Research Article

The Effect of Dissolved Humic Acids on Aluminosilicate Formation and Associated Carbon Sequestration

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1. Introduction

Complexation of Al with natural organic matter is important for the development of soils, influencing both the weathering and neogenesis of Al-bearing minerals [1] including aluminosilicate clays. The metastable clay minerals allophane and imogolite, when present, may control the solubility of both Al and Si relative to more stable phases such as gibbsite and kaolinite [2]. Allophane and imogolite are poorly crystalline hydroxyaluminosilicates with Al/Si ratios ranging from 0.5–4. They are composed of Si and Al polyhedral layers shaped into hollow tubes and spheres [3]. Imogolite, (OH) 2 Al 2 SiO 4 , which has long-range order, is tubular in shape and has an Al/Si ratio of 2. Allophane has short-range order and forms hollow spherules with a range of Al/Si ratios. Al-rich allophane is also called protoimogolite or imogolite-like allophane and has an Al/Si ratio of ~2 [4]. Imogolite and allophane occur frequently as, but are not limited to, what are termed allophanic horizons in volcanic soils such as andisols and spodosols [5]. Their occurrence is contingent upon conditions such as soil pH, the availability of sufficient Si, and the presence of organic material, which can either inhibit the formation of [5], or conversely, stabilize these minerals [6]. The large surface area and high reactivity of these minerals promote complexation with organic matter [6], the essential soil nutrients P and N, and toxic contaminants such as As, Cd, Cu, and Pb [7, 8].

Laboratory synthesis of aluminosilicate phases in the presence of organic constituents has been previously explored. Organic additives such as quercetin [9] and organometallic reagents such as aluminum-sec-butoxide (ASB) and tetraethoxysilane (TEOS) [10, 11] were used to synthesize aluminosilicates including kaolinite, halloysite, allophane, and imogolite. The specific phases that formed and their amounts depended on factors such as initial Al/Si ratio, pH, temperature, and aging time. The proposed precipitation mechanism involves the slowing of Al hydroxide polymerization by formation of stable Al-organo complexes.
These complexes are thought of as precursor species that have Al–O (and possibly Si–O) bonds required for attachment of alumina and silicate sheets [12]. This eliminates the need for conversion of Al–OH to Al–O bonds in systems predisposed to Al hydroxide precipitation and facilitates the formation of required Al–O–Si linkages with the organic material acting as a “catalyst” which is subsequently recycled. Conversely, addition of organic acids such as citric [13] and more complex, naturally occurring fulvics and humics [14] were observed to inhibit the formation of well-defined phases during synthesis at 96–100°C. The concentration of imogolite declined with increasing organic concentration, eventually giving way to the formation of only disordered aluminosilicates and pseudoboehmite [13, 14]. However, to be applicable to natural systems synthesis at low temperature is required. Uniquely, this study was conducted at 25°C to systematically explore the effect of dissolved organic carbon (DOC) from natural humic acid (HA) on the formation of aluminosilicate minerals. Results isolated the role of initial chemical composition on aluminosilicate formation, as a first step in deconvoluting the complexity of this process in natural soils.

2. Experimental Details

Stock solutions for batch experiments were prepared by diluting in deionized water (DI) 1000 mg/L Al in HNO₃, and 1000 mg/L Si in DI standard solutions. Suwannee River Humic Acid (SRHA, International Humic Substances Society) containing 53 wt % C was dissolved in DI water to produce a 250 mg/L DOC stock. Though a river humic acid was chosen for this study, the carboxylic content can be similar to that of soil humic acids. A matrix of experimental binary and ternary solutions was prepared with variable Al, Si, and DOC concentrations (Table 1). Appropriate amounts of the stock solutions were mixed in the sequence Si and/or Al stock solution followed by DOC stock solution to yield a total volume of 80 mL. Solution pH was adjusted to a value close to 6 (±0.5 pH unit) using <0.5 mL 0.1 or 1.0 M NaOH, and initial concentrations were corrected for this addition. Time-series data indicated that aqueous concentrations of all components in filtered (0.2 μm PTFE syringe filters) mixed solutions were invariant after 20 h; thus, all experiments were conducted for this time period. Solutions were stirred only during preparation and prior to filtration. Aqueous Al and Si concentrations were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) using a Perkin Elmer Optima 4300 instrument. All solutions were prepared and sampled in duplicate.

2.1. Thermodynamic Calculations. Based on results from small-volume batch experiments, solutions with selected concentrations of Al, Si, and DOC were chosen to generate large amounts of precipitates for subsequent analysis (Table 1). The initial aqueous speciation and saturation states with respect to potential solid precipitates were calculated using Visual MINTEQ ver 2.53 with the Thermo.vdb database [15]. For all calculations, initial concentrations of Al, Si, and DOC were entered, along with any base required for pH adjustment. The pH was calculated from the charge and mass balance in solution prior to precipitation, that is, the H⁺ concentration was adjusted until the charge difference was ≤0.01%. For DOC-bearing solutions, the Stockholm Humic Model (SHM) [16] was used to model metal-humic complexation. Acid dissociation constants for SRHA carboxylic and phenolic functional groups available from IHSS [17] were included.

2.2. Evaluation of Precipitate Phases. Experiments designed to generate sufficient material for compositional and mineralogical analysis (Table 1) were prepared in an 800 mL volume in triplicate and were treated with <1 mL 10 N NaOH for pH adjustment. After 20 h, each solution was vacuum-filtered using a 0.2 μm polycarbonate filter, the filtrate sampled for Al and Si analysis, and the precipitate recovered. The final mass of precipitate was placed in a drying oven at 40°C for several hours to expedite evaporation of excess moisture, then ground gently using a mortar and pestle. A portion of sample was dissolved using 0.1 M HNO₃ and the Al and Si concentrations determined by ICP-OES analysis. Total C content was determined using a Carlo Erba 2500 CHNS Elemental Analyzer. X-ray diffraction (XRD) data were collected from 2–65° 2-theta with a step size of 0.02° using a Siemens D5000 X-ray diffractometer. Fourier transform infrared (FTIR) spectroscopy data were collected in transmission mode for samples in a KBr background using a Perkin Elmer Spectrum 100 spectrometer.

Table 1: Concentrations of Al, Si, and DOC used for binary and ternary experiments (variable [DOC]), variables [Si] and [Al], and experiments used to generate precipitates for further analysis.

| Al (mM) | Si (mM) | DOC (mg/L) |
|---|---|---|
| Binary solutions | | |
| — | 0.3 | 6 |
| 0.3 | — | 6 |
| 0.3 | 0.3 | — |
| Ternary solutions: variable [DOC] | | |
| 0.3 | 0.3 | 3 |
| 0.3 | 0.3 | 6 |
| 0.3 | 0.3 | 9 |
| Variable [Si] | | |
| 0.3 | 0.05–1.5 | — |
| 0.3 | 0.05–1.5 | 6 |
| Variable [Al] | | |
| 0.05–1.5 | 0.3 | — |
| 0.05–1.5 | 0.3 | 6 |
| Solutions for precipitate recovery | | |
| 0.5 | 0.5 | — |
| 0.5 | 0.5 | 6 |
| 0.75 | 0.5 | — |
| 0.75 | 0.5 | 6 |
| 1.0 | 0.5 | — |
| 1.0 | 0.5 | 6 |

Both ²⁹Si and ²⁷Al nuclear magnetic resonance spectroscopy (NMR) data were collected for generated solids. The ²⁹Si single-pulse magic angle spinning (SP/MAS) and ²⁹Si [{¹H}] cross-polarization magic angle spinning
(CP/MAS) spectra were collected with a 400 MHz (9.4 T) Varian Inova spectrometer operating at 79.5 MHz for $^{29}$Si using a Varian/Chemagnetics T3 sample probe assembly configured for 3.2 mm (o.d.) rotors. The SP/MAS spectra were collected under quantitative acquisition conditions using a 90° pulse (5 μs) and 180 s relaxation delay at a spinning rate of 10 kHz. The CP/MAS spectra were obtained at spinning rates of 5 and 10 kHz using a ramp of the transverse $^1$H field during polarization transfer for contact times ranging from 0.5 to 15 ms. For the $^{27}$Al SP/MAS NMR spectra, a 500 MHz (11.7 T) Varian Infinity Plus spectrometer was used, operating at 130.3 MHz with the sample spinning at 18 kHz in 3.2 mm rotors. The acquisition parameters consisted of 1.0 μs pulses ($\pi/12$) and a 1.0 s relaxation delay, which correspond to uniform excitation and full relaxation of the central transition. Additional spectra were taken for the 1.0 mM Al samples at 217 MHz (19.5 T; Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, Tallahassee, FL, USA). These high-field spectra were taken at a 10 kHz spinning rate (4 mm spinning system) under low-power conditions using 4 μs pulses and 0.5 s relaxation delay for a total of 128 acquisitions.

3. Results

3.1. Al and Si Removal from Binary and Ternary Solutions. Results for ternary Al-Si-DOC and binary Al-Si, Al-DOC and Si-DOC experiments show that for all systems, Si is less susceptible to removal from the aqueous phase relative to Al (Figure 1). Comparison of results from the binary Al-Si, Si-DOC, and Al-DOC experiments indicates that aqueous Si concentration is reduced in the presence of Al but not DOC, whereas Al is removed from solution in the presence of Si, and to a greater extent in the presence of DOC.

Equal amounts of Al and Si precipitated from Al-Si solutions with 0 or 3 mg/L DOC. As DOC concentration increased from 3 to 6 mg/L, removal of both Al and Si was enhanced. At 9 mg/L DOC no additional Al was removed, and aqueous Si concentrations increased slightly, relative to the 6 mg/L DOC solution. These results suggest that removal of both Al and Si was optimized in the 6 mg/L DOC solution relative to binary and other ternary solutions, therefore 6 mg/L DOC was used in subsequent experiments in which initial concentrations of Al and Si were varied. The Al/Si ratios of precipitates from 0, 3, and 6 mg/L DOC solutions are 2.2–2.3, suggesting that precipitates formed both in the absence and presence of DOC may be similar in composition. The slightly higher Al/Si ratio of 2.8 in precipitates from 9 mg/L DOC solutions suggests the precipitation of additional Al, possibly caused by the higher concentration of DOC.

Comparing the results from binary and ternary systems indicates that in the latter Al may precipitate both as aluminosilicate and alumin-o-organic complexes. As Si does not appear to form insoluble complexes with DOC, enhanced Si removal in Al-Si-DOC solutions, with DOC > 3 mg/L, relative to Al-Si solutions appears to result by the formation of aluminosilicate complexes which may bind to the DOC by an Al-bridging mechanism (i.e., Si-Al-DOC). Coprecipitation of aluminosilicate with precipitating organics may also occur. Hence, significant reduction in both Al and Si concentrations in Al-Si-DOC solutions is likely caused by multiple complexation and precipitation pathways.

3.2. The Effect of Varying Al or Si Concentration in Solutions with 0 or 6 mg/L DOC. The effect of variable Si concentration from 0.05 to 1.5 mM Si was evaluated at a fixed initial Al concentration of 0.3 mM and fixed DOC concentration of 0 or 6 mg/L. The amount of Si remaining in solution after 20 h was slightly below the initial value in all cases with no obvious effect of DOC (Figure 3(a)). The final concentration of Al remained much lower than the initial value regardless of initial Si, with a slightly higher value (less removal) only at 1.5 mM Si (Figure 3(b)). Below 0.3 mM initial Si, aqueous Al concentration remained slightly higher for Al-Si relative to Al-Si-DOC solutions. This is consistent with the enhanced removal of Al in DOC solutions.

The effect of variable Al concentration from 0.05 to 1.5 mM was evaluated at an initial Si concentration fixed at 0.5 mM, a value anticipated to be sufficient for observing potential interactions with the higher concentrations of Al. Total Si concentration decreased with increasing initial Al (Figure 3(c)), with comparable behavior for 0 and 6 mg/L DOC solutions except from 0.6 to 0.9 mM initial Al where the final Si concentration of the Al-Si solutions without DOC increased abruptly (Figure 3(c)). A similar abrupt increase occurred for final Al in the same Al-Si solutions (Figure 3(d)). In the Al-Si-DOC solutions, the Si concentration abruptly increased at 1 mM initial Al (Figure 3(c)) to a value similar to that of the DOC-free solution. In
these solutions, Al concentration fell rapidly to a low value and remained relatively constant up to 1 mM initial Al (Figure 3(d)), above which it also increased to values similar to those in the DOC-free solution.

Solids recovered from Al-Si and Al-Si-DOC solutions with 0.5, 0.75, and 1.0 mM initial Al were analyzed to investigate further the deviation between Al-Si and Al-Si-DOC systems observed over the initial Al concentration range of 0.6–1.0 mM.

3.3. Speciation in and Saturation States of Initial Solutions Containing 0.5, 0.75, and 1.0 mM Al, 0.5 mM Si, and 0 or 6 mg/L DOC. Thermodynamic modeling was used to estimate initial aqueous speciation and predicted precipitates for the 0.5, 0.75, and 1.0 mM Al solutions with 0.5 mM Si and 0 or 6 mg/L DOC. The dominant initial aqueous Al and Si species are Al(OH)$_2^+$ and H$_4$SiO$_4^{0}$ (Table 2). With increasing Al concentration, the concentration of AlH$_4$SiO$_4^{2+}$ complexes increases subtly. The fraction of polymeric Al$_3$(OH)$_4^{5+}$ increases by a factor of 10 when the...
initial Al concentration is doubled from 0.5 to 1.0 mM. For initial Al-Si-DOC solutions, the overall fractions of dominant species, Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^{−}$, are somewhat lowered relative to those in Al-Si solutions, but otherwise the speciation trends are similar. Speciation of Al as the aluminum tridecamer Al$_{13}$ was negligible as formation of this species is limited in the presence of Si [18] and HA [19]. The calculated pH for all solutions ranged from pH 6.03 to 6.09, consistent with the measured pH of 6.00 ± 0.5 for all samples.

The predicted species for Al complexed with SRHA are primarily bidentate HA$_2$AlO$_2$H and HA$_2$Al$^+$ along with a small fraction (<1%) of electrostatically bound Al. The fraction of Al-HA complexes decreases with increasing initial Al concentration; however, the absolute concentration of Al complexed to HA, including electrostatic species, is ~0.027 mM for all initial Al concentrations (Table 2). The concentration of DOC involved in this complexation is about ~0.053 mM, corresponding to 0.6 mg/L or one-tenth of the initial DOC in solution.

The $^{13}$C NMR analysis of SRHA [23] indicates that 15% of the C occurs as carboxyl functional groups. For 6 mg/L (0.5 mM) DOC solutions approximately 0.07 mM of C would be associated with these groups. If Al complexes primarily with carboxyl functional groups [24], then the maximum concentration of C available for complexation with Al is 0.07 mM. Thus, the thermodynamic calculations suggest that ~70% of this C (0.05 mM) may be directly bonded to Al to form bidentate Al-HA complexes in solution.

The supersaturated mineral phases for all initial Al-Si and Al-Si-DOC solutions are kaolinite, halloysite, imogolite, allophane, diaspore, boehmite, gibbsite, amorphous Al(OH)$_3$1, and quartz. All solutions were undersaturated with respect to amorphous SiO$_2$. Though thermodynamically feasible, not all predicted phases will precipitate under the given solution conditions. For example, spontaneous precipitation of quartz is likely only in supersaturated solutions [25] well above the concentrations studied here, whereas that of diaspore is rare in the absence of stabilizing substituting ions such as Fe [26].

3.4. Precipitates from Initial Solutions with 0.5, 0.75, and 1.0 mM Al, 0.5 mM Si, and 0 or 6 mg/L DOC. Solids formed from the Al-Si solutions were white to colorless, whereas those from Al-Si-DOC solutions were dark brown, similar in color to the initial solutions. All precipitates were gel-like in consistency. Of Al, Si, and C, Al was highest in concentration by weight (wt %) in all samples (Table 3) and was highest for the samples formed in initial 0.75 mM Al solutions with and without DOC. The wt % Si decreased with increasing initial Al concentration for solids formed in Al-Si solutions and was highest in the solid formed in the 0.75 mM Al-Si-DOC solution. The wt % C in the solids also decreased with increasing initial Al consistent with the corresponding decrease in the calculated fraction of Al-HA complexes and suggesting that these complexes are precursors to Al-HA precipitates in the solids.

Precipitates from 0.5 mM initial Al solutions that contained DOC had less mass (58 mg), Al, and Si than precipitates (72 mg) from the solutions without DOC. The Al/Si mole ratio for the precipitates was 2.2. The mole ratio of Al/C in the precipitate from the DOC-bearing solution was 0.7. The lower mass of the Al-Si-DOC solids suggests that Al-HA complexation inhibits or slows the formation of aluminosilicate phases, but does not change the bulk inorganic composition of the precipitate compared to DOC-free solutions. If the HA is a simple coprecipitate in the solids, it would be associated with about 1 wt% of the precipitated Al, assuming the same bidentate stoichiometry with carboxyl groups as in the soluble Al-HA species. This would lower the Al/Si ratio in the inorganic precipitate to ~2.

At 0.75 mM initial Al, again the total mass of precipitate from the Al-Si solution was greater (190 mg) compared to the mass (169 mg) precipitated from the Al-Si-DOC solution. The fraction of precipitated Al and Si is higher in the Al-Si-DOC solid compared to the Al-Si solid, but the Al/Si ratio is the same within uncertainty. This Al/Si ratio is, however, slightly higher than the ratios in the 0.5 mM Al precipitates. Assuming an Al/Si mole ratio of 2 in the inorganic part of the precipitate, the excess Al is too high by a factor of ~8 to be solely in the form of bidentate Al-HA complexes, assuming there is no fractionation (i.e., selective precipitation of smaller molecules with higher proportions of Al-binding sites) of the HA during precipitation. This suggests that a small amount of an Al-(oxy)hydroxide phase may have
Table 2: Speciation of Al and Si in 0.5, 0.75, and 1.0 mM Al; 0.5 mM Si solutions with 0 (Al-Si) and 6 mg/L (Al-Si-DOC) as calculated using Visual MINTEQ ver 2.53 with the Thermo.vdb database.

| [Al] mM | H4SiO4 | AlH3SiO4 | Al(OH)2 | Al(OH)3 | Al(OH)4 | AlOH2+ | Al3+ | Al3(OH)4 | AlH3SiO4 | Al-HA | Al-HA C |
|---------|--------|----------|--------|--------|--------|--------|------|----------|----------|-------|--------|
| 0.5     | 98.1   | 1.8      | 48.9   | 23.0   | 14.6   | 9.0    | 0.9  | 1.6      | 1.8      |       |        |
| 0.75    | 96.9   | 3.1      | 48.5   | 20.5   | 11.8   | 10.2   | 1.2  | 5.3      | 2.1      |       |        |
| 1       | 96.0   | 4.0      | 46.0   | 19.0   | 11.0   | 10.1   | 1.3  | 10.0     | 2.0      |       |        |

| Al-Si-DOC | H4SiO4 | AlH3SiO4 | Al(OH)2 | Al(OH)3 | Al(OH)4 | AlOH2+ | Al3+ | Al3(OH)4 | AlH3SiO4 | Al-HA | Al-HA C |
|-----------|--------|----------|--------|--------|--------|--------|------|----------|----------|-------|--------|
| 0.5       | 98.1   | 1.9      | 47.2   | 21.1   | 12.6   | 9.2    | 1.0  | 5.3      | 0.026    | 0.052 |        |
| 0.75      | 96.9   | 3.1      | 47.2   | 19.1   | 10.6   | 10.4   | 1.3  | 3.5      | 0.027    | 0.053 |        |
| 1         | 95.9   | 4.0      | 45.0   | 18.0   | 10.1   | 10.2   | 1.3  | 2.0      | 0.027    | 0.053 |        |

1Source of thermodynamic data for aqueous species: Al hydrolysis species [20]; AlH3SiO42+ [21]; Al3(OH)45+ [22]. Organic complexation was calculated using the Stockholm Humic Model [16].

Table 3: Composition of precipitates derived from solutions with initial 0.5, 0.75, and 1.0 mM initial Al; 0.5 mM initial Si and 0 or 0.5 mM (6 mg/L) DOC.

| Initial Al | Precipitate | Al wt percent | Si wt percent | Al/Si1 | Al/Si1 | Al/C1 | Mass2 (mg) | Al wt percent | Si wt percent | C wt percent | Al/Si1 | Al/C1 |
|-----------|-------------|---------------|---------------|--------|--------|-------|------------|---------------|---------------|-------------|--------|------|
| 0.5       | 1           | 72            | 22.7          | 10.9   | 2.2    | 1     | 1          | 58            | 17.9          | 8.6         | 12.0   | 2.2  |
| 0.75      | 1.5         | 190           | 23.3          | 9.2    | 2.6    | 1.5   | 1.5        | 169           | 25.9          | 9.8         | 9.3   | 2.7  |
| 1         | 2.1         | 142           | 20.3          | 9.0    | 2.3    | 2     | 2          | 182           | 20.2          | 7.8         | 5.2   | 2.7  |

1Mole ratios.
2Uncertainty is ± 1 mg.

formed as predicted by the thermodynamic calculations. DOC appears to promote aluminosilicate precipitation, but the overall composition of the precipitate is similar to that of DOC-free solids.

At 1.0 mM initial Al, the mass of precipitate (142 mg) from the Al-Si solutions was less than that (182 mg) from the Al-Si-DOC solutions. The wt% of precipitated Al is the same for both DOC-free and DOC-bearing solids, but less than that for solids formed from solutions with initial Al of 0.75 mM. The Al/Si ratio of the Al-Si-DOC sample is similar to that of the solids formed in the initial 0.75 mM Al solutions. However, the Al/C ratio indicates less precipitated C relative to the 0.5 and 0.75 mM samples, which correlates with the decrease in the calculated fraction of Al-HA complexes in solution with increasing initial Al. Again, assuming an Al/Si ratio in the aluminosilicate of 2 and no fractionation of the HA during precipitation, the excess precipitated Al is about a factor of 6 too high to be complexed only to carboxyl C in coprecipitated HA suggesting the formation of a minor amount of Al-(oxy)hydroxide.

3.4.1. XRD Analysis. X-ray powder diffraction patterns show that all solids exhibited low crystallinity, with no notable differences as a function of Al concentration or in the absence or presence of DOC (Figure 2). Broad peaks centered at approximately 0.334 nm and 0.222 nm, characteristic of allophane [6, 7, 27], occur in all samples. Aluminum-rich allophanes (Al2O3·xSiO2·yH2O (x = 1; y = 2–5)) classified as protoimogolite or imogolite-like allophane [28] can have Al/Si ratios ranging from 2.3 to 2.7 [29], consistent with the observed range of 2.2 to 2.7. The observed XRD reflections are also common to imogolite, although there are additional imogolite reflections [30, 31] that are absent in the XRD patterns. The additional peaks are also significantly less intense than the observed peaks and would be close to background in these samples. Thermodynamic calculations indicated initial supersaturation with respect to allophone, imogolite, halloysite, and kaolinite. However, equilibration of halloysite and kaolinite is slow at room temperature [2, 12], whereas allophane readily forms in oversaturated solutions [31].

3.4.2. FTIR Analysis. Sample spectra reveal bands at ~3500, 970, 570, and 430 cm⁻¹, characteristic of allophane and imogolite [8, 32] (Figure 4). The diffuse band at 3000–3800 cm⁻¹ is indicative of OH stretching of Al–OH, Si–OH, and water [33], with an additional water band at ~1600 cm⁻¹. The peak at 970 cm⁻¹ is attributed to Si–O
Figure 4: FTIR spectra for solids derived from Al-Si and Al-Si-DOC solutions with 0.5, 0.75 and 1.0 mM Al; 0.5 mM Si; and 0 or 6 mg/L DOC.

Figure 5: $^{29}$Si SP/MAS NMR spectra of precipitates from solutions with 0.5 mM Si and (a-b) 0.5 mM Al; (c-d) 0.75 mM Al; (e-f) 1.0 mM Al; with and without 6 mg/L DOC as indicated. All spectra were taken under quantitative conditions with a 180 s relaxation delay and 10 kHz spinning rate.

stretches and shifts to higher wavenumbers at lower Al/Si ratios with the peak for 0.5 mM initial Al samples closer to 1000 cm$^{-1}$. The peaks in the 800–400 cm$^{-1}$ range are from Si–O–Al and Si–O–Si stretching. The broad band at 570 cm$^{-1}$ with shoulders at 690 and 430 cm$^{-1}$ indicates an imogolite-like structure observed in natural allophane and imogolite [27]. Compared to allophane, imogolite peaks are sharper with doublets at 970 and 570 cm$^{-1}$ [32, 34]. Sharper peaks for 0.75 mM initial Al solids may indicate more imogolite or imogolite-like material in these samples. The broadest peaks are observed for the 0.5 mM initial Al solid with no DOC, indicative of less imogolite-like material in this sample.

3.4.3. NMR Analysis. The $^{29}$Si SP MAS/NMR spectra of all the precipitates contain a narrow peak at a chemical shift of $\delta_{Si-29} = -78.3$ ppm (1.8 ppm full width at half maximum; FWHM) plus a broad signal at more negative chemical shifts that can be represented by two broad peaks, near $-82$ ppm and $-89$ ppm, and 9–17 ppm FWHM, in varying proportions (Figure 5). The narrow peak is characteristic of imogolite-like Si environments, in which a silicate tetrahedron is coordinated to three 6-coordinated Al ions and one hydroxyl ion [35, 36]. The broad peaks arise from polymerized Si, and resemble closely those reported previously for natural allophane [36, 37] and also for synthetic hydroxy-aluminosilicates [38, 39]. For the precipitates from solutions with 0.75 mM initial Al, (Figures 5(c) and 5(d)) the imogolite-like environments represent a greater proportion of the Si (20–23%) than for those with 1.0 mM initial Al (18–21%; Figures 5(e) and 5(f)) and 0.5 mM initial Al (10%; Figures 5(a) and 5(b); Table 4). For solids from 0.75 mM and 1.0 mM solutions, the fitted intensity of the imogolite-like peak is somewhat higher for the Al-Si-DOC relative to the Al-Si samples. Although the difference is subtle, the values for Al-Si-DOC samples are consistently higher than those of Al-Si samples (Table 4). For all pairs of Al-Si/Al-Si-DOC samples, the average chemical shift of the broad component was slightly more negative by 1-2 ppm for the Al-Si-DOC solids suggesting an increased tetrahedral Si/Al ratio in the polymerized structures. The $^{29}$Si$\{^{1}$H$\}$ CP/MAS spectra (not shown) are essentially identical to the corresponding SP/MAS spectra except for some minor differences in relative intensity, which varied only slightly with the NMR experimental contact time.

The aluminosilicate precipitates have $^{27}$Al MAS/NMR spectra that contain peaks centered near 5.5, 33, and 59 ppm, which are characteristic of Al in 6-, 5-, and 4-coordination, respectively (Figure 6). These values are the observed peak positions at 11.7 T. The peaks for 4- and 6-coordinated Al ($Al^{IV}$ and $Al^{VI}$) are similar to those reported for natural imogolite and allophane [29, 36] and for synthetic amorphous hydroxyaluminosilicates [38]. In addition to $Al^{IV}$ and $Al^{VI}$, a peak for 5-coordinated Al ($Al^{V}$) from allophane similar to that observed here has been reported [40] but would have been difficult to detect at the slower spinning rates used in the earlier studies. The integrated intensities of the three resonances were estimated by fitting the center
bands to lineshapes calculated from a random distribution of electric field gradients [41]. These simulations reproduce well the characteristic peak shapes, particularly the broad tail extending to lower chemical shifts most evident in the peak for AlVI. The best-fit lineshape parameters (Table 4) varied only slightly among the samples: \( \delta_{\text{iso}} \approx 7.9 \pm 0.3 \) ppm and mean quadrupolar coupling constant, \( C_q \approx 2.8 \) MHz for AlVI; \( \delta_{\text{iso}} \approx 63 \pm 1 \) ppm and \( C_q = 4.2 \) MHz for AlIV; \( \delta_{\text{iso}} \approx 36 \pm 1 \) ppm for AlVI. An average \( C_q \) value of 4.2 MHz was used to fit the AlV peak shape, which gave a constant relative intensity of 5% for all samples. These values are in reasonable agreement with high-field (217 MHz) spectra obtained for the 1.0 mM Al samples (Figures 6(g) and 6(h)), which give peak positions at 62.0, 34.0, and 6.0 ppm.

The 1.0 mM Al samples (Figures 6(e) and 6(f)) contain a lower proportion of AlVI (69–73%) and larger proportion of AlIV (22–26%) relative to other samples. The 0.75 mM samples (Figures 6(c) and 6(d)) contain 71–79% AlVI and 16–24% AlIV and the 0.5 mM samples (Figures 6(a) and 6(b)) 77–79% AlVI and 16–18% AlIV (Table 4). Small, but systematic, increases in the AlIV/Al total ratios were noted for samples precipitated with HA (Figures 6(a), 6(c), 6(e), and 6(g)) corresponding to 2–8% more AlIV compared to the samples precipitated from binary Al-Si solutions. In each case, the decrease in AlIV fraction correlates with a more negative chemical shift for the broad 29Si component, consistent with a decrease in the average number of Al IV bonded to polymerized Si. Other than these minor changes in relative intensity, virtually no difference in the 27Al spectra of samples coprecipitated with DOC was observed compared to those from HA-free solutions.

Results from 29Si MAS/NMR indicate the presence of both short-range ordered imogolite-like structures plus more polymerized Si environments, which is typical of allophane. The highest fraction of imogolite-like Si is observed in the 0.75 mM solids, consistent with inferences from FTIR analysis. Results from 27Al MAS/NMR also indicate the presence of AlIV in all samples. Tetrahedral Al is typically not observed in natural and synthetic imogolite phases [29, 39], and its occurrence along with that of polymerized Si suggests the presence of allophane or aluminosilicate gel [36]. For natural allophanes with Al/Si 2.3–2.70, the ratio of AlIV/Al total is typically 0.015–0.04 (1.5–4% AlIV) as determined by 27Al MAS/NMR [29]. Assuming that AlIV/Al total ratios are close to those of natural samples or synthetic imogolite-like allophane, AlIV concentrations in our samples are higher than expected if allophane was the only constituent. This result suggests that some fraction of AlIV could be associated with polymerized Si in a separate amorphous hydrated aluminosilicate gel in these samples.
Although the presence of an amorphous Al-(oxy)hydroxide cannot be ruled out, such materials generally contain lower Al\textsuperscript{IV}/Al\textsuperscript{VI} ratios than observed here. It should be noted that the role of Al\textsuperscript{VI} and polymerized Si in allophane remains uncertain, with some evidence that these signals arise from an impurity in natural allophane [42]. The Al\textsuperscript{III} that is observed for all samples could represent an intermediate product in the transition between allophane and imogolite which involves transformation of Al\textsuperscript{IV} to Al\textsuperscript{VI} [39]. The presence of Al\textsuperscript{VI} and the apparent coexistence of several phases demonstrate the transitional nature of these samples. The NMR data provide evidence for a mixture of imogolite-like structures, allophane, and aluminosilicate gel in all samples, with the fractions of both imogolite-like environments and Al\textsuperscript{IV} increasing with increasing initial Al concentration. For solids generated in the presence of HA, consistently lower Al\textsuperscript{IV}/Al\textsuperscript{VI} ratios combined with more imogolite-like Si suggest less aluminosilicate gel formed in these systems.

### 4. Discussion

#### 4.1. Al-Si Systems

In the experimental solutions, Si should have been dominantly monomeric (pH < 9; [Si] < 2-3 mM) [43], a form thought to have a low affinity for Al, and as a consequence Al-(oxy)hydroxide phases are expected to polymerize relatively rapidly [44]. However, the precipitates have low Al/Si ratios implying limited polymerization of separate Al-(oxy)hydroxide phases and instead enhanced formation of allophane and aluminosilicate gel.

The formation of poorly crystalline aluminosilicates in Al-Si solutions agrees with previous observations. For example, the Al/Si ratios of the initial solutions and precipitated solids for the 0.5 mM and 1.0 mM Al-Si samples are similar to those observed for pH 4.0-4.5 solutions aged for 7 years at 25°C [45]. Despite higher pH and shorter aging times, the current precipitates are compositionally similar to and thus may be the precursors of these precipitates [45]. The consistently higher fractions of imogolite-like Si observed in 0.75 and 1.0 mM Al-Si-DOC solids show that over short reaction times dissolved organic matter promotes the formation of imogolite-like material.

#### 4.2. Al-Si-HA Systems

At pH 6 HA is soluble, deprotonated, and thus able to complex with Al, which otherwise polymerizes rapidly [12]. Organics are known to inhibit Al polymerization, depending upon the affinity of the ligand for Al [46-48]. Because HA has a strong affinity for Al, polymerization is reduced, and the formation of amorphous Al phases is promoted [49, 50], as indicated by the thermodynamic modeling of the initial compositions of the experimental solutions. As Si alone also reduces Al polymerization, and the number of Al-HA binding sites is limited, Al-(oxy) hydroxide polymerization is further reduced in the presence of both Si and HA.

Precipitates in HA-bearing systems contain a significant portion of organic matter, suggesting insoluble metal-organo complexes. In pH 5-6, Si-free, Al-HA solutions, this can be attributed to chelation, sorption of humics on Al(OH)\textsubscript{3} flocs, and/or coprecipitation mechanisms [51]. The addition of Si and subsequent detection in the precipitate suggests that these mechanisms involve aluminosilicate material. Results from experiments with only Si and HA show no independent interaction of these two components. This is because Si prefers to be tetrahedrally coordinated and so forms weak complexes with HA carboxylic functional group oxygens, compared to the stable five-membered chelate rings that readily form with Al [52]. Because Si-HA complexation is negligible, any interaction of Si with HA is likely to proceed indirectly. Thus, the precipitation mechanisms for Si may involve insoluble Al-bridged Si-Al-HA complexes.

At low initial HA concentrations (~12 mg L\textsuperscript{-1} HA) and at 25°C for short reaction times (20 h), pure imogolite did not dominate the precipitate at any of the solution Al/Si ratios. However, concentrations of HA > 300 mg L\textsuperscript{-1} appeared to inhibit imogolite formation from solutions with Al/Si ratios of 2, heated to 96–100°C and aged for up to 110 hours [14]. Below this threshold pure imogolite was observed as the only detectable precipitate phase. The lower temperatures and shorter aging times in the current work are not conducive to the formation of pure imogolite, and therefore the role of HA is notably different from that reported previously. Results also suggest that any inhibitory effect of HA is shifted to lower concentrations relative to the published experimental results at higher temperature and much longer reaction time. For example, for 0.5 mM initial Al samples the presence of HA reduced the quantity of precipitate to a small extent. Though concentrations >12 mg L\textsuperscript{-1} HA were not used to generate solids for further analysis, observations from experiments with ~18 mg L\textsuperscript{-1} HA (9 mg/L DOC) suggest that more Al preferentially binds to the organics resulting in less Al-Si complexation and a reduction in aluminosilicate solid formation under these conditions. This may be interpreted as a slight inhibitory effect of HA on aluminosilicate formation at higher HA concentrations. On the other hand, the effect of HA on some solids characterized in this study was to produce a small but detectable increase in the production of imogolite-like material relative to aluminosilicate gel in comparison to HA-free systems.

#### 4.3. Relation to Natural Soil Systems

The studied conditions apply to those that may be observed in natural systems for allophane- and imogolite-bearing horizons of some andisols and spodosols. These soils are typically characterized by low DOC concentrations, pH on the order of 5-6.5, and sufficient Si to promote imogolite formation [5]. Current results show that although allophane can be produced in organic-free solutions, organic matter seems to promote the formation of imogolite-like structures when present in low concentrations. These structures in turn may be precursors to a pure imogolite phase. Organic matter may thus play an active role in the formation of both allophane and potentially imogolite in soils, which becomes evident in natural soils with high organic content. In some volcanic andisols, allophane production can be limited by enhanced Al-humic complexation, as observed for 0.5 mM Al solids,
phases such as feldspars and gibbsite. The stabilizing effect of allophane, inhibiting the formation of more crystalline aluminosilicate minerals by slowing not only Al-polymerization, but aluminosilicate polymerization which would otherwise increase the fraction of gel-like material, as observed in HA-free solutions. Hence, organic matter may stabilize and promote the formation of imogolite-like material, which can in turn facilitate the sequestration and storage of organic matter. This has implications for global warming and associated climate change, whereby enhanced soil weathering and productivity with increasing temperature can accelerate the production of allophanic soils which in turn can increasingly sequester organic carbon. In natural systems, the observed disparities in the role of organic material in allophane and imogolite synthesis may be attributed to factors such as parent material and climate, which are critical during soil formation processes [6]. In turn, these factors can dictate Al/Si and Al/C ratios in soil systems, which are based on results of the current study, determining the role of organic material in allophane and imogolite neogenesis.

Results of this study demonstrate the influence of HA on the formation of aluminosilicates under conditions applicable to certain soil systems. Allophane and imogolite-like material were successfully synthesized at ambient conditions in short reaction times, both in the presence and absence of HA at environmentally relevant concentrations of Al, Si, and DOC. Both Si and HA limit, if not prevent, the polymerization of Al-(oxy)hydroxide phases. HA further limits the polymerization of aluminosilicate gel and has a subtle, but consistent effect on increasing the fraction of imogolite-like material relative to HA-free systems. The influence of HA on the formation of poorly crystalline aluminosilicates, contingent upon initial Al/Si and Al/C ratios, along with a stabilizing effect of the mineral on the organic phase via chelation or coprecipitation, may explain the coincidence of allophonic soil horizons with organics in some soil systems. This in turn has implications for C storage and sequestration.

5. Conclusions

Solids with Al/Si ratios ranging from 2.2–2.7 were formed from solutions with 0.5, 0.75, and 1.0 mM initial Al, and aqueous Al/Si and Al/C ratios of 1, 1.5, and 2. Allophane was the dominant mineral in all solids, with the fraction of imogolite-like Si and aluminosilicate gel depending on initial solution composition. At 0.5 mM initial Al, the presence of HA did not significantly affect the composition of the precipitate or the fraction of imogolite-like material. At higher initial Al, formation of imogolite-like structures was enhanced, with slightly higher fractions observed in DOC-bearing solids, and the highest fraction for a solid formed from a solution of 0.75 mM Al, 0.5 mM Si, and 6 mg/L DOC. The amount of aluminosilicate gel increased with increasing initial Al concentration, but was reduced in the presence of HA.

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References

[1] G.F. Vance, F. J. Stevenson, and F. J. Sikora, “Environmental chemistry of aluminum-organic complexes,” in The Environmental Chemistry of Aluminum, G. Sposito, Ed., pp. 169–220, Lewis, Boca Raton, Fla, USA, 1995.
[2] H. Blinski, L. Horvath, N. Inghi, and S. Sjoberg, “Aluminosilicate phases during initial clay formation: H+–Al3+–oxalic acid–Silicic acid-Na+ system,” Journal of Soil Science, vol. 41, no. 1, pp. 119–132, 1990.
[3] K. Wada, “Structure and formation of non- and para-crystalline aluminosilicate clay minerals: a review,” in Clay Controlling the Environment, G. J. Churchman, R. W. Fitzpatrick, and R. A. Eggleton, Eds., pp. 443–448, CSIRO Publishing, Melbourne, Australia, 1995.
[4] R. L. Parfitt, “Allophane and imogolite: role in soil biogeochemical processes,” Clay Minerals, vol. 44, no. 1, pp. 135–155, 2009.
[5] F. C. Ugolini and R. A. Dahlgren, “Weathering environments and occurrence of imogolite/allophane in selected Andisols and Spodosols,” Soil Science Society of America Journal, vol. 55, no. 4, pp. 1166–1171, 1991.
[6] I. Basile-Doelsch, R. Amundson, W. E. E. Stone et al., “Mineralogical control of organic carbon dynamics in a volcanic ash soil on La Réunion,” European Journal of Soil Science, vol. 56, no. 6, pp. 689–703, 2005.
[7] Y. Arai, D. L. Sparks, and J. A. Davis, “Arsenate adsorption mechanisms at the allophane—Water interface,” Environmental Science and Technology, vol. 39, no. 8, pp. 2537–2544, 2005.
[8] L. Denai, I. Lamy, and J. Y. Bottero, “Structure and affinity towards Cd2+, Cu2+, Pb2+ of synthetic colloidal amorphous aluminosilicates and their precursors,” Colloids and Surfaces A, vol. 158, no. 3, pp. 315–325, 1999.
[9] C. J. Lind and J. D. Hem, *Effects of Organic Solutes on Chemical Reactions of Aluminum*, Geological Survey Water- Supply Paper 1827-G, United States Government Printing Office, Wash., USA, 1975.

[10] G. G. Lindner, H. Nakazawa, and S. Hayashi, "Hollow nanospheres, allophanes “all-organic” synthesis and characterization," *Microporous and Mesoporous Materials*, vol. 21, no. 4-6, pp. 381–386, 1998.

[11] G. H. Koenderink, S. G. J. M. Kluitmans, and A. P. Philipsse, "On the synthesis of colloidal imogolite fibers," *Journal of Colloid and Interface Science*, vol. 216, no. 2, pp. 429–431, 1999.

[12] J. D. Hem and C. J. Lind, "Kaolinite synthesis at 25°C," *Science*, vol. 184, no. 4142, pp. 1171–1173, 1974.

[13] K. Inoue and P. M. Huang, "Influence of citric acid on the natural formation of imogolite," *Nature*, vol. 308, no. 5954, pp. 58–60, 1984.

[14] K. Inoue and P. M. Huang, "Perturbation of imogolite formation by humic substances," *Soil Science Society of America Journal*, vol. 54, no. 5, pp. 1490–1497, 1990.

[15] J. P. Gustafsson, *Visual MINTEQ (VMINTEQ) Version 2.53*, KTH, Department of Land and Water Resources Engineering, Stockholm, Sweden, 2007.

[16] J. P. Gustafsson, "Modeling the acid-base properties and metal complexation of humic substances with the Stockholm Humic Model," *Journal of Colloid and Interface Science*, vol. 244, no. 1, pp. 102–112, 2001.

[17] J. D. Ritchie and E. Michael Perdue, "Proton-binding study of standard and reference fulvic acids, humic acids, and natural organic matter," *Geochimica et Cosmochimica Acta*, vol. 67, no. 1, pp. 85–93, 2003.

[18] F. Gérard, J. P. Boudot, and J. Ranger, "Consideration on the occurrence of the Al⊂₃ polycation in natural soil solutions and surface waters," *Applied Geochemistry*, vol. 16, no. 5, pp. 513–529, 2001.

[19] S. Hiradate and N. U. Yamaguchi, "Chemical species of Al reacting with soil humic acids," *Journal of Inorganic Biochemistry*, vol. 97, no. 1, pp. 26–31, 2003.

[20] D. K. Nordstrom and H. M. May, "Aqueous equilibrium data for mononuclear aluminum species," in *The Environmental Chemistry of Aluminum*, G. Sposito, Ed., pp. 29–55, CRC Press, Boca Raton, Fla, USA, 1989.

[21] G. S. Pokrovski, J. Schott, J. C. Harrichoury, and A. S. Sergeyev, "The stability of aluminum silicate complexes in acidic solutions from 25 to 150°C," *Geochimica et Cosmochimica Acta*, vol. 60, no. 14, pp. 2495–2501, 1996.

[22] R. M. Smith and A. E. Martell, in *NIST Critically Selected Stability Constants of Metal Complexes Database*, NIST, Gaithersburg, Md, USA, 7th edition, 2003.

[23] K. A. Thorn, D. W. Folan, and P. MacCarthy, "Characterization of the international humic substances society standard and reference fulvic and humic acids by solution state carbon-13 (13C) and hydrogen-1 (1H) nuclear magnetic resonance spectrometry," in *U.S. Geological Survey*, Water-Resources Investigations Report 89–4196, p. 93, 1989.

[24] J. P. Pinheiro, A. M. Mota, and M. F. Benedetti, "Effect of aluminum competition on lead and cadmium binding to humic acids at variable ionic strength," *Environmental Science and Technology*, vol. 34, no. 24, pp. 5137–5143, 2000.

[25] J. Ganor, T. J. Huston, and L. M. Walter, "Quartz precipitation kinetics at 180°C in NaCl solutions—Implications for the usability of the principle of detailed balancing," *Geochimica et Cosmochimica Acta*, vol. 69, no. 8, pp. 2043–2056, 2005.

[26] R. Gout and G. Verdes, "Effect of crystallinity on diaspore and boehmite relative stability," *European Journal of Mineralogy*, vol. 5, no. 2, pp. 215–217, 1993.

[27] F. Ohashi, S. I. Wada, M. Suzuki, M. Maeda, and S. Tomura, "Synthetic allophane from high-concentration solutions: nanoengineering of the porous solid," *Clay Minerals*, vol. 37, no. 3, pp. 451–456, 2002.

[28] R. L. Parfitt and J. M. Kimble, "Conditions for formation of allophane in soils," *Soil Science Society of America Journal*, vol. 53, no. 3, pp. 971–977, 1989.

[29] P. Ildefonse, R. J. Kirkpatrick, B. Montez, G. Calas, A. M. Flank, and P. Lagarde, "27Al MAS NMR and aluminum X-ray absorption near edge structure study of imogolite and allophanes," *Clays & Clay Minerals*, vol. 42, no. 3, pp. 276–287, 1994.

[30] F. Ohashi, S. Tomura, K. Akaku, S. Hayashi, and S. I. Wada, "Characterization of synthetic imogolite nanotubes as gas storage," *Journal of Materials Science*, vol. 39, no. 5, pp. 1799–1801, 2004.

[31] D. G. Lumsdon and V. C. Farmer, "Solubility characteristics of proto-imogolite solids: how silicic acid can de-toxify aluminium solutions," *European Journal of Soil Science*, vol. 46, no. 2, pp. 179–186, 1995.

[32] J. P. Gustafsson, E. Karlton, and P. Bhattacharya, "Allophane and imogolite in Swedish soils," Research Report TRITA-AMI 3046, Royal Institute of Technology, Stockholm, Sweden, 1998.

[33] H. He, T. L. Barr, and J. Klinowski, "ESCA and solid-state NMR studies of allophane," *Clay Minerals*, vol. 30, no. 3, pp. 201–209, 1995.

[34] M. Tani, C. Liu, and P. M. Huang, "Atomic force microscopy of synthetic imogolite," *Geoderma*, vol. 118, no. 3-4, pp. 209–220, 2004.

[35] P. F. Barron, M. A. Wilson, A. S. Campbell, and R. L. Frost, "Detection of imogolite in soils using solid state 29Si NMR," *Nature*, vol. 299, no. 5884, pp. 616–618, 1982.

[36] B. A. Goodman, J. D. Russell, B. Montez, E. Oldfield, and R. J. Kirkpatrick, "Structural studies of imogolite and allophanes by aluminum-27 and silicon-29 nuclear magnetic resonance spectroscopy," *Physics and Chemistry of Minerals*, vol. 12, no. 6, pp. 342–346, 1985.

[37] S. Hiradate, "Structural changes of allophane during purification procedures as determined by solid-state 27Al and 29Si NMR," *Clays and Clay Minerals*, vol. 53, no. 6, pp. 653–658, 2005.

[38] F. J. Doucet, C. Schneider, S. J. Bones et al., "The formation of hydroxyaluminosilicates of geochemical and biological significance," *Geochimica et Cosmochimica Acta*, vol. 65, no. 15, pp. 2461–2467, 2001.

[39] S. Strekopytov and C. Exley, "Thermal analyses of aluminium hydroxide and hydroxyaluminosilicates," *Polyhedron*, vol. 25, no. 8, pp. 1707–1713, 2006.

[40] C. W. Childs, S. Hayashi, and R. H. Newman, "Five-coordinate cation procedures as determined by solid-state 27Al and 29Si NMR," *Clays and Clay Minerals*, vol. 47, no. 1, pp. 64–69, 1999.

[41] D. Coster, A. L. Blumenfeld, and J. J. Fripiat, "Lewis acid sites and surface aluminum in aluminas and zeolites: a high-resolution NMR study," *Journal of Physical Chemistry*, vol. 98, no. 24, pp. 6201–6211, 1994.

[42] S. Hiradate and S. I. Wada, "Weathering process of volcanic glass to allophane determined by 27Al and 29Si solid-state
NMR,” *Clays and Clay Minerals*, vol. 53, no. 4, pp. 401–408, 2005.

[43] R. K. Iler, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, John Wiley & Sons, 1979.

[44] P. D. Taylor, R. Jugdaohsingh, and J. J. Powell, “Soluble silica with high affinity for aluminium under physiological and natural conditions,” *Journal of the American Chemical Society*, vol. 119, no. 38, pp. 8852–8856, 1997.

[45] S. I. Wada, “Imogolite synthesis at 25°C,” *Clays & Clay Minerals*, vol. 35, no. 5, pp. 379–384, 1987.

[46] F. Thomas, A. Masion, J. Y. Bottero, J. Rouiller, F. Montigny, and F. Genevrier, “Aluminum(III) speciation with hydroxy carboxylic acids. 27Al NMR study,” *Environmental Science and Technology*, vol. 27, no. 12, pp. 2511–2516, 1993.

[47] A. Masion, F. Thomas, J. Y. Bottero, D. Tchoubar, and P. Tekely, “Formation of amorphous precipitates from aluminum-organic ligands solutions: macroscopic and molecular study,” *Journal of Non-Crystalline Solids*, vol. 171, no. 2, pp. 191–200, 1994.

[48] A. Violante and P. Violante, “Influence of pH, concentration, and chelating power of organic-anions on the synthesis of aluminum hydroxides and oxyhydroxides,” *Clays Clay Miner*, vol. 28, pp. 425–434, 1980.

[49] M. R. Jekel, “Interactions of humic acids and aluminium salts in the flocculation process,” *Water Research*, vol. 20, no. 12, pp. 1535–1542, 1986.

[50] X. Lu, Z. Chen, and X. Yang, “Spectroscopic study of aluminium speciation in removing humic substances by Al coagulation,” *Water Research*, vol. 33, no. 15, pp. 3271–3280, 1999.

[51] M. Petrović and M. Kaštelan-Macan, “Interaction of humic substances and aluminum formation of insoluble associates,” *Food Technology and Biotechnology*, vol. 34, no. 2-3, pp. 81–85, 1996.

[52] G. S. Pokrovski and J. Schott, “Experimental study of the complexation of silicon and germanium with aqueous organic species: implications for germanium and silicon transport and Ge/Si ratio in natural waters,” *Geochimica et Cosmochimica Acta*, vol. 62, no. 21-22, pp. 3413–3428, 1998.

[53] S. Shoji, M. Nanzyo, and R. Dahlgren, “Volcanic ash soils. genesis. Properties and utilization,” in *Developments in Soil Science*, vol. 21, p. 288, Elsevier Press, Amsterdam, Netherlands, 1993.

[54] P. Broquen, J. C. Lobartini, F. Candan, and G. Falbo, “Allophane, aluminum, and organic matter accumulation across a bioclimatic sequence of volcanic ash soils of Argentina,” *Geoderma*, vol. 129, no. 3-4, pp. 167–177, 2005.
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