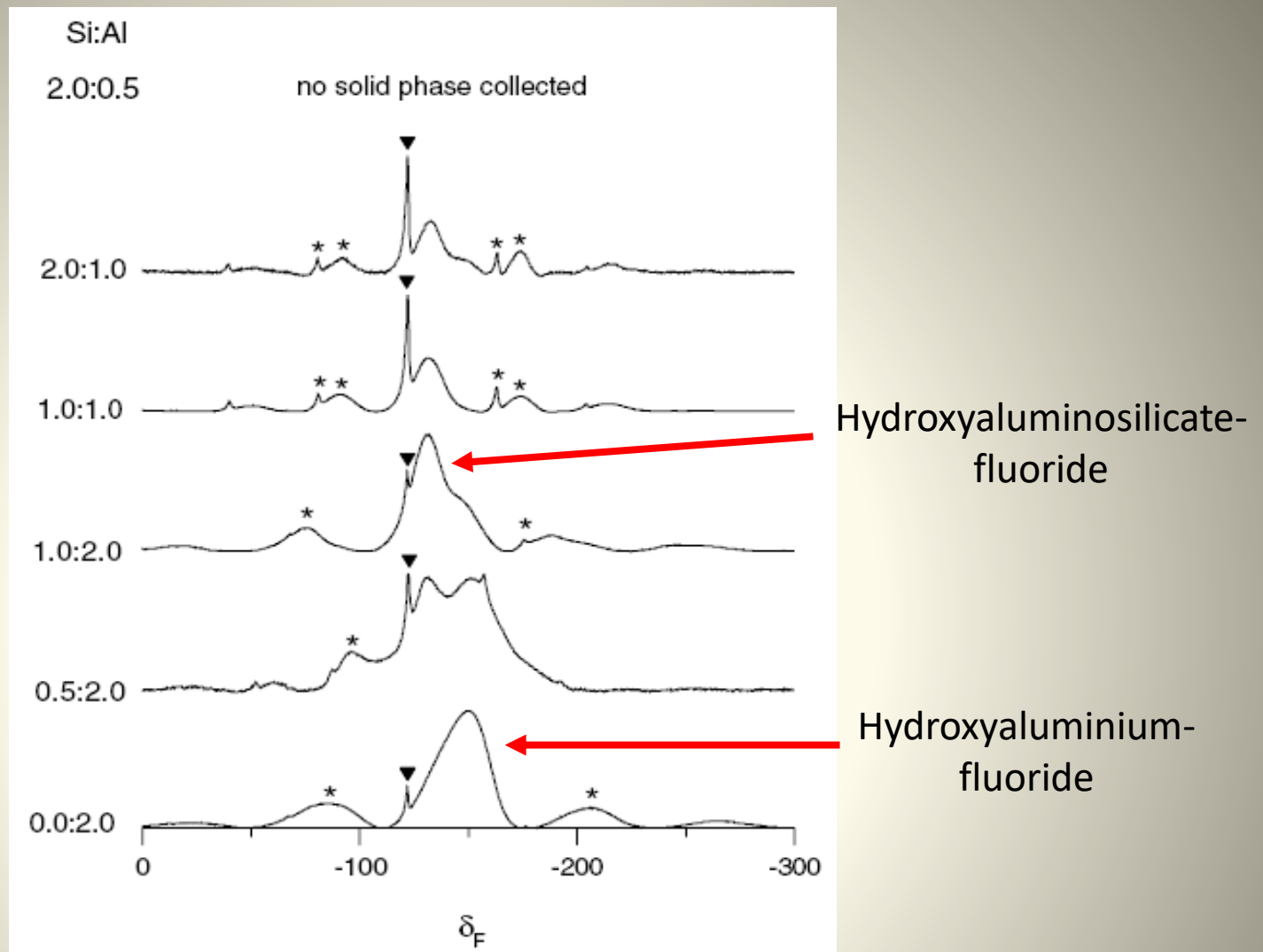


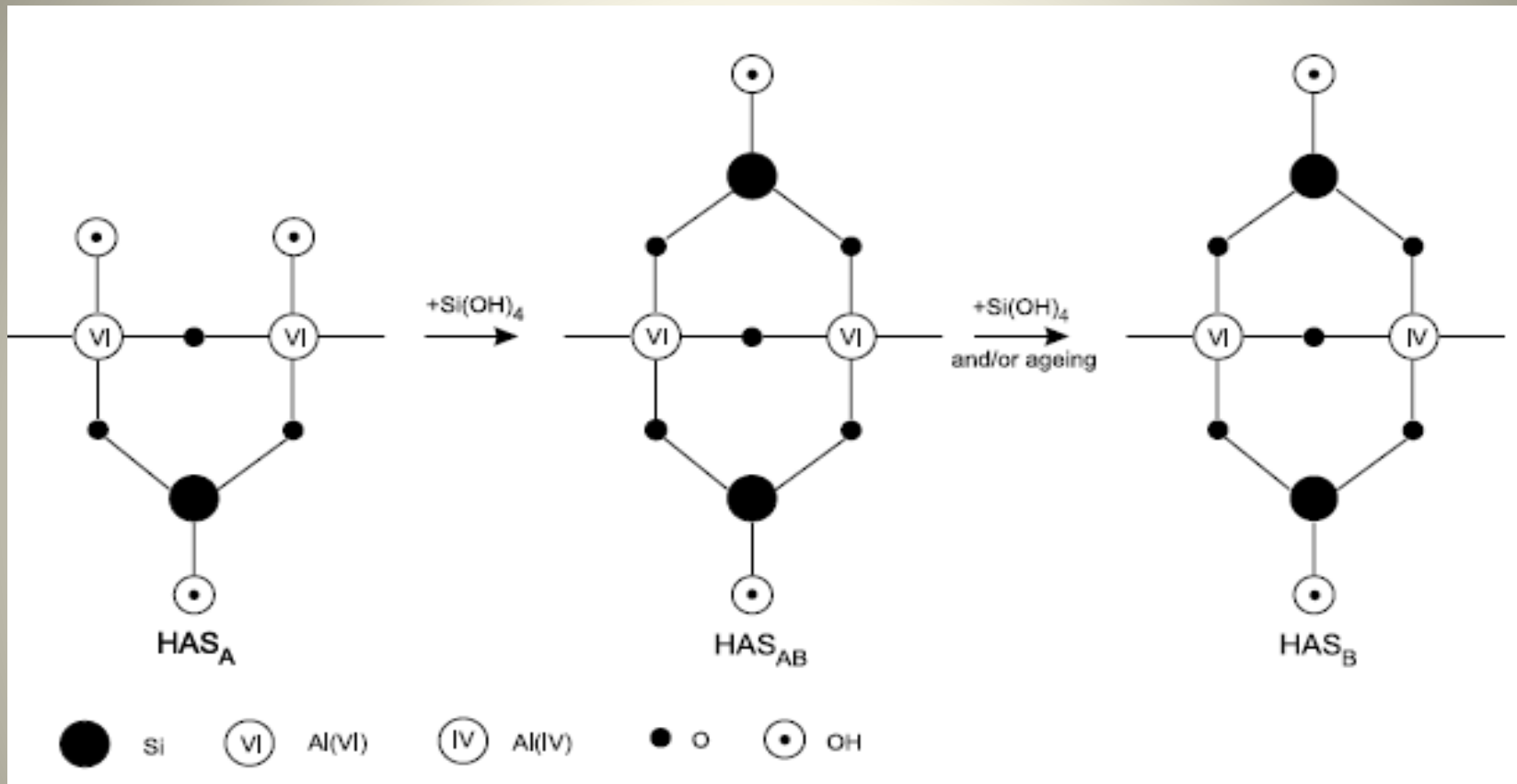
Fig. 4. ^{19}F MAS NMR spectra of solid phases prepared in the presence of F.

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_B from HAS_A involving a transitional form, HAS_{AB}, which undergoes a dehydroxylation fuelled by either ageing or a significant excess of Si(OH)₄.



Thermal analyses of aluminium hydroxide and hydroxyaluminosilicates

Stanislav Strekopytov¹, Christopher Exley*

Birchall Centre for Inorganic Chemistry and Materials Science, Lennard-Jones Laboratories, Keele University, Staffordshire ST5 5BG, UK

Received 16 September 2005; accepted 10 November 2005

Available online 22 December 2005

Abstract

Hydroxyaluminosilicates (HAS_A and HAS_B) are important secondary mineral phases in the biogeochemical cycle of aluminium. HAS_A is formed by the reaction of silicic acid (Si(OH)₄) with an aluminium hydroxide (Al(OH)_{3(s)}) template with further substitution of Si(OH)₄ into HAS_A resulting in HAS_B. 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 a hitherto unrecognised form of a purely amorphous Al(OH)_{3(s)} the thermal signature of which was a sharp exothermic peak (ca. 282 °C) which though present in HAS_A-like structures (260–275 °C) was absent from HAS_B-like structures. Solid-state NMR of heated HAS and Al(OH)_{3(s)} 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^(V) as a potential intermediate in the transformation of HAS_A to HAS_B.

The identification of a novel form of purely amorphous Al(OH)_{3(s)} 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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Polyhedron 25 (2006) 3399–3404



POLYHEDRON

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Further insight into the mechanism of formation of hydroxyaluminosilicates

Stanislav Strekopytov¹, Eve Jarry, Christopher Exley*

Birchall Centre for Inorganic Chemistry and Materials Science, Lennard-Jones Laboratories, Keele University, Staffordshire ST5 5BG, UK

Received 23 March 2006; accepted 16 June 2006

Available online 30 June 2006

Abstract

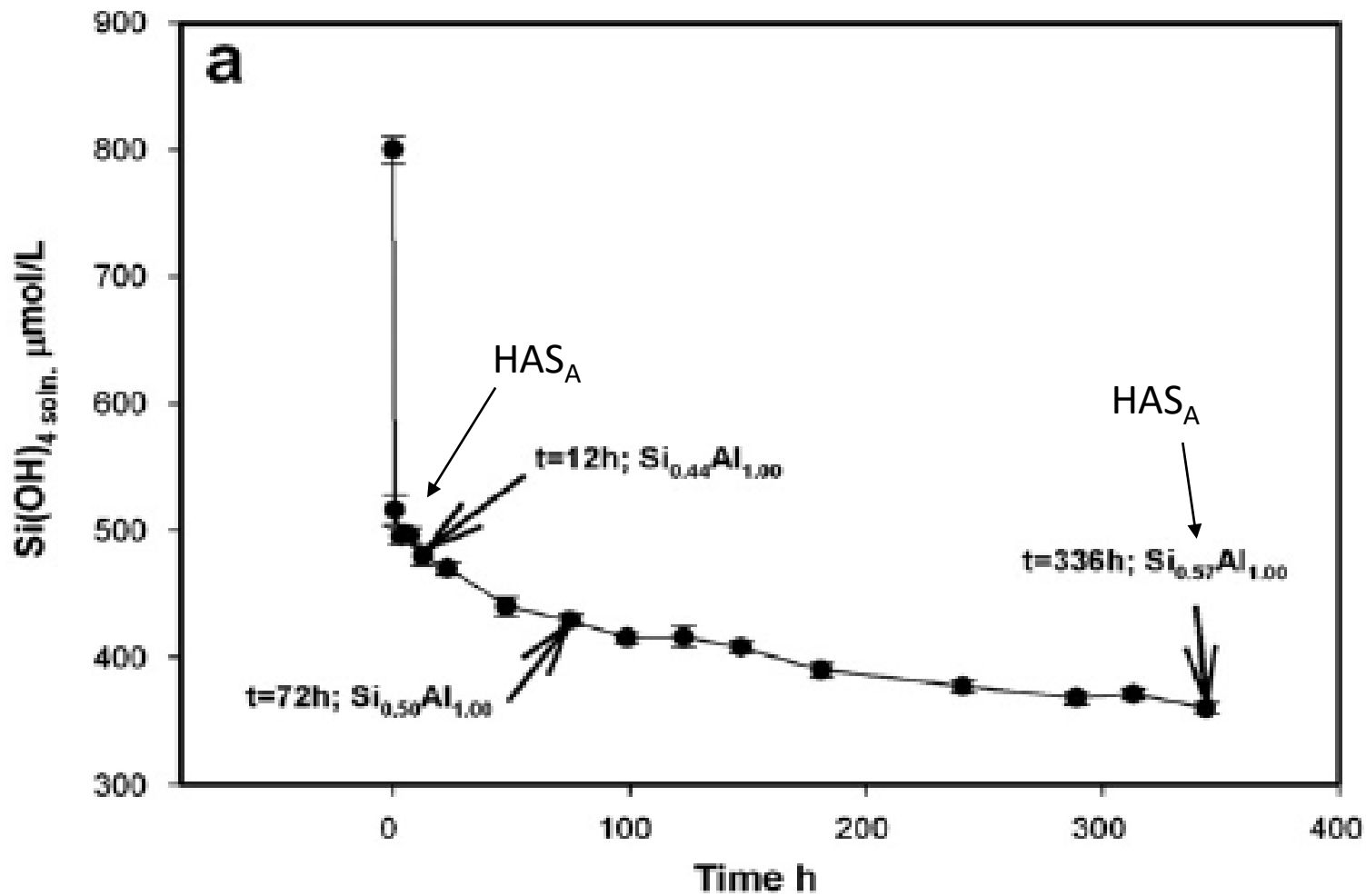
Hydroxyaluminosilicates (HAS) are formed by the reaction of silicic acid ($\text{Si}(\text{OH})_4$) with adjacent hydroxyl groups on an aluminium hydroxide ($\text{Al}(\text{OH})_{3(s)}$) framework or template. They are important secondary mineral phases in the biogeochemical cycling of aluminium and are extremely insoluble. Two discrete forms of HAS have been identified. HAS_A which is formed when $[\text{Si}(\text{OH})_4] \leq [\text{Al}]$ and HAS_B which is formed when $[\text{Si}(\text{OH})_4] \gg [\text{Al}]$. The formation of HAS_B has been suggested to involve the further reaction of $\text{Si}(\text{OH})_4$ with 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 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 (≥ 72 h ageing) only 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 HAS_A which, in turn, is the precursor to the formation of 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

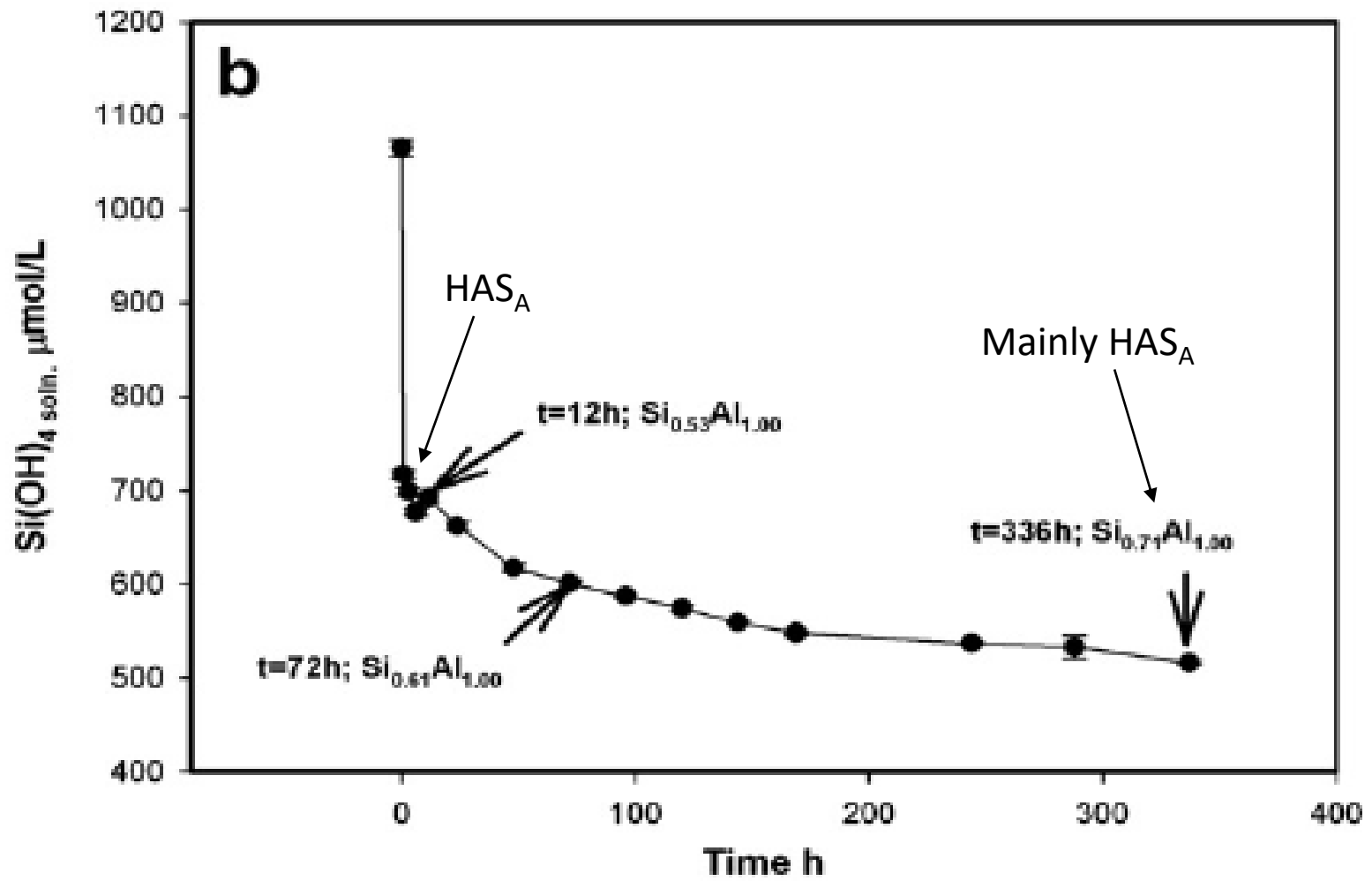
$\text{Al}(\text{OH})_{3(s)}$ is a prerequisite to $\text{HAS}_{A(s)}$ which is a prerequisite to $\text{HAS}_{B(s)}$

0.8 mM Al + 0.8 mM Si(OH)₄

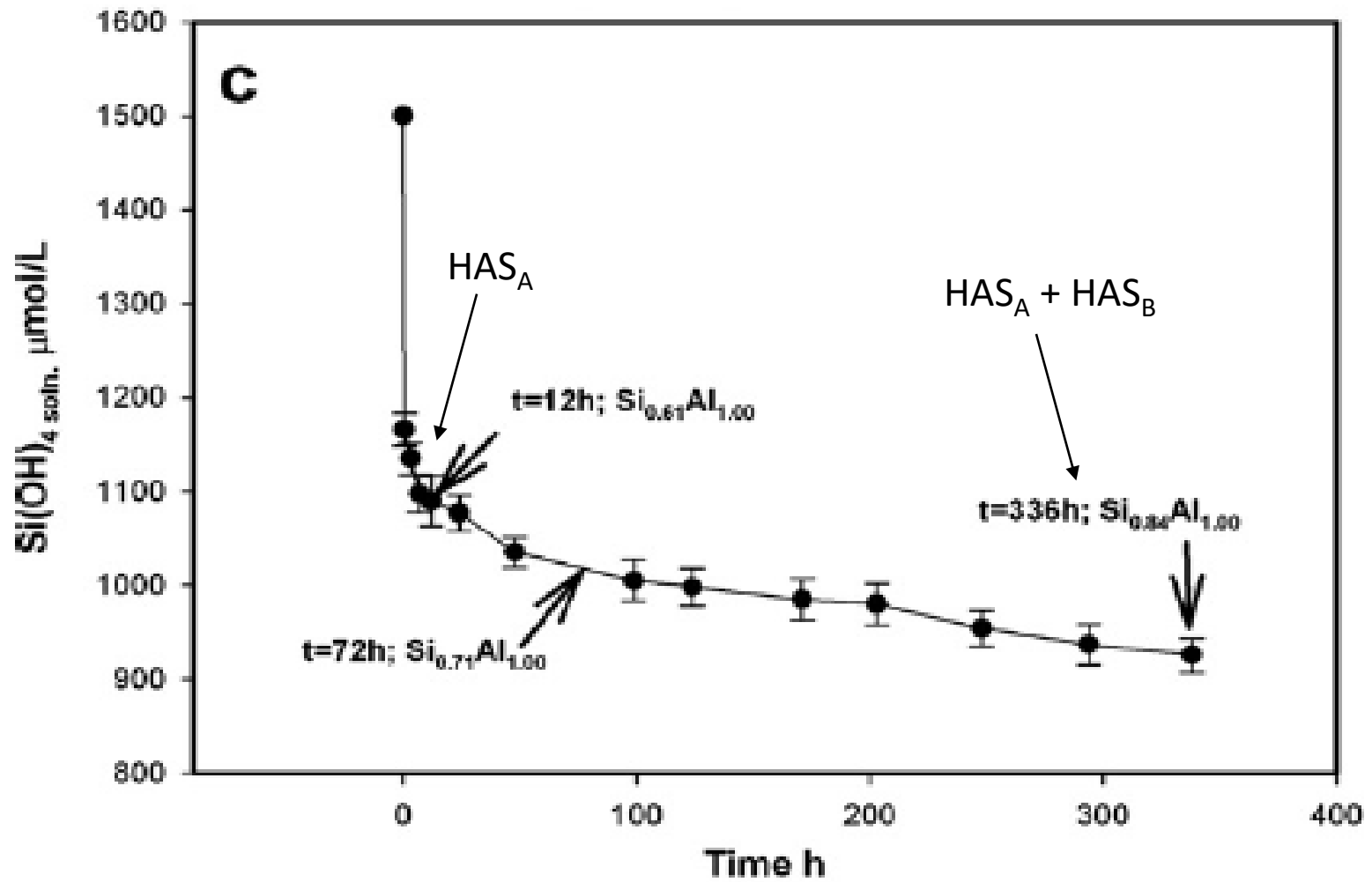


Which HAS is predicted/formed?

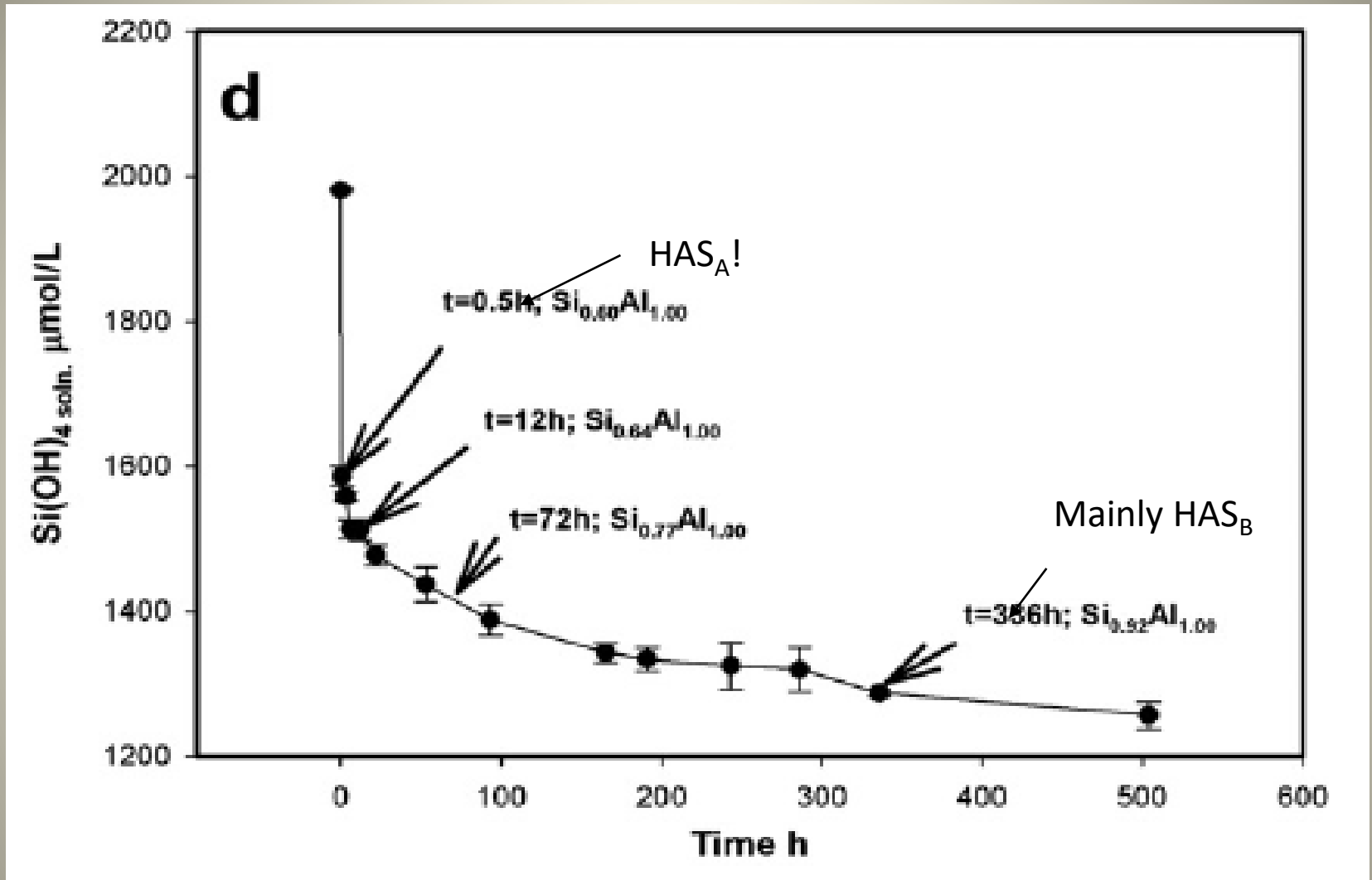
0.8 mM Al + 1.1 mM Si(OH)₄



0.8 mM Al + 1.5 mM Si(OH)₄



0.8 mM Al + 2.0 mM Si(OH)₄



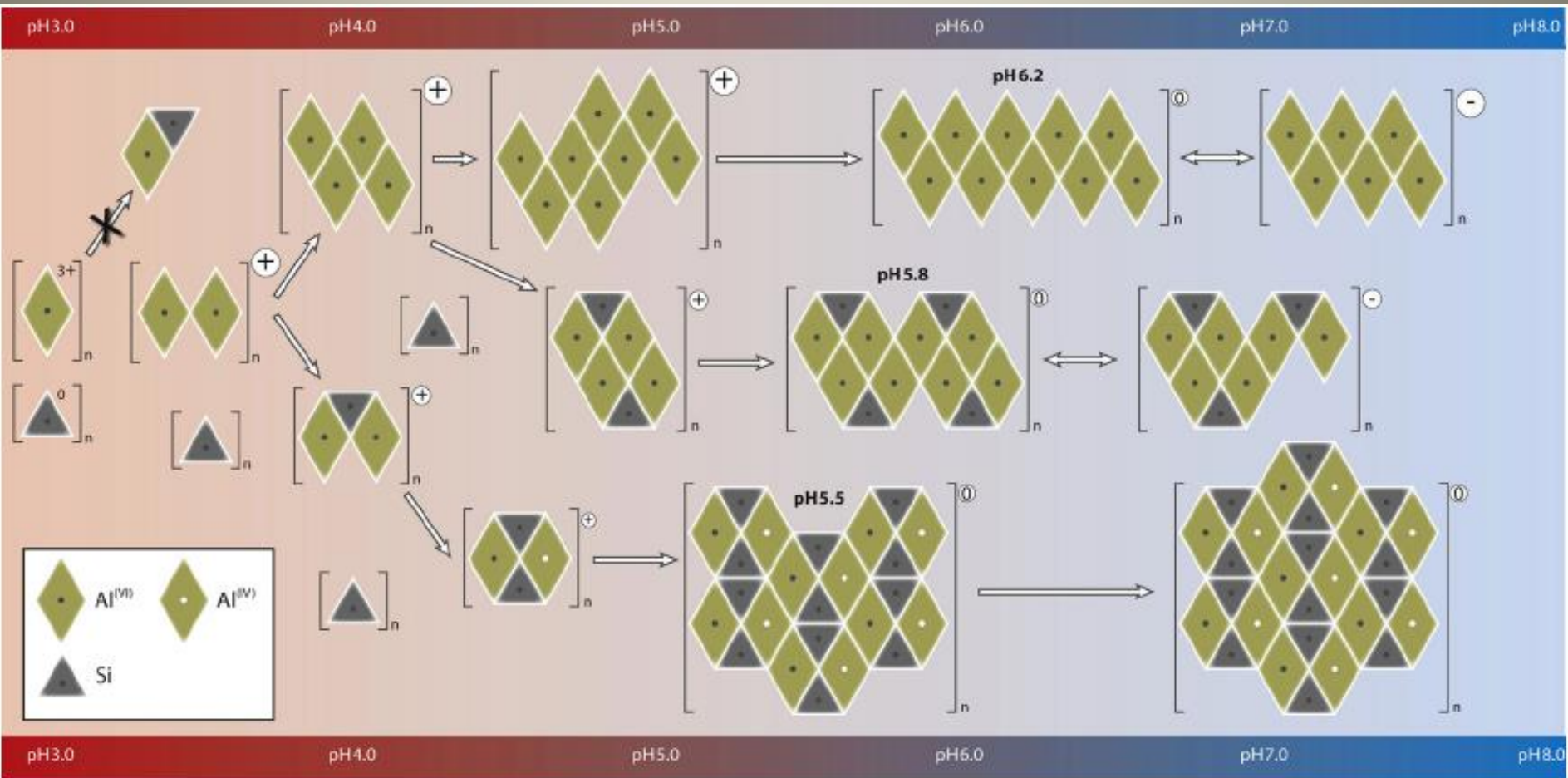
The earliest solid phase that can be collected from these solutions has the stoichiometry of 2 Al to 1 Si....HAS_A!!

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 Al_{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**.

Exley C (2012) Coordination Chemistry Reviews 256,82– 88.

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What is the mechanism of formation of hydroxyaluminosilicates?

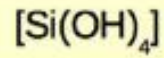
Received: 26 May 2016

Accepted: 08 July 2016

Published: 01 Aug 2016

James Beardmore¹, Xabier Lopez², Jon I. Mujika² & Christopher Exley¹

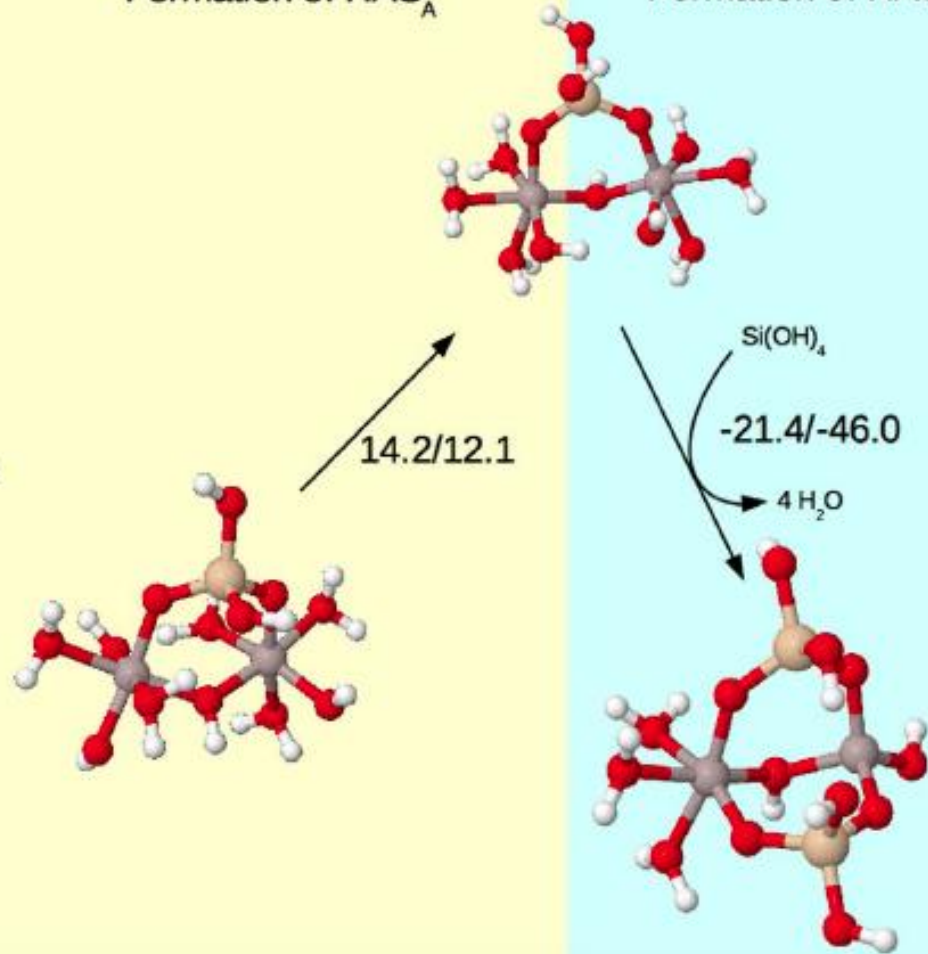
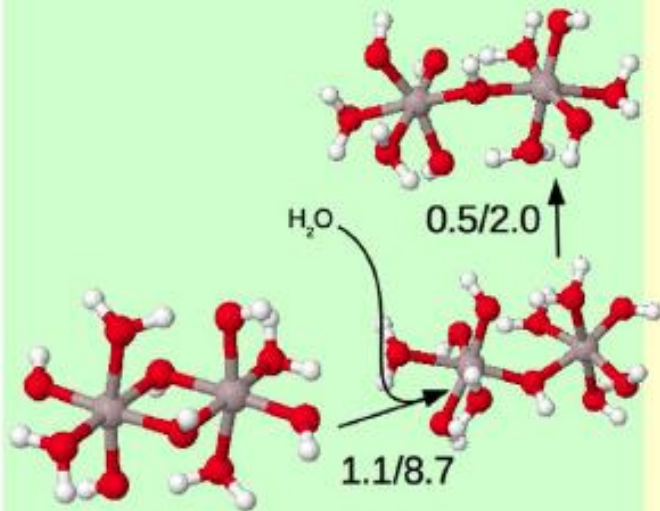
The formation of hydroxyaluminosilicates is integral to the biogeochemical cycles of aluminium and silicon. The unique inorganic chemistry which underlies their formation explains the non-essentiality in biota of both of these elements. However, the first steps in the formation of hydroxyaluminosilicates 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.



Absence of Si(OH)₄:
Formation of Al Hydroxides

Presence of Si(OH)₄:
Formation of HAS_A

Excess of Si(OH)₄:
Formation of HAS_B



And Finally Translational Research!

Journal of Alzheimer's Disease 33 (2013) 423–430
DOI 10.3233/JAD-2012-121231
IOS Press

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

Samantha Davenward^a, Peter Bentham^b, Jan Wright^b, Peter Crome^c, Deborah Job^c,
Anthony Polwart^d and Christopher Exley^{a,*}

^a*The Birchall Centre, Lennard-Jones Laboratories, Keele University, Stoke-on-Trent, Staffordshire, UK*

^b*Birmingham and Solihull Mental Health NHS Foundation Trust, The Barberry Centre, Birmingham, UK*

^c*North Staffordshire Combined Healthcare NHS Trust, Harplands Hospital, Stoke-on-Trent, UK*

^d*Life Sciences, Keele University, Stoke-on-Trent, Staffordshire, UK*



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