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

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Abstract

Hydroxyaluminosilicates (HAS) are important secondary mineral phases formed by the reaction of silicic acid ($Si(OH)_4$) 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 $Si(OH)_4$ 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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1. Introduction

Silicic acid ($Si(OH)_4$) reacts with aluminium to form hydroxyaluminosilicates (HAS) [1]. The reaction is not with $Al^{3+}_{(aq)}$ but involves the competitive condensation of $Si(OH)_4$ across hydroxyl groups on adjacent Al atoms which are part of an aluminium hydroxide ($Al(OH)_{3(s)}$) framework [2]. The reaction is described as competitive in that $Si(OH)_4$ must compete with hydroxyaluminium complexes such that $Si(OH)_4$ has been described as an inhibitor or poison of the growth of $Al(OH)_{3(s)}$ [1]. Thus when $Si(OH)_4$ is present in solutions in which $Al(OH)_{3(s)}$ is rapidly forming it reacts with the earliest precursors to the solid phase to slow down their growth and precipitation from solution whilst when $Si(OH)_4$ is added to preformed aggregates of $Al(OH)_{3(s)}$ it reacts with the solid phase breaking it down into smaller individual units [2]. The reaction of $Si(OH)_4$ with Al has been known for some time [3] without significant progress being made in either the characterisation of the reaction products or their mechanisms of formation. A significant obstacle has been the acceptance that the reaction is with $Si(OH)_4$ and not with either silicates or polysilicic acids [4]. Both of these will bind Al but in neither case

will HAS be formed [5]. To ensure that $Si(OH)_4$ is the reactant it is important that the solution is both below pH 9.0 (pK_a for $Si(OH)_4$ is about 9.6) and undersaturated with respect to the solubility of $Si(OH)_4$ (it will autocondense at $[Si(OH)_4] > 2.0$ mmol/L). When these criteria are met HAS of distinct stoichiometry and structure are formed and can be precipitated from solution [6]. There are only two basic types of HAS and which of these will form is dependent upon the ratio of $Si(OH)_4$ to Al in the parent solution. When Al is in excess HAS_A is formed. This has a Si:Al ratio of 0.5 and is composed of octahedral assemblies of Al atoms linked to Si through, predominantly, $Q_3(3Al)$ linkages. When $Si(OH)_4$ is present to a twofold excess or more HAS_B is formed. This has a Si:Al ratio of 1.0 and is composed of both octahedral and tetrahedral assemblies of Al atoms, in approximately equal amounts, linked to Si through, predominantly, $Q_3(1-2Al)$ linkages. The formation of HAS_B involves a dehydroxylation reaction which, at room temperature and pressure, appears to be fuelled by the excess of $Si(OH)_4$ in solution. When the concentrations of Al and $Si(OH)_4$ in parent solutions are either equal or favour $Si(OH)_4$ by less than a factor of two both types of HAS are present in the solid phase. The latter observation prompted the suggestion that HAS_B was formed via the competitive condensation of $Si(OH)_4$ across hydroxyl groups on HAS_A and subsequent research has tended to support this notion [6,7].

Both HAS_A and HAS_B appear to have analogues in the natural environment, protoimogolite and protoimogolite allophane, respectively [8], though their formation and persistence in natural waters has not been demonstrated unequivocally. There have been numerous references to the presence of HAS-like phases in natural environments without any direct confirmation that they are analogous to synthetic HAS. It is our contention that HAS similar in nearly all respects to HAS_A and HAS_B are significant secondary mineral phases which when formed in the natural environment are major players in the biogeochemical cycle of Al and in the biological availability of Al in general [9]. We have recently determined a solubility expression for HAS_B [10] which supports such a notion and will help to explain how Al is successfully retained within the lithospheric cycle and excluded from biota. However, if HAS are formed in nature then it is likely that, unlike in the laboratory, their form and persistence will be influenced by other ligands for Al, both organic such as humic and fulvic acids and inorganic such as fluoride and phosphate. We have taken the first steps to understand how the latter, fluoride and phosphate, when present at equimolar concentrations to $Si(OH)_4$, might influence the formation of synthetic HAS.

2. Experimental

2.1. Preparation of parent solutions

All reagents were of the highest purity available. Each of the parent solutions listed in Table 1 was prepared using ultra pure water (conductivity < 0.067 μS/cm, Elga UK) which included 100 mmol/L KNO_3 as a background electrolyte and was buffered at pH 6.0 with 25 mmol/L of piperazine-N,N′-bis (2-ethanesulphonic acid) (PIPES). $Si(OH)_4$ solutions, maximum concentra-

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)		Soid 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.

tion 2.0 mmol/L, were prepared by cation exchange of Na_4SiO_4 and either diluted as required (0.5 and 1.0 mmol/L) or used in place of pure water (2.0 mmol/L). Al was added from a freshly prepared 1 mol/L stock of $Al(NO_3)_3 \cdot 9H_2O$ in 1% HNO_3 and phosphate (HPO_4^{2-}) and fluoride (F^-) were added as $NaH_2PO_4 \cdot H_2O$ and NaF, respectively. We have used an established method of HAS preparation [2] in which the respective constituents of parent solutions are mixed at ca. pH 3.0 and then titrated to pH 6.0 using NaOH. In this way as soon as Al hydrolysis begins and hydroxy-aluminium templates are formed $Si(OH)_4$ will be available to react with them to give HAS.

To determine when any reaction involving the formation of HAS was complete and, therefore, facilitating thereafter the collection of the solid phase by filtration, pilot experiments were run for each parent solution in which the rate of formation of HAS was determined by measuring the change in $[Si(OH)_4]$ over time. One replicate of each solution was prepared in a 1 L PTFE container (Cowie Technology Ltd., UK) and placed in an incubator at 20.0 ± 0.1 °C. The solution was filtered periodically using syringe filters (Millipore) incorporating 0.1 μm polyvinylidene fluoride membrane filters (Durapore) and $[Si(OH)_4]$ determined as molybdate-reactive Si [11]. When $[Si(OH)_4]$ was observed to plateau (see Fig. 1 for representative examples) the reaction was considered complete and the requisite time period was chosen for the full scale experiments. In these the idea was to use the $[Si(OH)_4]$ at equilibrium with the solid phase to discriminate between the different parent solutions. Thus, if F^- were to influence the formation of HAS this might be evident from the equilibrium $[Si(OH)_4]$. To give this idea
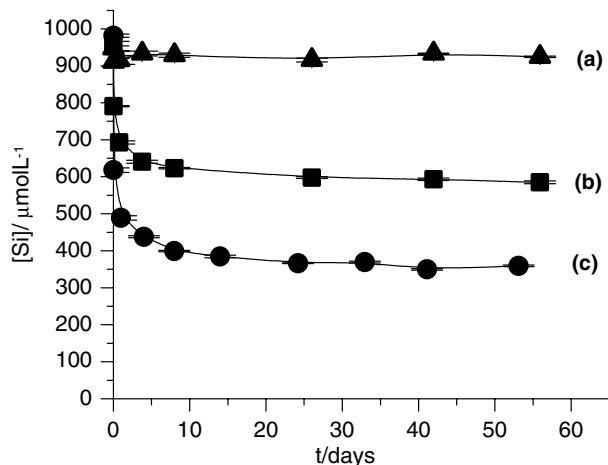
the greatest possibility of being effective nine replicates of each parent solution were prepared in 200 mL PTFE containers and placed in an incubator at 20.0 ± 0.1 °C. Following incubation of the solutions for the pre-determined time period (ca. 60 days) the equilibrium $[Si(OH)_4]$ was determined in each of the nine replicates though not following filtration (as in the pilot) but by using equilibrium dialysis. A dialysis chamber of volume 500 μL and MWCO 1000 Da (Spectra/Por® DispoDialyzer®) was immersed in the solution and allowed to equilibrate for 72 h. Previous control experiments had shown that $Si(OH)_4$ equilibrated across the membrane in this time interval and that the equilibrium was not influenced by the presence of 2.0 mmol/L F^- but that the same amount of HPO_4^{2-} resulted in an underestimation of the equilibrium $[Si(OH)_4]$. The latter resulted in filtration and not dialysis being used to determine the equilibrium $[Si(OH)_4]$ in parent solutions which included HPO_4^{2-}. Following equilibrium dialysis and the collection of samples for the determination of dialysable $Si(OH)_4$ and Al the solutions were filtered through 0.1 μm membrane filters (Durapore) and the filtered solutions were analysed for F^- and HPO_4^{2-} (see Table 1) whereas the solid phases were dried to a constant weight at 37 °C and stored in a desiccator for subsequent elemental composition by microprobe and solid state NMR.

2.2. Determination of $Si(OH)_4$, Al, F^- and HPO_4^{2-} in solution

$Si(OH)_4$ was determined spectrophotometrically (λ_{max} 810 nm) as the reduced blue molybdosilicic acid complex [11]. Single use plastic cells of 10 mm pathlength were used. Calibration curves using standards prepared from a certified Si stock solution (1000 mg/L; Perkin–Elmer) were plotted for both semi-micro (1.5 mL) and standard (4.0 mL) cuvettes. Confidence limits (95%) for nine replicates at two different [Si] were: 0.6 mg/L Si – 0.603 ± 0.004 mg/L and 0.2 mg/L Si – 0.194 ± 0.003 mg/L.

Al was determined by graphite furnace atomic absorption spectrometry (GFAAS) using matrix-matched standards and a programme developed by the authors [12].

Total F^- was measured using an ion selective electrode (Sentek, UK) calibrated against standard solutions containing 0.1–100 mg/L F^-. It was measured by the method of standard additions after mixing the sample with total ionic strength adjustment buffer which included 15 g/L *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid monohydrate (CDTA) and 58 g/L NaCl in acetate buffer at pH 5.0.

Total HPO_4^{2-} was measured spectrophotometrically (λ_{max} 880 nm) as the blue heteropoly complex [13].

Fig. 1. Change in $[Si(OH)_4]$ during 60 days incubation at 20.0 ± 0.1 °C for: (a) 1 mmol/L $Si(OH)_4$/1 mmol/L Al + 1 mmol/L HPO_4^{2-}; (b) 1 mmol/L $Si(OH)_4$/1 mmol/L Al + 1 mmol/L F^-; and (c) 1 mmol/L $Si(OH)_4$/1 mmol/L Al + no added anion. Mean and SD are plotted, $n = 5$.

2.3. Elemental composition of solid phases

Electron microprobe analysis was conducted on a Cameca SX100 electron probe microanalyser. Ground samples were pressed into pellets and the contents of Si, Al, F and P were determined for 20 different 5 μm spots on each pellet. Average atomic percentages were calculated for each sample ($n = 20$, RSD $\leqslant$ 5% for Al and Si) and normalized to Si = 1 (Table 1).

2.4. Solid state NMR

Solid state magic angle spinning (MAS) NMR was performed on a Varian UNITY Inova spectrometer with a 7.05 T Oxford Instruments magnet. Three probes have been used. The diameters of rotors are: 7.5 mm (Varian; ^{29}Si), 5 mm (Doty Scientific; ^{19}F with proton decoupling) and 4 mm (Varian; ^{27}Al, ^{31}P). Spin rates used were 5 kHz with the 7.5 mm probe, 11.6 kHz for the 5 mm probe and 10–14 kHz for the 4 mm probe. The frequencies for the individual nuclei are: ^{27}Al, 78.1; ^{29}Si, 59.6; ^{19}F, 282.1; ^{31}P, 121.4 MHz. Chemical shifts were referenced to: ^{27}Al, 1 M AlCl$_3$; ^{29}Si, (CH$_3$)$_4$Si; ^{19}F, CFCl$_3$; ^{31}P, 85% H$_3$PO$_4$. All spectra were obtained with direct-polarisation experiments and with 90° excitation pulses except for ^{27}Al where a 20° pulse was used. Recycle delays of 60–120 s were used for the ^{29}Si spectra, 1 s for the ^{19}F, 0.2 s for ^{27}Al and 60 s for ^{31}P.

3. Results

3.1. Influence of fluoride, F^-

Dialysis and membrane filtration were used to discriminate between HAS formed in the absence of F^- and HAS formed in the presence of equimolar F^- and Si(OH)$_4$. For each of the parent solutions the inclusion of F^- significantly increased dialysable [Si(OH)$_4$] and [Al] whereas [F^-] following filtration were reduced. For example, for parent solutions which included (in mmol/L) 1.0Si/2.0Al ± 1.0F dialysable [Si(OH)$_4$] and [Al] were, respectively, 73 and < 1 μmol/L in the absence of F^- and 141 and 66 μmol/L in the presence of F^- whereas the [F^-] following filtration had fallen from 1.0 mmol/L to 404 μmol/L (Table 1). Precipitates were collected by filtration from each combination of Al, Si(OH)$_4$ ± F^- except where the stoichiometry of the parent solution was 2.0Si/0.5Al/2.0F where no filterable precipitate was formed. Chemical composition using electron microprobe analysis confirmed the presence of F^- in solid phases (Table 1) and suggested the formation of HAS$_A$ (Si:Al ca. 0.5) and HAS$_B$ (Si:Al ca. 1.0) for parent solutions in which [Al] $\geqslant$ [Si(OH)$_4$] and [Al] < [Si(OH)$_4$], respectively [6]. Solid phase Si:Al ratios which

were significantly lower than 0.5, for example the parent solution of stoichiometry 0.5Si/2.0Al 0.5F, suggested that precipitates were composed of both HAS$_A$- and Al(OH)$_{3(s)}$-like phases. Solid state NMR (^{27}Al, ^{29}Si, ^{19}F) of precipitates (Figs. 2–4) identified the formation of Al(OH)$_{3(s)}$ (^{27}Al δ_{max} 0–10 ppm), HAS$_A$ (^{27}Al δ_{max} 0–3.4 ppm and ^{29}Si δ_{max} ca. −78 ppm) and HAS$_B$ (^{27}Al δ_{max} 0–3.4 ppm + ca. 55 ppm and ^{29}Si δ_{max} ca. −90 ppm) [6,14] and the incorporation of F^- (^{19}F δ_{max} −150 and −131 ppm) into solid phases [15] (Table 2).

3.2. Influence of phosphate, HPO_4^{2-}

The concentrations of filtered Si(OH)$_4$ were extremely high in solutions containing equimolar Si(OH)$_4$ and HPO$_4^{2-}$ and, in all but one of the parent solutions

Fig. 2. ^{27}Al MAS NMR spectra of solid phases prepared in the absence (a) and presence (b) of F^-. Si:Al – indicates the concentrations of Si(OH)$_4$ and Al in parent solutions. For (b) [F^-] = [Si(OH)$_4$] except, if [Si(OH)$_4$] = 0, then [F^-] = 0.5 mmol/L.
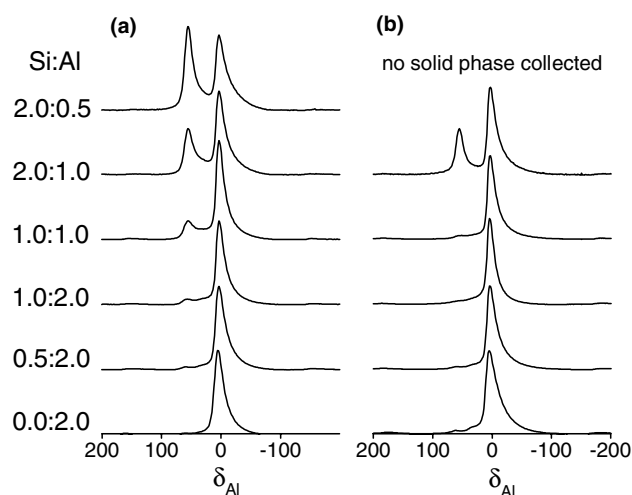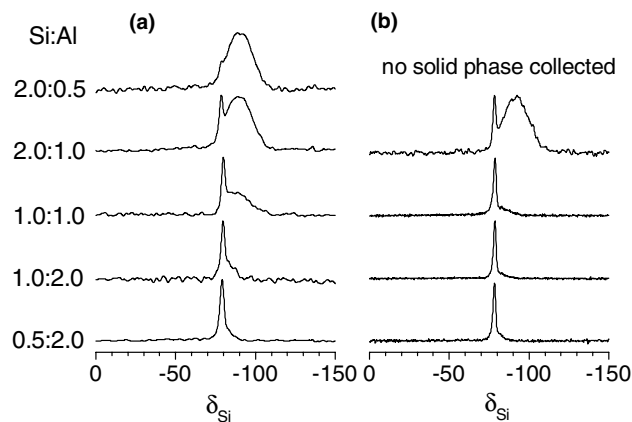
Fig. 3. ^{29}Si MAS NMR spectra of solid phases prepared in the absence (a) and presence (b) of F^-. Si:Al – indicates the concentrations of Si(OH)$_4$ and Al in parent solutions. For (b) [F^-] = [Si(OH)$_4$].

the solution studies and suggested that Al was precipitated as hydroxyaluminium phosphate from each of the parent solutions (Table 1). Si was only found as a significant component of the solid phase (Si:P ca. 0.5) when the concentration of Al in the parent solution exceeded the combined concentration of $Si(OH)_4$ and HPO_4^{2-} (2.0Si/0.5Al/2.0P). Solid state NMR (^{27}Al, ^{29}Si, ^{31}P) of this precipitate confirmed the formation of an hydroxyaluminium phosphate (^{27}Al δ_{max} 0.4 ppm; ^{31}P δ_{max} −10.6 ppm) and the probable 'contamination' of this phase with a small amount of HAS_A (^{29}Si δ_{max} −78.6 ppm) (Table 2).

4. Discussion

Dialysis demonstrated that HAS formed in the presence of equimolar F^- and $Si(OH)_4$ were in equilibrium with significantly higher concentrations of dialysable $Si(OH)_4$ and Al. The high concentrations of dialysable Al were most probably due to the formation of soluble complexes of aluminium fluoride and, possibly, hydroxyaluminium fluorides [16]. The assumption must be that whilst these complexes remain in solution there will be no opportunity for $Si(OH)_4$ to condense across hydroxyl groups on adjacent Al atoms to form HAS. As such the concomitant higher concentrations of dialysable $Si(OH)_4$ were probably indicative of F^- limiting the availability of hydroxyaluminium templates for the subsequent formation of HAS. The propensity for F^- to react with Al to form soluble complexes and so prevent the formation of HAS was best exemplified in the parent solution which included (in mmol/L) 2.0Si/0.5Al/2.0F in which approximately 50% of the original Al was dialysable and, consequently, no solid phase could be separated following filtration (Table 1). However, this was the only stoichiometry which appeared to prevent the formation of HAS and in each of the other parent solutions the evidence pointed towards the incorporation of F^-
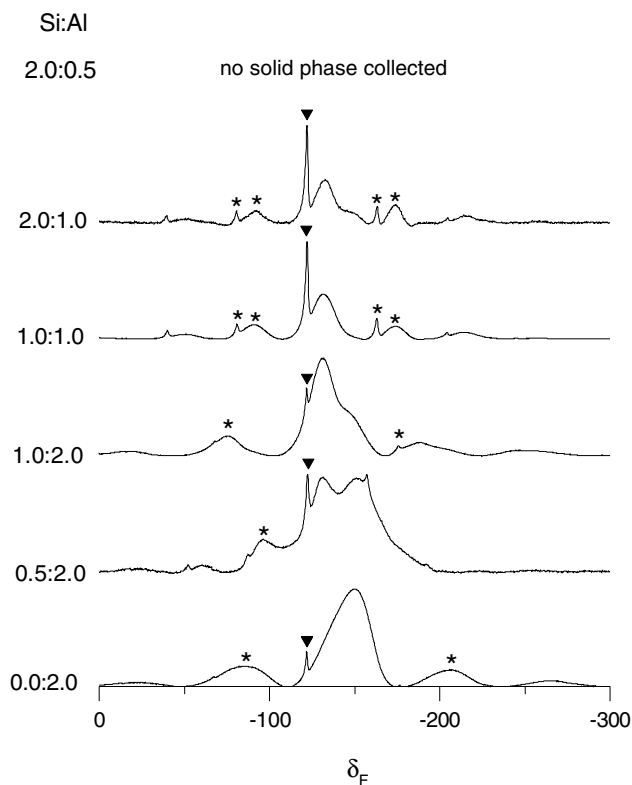

Fig. 4. ^{19}F MAS NMR spectra of solid phases prepared in the presence of F^-. Si:Al – indicates the concentrations of $Si(OH)_4$ and Al in parent solutions. $[F^-] = [Si(OH)_4]$ except, if $[Si(OH)_4] = 0$, then $[F^-] = 0.5$ mmol/L. Asterisks mark positions of sidebands and inverted triangles mark the position of chemical shift corresponding to contaminating PTFE.

(0.5Si/2.0Al/0.5P), showed that very little $Si(OH)_4$ was precipitated in solid phases (Table 1). All Al was precipitated from each of the parent solutions whereas the concentrations of soluble HPO_4^{2-} in equilibrium with solid phases loosely reflected the Al:P ratio of parent solutions. Chemical composition of precipitates using electron microprobe analysis confirmed the results of

Table 2
Assignments and abundances of ^{27}Al, ^{29}Si, ^{19}F and ^{31}P MAS NMR chemical shifts for each solid phase

Stoichiometry of parent solution (mmol/L)				δ^{27}Al		δ^{29}Si		δ^{19}F		δ^{31}P
Si	Al	F	P	Al^{IV}	Al^{VI}	Q^3(3Al)	Q^3(1-2Al)	Al(OH)$_3$–F	HAS–F	PO$_4$
0.5	2.0				2.5 (100%)	−79.1 (47%)	−81.1 (53%)			
0.5	2.0	0.5			2.7 (100%)	−78.2 (85%)	−82.1 (15%)	−151.1	−131.6	
0.5	2.0		0.5		0.4 (100%)	−78.6 (54%)	−85.0 (46%)			−10.6 (100%)
1.0	2.0				2.5 (100%)	−79.6 (38%)	−82.3 (62%)			
1.0	2.0	1.0			3.4 (100%)	−78.6 (83%)	−81.7 (17%)	−150	−131.1	
1.0	1.0			53.8 (8%)	2.5 (92%)	−79.9 (23%)	−88.8 (77%)			
1.0	1.0	1.0			2.7 (100%)	−78.7 (63%)	−82.1 (37%)		−131.9 (100%)	
2.0	1.0			55.0 (28%)	2.5 (72%)	−78.6 (7%)	−90.3 (93%)			
2.0	1.0	2.0		54.6 (31%)	2.1 (69%)	−78.3 (8%)	−91.7 (92%)		−132.8 (100%)	
2.0	0.5			55.0 (40%)	2.5 (60%)	−78.7 (1%)	−90.9 (99%)			
	2.0				5.0 (100%)					
	2.0	0.5			10.0 (100%)			−150.1 (100%)		

into the solid phase and more particularly into HAS. To understand how F^- influenced HAS formation it is informative to compare solid phases formed for each parent solution stoichiometry in the absence and presence of fluoride.

(i) *0.5Si/2.0Al ± 0.5F* – In the absence of F^- the solid phase was predicted to be a mixture of HAS_A and $Al(OH)_{3(s)}$ and this was borne out by a Si:Al ratio of 0.27 in the solid phase. Further confirmation of the presence of HAS_A was that all Al was present in octahedral geometry (^{27}Al δ_{max} 2.5 ppm) and Si was present in equal mixture of $Q_3(3Al)$ (^{29}Si δ_{max} −79.1 ppm) and $Q_3(2Al)$ (^{29}Si δ_{max} −81.1 ppm). In the presence of F^- the Si:Al ratio of the solid phase was 0.25 which again suggested a mixed phase. Interestingly, the ratios of Si:F and Al:F in the solid phase were ca. 2.0 and 8.5, respectively, and these may prove to be helpful in identifying the location of F in the solid phases. Again all Al was in octahedral geometry (^{27}Al δ_{max} 2.7 ppm) and the presence of HAS_A was confirmed by Si NMR, though this time the proportion of $Q_3(3Al)$ (^{29}Si δ_{max} −78.2 ppm) was very much higher than $Q_3(2Al)$ (^{29}Si δ_{max} −82.1 ppm). ^{19}F NMR gave δ_{max} at −151.1 ppm, which, based upon the chemical shift (^{19}F δ_{max} −150.1 ppm) we obtained for a pure precipitate of aluminium hydroxyfluoride, was probably indicative of F associated with $Al(OH)_{3(s)}$, and −131.6 ppm which we believe showed F associated with HAS_A.

(ii) *1.0Si/2.0Al ± 1.0F* – In the absence of F^- the solid phase was predicted to be primarily HAS_A and this was supported by a Si:Al ratio of 0.43 and characteristic chemical shifts for both ^{27}Al NMR (δ_{max} 2.5 ppm) and ^{29}Si NMR (δ_{max} −79.6 and −82.3 ppm). In the presence of F^- the Si:Al ratio of the solid phase was 0.41 which was indicative of HAS_A and the Si:F and Al:F ratios were ca 2.0 and 5.5, respectively. The lower ratio of Al to F in this phase was probably indicative of a higher $[F^-]$ to [Al] in the parent solution whereas this effect was limited by a significant reduction in the proportion of aluminium hydroxyfluoride in the mixed phase as was suggested by the almost complete disappearance of the ^{19}F NMR chemical shift at ca. −150 ppm. Solid state ^{27}Al, ^{29}Si and ^{19}F NMR showed that this precipitate was almost identical to that isolated from the previous parent solution (0.5Si/2.0Al/0.5F) except that the majority of F was now associated with HAS_A (^{19}F NMR δ_{max} −131.1 ppm).

(iii) *1.0Si/1.0Al ± 1.0F* – In the absence of F^- the solid phase was predicted to be HAS_A with perhaps some HAS_B and the latter was borne out by a Si:Al ratio of 0.63. Again the presence of a proportion of HAS_B was supported by both ^{27}Al NMR, which indicated a small amount of Al in tetrahedral geometry (^{27}Al NMR δ_{max} 53.8), and ^{29}Si NMR which showed that Si was now coordinated through both $Q_3(3Al)$ and $Q_3(1-2Al)$ linkages [6]. The presence of F^- appeared to reverse the

trend towards the formation of HAS_B such that structural (NMR) and compositional (microprobe) analyses of the solid phase showed that it was approximately identical to that precipitated from the previous parent solution (1.0Si/2.0Al/1.0F).

Thus in spite of quite obvious differences in the solid phases formed in the absence of added F^- the structure and composition of HAS formed in its presence were approximately identical, probably an HAS_A-like structure which included F in a single chemical environment (^{19}F NMR δ_{max} ca. −131 ppm) at a Si:F ratio of ca. 2–3 and Al:F ratio of ca. 5–6.

(iv) *2.0Si/1.0Al ± 1.0F* – In the absence of F^- the solid phase was predicted to be predominantly HAS_B and some HAS_A. The Si:Al ratio of the solid phase, ca. 0.94, confirmed the presence of the former and this was supported further by solid state ^{27}Al and ^{29}Si NMR which showed that Al was present in both octahedral (δ_{max} 2.5 ppm) and tetrahedral (δ_{max} 55.0 ppm) geometries and that Si was coordinated primarily through $Q_3(1-2Al)$ linkages (δ_{max} −90.3 ppm). Microprobe and NMR characterisation of the solid phase which formed in the presence of F^- showed that in respect of both Al and Si it was identical to that formed in the absence of F^-. This was unusual in that for previous parent solutions the additional presence of F^- had always resulted in structural changes manifested as increases in the proportion of $Q_3(3Al)$ linkages relative to $Q_3(1-2Al)$. No such changes occurred when F was incorporated into the predominantly HAS_B-like phase precipitated from this parent solution. However, the ^{19}F NMR chemical shift at δ_{max} −132.8 ppm was similar to those obtained for substitution of F^- into HAS_A-like structures (−131.6, −131.1 and −131.9 ppm) and this may indicate that F was present in a similar chemical environment in both HAS structures. The solid phase was different from the F-containing HAS_A-like solid phases in that the ratio's of Si:F (ca. 4) and Al:F (ca. 4) showed an increase in Si and a decrease in Al relative to F when compared with HAS_A-F. These apparently contradictory changes in the content of F in the solid phase relative to both Si and Al may actually be informative in respect of the mechanism of formation of HAS_B via HAS_A. For example, it was assumed that the solid phase which formed in the absence of F^- was a mixture of HAS_B and HAS_A and this was supported by NMR. However, the Si:Al ratio of this 'mixed' phase was very close to 1.0 and this may indicate that the predominant forms of HAS were actually HAS_B (ca. 60% of the total) and an intermediate form HAS_{AB} (ca. 40% of the total) in which the further incorporation of $Si(OH)_4$ has not yet triggered the dehydroxylation reaction which would result in 50% of its constituent Al switching from an octahedral to a tetrahedral geometry (Fig. 5). It is our understanding to date that the rate at which dehydroxylation takes place is highly dependent upon the $[Si(OH)_4]$ which is free to

exchange with the solid phase. In the presence of F^- the Si:Al ratio of the mixed solid phase was very close to 1.0 whilst the NMR again suggested that Al was predominantly present in octahedral coordination. In addition, the presence of F^- in the parent solution did not influence the coordination of Si in the solid phase. In each of the previous parent solutions the presence of F^- promoted the coordination of Si through $Q_3(3Al)$ as opposed to $Q_3(1-2Al)$ linkages. Considering that this was the first parent solution in which $[F^-] > [Al]$ it is conceivable that a higher proportion of Al–OH will be replaced by Al–F in the solid phase and this would explain the observed increase in the ratio of F to Al. The reason why the F to Si ratio was concomitantly reduced could be that the HAS_B structure only has one potential binding site for F and this is associated with octahedrally coordinated Al in this structure whilst HAS_{AB}, which only includes octahedral Al, retains two potential binding sites for F. In this way, considering the relative proportions of HAS_B and HAS_{AB} in the solid phase, it was possible for the ratio of F to Si to be reduced and the ratio of F to Al to be increased relative to solid phases which were formed from parent solutions in which $[Al] \geqslant [F^-]$, the predominant precipitate would be HAS_A and the lower $[F^-]$ would dictate that Al–OH groups on this phase would only be partially substituted for Al–F.

(v) *2.0Si/0.5Al ± 2.0F* – In the absence of F^- a solid phase was precipitated with a Si:Al ratio of 1.1 and NMR chemical shifts which demonstrated that it was composed of at least 80% HAS_B. We would contend that the remainder was HAS_{AB} and that the higher proportion of tetrahedrally coordinated Al in this mixed phase was the result of an accelerated dehydroxylation reaction which was fuelled by a high concentration of free to exchange $Si(OH)_4$ (ca. 850 μmol/L as compared to ca. 600 μmol/L for the 2.0Si + 1.0Al parent solution).

In the presence of F^- we were not able to collect any solid phase and this may have been due to the fourfold excess of F^- preventing the formation of hydroxyaluminium templates required for HAS formation or possibly the substitution of F into preformed HAS_B such that it prevented the aggregation of the solid phase towards a filterable size.

To try to identify the location of F in our HAS we have carried out F–Si CP NMR and we obtained the same spectrum as for DP NMR. The most likely explanation for this is that F was not specifically associated with Si and that the ^{19}F NMR chemical shift in the range -131 to -133 ppm was due to Al–F with Al being linked to Si through varying combinations of $Q_3(1-3Al)$. We obtained further support for this possibility by carrying out F–Al CP NMR which strongly suggested that, not only was F coordinated through Al but that it was only associated with octahedral Al. The association of F with Al and not with Si was again supported by the observation that concomitant with an increase in the Si:Al ratio of the solid phase was an increase in the Si:F ratio and the propensity for F in the solid phase to promote the characteristic HAS_A (^{29}Si NMR δ_{max} -78 ppm) structure. Thus F^- may be competitive with $Si(OH)_4$ in inhibiting/promoting the formation of HAS_B via the putative intermediate HAS_{AB}. This competitive edge to F^- was lost when the rapid formation of HAS_B (via HAS_{AB}) was favoured (i.e., where the $[Si(OH)_4]$ of the parent solution was at least double that of the [Al]) and under these conditions the substitution of F for OH would be limited by the $Si(OH)_4$-directed dehydroxylation reaction in which up to 50% of octahedrally coordinated Al rearranges to give tetrahedrally coordinated Al in the solid phase. The probable role of F^- in the formation of HAS is summarised in the scheme in Table 3. It predicts the formation of a number of different solid phases which though unlikely to be
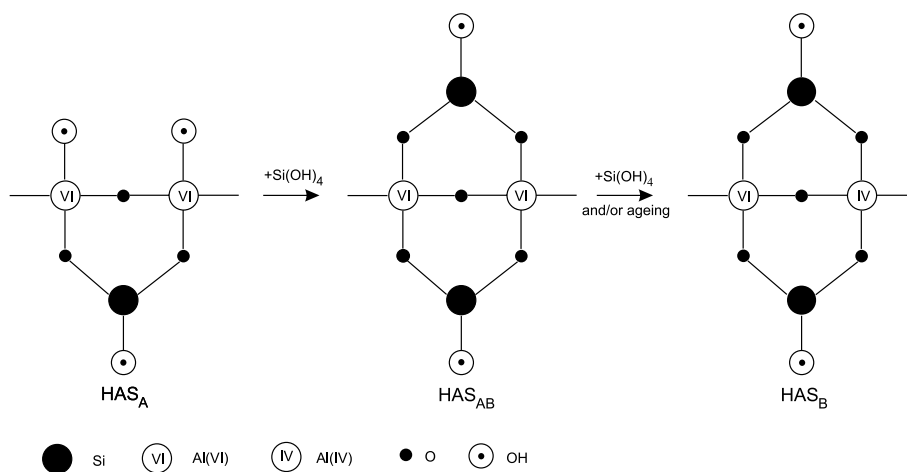

Fig. 5. Suggested scheme for the formation of HAS_B from HAS_A involving a transitional form, HAS_{AB}, which undergoes a dehydroxylation fuelled by either ageing or a significant excess of $Si(OH)_4$.

Table 3
Summary of the suggested role of fluoride in the formation of fluoride-substituted hydroxyaluminosilicates

Conditions	Reactants		Solid phase	Elemental ratio
$[F^-] < [Al]$ $[Si(OH)_4] = 0$	$Al^{3+}_{(aq)} + F^-_{(aq)}$	$\xrightarrow{OH^- \rightarrow pH\ 6.0}$	$Al_4(OH)_{12-x}F_x$	Al:F < 2.0
$[F^-] < [Al]$ $[Si(OH)_4] \leqslant [Al]$	$Al^{3+}_{(aq)} + F^-_{(aq)} + Si(OH)_4$	$\xrightarrow{OH^- \rightarrow pH\ 6.0}$	$(HAS_A)_4F$	Al:F = 8.0 Al:Si = 0.5 Si:F = 4.0
$[F^-] > [Al]$ $[Si(OH)_4] > [Al]$	$Al^{3+}_{(aq)} + F^-_{(aq)} + Si(OH)_4$	$\xrightarrow{OH^- \rightarrow pH\ 6.0}$	$(HAS_{AB})_4F_2$[a]	Al:F = 4.0 Al:Si = 1.0 Si:F = 4.0
$[F^-] < [Al]$ $[Si(OH)_4] > [Al]$	$Al^{3+}_{(aq)} + F^-_{(aq)} + Si(OH)_4$	$\xrightarrow{OH^- \rightarrow pH\ 6.0}$	$(HAS_B)_4F$	Al:F = 8.0 Al:Si = 1.0 Si:F = 8.0

[a] In the presence of an excess of $Si(OH)_4$ this phase will undergo a slow dehydroxylation in which up to 50% of the constituent Al adopts tetrahedral geometry and F will be titrated from the solid phase. The resulting phase will be a mixture of $(HAS_{AB})_4F_{2(s)}$ and $(HAS_B)_4F_{(s)}$.

precipitated as single phases are not too dissimilar in elemental composition and structure to those we have identified and characterised herein (Tables 1 and 2).

Further research will be required to understand fully the mechanism of formation of fluorine-substituted HAS whereas under the conditions used in this study HPO_4^{2-}, when equimolar to $Si(OH)_4$, prevented HAS formation in all but one of the parent solutions. When Al was present to a fourfold excess of HPO_4^{2-} (0.5Si/2.0Al/0.5P) the resulting solid phase included primarily aluminium hydroxyphosphate [17] but it also contained a significant component of HAS_A. Phosphate is a bulky ligand in comparison to F^- and its ligation by Al was generally sufficient to promote the precipitation of an hydroxyphosphate and to prevent any reaction of $Si(OH)_4$ across any remaining Al–OH groups. Whether HPO_4^{2-} would be competitive when $Si(OH)_4$ was present to excess remains to be determined.

In the experiments described herein both F^- and HPO_4^{2-} were present at equimolar concentration to $Si(OH)_4$ and, as such, were given maximal opportunity to influence the formation of HAS. The results have identified the formation of fluorine-substituted HAS, which may have some significance to both the biogeochemistry of Al and also to materials science, and the inhibition of the formation of HAS by HPO_4^{2-}. In the natural environment the concentration of $Si(OH)_4$ is likely to be significantly in excess of both F^- and HPO_4^{2-} and further experiments using more environmentally realistic concentrations of these ligands will be needed to confirm that fluorine-substituted HAS could form in soil and surface waters and similarly that HPO_4^{2-} might prevent or influence HAS formation.

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