# SYNTHESIS AND CHARACTERIZATION OF A HOLLOW SPHERICAL FORM OF MONOLAYER ALUMINOSILICATE

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**Abstract**—Hollow spherical particles of aluminosilicate having diameters of 80 to 100 Å and high electric charge were synthesized by heating solutions containing Si and Al concentrations of about 2 mM (Si/Al molar ratio = 1.0–1.2; pH = 9.0) at 95°–100°C for 7 days. Electron microscopy, X-ray powder diffraction, and infrared spectroscopy suggested that the walls of the spherical particles consisted of monolayer aluminosilicate, most probably having a 1:1 layer structure. Chemical analysis supported this supposition but indicated modifications as shown in the formula $(Si_{1.85}Al_{0.62})^{IV}(Al_{1.38})^{VI}(OH)_{4.10}O_{4.96}Na_{0.62}$, compared with $(Si_2)^{IV}(Al_2)^{VI}(OH)_4O_5$ for an ideal 1:1 layer silicate. High-resolution $^{29}Si$ and $^{27}Al$ nuclear magnetic resonance spectroscopy indicated the substitution of Al for Si in the tetrahedral sheet, the presence of $Al^{IV}$ and $Al^{VI}$, and the presence of Si bonded through oxygen to three Al atoms and one H. A natural counterpart of the synthesized aluminosilicate may be a precursor of halloysites formed by weathering of volcanic ash and pumice and have a close structural relation with allophane and imogolite.

**Key Words**—Allophane, Aluminosilicate, Halloysite, Imogolite, Infrared spectroscopy, Nuclear magnetic resonance, Synthesis, Transmission electron microscopy.

要約 — Si，Al を約 2 mM の濃度で含む溶液（Si／Al モル比＝1.0 - 1.2；pH＝9.0）を7 日間加熱することによって，直径 80 - 100 Å の中空球状粒子より成り，高い負電荷をもつケイ酸アルミニウムを合成した。電子顕微鏡観察，X 線粉末回折及び赤外吸収スペクトル分析は，中空球状粒子の球壁が，恐らくは 1：1 型層構造をもつケイ酸アルミニウムの単分子層より成ることを示唆した。化学分析は，このケイ酸アルミニウムが，理想的な 1：1 型構造の組成式 $(Si_2)^{IV}(Al_2)^{VI}(OH)_4O_5$ と対比すれば，$(Si_{1.85}Al_{0.62})^{IV}(Al_{1.38})^{VI}(OH)_{4.10}O_{4.96}Na_{0.62}$ で表されることを示した。高分解能 $^{29}Si$ 及び $^{27}Al$ 核磁気共鳴スペクトル分析は，四面体シートで Al による Si の置換，$Al^{IV}$ と $Al^{VI}$ の共存，酸素を介して 3 Al，1 H と結合している Si の存在を示した。合成されたケイ酸アルミニウムと対比できるものは，自然では火山灰，浮石の風化でハロイサイトの先駆体として生ずる可能性があり，アロフェン，イモゴライトと構造上密接な関係をもっている。

## INTRODUCTION

Hydrous aluminosilicates which can be called "embryonic halloysites" have been found in soils rich in "exchangeable base" that have been derived from volcanic ash in Ecuador (Wada and Kakuto, 1985), Japan (Wada *et al.*, 1985), Kenya (Wada *et al.*, 1987), and Rwanda (Wada and Kakuto, 1986). The clay fractions of these soils contain morphologically different particles, among which are hollow spherical particles having diameters of about 100 Å. These particles were not isolated in the above studies, and the mineral constituting them has not been identified.

In the present study we attempted to synthesize and characterize an aluminosilicate mineral forming such hollow spherical particles and showing an infrared (IR) spectrum similar to those of the "embryonic halloysites." The synthesis was carried out by heating dilute, near neutral to weakly alkaline solutions containing Si and Al at 95°–100°C. The products were characterized by transmission electron microscopy (TEM), IR spec-

troscopy, X-ray powder diffraction (XRD), and $^{29}Si$ and $^{27}Al$ nuclear magnetic resonance (NMR) spectroscopy and by chemical and thermal analyses. The elucidated structure of the mineral was compared with those of imogolite, allophane, and halloysite.

## METHODS

### Synthesis

A 0.1 M solution of sodium aluminate (Wada and Wada, 1983) and a 0.1 M solution of sodium silicate were mixed and diluted with water to give Si/Al molar ratios ranging from 0.5 to 3.0 and Si and Al concentrations of about 2 mM. Then, a 1 M solution of $CH_3COOH$ or HCl was added to 200 ml of the stirred solution at the rate of about 0.2 ml/min to adjust the pH of the solution to different values ranging from 6.5 to 9.0. The solution was heated for 7 days at 95°–100°C in a flask under a reflux condition. The product formed in the solution was collected by filtration through a 250-Å pore-size Millipore filter, washed with water,

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and freeze-dried. Two allophanes having Si/Al molar ratios of 0.95 and 0.55 were also synthesized using the method described by Wada *et al.* (1979). These allophanes together with allophane and spherical halloysite separated from weathered pumice (Henmi and Wada, 1976; Wada *et al.*, 1977), were used as reference materials for IR and NMR spectroscopy.

## Characterization

The products collected on the filter were dispersed in water and dried on a collodion film or microgrid for TEM. IR spectra were obtained from the freeze-dried samples incorporated in KBr discs and XRD patterns from those mounted in aluminum holders. The Si, Al, and Na contents of the samples were determined by dissolution with aqua regia and HF according to the Bernas (1968) method; however, the dissolution was carried out at 50°C for 4 hr in a polyethylene volumetric flask having an airtight cap. The $H_2O+$ content was calculated by substracting the sum of $SiO_2$, $Al_2O_3$, and $Na_2O$ from the weight of the sample heated at 105°C.

High-resolution solid-state NMR spectra were obtained with a Bruker CXP300 spectrometer operated at 78.1 MHz for $^{27}Al$ and 59.59 MHz for $^{29}Si$. Single resonance (Bloch decay) experiments were performed with high-power proton decoupling. A 2-$\mu$s pulse was used for $^{27}Al$, and a 3-$\mu$s (45°) pulse was used for $^{29}Si$ excitation, with recycle times of 1 and 10 s, respectively. About 500 scans for $^{27}Al$ and 10,000 scans for $^{29}Si$ were collected. Data were collected in 1 K points, zero filled to 4 K, and Fourier transformed using a line broadening of 50 Hz. Four left shifts were needed to remove an underlying broad resonance in $^{27}Al$ spectra.

Differential thermal analysis and thermogravimetry were carried out using 10-mg samples and a heating rate of 10°C/min in air.

## RESULTS AND DISCUSSION

### Synthetic products and conditions for formation

The synthetic products can be classified into five groups based on transmission electron micrographs (Figure 1), IR spectra (Figure 2), and XRD patterns (Figure 3). Group I products contained exclusively hollow spherical particles having diameters of about 100 Å (Figure 1a). The IR spectra (Figure 2a) resembled those exhibited by "embryonic halloysites" (Wada and Kakuto, 1985; Wada *et al.*, 1985) and the XRD patterns showed reflections at 4.3–4.4, 2.5–2.6, and 2.3 Å and a strong, broad reflection at 3.3–4.4 Å (Figure 3a). Group III products consisted of fine granules having diameters of <100 Å (Figure 1b) with or without fibrous and platy particles. The IR spectra of the products (Figure 2b) resembled those of natural and synthetic allophanes (Wada *et al.*, 1979). The XRD patterns showed the reflections of 6.12, 3.16, 2.34, and 1.86 Å

of boehmite in addition to a broad reflection at 3.3–3.5 Å (Figure 3b). Group V products consisted of large granules having diameters of >100 Å (Figure 1c). The IR spectra (Figure 2c) resembled those of "hydrous feldspathoids" formed from alkaline solutions having Si/Al molar ratios greater than 1.0 (Farmer *et al.*, 1979). The XRD patterns showed two broad reflections at 3.3–3.4 and 8–10 Å. Group II and IV products show features intermediate between those of group I and III products and group I and V products, respectively. Particles that appeared to be hollow but varied in shape and size were also found in group IV products (Figure 4a). These particles were similar to those found in some Kenyan and Rwanda soils (Figure 4b).

Figure 5 shows the classified synthetic products formed from the solutions having different Si/Al ratios and pHs. Hollow particles (groups I, II, and IV), either spherical or somewhat distorted, formed from solutions having Si/Al ratio of 0.8–2.0 and pHs of 6.5–9.0, but only hollow spherical particles having diameters of about 100 Å (group I) formed from solutions having Si/Al ratios of 1.0 or 1.2 and pHs of 9.0 after heating at 95°–100°C for 7 days (formation started at 3–4 days). These materials were not formed in more concentrated solutions (e.g., Si and Al concentrations of 0.01 M). If heating the solution only accelerated the reaction at lower temperatures as was found for imogolite (5 days at 95°–100°C vs. 7 yr at 25°C; Wada, 1987), the formation of the hollow spherical particles may correlate with the formation of "embryonic halloysites" in soils rich in "exchangeable base" and silica derived from volcanic ash (Wada and Kakuto, 1985; Wada *et al.*, 1985; Wada *et al.*, 1987).

### Characterization of hollow, spherical aluminosilicate (HSAS)

*X-ray powder diffraction and electron microscopy.* HSAS is distinctly different from either "allophanes" (group III), "hydrous feldspathoids" (group V), or their mixture not only in its morphology (Figure 1) but also in IR spectra (Figure 2) and XRD patterns (Figure 3). As shown in Figure 3a, HSAS in group I products gave reflections at 4.4–4.3, 2.6, and 2.3 Å, comparable to the 02, 11, and 13,20 reflections of halloysite. These reflections are broad, but not as broad as the reflection at 3.4 Å, suggesting the development of two-dimensional order. No 00$l$ reflections were observed, as expected from the particle size and shape observed by TEM. High-resolution TEM showed that the spherical particles have a diameter of 80–100 Å and wall thicknesses only 10–12 Å (Figure 6), indicating that HSAS is a spherical form of monolayer aluminosilicate.

*Chemical analysis.* The chemical compositions of HSAS in a group I product and a "hydrous feldspathoid" in a group V product yield the following formulae, respectively: $1.85SiO_2 \cdot Al_2O_3 \cdot 0.31Na_2O \cdot 2.05H_2O+$ and
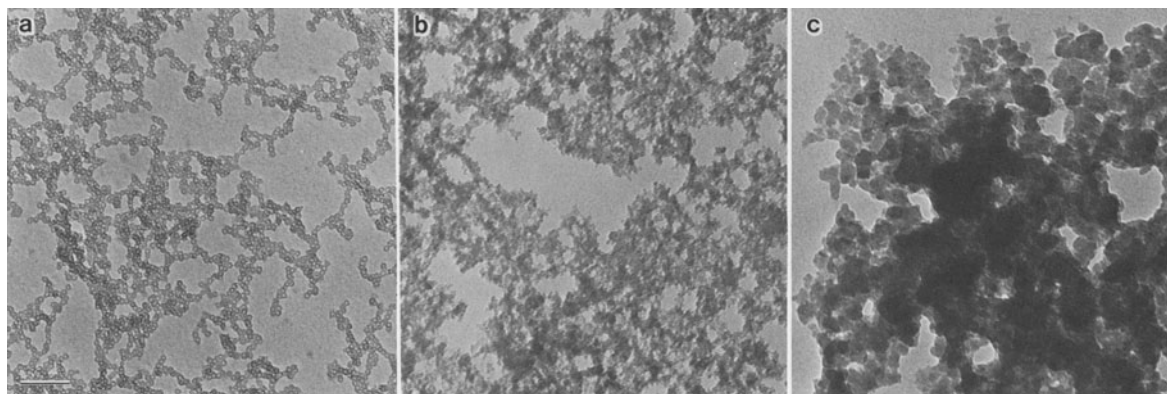
Figure 1.    Transmission electron micrographs of (a) group I product, (b) group III product, and (c) group V product. Bar = 1000 Å.

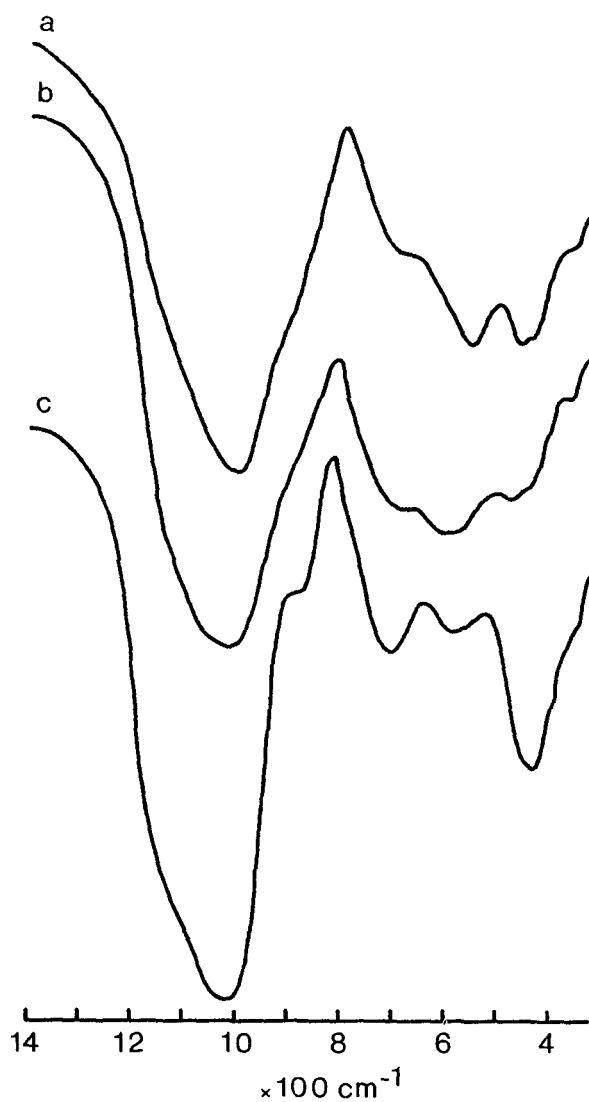

Figure 2.    Infrared spectra of (a) group I product, (b) group III product, and (c) group V product.

$4.24SiO_2 \cdot Al_2O_3 \cdot 0.30Na_2O \cdot 2.70H_2O+$. These formulae were recalculated into the following structural formulae, respectively, by assuming that $Na^+$ is retained by negative charge arising from substitution of Al for Si in the tetrahedral sheet: $(Si_{1.85}Al_{0.62})^{IV}Al^{VI}_{1.38}(OH)_{4.10}$ $O_{4.96}Na_{0.62}$, and $(Si_{4.24}Al_{0.60})^{IV}Al^{VI}_{1.40}(OH)_{5.40}$ $O_{9.08}Na_{0.60}$,
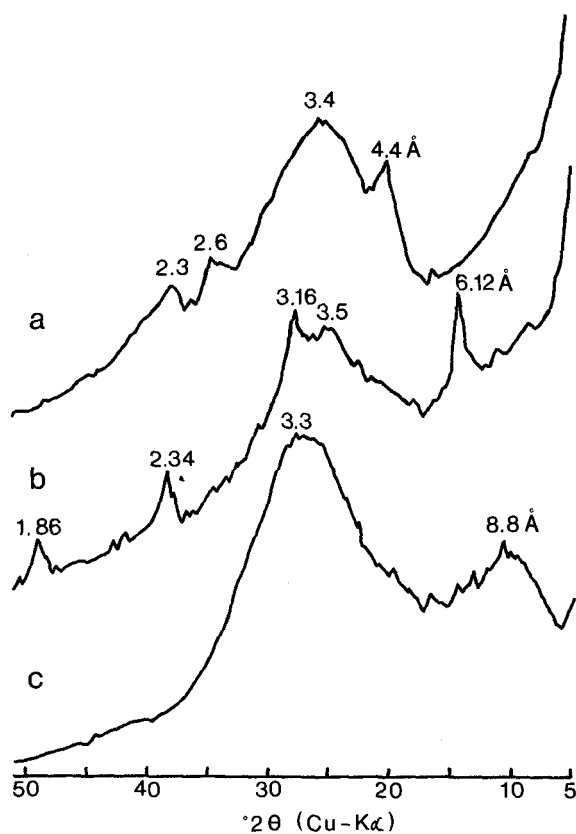


Figure 3.    X-ray powder diffraction patterns of (a) group I product, (b) group III product, and (c) group V product. Random orientation.

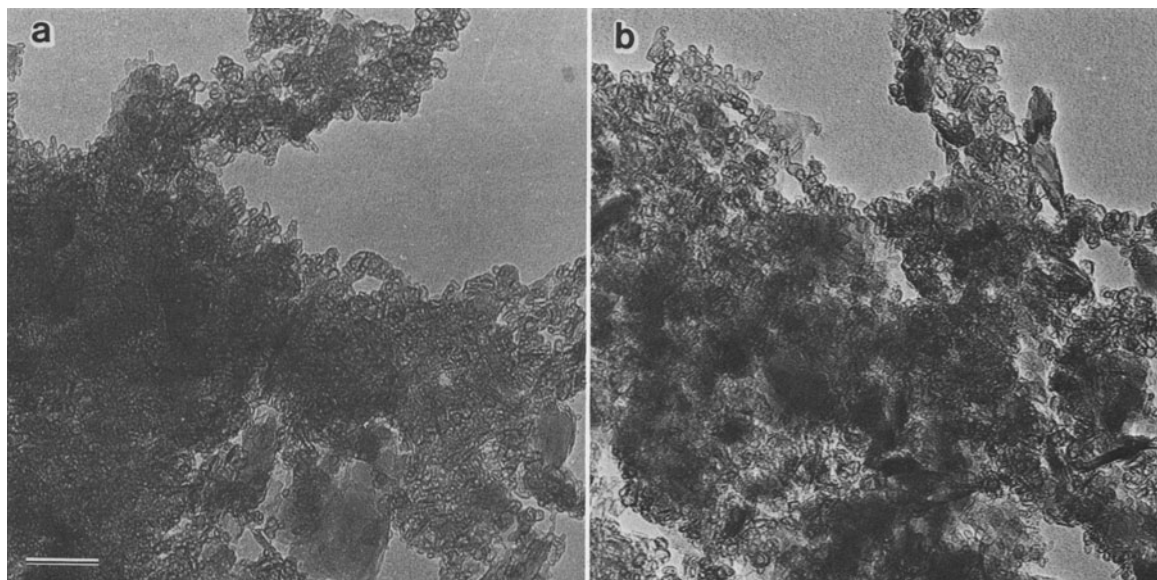Figure 4.   Transmission electron micrographs of (a) group IV product and (b) fine clay (<0.1 μm; dithionite-citrate-bicarbonate treated) of a Rwanda soil (Visoke series, Bw horizon). Bar = 1000 Å.

where the superscripts IV and VI denote the coordination number. These calculated structural formulae may be compared with the structural formulae for idealized 1:1 and 2:1 layer silicates, containing no cationic substitutions: 1:1 layer silicate = $(Si_2)^{IV}Al^{VI}_2$ $(OH)_4O_5$ and 2:1 layer silicate = $(Si_4)^{IV}Al^{VI}_2(OH)_2O_{10}$. On the basis of this comparison HSAS appears to be a 1:1 layer structure having considerable substitution of Al for Si which results in an excess of Si in the tetrahedral sheet and a deficit of Al in the octahedral sheet. Neither the 1:1 nor the 2:1 layer structure could be assigned to the "hydrous feldspathoid," which probably consists more or less of a three-dimensional silicate framework. The 1:1 layer structure assigned to HSAS could account for its spherical shape, if the Si(Al) tetrahedral sheet and Al octahedral sheet form, respectively, the outer and inner parts of the curved unit layer. Like allophane, most of HSAS dissolved (about 90% of Si and Al) by 4-hr extraction with 0.2 M ammonium oxalate-oxalic acid (pH 3.0) in the dark. This dissolution of Si as well as Al is different from "embryonic halloysites" in soils which showed dissolution of Al but only a small amount of Si (Wada and Kakuto, 1985; Wada *et al.,* 1985).

HSAS adsorbed 32% of water on the oven-dry basis at 51% relative humidity. The adsorbed water: $Al_2O_3$ molar ratio of 4.8, more than twice that of fully hydrated halloysite (2.0), is in accord with its monolayer structure. HSAS contained 7.16% $Na_2O$ which is equivalent to 2.31 meq $Na^+$/g. Sodium was retained against washing with water on the Millipore filter, and the contribution of Na in the entrained solution was estimated to be <0.01 meq/g. All retained $Na^+$ was

found to be exchangeable with $Mg^{2+}$, indicating that HSAS has a high cation-exchange capacity.

*Nuclear magnetic resonance spectroscopy.* The $^{29}Si$ spectrum of HSAS has a broad resonance extending from about −80 to −95 ppm (Figure 7). There appears to be some resolution into separate resonances at −90 and −87 ppm and possibly at −85 ppm. These resonances may arise from a range of Al-substituted sili-
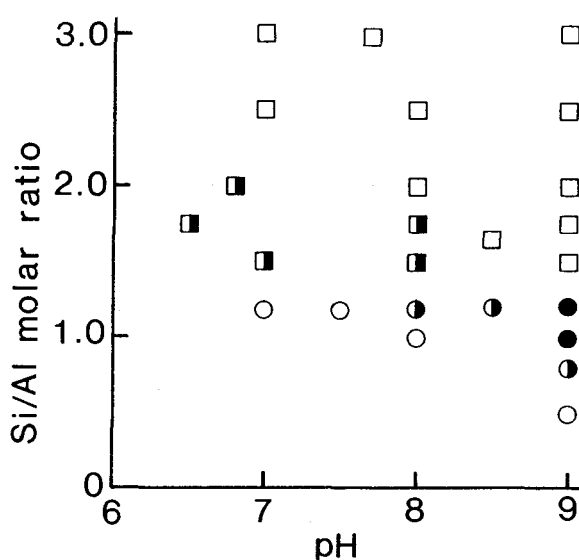


Figure 5.   Synthetic products formed from solutions having different Si/Al molar ratios and pHs. ● = group I product; ◑ = group II product; ○ = group III product; ◪ = group IV product; □ = group V product.
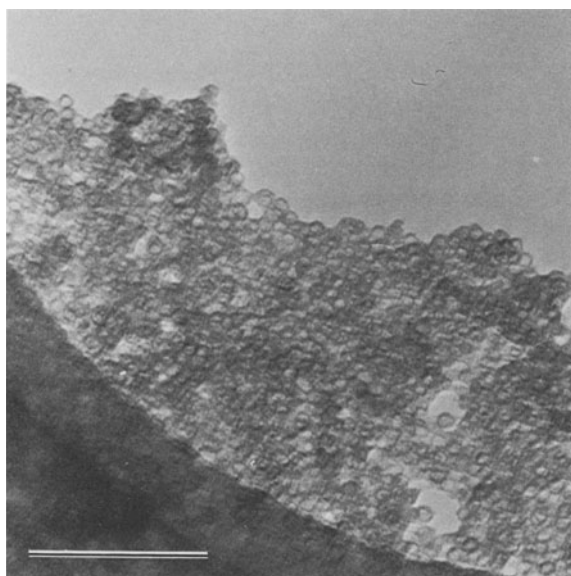
Figure 6.   High-resolution transmission electron micrograph of hollow spherical particles (group I product). Bar = 1000 Å.

cates, but are consistent with a layer silicate with a high degree of Al-substitution in the tetrahedral sheet (Barron et al., 1983; Kinsey et al., 1985; Lippmaa et al., 1980). A similar broad resonance was also found for a synthetic "hydrous feldspathoid" by Goodman et al. (1985). Group I products contained, however, no appreciable amount of particles other than hollow spherical particles, such as those found in group V products (Figure 1c), which have IR spectra resembling "hydrous feldspathoid." The poor resolution of the $-80$ to $-90$ ppm resonances may reflect a wide range of substitution patterns of $Al^{IV}$ for Si, that is, lack of Si-Al ordering in the tetrahedral sheet (Kinsey et al., 1985) and a range of Si–O–Si(Al) bond angles (Goodman et al., 1985; MacKenzie et al., 1985).

The $^{29}Si$ spectrum also has a resonance at $-78$ ppm (Figure 7), characteristic of $(OH)Si(OAl^{VI})_3$ structures found in imogolite or its less-ordered relatives (Barron et al., 1982; Goodman et al., 1985). In imogolite, a tubular monolayer aluminosilicate, every Si is bonded to one OH group and three O atoms on the inner surface of an octahedral sheet (Cradwick et al., 1972). The Si/Al elemental ratio in imogolite is 0.5. From the spectra 25% of Si in HSAS is estimated to be in the imogolite $(HO)Si(OAl^{VI})_3$ structures. The fraction of Al in the imogolite (Im) structures (f(Al-Im)) can also be calculated directly from the fraction of Si (f(Si-Im)) and the elemental Si/Al ratio of the sample, because:

$$f(Al\text{-}Im) = 2f(Si\text{-}Im) \cdot Si/Al$$
$$= 2 \times 0.25 \times 1.85/2$$
$$= 0.46.$$

The $^{27}Al$ spectrum shows two peaks at 5 and 59 ppm

(Figure 7) from octahedral and tetrahedral Al ($Al^{VI}$ and $Al^{IV}$), respectively. The amount of $Al^{VI}$ estimated from the spectrum is $\sim 50\%$. Thus, only about 4% of the $Al^{VI}$ in the sample is not in the imogolite structures. Assuming that 25% of the Si in the HSAS is in the imogolite structures, the calculated structural formula suggests that 33% of $Al^{VI}$ is not in the imogolite structures.

The difference in the estimation of $Al^{VI}$ which is not in the imogolite structures suggests that not all of the Al is observed by NMR. Linewidths of Al species in which the octahedron is distorted may be so broad as to be unobservable. Unseen Al cannot be part of a regular octahedral sheet, such as that expected for a typical 1:1 layer silicate. MacKenzie et al. (1985) found a sharp decrease of the integrated intensity of Al resonances for dehydroxylated kaolinite and interpreted it in terms of the effect of electric field gradients set up by crystallographic distortions and/or defect formation. They proposed a model structure of metakaolinite which consists of a flattened Si–O sheet and an Al–O,OH sheet containing randomly occurring disorganized regions. Although the causes and the resulting structures are different, the octahedral sheet in HSAS must also be poorly organized and contain numerous defects.

Like HSAS, the synthetic allophanes showed two resonances in the $^{29}Si$ spectrum (Figure 7), although the $-78$ to $-79$ ppm resonance was stronger, particularly for the allophane having a Si/Al ratio of 0.55. Goodman et al. (1985) obtained similar NMR spectra for natural allophanes. They attributed the $-78$ to $-79$ ppm peak to imogolite species and the broader resonance to more polymerized Si species, mostly framework aluminosilicates. Inasmuch as allophane is a hollow spherical form of monolayer aluminosilicate (Wada and Wada, 1977), the structures giving rise to the broad resonance can be attributed to tetrahedral sheets in which Al substitutes for Si.

In contrast, the spherical halloysite has a single if broadened resonance at $-93$ ppm. Sidebands are present probably because the sample contains some paramagnetic material; however, the sample may have an unusually high chemical-shift anisotropy. The chemical shift ($-93$ ppm) of spherical halloysite is similar to that of other 1:1 layer aluminosilicates ($-91$ to $-92$ ppm); thus bond distortions brought about by sphere formation are insufficient to cause chemical shift changes. Although the spheres are smaller for HSAS, the shift to $-87$ ppm found for HSAS may be mainly caused by substitution of Al for Si.

*Infrared spectroscopy.* The IR spectrum of HSAS, natural spherical halloysite and allophane are shown in Figures 8a, 8b, and 8c, respectively. HSAS and spherical halloysite have similar absorption bands resolved at 680, 550–560, 460–470, and 430–440 cm$^{-1}$, whereas
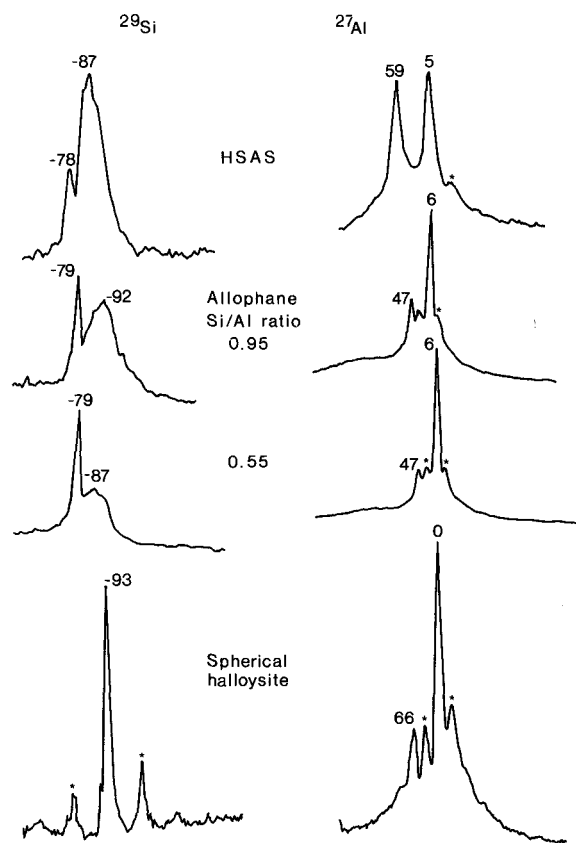
Figure 7.   High-resolution $^{29}Si$ and $^{27}Al$ nuclear magnetic resonance spectra of synthetic hollow spherical form of aluminosilicate (HSAS), synthetic allophanes, and natural spherical halloysite (weathered pumice). ⋆ = spinning-sidebands.
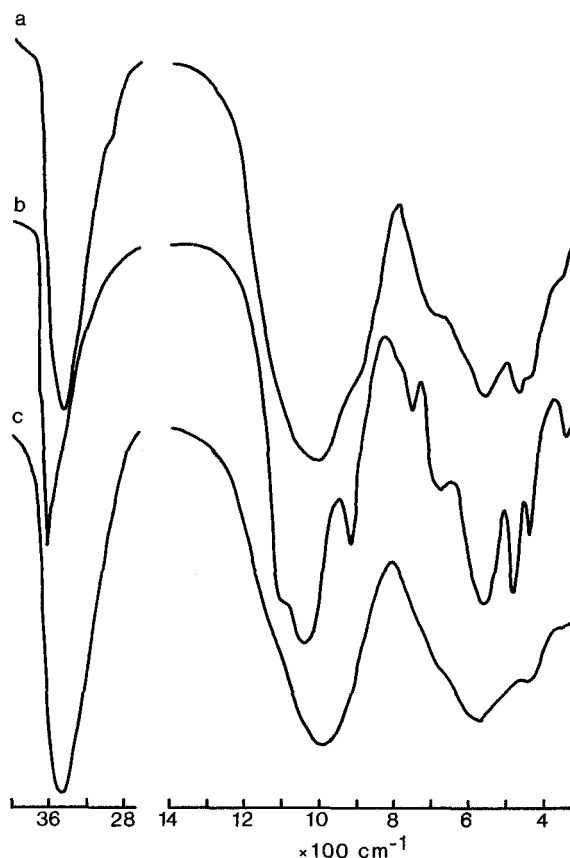


Figure 8.   Infrared spectra of (a) synthetic hollow spherical form of aluminosilicate, (b) natural spherical halloysite, and (c) allophane having Si/Al molar ratio of about 1.0 (weathered pumice).

the allophane has a broad absorption at 570 cm$^{-1}$ and weak shoulders at 670 and 430 cm$^{-1}$. The difference between the IR spectra of HSAS and "hydrous feldspathoid" is shown in Figure 2. The latter has absorption bands at 700, 580, and 435 cm$^{-1}$. Inasmuch as spherical halloysites and other kaolin minerals show common spectral features in this region, the IR pattern of HSAS suggests that an incipient 1:1 layer structure is present.

On the other hand, important differences exist between the IR spectra of HSAS and spherical halloysite in the OH-stretching (3450 vs. 3680, 3630, and 3550 cm$^{-1}$) and OH-bending (880 vs. 915 cm$^{-1}$) bands and in the major Si(Al)–O band (1000 vs. 1040 cm$^{-1}$) (Figure 8). The broad and poorly resolved OH-related bands of HSAS are attributed to the presence of a large amount of adsorbed water and the defects in the octahedral sheet which were indicated by chemical analysis and NMR spectroscopy. The shift of the Si(Al)–O band toward low wavenumber is likely due to more substitution of Al for Si in the tetrahedral sheet (Stubican and Roy, 1961) and the presence of Si in the imogolite

structures (Cradwick *et al.,* 1972), which were indicated by $^{29}Si$ and $^{27}Al$ NMR spectroscopy.

*Thermal analyses.* Like allophane, dehydration and dehydroxylation could not be distinguished for HSAS by differential thermal analysis and thermogravimetry. About 90% of the weight loss due to these reactions took place continually on heating to 330°C. This continuous dehydration and dehydroxylation may be related to the presence of defects in the octahedral sheet, because imogolite, a monolayer aluminosilicate having no defects in the octahedral sheet, shows a clear endothermic effect and a weight loss due to dehydroxylation (Yoshinaga and Aomine, 1962). TEM showed that HSAS maintained its hollow spherical shape after dehydroxylation as did allophanes (van der Gaast *et al.,* 1985).

## CONCLUSIONS AND IMPLICATIONS

On the basis of the foregoing characterization, the group I product appears to be a hollow, spherical form of monolayer aluminosilicate. The term monolayer

Table 1. Particle morphology and structural formulae of monolayer aluminosilicates.

| Mineral | Particle | | Approximate structural formula |
| | Shape | Diameter (Å) | |
| --- | --- | --- | --- |
| Kaolin | — | — | $Si^{IV}_2$     $Al^{VI}_2$                          $(OH)_4 O_5$ |
| HSAS[1] | Sphere | 80–100 | $(Si_{1.5}Al_{0.5})^{IV}Al^{VI}_{1.4}(Si^{IV}\text{-}OH)_{0.4}(OH)_{3.5}O_{5.0}$ |
| Allophane | Sphere | 30–50 | $(Si_{1.2}Al_{0.2})^{IV}Al^{VI}_{1.4}(Si^{IV}\text{-}OH)_{0.4}(OH)_{2.8}O_{4.1}$ |
| Allophane | Sphere | 30–50 | $(Si_{0.4}Al_{0.1})^{IV}Al^{VI}_{1.4}(Si^{IV}\text{-}OH)_{0.4}(OH)_{2.6}O_{2.4}$ |
| Imogolite | Tube | 20 | $Al^{VI}_2 (Si^{IV}\text{-}OH)_1 (OH)_3 O_3$ |

[1] Hollow, spherical aluminosilicate.

aluminosilicate as used here refers to the wall of the spherical particle which consists of a unit layer, but not of the assemblage of the unit layers, such as that found for spherical halloysites. The curved unit layer of HSAS is a 1:1 type in which the tetrahedral and octahedral sheets constitute, respectively, its outer and inner parts and which are characterized by: (1) substitution of Al for Si in the tetrahedral sheet; (2) defects in the octahedral sheet; and (3) attachment of Si–OH tetrahedra to the inner surface of the octahedral sheet, each through three O atoms. These are shown in the structural formula which is compared in Table 1 with that of an ideal kaolin mineral.

Table 1 lists the particle size and shape and approximate structural formulae of three monolayer aluminosilicates—HSAS, allophane, and imogolite. The structure of imogolite was elucidated by Cradwick et al. (1972), whereas those of allophanes having different Si/Al ratios have not been worked out completely. Parfitt and Henmi (1980) and Parfitt et al. (1980) suggested that allophane having a molar Si/Al ratio close to 0.5 is made up of distorted imogolite structural units and that allophane having a Si/Al ratio close to 1.0 contains condensed silicate units, either on the outside surface of the Al octahedral sheet giving rise to a halloysite-like structure, or bonded on the inside surface of an imogolite structure. The structural formulae for allophanes having Si/Al ratios of 1.0 and 0.5 were calculated by assuming a $H_2O+/Al_2O_3$ ratio of 2.0 and using the $^{29}Si$ and $^{27}Al$ NMR data obtained for the two synthetic allophanes (Figure 7). These formulae suggest that (1) the framework common to the two allophanes is the Al octahedral sheet with defects; (2) the two species of allophanes are different in the development of the outer Si(Al) tetrahedral sheet; and (3) the development of structural order in allophane is inhibited by defects in both the octahedral and tetrahedral sheets.

In all three minerals, the number of the innermost Si(OH) tetrahedra and the development of the outer Si(Al) tetrahedral sheet seem to determine the curvature of the unit layer, and hence, the diameter of the tube or spheres. This observation also holds for spherical halloysite in which the absence of the innermost Si(OH) tetrahedra was indicated in the $^{29}Si$ NMR spectrum (Figure 7). Thus, the minimum inner diameter is much larger and found to be 150 to 200 Å (Wada

et al., 1977). Cradwick et al. (1972) pointed out for imogolite that the bonding of the Si(OH)-tetrahedra on the inside surface of the Al octahedral sheet results in a considerable shortening of the O–O distance around the vacant octahedral site and an increase of the curvature of the composite layer. The present observation further suggests that the development of the tetrahedral sheet, particularly the one having a greater substitution of Al for Si, stretches the curved layer for allophanes and HSAS.

HSAS and hollow particles found in group II and IV products may be precursors of halloysite. As shown in Figure 4, hollow particles that vary in shape and size were found in some soils derived from volcanic ash in which "embryonic halloysites" are present. The formation of HSAS (group I) and group II, III, and IV products shown in Figure 5 suggest that the pH and Si/Al ratio of solutions can control the formation of halloysite and allophane in weathering of volcanic ash.

## ACKNOWLEDGMENT

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