

A STRUCTURAL SCHEME OF SOIL ALLOPHANE

KOJI WADA

Faculty of Agriculture, Kyushu University, Fukuoka, Japan.

ABSTRACT

Chemical, infrared spectroscopy and morphological data for well-characterized soil allophane suggest two end-members with chemical composition $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and a structural scheme common to the two end-members and intermediate compositions.

The proposed structure for allophane with the Si/Al ratio 1/1 is composed of a silica tetrahedral chain and an alumina octahedral chain sharing a corner of the respective tetrahedron and octahedron. Addition of another alumina octahedral chain to the silica tetrahedral chain results in formation of allophane with the Si/Al ratio 1/2. Noncrystalline and poorly crystalline X-ray patterns of allophane with the Si/Al ratio 1/1 and 1/2 are interpreted in terms of the differences in the ease with which the respective unit chains are aligned. This structural scheme accounts for most observed bonding and morphological features as well as surface characteristics of soil allophane. A genetic transformation from allophane with the Si/Al ratio 1/1 to "imogolite" or hydrated halloysite can well be understood on the basis of the development or the rearrangement of the chain structure units.

INTRODUCTION

The amorphous or nearly amorphous aluminum silicate allophane, as a principal clay constituent in volcanic ash soils, is of great importance in determining the physical and chemical properties of these soils. During the past fifteen years, a considerable volume of information has been obtained on soil allophane by various methods. Soil allophane is now known to possess a range of chemical composition and different degrees of order (Kuwano and Matsui, 1957; Aomine, 1958; Kanno *et al.*, 1960; Osaka, 1960; Yoshinaga and Aomine, 1962*b*; Aomine and Miyauchi, 1965; Yoshinaga, 1966; Miyauchi and Aomine, 1966; Wada, 1966). A component named "imogolite"¹ which shows several broad X-ray reflections (Table 1), gives an endotherm at 410 to 430°C and appears as thread-like particles of diameter 100 to 200 Å in electron micrographs (Yoshinaga and Aomine, 1962*b*). However, no attempt has been made previously to evaluate these data in relation to any structural organization that might be present in allophane and "imogolite."

The first part of this article summarizes chemical, infrared spectroscopy and morphological data obtained for well-characterized specimens of allophane and "imogolite." Evaluation of these data led to a postulate of two end-members and to a structural scheme common to these end-members and the intermediate compositions. In the second part, their

¹ Although the use of the name "imogolite" as a distinct mineral species has not been approved (Fleischer, 1963), it is used in this article for convenience to denote a component in soil allophane showing the characteristics described here.

validity and implications as working hypotheses in the study of soil allophane are discussed.

Allophane other than that formed in weathered volcanic ash and pumice beds is not included in this study. Presence of some regularity in chemical composition (Ossaka, 1960; Marshall, 1964) and structural organization (Collins quoted by Grim, 1961) has also been noted for the former allophane. However, a similar analysis of this material will be less successful, partly because of an extreme diversity in genesis (from hy-

TABLE 1. X-RAY POWDER DATA FOR "IMOGOLITE"

d_{obs}	I_{obs}	B_{obs}^1	d_{calc}	(hkl)
13.0-18 Å	7	3.5°	17Å	01
7.6-7.8	4	2.5	8.5	02
5.5-5.6	2	2	7.4	10
4.4 ²	0.5	—	5.7	03
			4.25	04
4.0 ²	0.5	—		
3.7	2	2	3.7	20
3.26 ²	10	4	—	—
2.26 ²	2.5	2.5	—	—
1.40 ²	1	3	—	—

Air-dried, Na-saturated, <0.2 μ fraction of Uemura soil in random orientation (Yoshinaga and Aomine, 1962b).

¹ Angular width at half-maximum intensity.

² Reflections common to "imogolite" and allophane.

drothermal alteration to simple precipitation) and hence in nature and properties, and partly because of a lack of extensive or reliable data.

SUMMARY OF ANALYTICAL AND MORPHOLOGICAL DATA

Chemical analysis. The analyses evaluated were those from studies of amorphous or nearly amorphous fine clay fractions (<0.2 μ) derived from recent volcanic deposits by weathering (Yoshinaga and Aomine, 1962a,b; Aomine and Miyauchi, 1965; Yoshinaga, 1966; Miyauchi and Aomine, 1966). For these specimens, X-ray and other data were also reported and in most cases, amorphous oxides were largely removed by Na₂S₂O₄-NaHCO₃-Na citrate and 2 percent Na₂CO₃ treatments (Jackson, 1956).

For evaluation, the numbers of Si, Al (+Fe) and H (in H₂O+) per 18 oxygens were first calculated and plotted (Figs. 1 and 2). These were compared with those for kaolinite and halloysite (Bates, 1959; Aomine

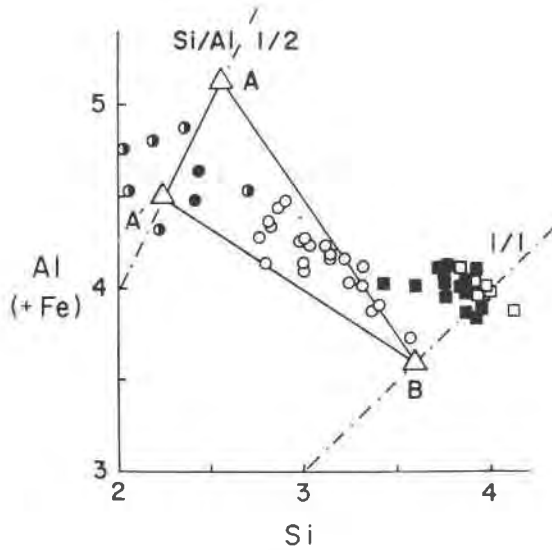


FIG. 1. Relationships between the number of Al (+Fe) and Si per 18 oxygens for soil allophane and kaolin minerals. Legends; ●: "imogolite"; ●: "imogolite" plus allophane (extractable oxides are not removed); ○: allophane; ■: hydrated halloysite; □: kaolinite; △: ideal allopheane with the formula shown in Fig. 5.

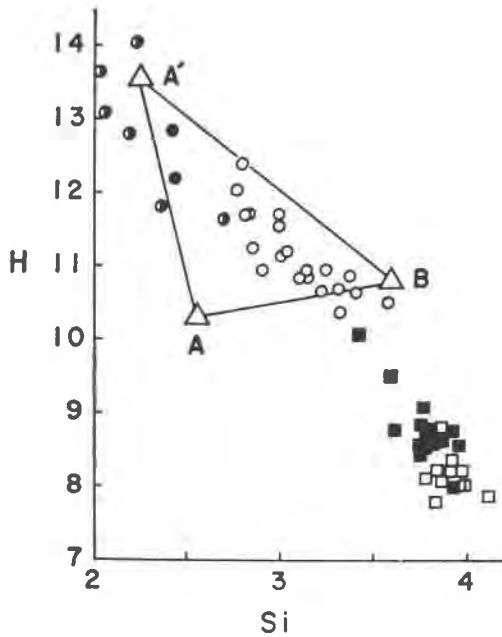


FIG. 2. Relationships between the number of H (in H₂O) and Si per 18 oxygens for soil allophane and kaolin minerals. Legends as in Fig. 1.

and Wada, 1962), with a structural unit containing 18 oxygens. The amount of Fe in soil allophane is rather insignificant, except for specimens analyzed without removal of extractable oxides.

From Figures 1 and 2, it is evident that soil allophane as a whole has its own composition region, just as halloysite and kaolinite. The specimens containing "imogolite" can be differentiated from the others on the basis of their chemical composition. The fact that the Si/Al ratio for soil allophane is in the range from 1/1 to 1/2 strongly suggests some regularity in bonding between Si and Al through oxygen, in the structural organization of soil allophane. Apparent exceptions are the specimens from which extractable oxides were not removed, although the ratio Si/Al, not Si/(Al+Fe), for these specimens are also in the above range. Note that the observed regularity is essentially not dependent on the fractionations and pretreatments, though these have undoubtedly helped to narrow the range. Birrell and Fieldes (1952) reported the Si/Al ratio 1/0.83 to 1/1.98 for allophane in New Zealand soils, with minor amounts of impurities, and Ossaka (1960) quoted the value 1/0.68 to 1/2.22 for twenty specimens of soil allophane.

Now, we can reasonably assume that the two end-members with the Si/Al ratio 1/1 and 1/2 associated with a definite number of hydrogen and oxygen are present in soil allophane. The former may correspond to Brown's allophane (1955) and the latter to an ideal "imogolite."

Infrared spectroscopy. A striking feature of the chemical composition of soil allophane is its high content of hydrogen as illustrated in Figure 2. Knowledge of its forms (adsorbed water vs. structural OH groups), locations (surface vs. internal) and bondings (Al-OH vs. Si-OH) is of primary importance in setting up of any structural scheme for allophane and "imogolite."

In this respect, infrared spectroscopy combined with deuteration gave useful information (Wada, 1966). After deuteration with D₂O, a nearly complete removal of adsorbed D₂O was effected at the relatively low temperatures of 75 to 100°C. All the OH groups in allophane and "imogolite" were replaced by OD, whereas very minor and partial replacements resulted for montmorillonite and hydrated halloysite, respectively. In addition, the presence of an OH-bending band in allophane and "imogolite," with a maximum at 830 to 850 cm⁻¹, was shown by its frequency shift upon deuteration to 700 cm⁻¹. Ordinarily, this absorption maximum could not be specified even as a shoulder on the intense but broad absorption band in the 1200 to 800 cm⁻¹ region. The corresponding Al-OH absorption band appears at 940 to 910 cm⁻¹ for the layer silicates.

These observations on the state of hydrogen in soil allophane lead to

the following two conclusions: first, from the structural point of view, a sharp line exists between the structural OD groups and the adsorbed D_2O , and hence the structural OH groups and the adsorbed H_2O . This implies that the amount of H_2O (+) gives a measure of the hydrogen largely in the structural OH groups. Second, all the structural OH groups locate at the surface, and their arrangement differs in principle from those known so far for the layer crystalline silicates.

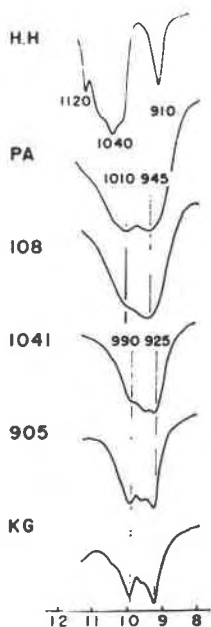


FIG. 3. Infrared spectra of hydrated halloysite (H.H.), allophane (PA, 108), allophane plus "imogolite" (1041, 905) and "imogolite" (KG) recorded by the use of D_2O as a mulling medium (Wada, 1966). Ordinate: transmittance; abscissa: wave number (cm^{-1}) $\times 10^{-2}$.

Aside from the OH-related absorptions, the principal differences between allophane and "imogolite," as well as between them and the layer silicates, were found in the Si-O stretching absorption band (Wada, 1966). Allophane with the Si/Al ratio 1/1 to 1/1.3 shows broad absorption maxima at 1010 and 945 cm^{-1} , whereas the specimens with the lower Si/Al ratio containing predominantly "imogolite" show rather well-defined absorption maxima at 990, 955 and 925 cm^{-1} (Fig. 3). Most aluminum silicates with 1:1, 2:1 and 2:2 layer structure show their main Si-O absorption maxima at frequencies higher than 1000 cm^{-1} .

This difference alone does not disprove the development of the layer

structure in allophane and "imogolite," since the increasing Al for Si substitution in the layer silicates results in the displacements of the Si-O band toward lower frequencies. However, the displacement to the frequencies as low as 940 to 925 cm^{-1} requires a high Al for Si substitution in the tetrahedral sheet at the rate of about 1 to 1 (Stubican and Roy, 1960; Farmer and Russell, 1964). Of course, we can not expect this situation for soil allophane. Rather, the low Si-O stretching frequencies should simply be interpreted in terms of the increasing replacement of Si-O-Si linkages with Si-O-Al linkages, as pointed out by Mitchell *et al* (1964). This may be possible only in the structural schemes different from those known for the crystalline layer silicates.

Electron microscopy. A diverse morphology has been reported for allophane and related mineraloids. This diversity is undoubtedly due to differences in the exact nature of the specimens examined, but partly due to those in dispersion, pretreatments and mounting in preparation. Recent studies on well-characterized and well-dispersed specimens (Yoshinaga and Aomine, 1962*a,b*; Aomine and Miyauchi, 1965; Miyauchi and Aomine, 1966) show that a fairly good correlation exists between morphology, chemical composition and development of structural order.

The result may be summarized as follows: "imogolite" develops smooth, curved and often branched threads with diameter about 50 to 200 Å (Fig. 4, above). These threads may extend to as long as several microns. With the increasing Si/Al ratio, the tendency to appear as the thread is gradually lost, but not completely, and minute particles with diameter 50 to 500 Å in aggregated masses (Fig. 4, below) or thin films appear dominantly. The thread-like feature is observed even for allophane with the Si/Al ratio 1/1 (Aomine and Wada, 1962), though an apparent constitution of these threads differs from that known for "imogolite." From the structural point of view, the fibrous morphology of "imogolite" is of particular importance. It strongly suggests one-dimensional regularity in the structural organization developed in this species.

STRUCTURE OF SOIL ALLOPHANE

Presence of prototypic layer structures with a low degree of order in soil allophane has long been considered by many investigators, but by implication rather than definite evidence. Here, a structural scheme common to allophane with the Si/Al ratio 1/2 to 1/1 based on a chain structure has been developed on the basis of simplicity and consistency with the foregoing data. The basic structure unit is a chain illustrated in Figure 5 that is compounded with a silica tetrahedral chain and an alumina octahedral chain. In allophane with the Si/Al ratio 1/2, R is substituted

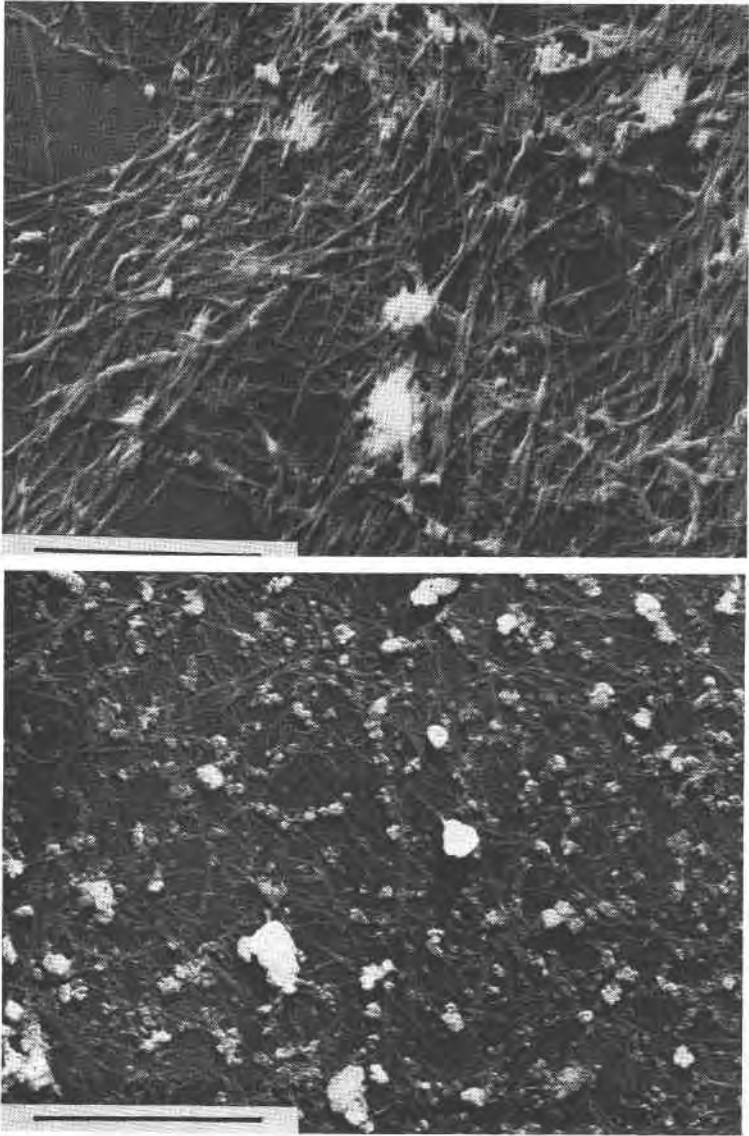
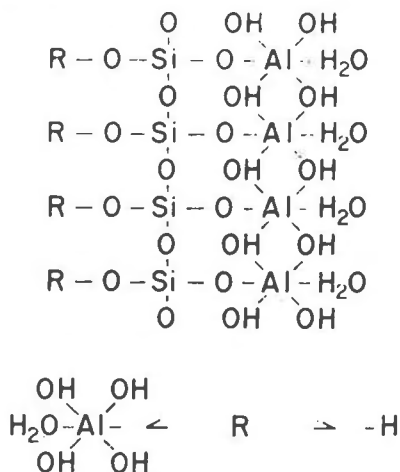


FIG. 4. Electron micrographs of "imogolite" and allophane: above: "imogolite" formed as gel films in the weathered Kanuma pumice bed (Miyachi and Aomine, 1966); below: "imogolite" plus allophane appeared in a glassy volcanic ash soil (Lab. No. 242) (Aomine and Miyachi, 1965). Line indicates 1 μ .

by another alumina octahedral chain (chain unit A), whereas in allophane with the Si/Al ratio 1/1, R is substituted by hydrogen (chain unit B).

Elemental composition. The elemental composition of the units A and B (Fig. 5) can be expressed in the chemical formulae $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, respectively. The latter can be comparable with that



	Formula A		Analysis A	Formula B	Analysis B
Si	4	3.5	3.8	4	4.0
Al	8	7.0	7.1	4	4.1
H	16	21.0	19.5	12	11.6
O	28	28.0	28.0	20	20.0

FIG. 5. Structural formula for allophane with the Si/Al ratio 1/2 (formula A and A') and 1/1 (formula B). Analyses: (A) Yoshinaga and Aomine (1962b); Miyauchi and Aomine (1966), and (B) Yoshinaga (1966).

of Brown's allophane $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ (1955). The agreement between the formula compositions and those actually found for the corresponding end-members is rather satisfactory. Some discrepancy between the formula A and its nearest natural specimens may partly be ascribed to the replacements of Al and Si by H in the development of the structural organization. This results in the formation of vacant octahedra and tetrahedra as one of likely occurring defects. Formula A' is thus calculated assuming the replacements of (1 Al + 1/2 Si) by 5 H per formula composition A. On the other hand, the H content estimated from the H_2O (+)

measurement likely involves the H in the form of adsorbed H₂O. This may also contribute to the above discrepancy though less in the magnitude.

The latter situation exists equally or to some greater extent to the end-member corresponding to the formula B (Wada, 1966). Thus, the apparent agreement between the formula composition and the analysis (Fig. 5) suggests an occurrence of the compensating replacement of H that probably occurs at R by Si and/or Al. It, in turn, may result in some two or three dimensional organization of the short chain units depicted schematically in Figure 9.

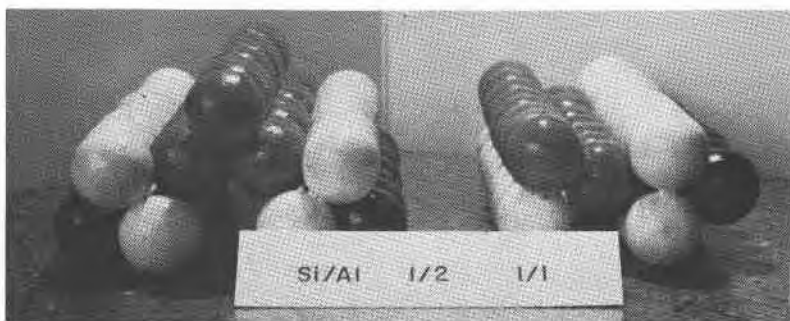


Fig. 6. Structural models of allophane with the Si/Al ratio 1/2 and 1/1. Si and Al are not shown, white balls show OH, gray oxygen, and black H₂O.

Plots of the formula compositions on Figures 1 and 2 indicate that the proposed chain units and its mixing development can explain the variation of the chemical composition found for the natural specimens. Exceptions are those not removed extractable oxides, mainly iron oxides. If the proposed structural scheme is correct, it means that most extractable Fe is not involved in the structural organization of "imogolite" and allophane.

Structural features. An exact orientation of the alumina octahedral chain relative to the silica tetrahedral chain in the structure units is not known, and Fig. 6 shows only one of possible orientations. Thus, the approximate size of the cross section viewed along the chain axis for the structure units A and B can vary 11.8×8.9 to 14.6×6.3 Å and 9.7×5.6 to 10.0×5.5 Å, respectively.

In the case of "imogolite", several reflections characteristic to this species appear on the X-ray diffraction pattern (Table 1). Its simplicity and diffuseness make detailed interpretation difficult. The diffraction pattern, however, suggests a possible presence of the two-dimensional reg-

ularity that may result from the grouping of the chain unit A with random orientation along the chain axis c . An ideal *average* unit cell with the cell dimensions $a=7.4$ and $b=17.0$ Å may be related to the structure unit A as illustrated in Figure 7. The cell dimensions may vary according to the variations in the orientation of the tetrahedral and octahedral chains. This type of disorder associated with the defects suggested from the deviations from an ideality in chemical composition may account for a least partly the broadness of the diffraction patterns, and the lack of the

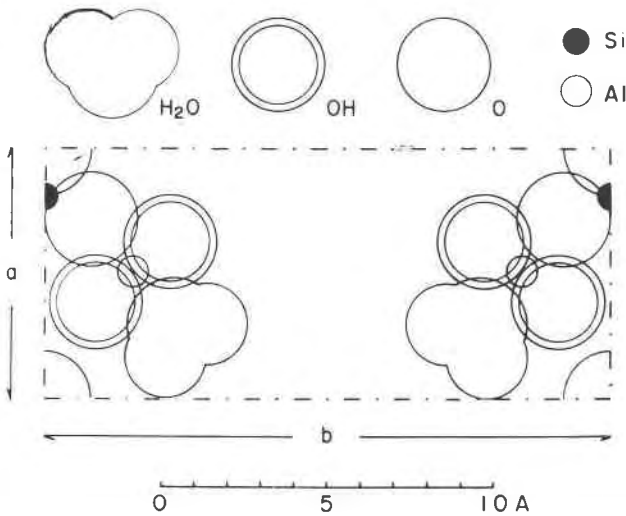


Fig. 7. The ideal *average* unit cell for "imogolite" seen in projection along the chain axis.

(hk) reflections. Other reflections common to allophane with the higher Si/Al ratio suggest presence of less ordered regions in the specimens of "imogolite" examined. An analogous situation, that is, the presence of crystalline and non-crystalline regions, has been reported in many organic chain-polymers.

No change in the spacing has been reported for "imogolite" either in the presence of water or ethylene glycol (Yoshinaga and Aomine, 1962*b*; Miyauchi and Aomine, 1966). This observation accords well with the very loose packing of the unit chains which can accommodate polar molecules in their interstitial portions (Fig. 7), although the mechanism for the maintenance of the chain separation can not be accounted for at present. A structural disposition shown in Figure 7 can accommodate 20 water molecules including those in the octahedral coordination, or 4 molecules of ethylene glycol per structure unit A. No pertinent data on

the well-defined specimens has been available at hand, but qualitatively this picture accounts for the high retention of polar solvent molecules known for soil allophane (Table 2).

Heating of "imogolite" from 100 to 300°C results in development of a fairly sharp and intense 18 Å reflection from the broad 13 to 18 Å reflection band (Yoshinaga and Aomine, 1962b; Miyauchi and Aomine, 1966). It attains to a maximum at about 50 percent of dehydroxylation, and concurrently, no significant change occurs for the reflections at 7.6 to 7.8 and 5.5 to 5.6 Å. Simple dehydroxylation and reorganization of the struc-

TABLE 2. ADSORPTION OF POLAR SOLVENTS ON SOIL ALLOPHANE

Solvent	Equilibrium conditions	Retention measured (oven-dry basis)	Solvent molecules calculated per		Reference
			Unit A	Unit B	
Water	R.H. 96%	49.5%	22	15	(1)
	R.H. 50%	25.9	10	8	
Water	R.H. 50%	18.3-26.2	8-11.5	5.5-8	(2, 3)
Ethylene glycol	Vacuum over CaCl ₂	13.3-25.5	1.7-3.0	1.2-2.1	(4, 5)
Glycerol	110°C	14.6	1.3	0.9	(6)

Reference (1) Aomine and Otsuka (Unpublished); (2) Yoshinaga and Aomine (1962a, b); (3) Yoshinaga (1966); (4) Aomine and Yoshinaga (1955); (5) Egawa *et al.*, (1952); (6) Kinter and Diamond (1958)

ture unit A can not produce such a long-range regularity, and this difficulty remains to be solved in future studies.

Besides this, much work remains to be done for "imogolite" in the determination of its structural identity. Among them, syntheses of an ideal "imogolite" will be required at first. If its crystallization occurs according to the present structural scheme, analyses of fiber diffraction as well as electron diffraction patterns will play a big part. In addition, a careful examination of the transitional stage upon dehydration and dehydroxylation will be required, and density data will help an interpretation of the obtained result.

The presence of the structural organization shown in Figure 5 in allophane with the Si/Al ratio 1/1, can of course not be proved directly from its X-ray pattern (Table 1). However, this may be inferred indirectly from its structural transformation to hydrated halloysite that could occur in an orderly manner shown in Figure 8. The reaction involves a unification of the adjacent chain units resulting in liberation of water from the OH groups bonded to Si. Then, the shaded OH groups are lost and the

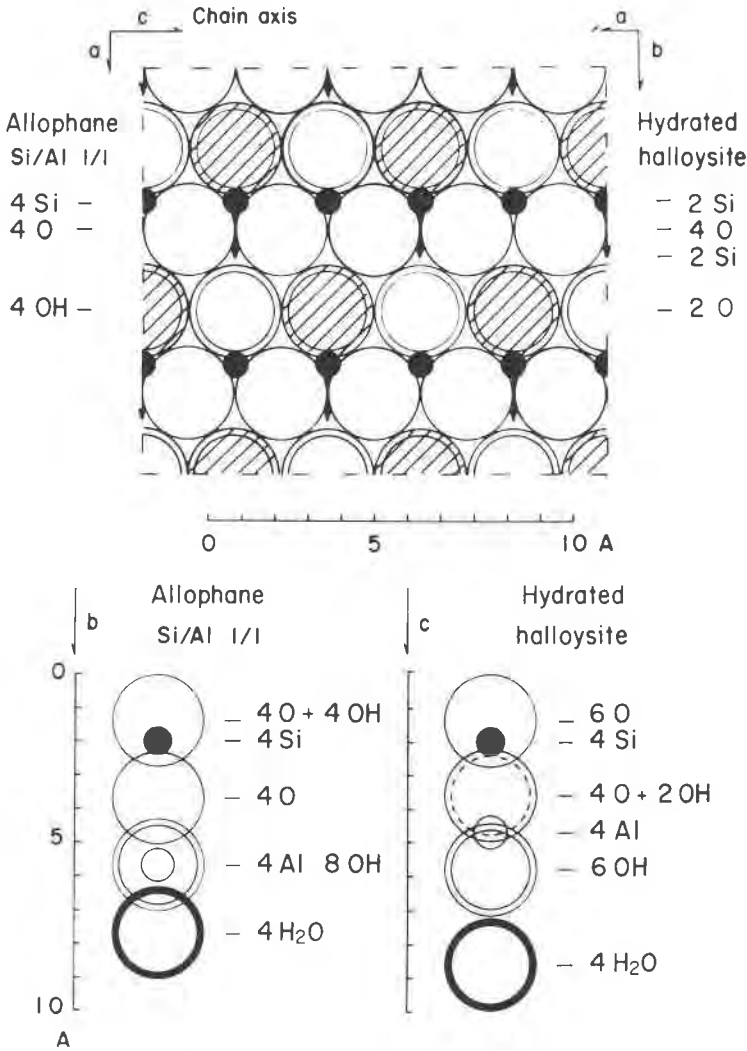


FIG. 8. Orientation relationships in the transformation of allophane with the Si/Al ratio 1/1 to hydrated halloysite. Above: Changes occurring in the Si-O,OH sheet. Below: Atom stacking diagrams along the *b*-axis of allophane and the *c*-axis of hydrated halloysite.

remainings change to oxygen (Fig. 8, above). A concurrent movement of the Si atoms as indicated by arrows forms a hexagonal net work of the silica tetrahedra and subsequent rearrangement of the Al-octahedra results in the formation of the kaolin structure (Fig. 8, below).

It is well-known that the hydrated halloysite derived from allophane

gives a rather sharp and strong (001) reflection despite of its very thin sheet appearance (Sudo and Takahashi, 1956; Aomine and Wada, 1962). It suggests that this form of hydrated halloysite already shows a high regularity in the layer stacking along its *c*-axis. The extreme weakness of (*hk*) reflections for the oriented specimen (Wada, Unpublished) indicates that the *c*-axis is perpendicular to the plane of the developing sheet as seen in the well-developed tubular halloysites (Honjo *et al.*, 1954). By inference, the structure unit B can probably form a particular sheet structure in this case, wherein its *a*- and *c*-axes are in the plane of the developing sheet (Figs. 8 and 9) and the hydrogen bond through water molecules plays an important role.

Bonding. Turning to the bonding features, the proposed structure satisfies those postulated by infrared spectroscopy. Evidently all the structural OH groups are exposed at surface, and their arrangements have a feature common to the two end-members and the intermediates, but quite different from those found in the layer silicates (Figs. 5 and 6). The high proportion of the Si-O-Al linkage relative to the Si-O-Si linkage, particularly in allophane with the Si/Al ratio 1/2, would result in the observed shift of the Si-O stretching absorption toward the lower frequencies (Fig. 3).

The presence of Al in 4-fold coordination in soil allophane has been inferred from its mode of origin from feldspars and glasses and from the development of its negative charge with the increasing pH (Fieldes and Schofield, 1960; Iimura, 1961). Actually, the coordination data for Al in soil allophane are very scarce. Egawa (1964) concluded from his X-ray fluorescence spectroscopy on a Kanuma allophane ($< 2\mu$) with the Si/Al ratio 1/0.85 that Al is present in both the two coordination states 4 and 6, and that its proportion is nearly 1 to 1. He did not specify for his specimen, however, the state of hydration and presence or absence of primary minerals such as glass and feldspar. The corresponding data on a synthesized silicoalumina gel with the Si/Al ratio, 1/1.72, were obtained by Léonard *et al.* (1964). In this particular gel, the percent of Al in 4-fold coordination was 56 ± 6 and 95 ± 10 at 100°C and 350°C , respectively. In these analyses, however, the resolution in spectroscopy does not permit differentiation of Al in 5-fold coordination from that in the mixed 4- and 6-fold coordinations. A development of surface acidity ($\text{pK} \doteq 3.3$) due possibly to a change of Al coordination was also reported upon heating various allophanic specimens from 100 to 420°C (Yamamoto, 1960). The present structural scheme predicts the transformation of Al coordination from 6 to 5 upon dehydration and further to 4 upon dehydroxylation (Fig. 5).

Morphology. Morphological relationships between "imogolite," allophane with the Si/Al ratio 1/1, and hydrated halloysite are schematically shown in Figure 7. The thread-like feature of "imogolite" appeared on the electron micrographs (Fig. 4; above) can well be expected from the organization of the structure unit A, where a silica tetrahedral chain is bonded to two alumina octahedral chains (Fig. 5) and chances to develop two or three dimensional structures are very few. The observed diameter of the thread 50 to 200 Å suggests alignment of about 5 to 20 chain units along the diameter.

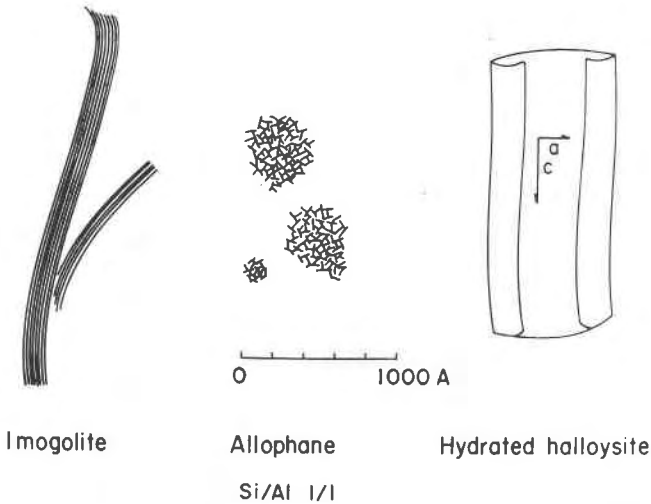


FIG. 9. A schematic representation of the morphological transition between "imogolite," allophane with the Si/Al ratio 1/1 and hydrated halloysite.

On the other hand, developments of three dimensional arrays readily occur for the structure unit B (Fig. 9). Replacement of H at R by Si or Al (Fig. 5) and subsequent chain development to other directions have already been suggested for allophane with a relatively high Si/Al ratio on the basis of its cation composition. This picture accords well with the frequent appearance of minute particles with irregular outlines on the electron micrographs (Fig. 4; below) and the lack of crystalline diffraction effects. The two dimensional array of the structure unit B along its *c*- and *a*-axes (Fig. 8) less likely occurs, but its occurrence has been inferred from the structural transformation to hydrated halloysite. This arrangement results in the formation of very thin sheets and films.

Ion-exchange and adsorption. Dependence of the cation- and anion-exchange capacities of soil allophane on the solution pH has been inter-

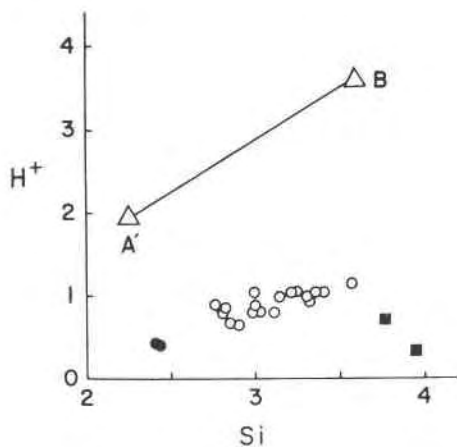


FIG. 10. Relationships between the number of dissociable H^+ at pH 10.5 and Si per 18 oxygens for soil allophane and hydrated halloysite. Legends as in Fig. 1.

preted in terms of the development of negative and positive charges resulting from the dissociation and uptake of H^+ through the edge OH groups bonded to Si and Al (Wada and Ataka, 1958; Aomine and Jackson, 1959; Fieldes and Schofield, 1960; Iimura, 1961; Birrell, 1961*a*). The published data suggest the following state of ionization:

pH	<i>State of ionization</i>	
< 3	$\equiv Si-OH$	$\equiv Al=(OH_{2+0.5})_2$
7	$\left\{ \begin{array}{l} \equiv Si-OH \\ \equiv Si-O^- \end{array} \right.$	$\left\{ \begin{array}{l} \equiv Al=(OH_{2+0.5})_2 \\ \equiv Al=(OH_{1.5})_2 \end{array} \right.$
10	$\left\{ \begin{array}{l} \equiv Si-OH \\ \equiv Si-O^- \end{array} \right.$	$\equiv Al=(OH_{1.5})_2$
>12-13	$\equiv Si-O^-$	$\left\{ \begin{array}{l} \equiv Al=(OH^{-0.5})_2 \\ \rightleftharpoons \\ \equiv Al-O^- \end{array} \right.$

The number of dissociable hydrogen upon treatment with 2 percent Na_2CO_3 (Jackson, 1956) per structure unit containing 18 oxygens is calculated from the Na content of the specimens thus treated (Wada and Aomine, 1962; Yoshinaga and Aomine, 1962*a,b*; Yoshinaga, 1966; Miyauchi and Aomine, 1966) and plotted against the number of Si in the same unit (Fig. 10). Its decrease with the Si/Al ratio is somewhat parallel with the decreasing number of the Si-OH groups calculated for the A', B and intermediate compositions (Fig. 5). The measured cation-exchange capacity values about 80 to 250 me per 100 g of clay correspond to about

20 to 30 percent of ionization of all the Si-OH groups at pH 10.5 in the respective specimens. The latter ionization figures may be compared with the $pK_1=9.7$ known for silicic acid (Iler, 1955).

The available data are not sufficient to fix the anion-exchange sites in the present structural scheme. It is unlikely, however, that the anion-exchange capacity of soil allophane exceeds 100 me per 100 g of clay unless its structure is disrupted. This suggests that the ionizable Al-OH groups may locate only at the ends of each chain units as well as at the vacant octahedral sites.

A very rapid and remarkable fixation of anions, particularly phosphate and fluoride, has been noted for soil allophane (Wada, 1959; Egawa *et al*, 1960; Birrell, 1961*b*). The reaction proceeds to a complete breakdown of allophane structure and to the formation of the new insoluble phases that contain Al as a main constituent. The high Al specific surface area of the present structural scheme is quite consistent with these observations.

Finally, physical adsorption of salt molecules in allophane (Birrell and Gradwell, 1956; Wada and Ataka, 1958) can be visualized as penetration of salt molecules into the interstitial portions of the structural units (Figs. 7 and 9) where an additional stability due to *van der Waal's* interaction may be conferred to the salt molecules. A similar situation can also exist to sorption of humic materials (Wada and Inoue, 1967).

GENETIC IMPLICATIONS

Linear polymers can be formed in polymerization of both silicic acid (Iler, 1955) and aluminohydronium ion (Jackson, 1960) under suitable environmental conditions. Formation of allophane with the Si/Al ratio 1/1 or higher probably occurs under these conditions from viscous liquids or jellies containing Si and Al released from primary minerals. Then, it is less difficult to assume a crystallization of "imogolite" or hydrated halloysite from this allophane on the basis of a continuous transition in their structure and morphology. The former process has been illustrated in the weathering of the glassy volcanic ash (Aomine and Miyauchi, 1965), and the latter, in the weathering of the glassy tuff (Sudo and Takahashi, 1956) as well as of the volcanic ash and pumice (Aomine and Wada, 1962). Also, "imogolite" can form directly from coprecipitation of Si and Al, and its typical occurrence as a gel can be seen in weathered pumice beds (Miyauchi and Aomine, 1966; see also, Kuwano and Matsui, 1957; Kanno *et al*, 1960).

The direction of weathering to form "imogolite" or hydrated halloysite may primarily be determined by relative proportion of Si and Al available in the system. However, the continuous structural relationships suggest that major environmental conditions are not much differ-

ent for their formation. Actually, all the reaction can proceed at pH 5 to 6 under well-drained conditions. The type of parent ash and pumice is not critical except that the glassy material often favors formation of "imogolite" (Yoshinaga and Aomine, 1962b; Miyauchi and Aomine, 1966). In addition, a local segregation of manganese and iron oxides as concretions is known to occur concurrently with the formation of hydrated halloysite (Aomine and Wada, 1962).

On the other hand, an accumulation of gibbsite in weathered volcanic ash likely occurs under distinctly acid conditions, namely pH 4 to 5, and in the presence of layer crystalline silicates, preferably with 2:1 type structure (Kanno, 1961; Wada and Aomine, 1966). These may reflect a lack of continuous structural relationships between gibbsite and allophane including "imogolite."

Different mechanisms for formation of hydrated halloysite from allophane have been suggested by several investigators (Tamura and Jackson, 1953; Fieldes, 1955; Aomine and Wada, 1962). These are different in detail, but commonly assume the formation of a gibbsite-like sheet structure in silica-alumina gel at first and subsequent addition and orientation of silica tetrahedra. Also, the development of order in "imogolite" has been interpreted in terms of that of a prototypic 2:1 layer structure (Kanno *et al.*, 1960). However, there is really no definite evidence that either the gibbsite-like sheet or the prototypic 2:1 layer structure occurs in soil allophane.

ACKNOWLEDGMENT

The author is greatly indebted to Professor S. Aomine for helpful discussions and for the use of electron micrographs and unpublished data. The research was supported in part by a grant from the Science Research Fund of the Japanese Ministry of Education.

REFERENCES

- AOMINE, S. (1958) Allophane in soils. *J. Sci. Soil Manure, Japan* **28**, 508-516.
- AND M. L. JACKSON (1959) Allophane determination in Ando soils by cation-exchange capacity delta value. *Soil Sci. Soc. Am. Proc.* **23**, 210-214.
- AND N. MIYAUCHI (1965) Imogolite of imogo-layers in Kyushu. *Soil Sci. Plant Nutr. (Tokyo)* **11**, 212-219.
- AND K. WADA (1962) Differential weathering of volcanic ash and pumice, resulting in formation of hydrated halloysite. *Amer. Mineral.* **47**, 1024-1048.
- AND N. YOSHINAGA (1955) Clay minerals of some well-drained volcanic ash soils in Japan. *Soil Sci.* **79**, 349-358.
- BATES, T. F. (1959) Morphology and crystal chemistry of 1:1 layer lattice silicates. *Amer. Mineral.* **44**, 78-114.
- BIRRELL, K. S. (1961*a*) The adsorption of cations from solution by allophane in relation to their effective size. *J. Soil Sci.* **12**, 307-316.

- (1961*b*) Ion fixation by allophane. *N. Z. J. Sci.* **4**, 393–414.
- AND M. FIELDS (1952) Allophane in volcanic ash soils. *J. Soil Sci.* **3**, 156–167.
- AND M. GRADWELL (1956) Ion-exchange phenomena in some soils containing amorphous mineral constituents. *J. Soil Sci.* **7**, 130–147.
- BROWN, G. (1955) Report of the Clay Minerals Group Sub-committee on Nomenclature of Clay Minerals. *Clay Miner. Bull.* **2**, 294–302.
- EGAWA, T. (1964) A study on coordination number of aluminum in allophane. *Clay Sci. (Tokyo)* **2**, 1–7.
- Y. WATANABE AND A. SATO (1952) Studies on the clay minerals of some upland soils in Japan. *Bull. Nat. Inst. Agr. Sci.* **B5**, 39–107.
- A. SATO AND T. NISHIMURA (1960) Release of OH ions from clay minerals treated with various anions, with special reference to the structure and chemistry of allophane. *Adv. Clay Sci. (Japan)* **2**, 252–262.
- FARMER, V. C. AND J. D. RUSSELL (1964) The infrared spectra of layer silicates. *Spectrochim. Acta* **20**, 1149–1173.
- FIELDS, M. (1955) Clay mineralogy of New Zealand soils, Part II: Allophane and related mineral colloids. *N. Z. J. Sci. Tech.* **37**, 336–350.
- AND R. K. SCHOFIELD (1960) Mechanisms of ion adsorption by inorganic soil colloids. *N. Z. J. Sci.* **3**, 563–579.
- FLEISCHER, M. (1963) New Mineral Names. *Amer. Mineral.* **48**, 434.
- GRIM, R. E. (1962) *Applied Clay Mineralogy*. McGraw-Hill Book Co. Inc. New York, N. Y.
- HONJO, G., N. KITAMURA AND K. MIHAMA (1954) A study of clay minerals by means of single-crystal electron diffraction diagrams—The structure of tubular kaolin. *Clay Miner. Bull.* **2**, 133–141.
- IMURA, K. (1961) Acidity and ion exchange in allophane. *Adv. Clay Sci. (Japan)* **3**, 90–102.
- ILER, R. K. (1955) *The Colloid Chemistry of Silica and Silicates*. Cornell Univ. Press, Ithaca, N. Y.
- JACKSON, M. L. (1956) *Soil Chemical Analysis—Advanced Course*. Published by the author, Madison, Wisc.
- (1960) Structural role of hydronium in layer silicates during soil genesis. *Trans. Intern. Congr. Soil Sci.*, *7th* **2**, 445–455.
- KANNO, I. (1961) Genesis and classification of main genetic soil types in Japan. I. Introduction and Humic Allophane Soils. *Bull. Kyushu Agr. Exp. Sta.* **7**, 1–185.
- KUWANO, Y. AND Y. HONJO, (1960) Clay minerals of gel-like substances in pumice beds. *Adv. Clay Sci. (Japan)* **2**, 355–365.
- KINTER, E. B. AND S. DIAMOND (1958) Gravimetric determination of monolayer glycerol complexes of clay minerals. *Proc. Nat. Conf. Clays Clay Miner.* **5**, 318–333.
- KUWANO, Y. AND T. MATSUI (1957) Clay mineralogy of pumice beds intercalated in the Kanto volcanic ash formations. *Misc. Rep. Res. Inst. Nat. Resources (Tokyo)* **45**, 33–42.
- LÉONARD, A., S. SUZUKI, J. J. FRIPIAT AND C. DE KIMPE (1964) Structure and properties of amorphous silicoaluminas. I. Structure from x-ray fluorescence spectroscopy and infrared spectroscopy. *J. Phys. Chem.* **68**, 2608–2617.
- MARSHALL, C. E. (1964) *The Physical Chemistry and Mineralogy of Soils*. Volume I. Soil Materials. John Wiley and Sons, Inc., New York, N. Y.
- MITCHELL, B. D., V. C. FARMER AND W. J. MCHARDY (1964) Amorphous inorganic materials in soils. *Adv. Agron.* **16**, 327–383.
- MIYAUCHI, N. AND S. AOMINE (1966) Mineralogy of gel-like substances in the pumice bed in Kanuma and Kitakami Districts. *Soil Sci. Plant Nutr. (Tokyo)* **12**, 187–190.
- OSSAKA, J. (1960) On the hydro-alumina silicate minerals from Mt. Asama. *Adv. Clay Sci. (Japan)* **2**, 339–349.

- STUBICAN, V. AND R. ROY (1961) Infrared spectra of layer-structure silicates. *J. Amer. Ceram. Soc.* **44**, 625-627.
- SUDO, T. AND H. TAKAHASHI (1956) Shapes of halloysite particles in Japanese clays, *Clays Clay Miner. Proc. Nat. Conf.* **4**, 67-79.
- TAMURA, T. AND M. L. JACKSON (1953) Structural and energy relationships in the formation of iron and aluminum oxides, hydroxides and silicates. *Science* **117**, 381-383.
- WADA, K. (1959) Reaction of phosphate with allophane and halloysite. *Soil Sci.* **87**, 325-330.
- (1966) Deuterium exchange of hydroxyl groups in allophane. *Soil Sci. Plant Nutr. (Tokyo)* **12**, 176-182.
- AND S. AOMINE (1966) Occurrence of gibbsite in weathering of volcanic materials at Kuroishibaru, Kumamoto. *Soil Sci. Plant Nutr. (Tokyo)* **12**, 151-157.
- AND H. ATAKA (1958) The ion uptake mechanism of allophane. *Soil Plant Food (Tokyo)* **4**, 12-18.
- AND T. INOUE (1967) Retention of humic substances derived from rotted clover leaves in soils containing montmorillonite and allophane. *Soil Sci. Plant Nutr. (Tokyo)* **13**, 9-16.
- YAMAMOTO, D. (1960) On the surface acidity of allophane and a coloration of Vitamin A with the clay. *Clay Sci. (Tokyo)* **1**, 32-36.
- YOSHINAGA, N. (1966) Chemical composition and some thermal data of eighteen allophanes from Ando soils and weathered pumices. *Soil Sci. Plant Nutr. (Tokyo)* **12**, 47-54.
- AND S. AOMINE (1962a) Allophane in some Ando soils. *Soil Sci. Plant Nutr. (Tokyo)* **8**(2), 6-13.
- AND ——— (1962b) Imogolite in some Ando soils. *Soil Sci. Plant Nutr. (Tokyo)* **8**(3), 22-29.

Manuscript received, June 29, 1966; accepted for publication, January 23, 1967.