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Morphology and composition of allophane

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Abstract

Sixteen clay samples separated from different weathered volcanic ashes and pumices were studied by electron microscopy, chemical analysis, infrared spectroscopy, and X-ray fluorescence spectroscopy. In electron micrographs, allophane appeared as fine, ring-shaped particles with diameters 35–50 Å which, in three dimensions, may be hollow spherules or polyhedrons. These particles formed aggregates of various shapes and sizes, either by themselves or with other constituents. The chemical analysis of the fine clays (<0.2 μm) showed that allophane has a SiO_2/Al_2O_3 ratio (mole) ranging at least from 1 to 2, while coexisting imogolite has a SiO_2/Al_2O_3 ratio close to 1.0. Allophane-like constituents dissolved by dithionite-citrate and Na_2CO_3 treatments were not morphologically differentiated from the remaining allophane. Electron micrographs of the coarse clays (0.2–2 μm) showed that allophane forms within weathered glass shards. Of allophane samples, those separated from the pumice grains gave each a relatively narrow Si–O absorption maximum with a frequency that showed a good linear correlation with the SiO_2/Al_2O_3 ratios. X-ray fluorescence spectroscopy indicated that aluminum in allophane is in both 4- and 6-fold coordinations, while nearly all aluminum in volcanic glass and imogolite is in 4- and 6-fold coordinations, respectively. The content of aluminum in 4-fold coordination in allophane increased with its SiO_2/Al_2O_3 ratio and amounted to 50 percent of the total aluminum.

Implications of these observations to the structure and the charge characteristics of allophane are briefly discussed.

Introduction

Grim (1968) stated in his book: "As would be expected, allophane with little or no structural organization is found in particles without any definite and regular shape. Electron micrographs generally show fluffy aggregates with a rounded nodular appearance." A number of investigators obtained electron micrographs of allophane derived from weathered volcanic ash and pumice, and suggested that allophane consists of aggregates of very fine particles (*e.g.* Birrell and Fieldes, 1952; Aomine and Yoshinaga, 1955; Egawa and Watanabe, 1964; Bates, 1971). Birrell and Fieldes (1952) recognized particles of 50 Å diameter or less in an electron micrograph of an allophane sample, separated from a volcanic ash soil in New Zealand. Sudo (quoted by Bates, 1971) found rounded grains or particles (0.1–0.3 μm) usually composed of fine allophane particles (about 0.05 μm diameter) in the Kanto volcanic ash soils.

Wada and Yoshinaga (1969) and Wada *et al.* (1972) noted the presence of ring-shaped particles in high-resolution electron micrographs of samples containing allophane. Kitagawa (1971) observed similar objects in the clays separated from five samples of weathered pumices and suggested that allophane consists of a hollow "unit particle" with a diameter of 55 Å. These observations suggest that further studies should consider the possibility that allophane is a clay mineral with a unique morphology, and hence, with a unique structure.

The purpose of the present study was to obtain information about morphology and composition of structure units which may be present in allophane, as compared with those of the structure unit of imogolite. Clays separated from weathered volcanic ashes and pumices of different lithologic compositions, ages and origins were subjected to electron microscopy, chemical analysis, infrared spectroscopy and X-ray fluorescence spectroscopy.

Materials and methods

Brief descriptions of samples from which clays were separated are given in Table 1. Among the sam-

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ples, those with the suffix P and G were respectively pumice grains and gel films, separated from the same pumice beds. All the samples were treated with H_2O_2 to remove organic matter and dispersed at pH 4 (HCl) or pH 10 (NaOH) by sonic wave treatment (20 kHz). Clays (<2 μm) were first collected by sedimentation, followed by flocculation with NaCl. Aliquots of these clay suspensions were washed with water until the clays dispersed again, and the fine (<0.2 μm) and coarse (0.2–2 μm) clays were collected by centrifugation. The clay suspensions were used for the analysis either as such or after freeze-drying.

Electron microscopy

A JEM 100B electron microscope with decontamination devices was used at 100 kV. In order to obtain a general view, a drop of the clay suspension was dried on a collodion film reinforced with carbon and observed at an electron optical magnification of 10,000. Electron diffraction patterns were also obtained using this specimen. For high-resolution electron microscopy, a drop of the clay suspension was dried on a microgrid prepared by Fukami and Adachi's method (1965) and observed at an electron optical magnification of 50,000 or 100,000. Exposure for photographing was made at the lowest current and within the shortest time possible.

Chemical analysis

The clay suspension containing 20 to 30 mg of the fine clay was taken in a polyethylene centrifuge tube for determination of the molar SiO_2/Al_2O_3 ratio. Sodium chloride was then added, and the clay and supernatant were separated by centrifugation. The clay was treated with 50 ml of 0.15 *M* sodium oxalate–oxalic acid mixture (pH 3.5) at 90°C for 2 hours. This treatment resulted in a complete dissolution of all the examined clays. The Si and Al in the resulting solution were determined using an AA-610 atomic absorption spectrophotometer in nitrous oxide–acetylene flame. The recovery of Si and Al in the presence of oxalate, of Al in the presence of Si and *vice versa* was tested in a preliminary determination.

TABLE 1. Descriptions of samples

Abbreviation; and/or laboratory number	SiO_2/Al_2O_3 ratio of fine clay	Locality; and horizon or layer	Material*; and approximate age (y)	Reference**
Ohakune; W-133.2	0.83	Rangitaua, New Zealand; B	A (And); 5000	1
905	0.91	Uemura, Kumamoto, Japan; BC	A (And); 4000-5000	2, 3, 4
1041	1.03	Choyo, Kumamoto, Japan; BC	A (And); <5000	2, 3, 5
A.P.; W-164.2	1.12	Andies Prairie, Oregon, U.S.A.; C2	A (Dac); 6600	6
Ki-P	1.19	Kitakami, Iwate, Japan; III	P (Dac)	7
Ki-G	0.96		G	
Ku-P	1.22	Kurayoshi, Tottori, Japan; IV	P; 32000	8, 9
Ku-G	1.02		G	
Tirau; W-130.2	1.26	Tirau, New Zealand; B	A (Rhy-And); <13000-14000	1
Taupo; W-132.3	1.29	Wharepaina, New Zealand; B	P (Rhy); 1700	1
Ka-P	1.30	Hangandai, Tochigi, Japan; VII	P (And)	10
Mt. Schank; W-139.3	1.31	Mt. Schank, South Australia; B	A (Bas); <5000-6000	5, 11
PA	1.54	Choyo, Kumamoto, Japan; XVI	P (And); >9000	12
PA-P	1.75			
VA	1.77	Choyo, Kumamoto, Japan; XIV	A (And); >9000	4, 12
Mazama; W-159.3	1.97	Crescent Lake Site, Oregon, U.S.A.; C2	P (Dac); 6600	6

* A; weathered volcanic ash, G; gel films, P; weathered pumice, (And); andesitic, (Bas); basaltic, (Dac); dacitic, (Rhy); rhyolitic.

** 1; Gibbs (1968), 2; Aomine and Yoshinaga (1955), 3; Yoshinaga and Aomine (1962a, b), 4; Wada and Tokashiki (1972), 5; Wada and Greenland (1970), 6; Dudas (1973), 7; Wada and Matsubara (1968), 8; Yoshinaga and Yamaguchi (1970), 9; Tazaki (1971), 10; Aomine and Mizota (1973), 11; Hamblin and Greenland (1972), 12; Aomine and Wada (1962).

Infrared spectroscopy

A disc was prepared by mixing 2 mg of the freeze-dried fine clay with 600 mg of KBr and by pressing this mixture at 500 kg/cm^2 for 15 min. The infrared spectrum was obtained from the KBr disc using an IR-S spectrophotometer with double NaCl prisms.

X-ray fluorescence spectroscopy

A flat layer of the freeze-dried clay (100–200 mg) was placed on the plate of a sample holder and covered with a Mylar film fixed to the plate with a metal ring. The position of Al$K\alpha$ in 2θ units was determined using a Geigerflex KG-3 X-ray fluorescence spectrometer. The sample was placed in an evacuated chamber and irradiated with X-rays from a tungsten tube target operated at 50 kV and 45 mA. An EDDT crystal was used as an analyzing crystal. The same determination was carried out with kaolinite, gibbsite, orthoclase, anorthite and their mixtures as reference materials.

Results and discussion

Electron microscopy

Figure 1 shows the electron micrographs of the four fine clays obtained at a low magnification. These micrographs show the range in morphological variation of the clay samples, which are composed of fine, rounded particles and threads. The relative content of the rounded particles and threads markedly varies from one sample to another with the proportion of the rounded particles decreasing in the following order: Mazama, PA–P > PA, VA, Ka–P, Ki–P > Taupo, A. P., Ohakune > Tirau > Mt. Schank, 1041 > 905 > Ki–G, Ku–G.

Figure 2a is a high resolution electron micrograph of the 905 fine clay which is a mixture of the threads and the rounded particles in nearly equal amounts (Fig. 1b). These two micrographs show that the threads are composed of bundles of parallel fiber pairs with a separation of about 20 Å. This feature was observed with imogolite and interpreted as an

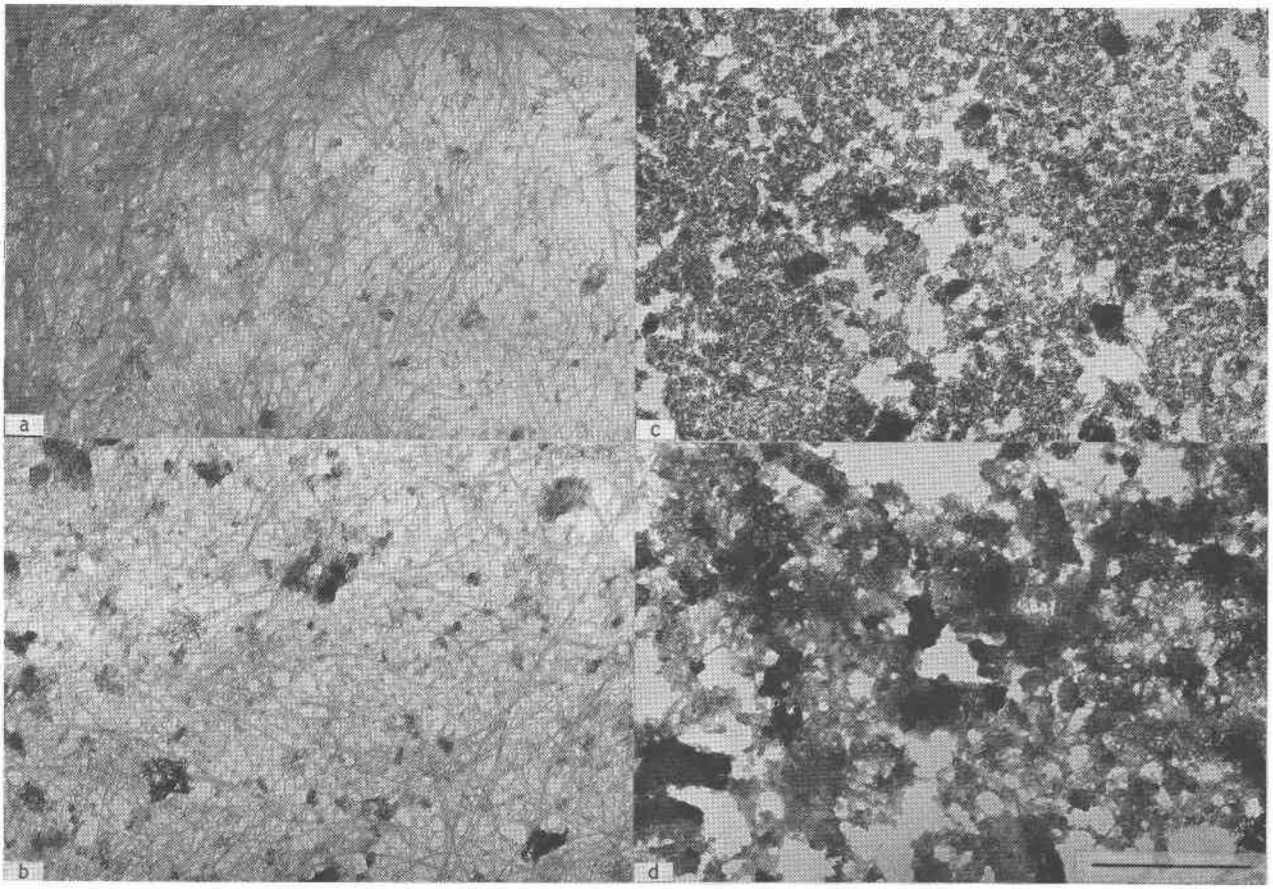

FIG. 1. Low-magnification electron micrographs of fine clays differing in the relative contents of imogolite and allophane. Scale marker: 1 μm. a. Ki–G. b. 905. c. VA. d. Mazama.

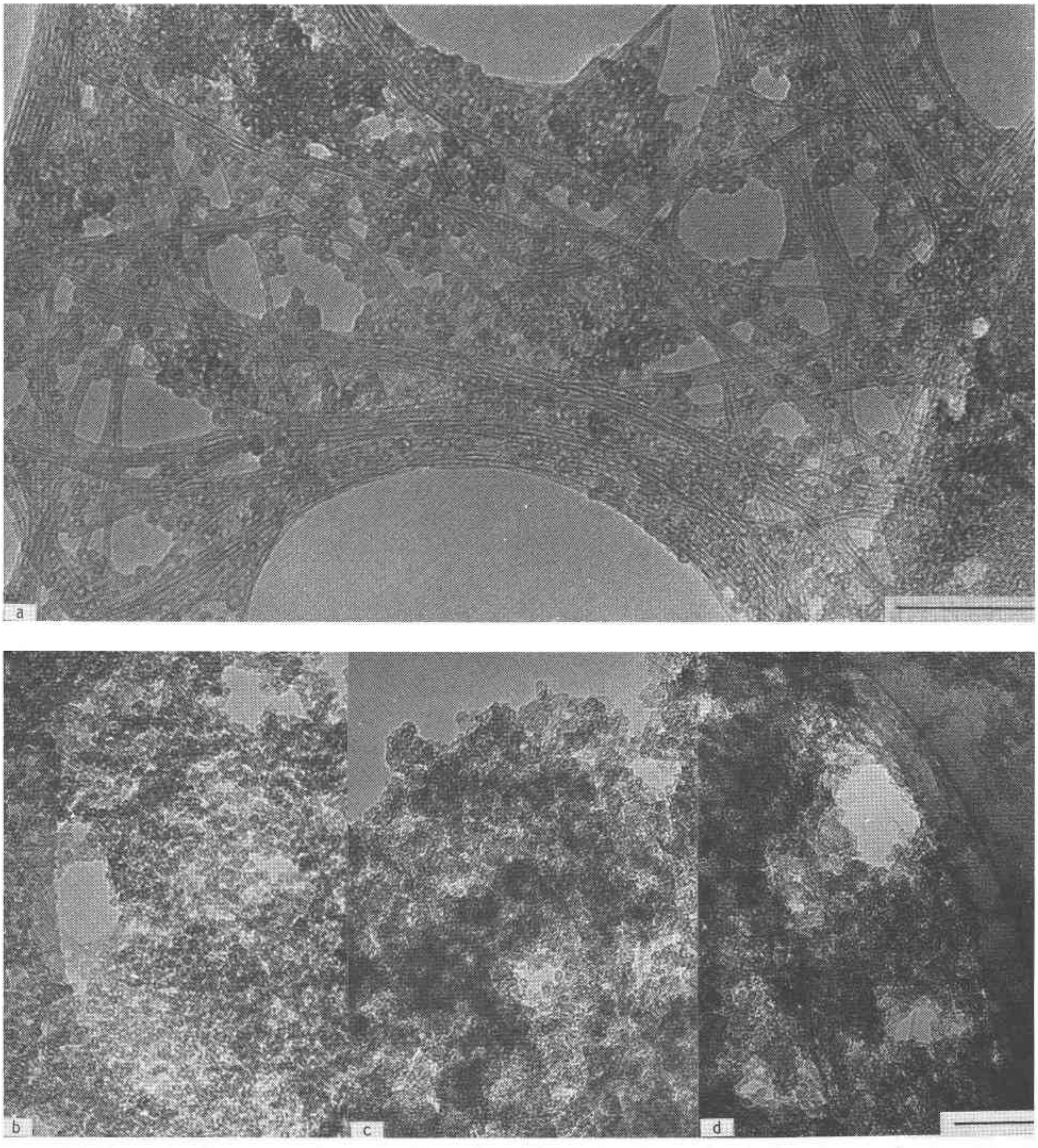

FIG. 2. High-magnification electron micrographs of imogolite and/or allophane in fine clays. Scale marker: 500 Å. a. 905. b. Ka–P. c. VA. d. Mazama.

indication that it consists of bundles of tubes, each 20 Å in diameter (Wada *et al.*, 1970). Of the examined fine clays, the Ku–G, Ki–G and 905 clays gave a series of well-defined diffraction rings at 1.4, 2.1, 2.3, 3.3, 3.7, 4.1, and 5.7 Å, which provided evidence for imogolite in them. The small amounts of imogolite in the 1041 and Mt. Schank clays were also indicated by electron diffraction. On the other hand, the tube was found in all the clays and was very useful for detection of imogolite even when present in very small amounts as shown in Figures 2b and 2d. Actually, the presence of imogolite has not been reported for some of these clays. No fibrous particle other than imogolite was found at the higher magnifications. All the threads found at the low magnification were therefore identified as imogolite.

The fine clays in which the rounded particles predominated gave broad diffraction rings at 1.45, 2.25, and 3.35 Å, which are typical of allophane. These diffraction rings were broad as compared with those from imogolite, but not as broad as those from carbon evaporated on the collodion film, implying that the coherent scattering unit is larger in allophane than in the evaporated carbon. Figures 2a–2d show the finer structure of the allophane particles; there are many ring-shaped particles with diameters of 35–50 Å. They are often deformed and aggregated, and in three dimensions may be hollow spherules or polyhedrons. Close inspection shows even finer structure within the wall of the ring-shaped particles. However, the electron optical magnification of 100,000 or 50,000 does not ensure that this imaged structure exceeds noise in the electron beam/recording system, and therefore, it can not be considered the true structure (Alderson, 1974). Similar ring-shaped particles were observed in all the clays examined, irrespective of the lithologic composition, ages, and origins of volcanic ashes and pumices from which they were separated. It would be reasonable to consider that these fine particles represent structure units of allophane.

The question of whether the fine allophane particles are rings or spherules has not been resolved. Application of replica and shadowing techniques has not been rewarded, partly because of insufficient resolution of either replica or shadowed micrographs, and partly because of failure in obtaining good dispersion of the particles. The obtainable higher resolution of replica micrographs ranges from 20 to 50 Å (Goodhew, 1972), which is about the same in size or larger than the relief of interest. Final conclusion must, therefore, await further improvement of the techniques for specimen preparation and independent checks by other techniques. However, the absence of the isolated, imaged particles which may represent a side view of the ring-shaped particles suggests the possibility that they are hollow spherules or polyhedrons.

Such fine "spherules" and tubes described above and the overlapping of them may explain most, but not all, of the images appearing in Figures 2a–2d. The slight differences in their appearance and size from one micrograph to another is largely due to the differences in focus setting, resolution, and exposure to the electron beam. The micrographs provide evidence that the specimen damage and contamination due to the electron beam is minimum at least for imogolite, but this does not prove the same for allophane. The question of whether allophane is composed of only the fine "spherules" has therefore not been resolved. On the other hand, no sample contained gel material, as observed by Jones and Uehara (1973) in soils derived from volcanic ash in Hawaii. This material appeared to be "amorphous" even in high resolution electron micrographs.

Kitagawa (1971) obtained electron micrographs of allophane similar to those shown in Figures 2b, 2c, and 2d. An agreement between the diameter of the spherules measured by electron microscopy and that calculated from the measured surface area (600 m^2/g) and specific gravity (1.9) was considered as a support for the 55 Å "unit particle" in allophane. No contribution of the internal surface of the hollow sphere to the measured surface area was allowed for. The measured surface areas of allophane have also been known to vary considerably according to the methods of measurement and sample preparation (*e.g.* Aomine and Otsuka, 1968; Egashira and Aomine, 1974).

No significant amounts of opaline silica with characteristic disc and ellipsoid shapes (Shoji and Masui, 1969) and unweathered volcanic glass shards were found in the fine clays. Very rarely, halloysite spherules with diameters 400–1600 Å were found in the VA, 1041, and PA fine clays. As shown in Figure 3, these spherules were characterized by a concentric structure with a circumferential lattice image of 7 Å spacing. The coexistence of imogolite, allophane, and halloysite may illustrate a heterogeneous weathering

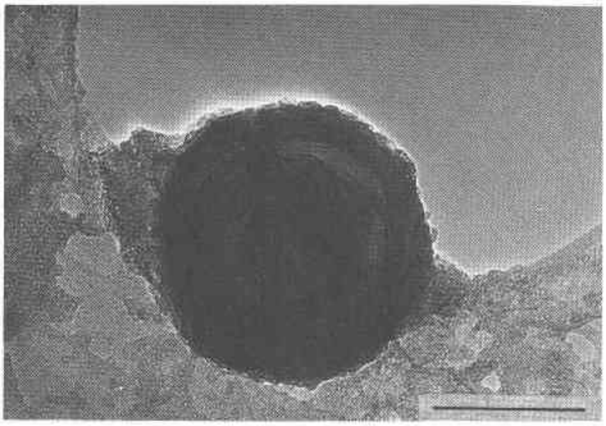

FIG. 3. High-magnification electron micrographs of halloysite, allophane, and imogolite in the 1041 fine clay. Scale marker: 1000 Å.

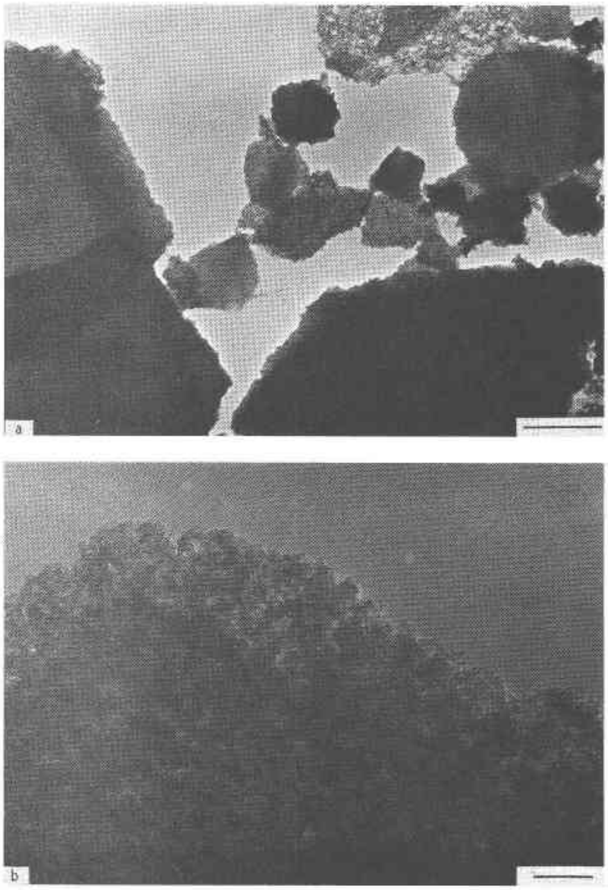

FIG. 4. Electron micrograph of weathered volcanic glass in the PA coarse clay. a. Low magnification. Scale marker: 1 μm. b. High magnification. Scale marker: 500 Å.

environment, even in one deposit of volcanic ash or pumice.

Volcanic glass shards, diatoms, opaline silica, and unidentified mineral fragments were found in the coarse clays. As shown in Figure 4a, some of the glass shards are thick, but some are thin enough to be translucent to the electron beam. The latter show a fine granular structure; and the imogolite threads are found outside, but not inside, these weathered glass shards, unless they are broken down into fragments. Viewed at higher magnifications, this fine granular structure is seen to be composed of dense packing of "spherules," similar to the allophane "spherules" observed in the fine clays (Fig. 4b). These observations suggest that allophane forms first by hydrolysis of volcanic glass, followed by *in situ* precipitation from the resulting hydrolysate. Imogolite may be formed either by alteration of allophane or by precipitation from the hydrolysate outside the glass shard. A similar but megascopic differential formation of allophane and imogolite inside and outside the pumice grains was seen in the large differences in their contents between the Ki–P and Ki–G clays or the Ku–P and Ku–G clays.

Chemical analysis

As shown in Table 1, the SiO_2/Al_2O_3 ratios of the fine clays range from 0.83 to 1.97. In Figure 5, the SiO_2/Al_2O_3 ratios are plotted against the relative content of allophane, estimated from the electron micrographs of the specimens deposited on the carbon-coated collodion film. Two inferences may be drawn from this plot: the first, the higher the imogolite content, the lower the SiO_2/Al_2O_3 ratio of the fine clay; the second, imogolite has a SiO_2/Al_2O_3 ratio close to 1.0, while allophane has a SiO_2/Al_2O_3 ratio ranging at least from 1 to 2. Within the limit of resolution attained in the electron microscopy, there was no apparent morphological difference between the allophane "spherules" in the samples with different SiO_2/Al_2O_3 ratios, as illustrated in Figures 2a–2d.

Wada and Yoshinaga (1969) showed that the SiO_2/Al_2O_3 ratios of the fine clays (<0.2 μm) in which allophane predominated were in a range from 1.3 to 2.0, while those of the fine clays in which imogolite predominated were in a fairly narrow range from 1.05 to 1.15. Chemical analysis data for clays fractionated at 2 μm were also provided; Iimura (1969) gave SiO_2/Al_2O_3 ratios 0.89–1.43 for five allophanic clays. Kitagawa (1974) gave SiO_2/Al_2O_3 ratios 1.40 and 1.46 for two allophanic clays in which he did

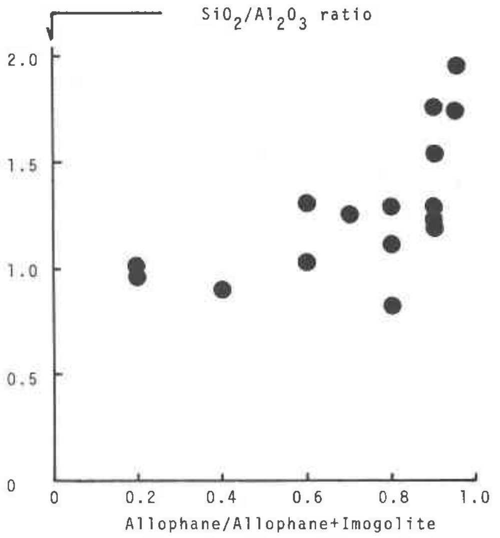

FIG. 5. The relationship between the SiO_2/Al_2O_3 ratio and the relative contents of allophane and imogolite of fine clays.

not recognize imogolite and other impurities by electron microscopy. The higher SiO_2/Al_2O_3 ratios for imogolite, 1.5 (Russell *et al.,* 1969) and 1.29–1.32 (Tazaki, 1971), and the lower SiO_2/Al_2O_3 ratios close to 1.0 for allophane (*e.g.* Russell *et al.,* 1969; Lai and Swindale, 1969) were also reported.

It was shown that dithionite–citrate (Mehra and Jackson, 1960) and Na_2CO_3 (Wada and Greenland, 1970) treatments resulted in dissolution of allophane-like constituents from clays in which allophane and/or imogolite predominated. These constituents were characterized by relatively low SiO_2/Al_2O_3 ratios, mostly 0.4–1.4 (Tokashiki and Wada, 1972) and by a similarity of infrared spectra to allophane (Wada and Greenland, 1970). However, the question of whether these allophane-like constituents are present as discrete particles or surface phases was not resolved. The VA and Ki–G fine clays before and after the dithionite–citrate and Na_2CO_3 treatments were therefore observed by electron microscopy. By these treatments, the spherules decreased considerably as compared with the tubes, but no particular morphological change was found in the remaining spherules and tubes. This observation suggests that both allophane and allophane-like constituents are composed of morphologically similar particles.

Infrared spectroscopy

The infrared spectra in the Si–O stretching region of some fine clays differing in the allophane content are shown in Figure 6. Figure 7a shows the frequencies of the main absorption maximum in this region plotted against the SiO_2/Al_2O_3 ratio for all the fine clays. Only the Ku–G, Ki–G, and 905 clays show a flat absorption maximum extending from 945 to 990 cm^{-1}, which has been considered to be typical of imogolite (Russell *et al.,* 1969; Wada *et al.,* 1972). This feature has been attributed to the presence of isolated orthosilicate groups with their silicon to apical oxygen bonds perpendicular to the fiber axis (Cradwick *et al.,* 1972).

Of the samples in which allophane predominated, those separated from the pumice grains, marked with small circles in Figure 7a, give a relatively narrow maximum, and the frequency of the absorption maximum shows a good linear correlation with the SiO_2/Al_2O_3 ratio. A similar composition–spectrum relationship was noted by Kanno *et al.* (1968), Lai and Swindale (1969) and Tokashiki (1974). The present observation may have importance in suggesting: first, the broad Si–O absorption maximum signifies a multiplicity in the chemical composition of the allophane "spherules" in one sample; and second, the latter multiplicity is associated with that of microenvironment of their formation. The interior of pumice grains or glass shards would provide a relatively uniform environment for the formation of the allophane "spherules."

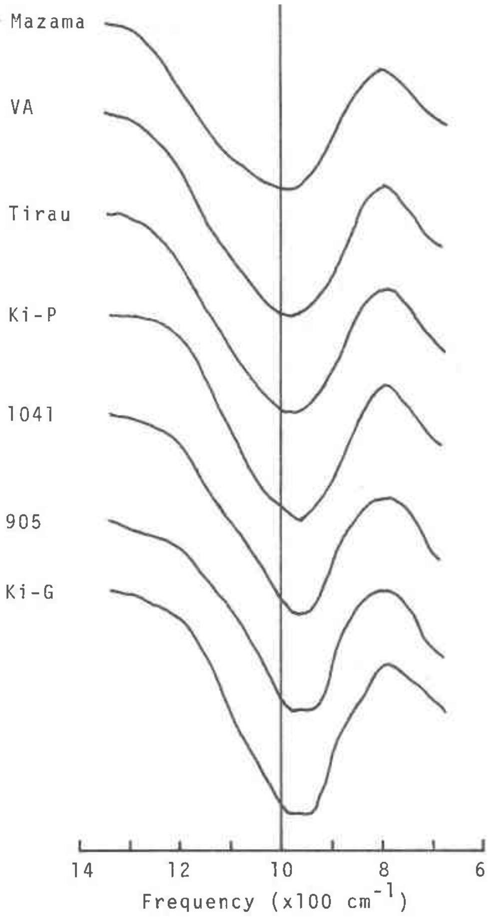

FIG. 6. Infrared spectra of fine clays differing in the relative contents of allophane and imogolite.

Figure 7b shows that the ratio of the absorbance at 1100 cm^{-1} to that at 940 cm^{-1} increases with the increasing SiO_2/Al_2O_3 ratio of the fine clays, irrespective of the predominance of allophane or imogolite. This absorbance ratio may be used for estimating the gross SiO_2/Al_2O_3 ratio of such clays.

X-ray fluorescence spectroscopy

Figure 8 shows 2θ positions of Al$K\alpha$ from clay samples which are different in particle size, previous treatments, and allophane and imogolite contents. The 2θ values for the untreated fine clays range from those for kaolinite and gibbsite to those for anorthite and orthoclase, and increase with increasing allo-

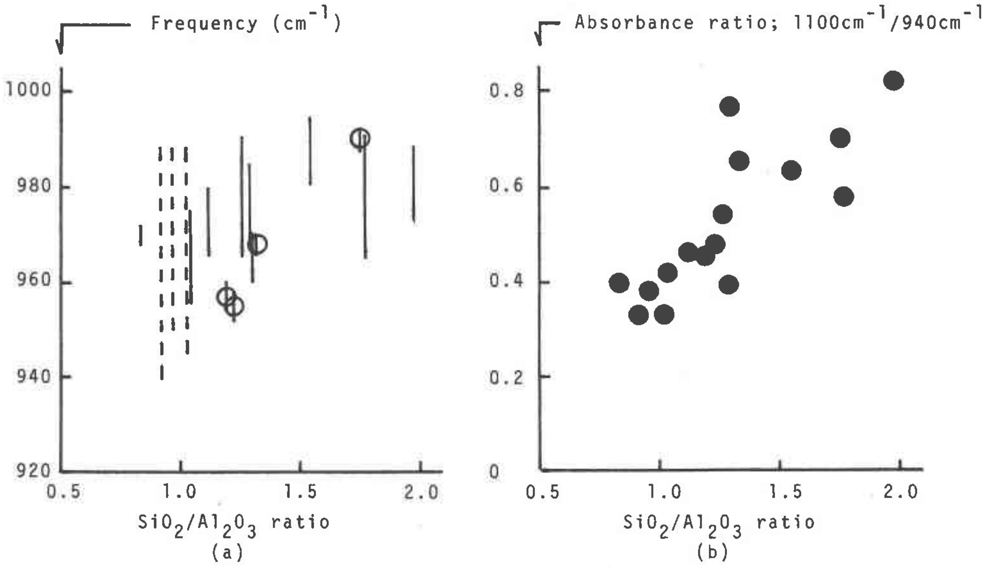

FIG. 7. (a) The relationship between the frequency of the Si-O absorption maximum and the SiO_2/Al_2O_3 ratio of fine clays. Broken lines; Ki-G, Ku-G and 905. Encircled; Ki-P, Ku-P, Ka-P and PA-P. (b) The relationship between the ratio of absorbance at 1100 cm^{-1} to that at 940 cm^{-1} and the SiO_2/Al_2O_3 ratio of fine clays.

phane content in the sequence Ki-G, Ku-G < 905, 1041 < Ki-P, Ku-P < PA, VA. The Ki-G and Ku-G clays subjected to the dithionite-citrate and Na_2CO_3 treatments, nearly pure imogolite samples, gave low 2θ values comparable to those of kaolinite and gibbsite. These observations indicate that nearly all aluminum in imogolite is in 6-fold coordination, while aluminum in allophane is probably in both 6- and 4-fold coordinations.

Since there was a linear relationship between the 2θ positions of Al*Kα* and the Al(IV) content of kaolinite, anorthite, and their mixtures, the Al(IV) content of the samples could be estimated from Figure 8. There is a trend for allophane in that the higher the SiO_2/Al_2O_3 ratio the greater the Al(IV) content. The Al(IV) content is as high as 50 percent of the total aluminum in allophane with a SiO_2/Al_2O_3 ratio close to 2. The dithionite-citrate and Na_2CO_3 treatments result in a slight decrease in the 2θ values for the clays containing allophane, imogolite, and allophane-like constituents. This may suggest that allophane-like constituents, even those with relatively low SiO_2/Al_2O_3 ratios, contain small but significant amounts of aluminum in 4-fold coordination. Sample 905 is an exception, the reason being not accounted for.

The 2θ values of Al*Kα* for the coarse clays are higher than those for the fine clays from the same samples (Fig. 8). Electron microscopy indicated that the coarse clays contain substantial amounts of volcanic glass, both weathered and unweathered (Fig. 4). Nearly all aluminum in unweathered volcanic glass may be in 4-fold coordination, as shown by the high 2θ value for the fine sand separated from sample 905, which primarily consists of unweathered volcanic glass.

Several investigators studied Al coordination status in allophanic clays, though they did not give data on the contents of imogolite, volcanic glass, and other impurities in their samples. Egawa (1964) and Udagawa *et al.* (1969) separated allophanic clays from the Kanuma pumice bed. Their samples differed in SiO_2/Al_2O_3 ratios, 2.37 and 1.67, but were alike in the coordination status, about 50–60 percent of aluminum being estimated to be in 4-fold coordination at room temperature and at *ca* 200°C. Okada *et al.* (1975) analyzed an allophanic clay from the same pumice bed and obtained the SiO_2/Al_2O_3 ratio of 1.38 and the Al coordination number of 6.00. They also found the Al coordination number being 5.4 and 5.5 for two allophanic clays with the SiO_2/Al_2O_3 ratios of 1.60 and 1.64, respectively. In this determination, soda glass was used as a reference material in which all aluminum is in 4-fold coordination.

Conclusions and implications

High-resolution electron microscopy showed that allophane in the samples studied consists of morpho-

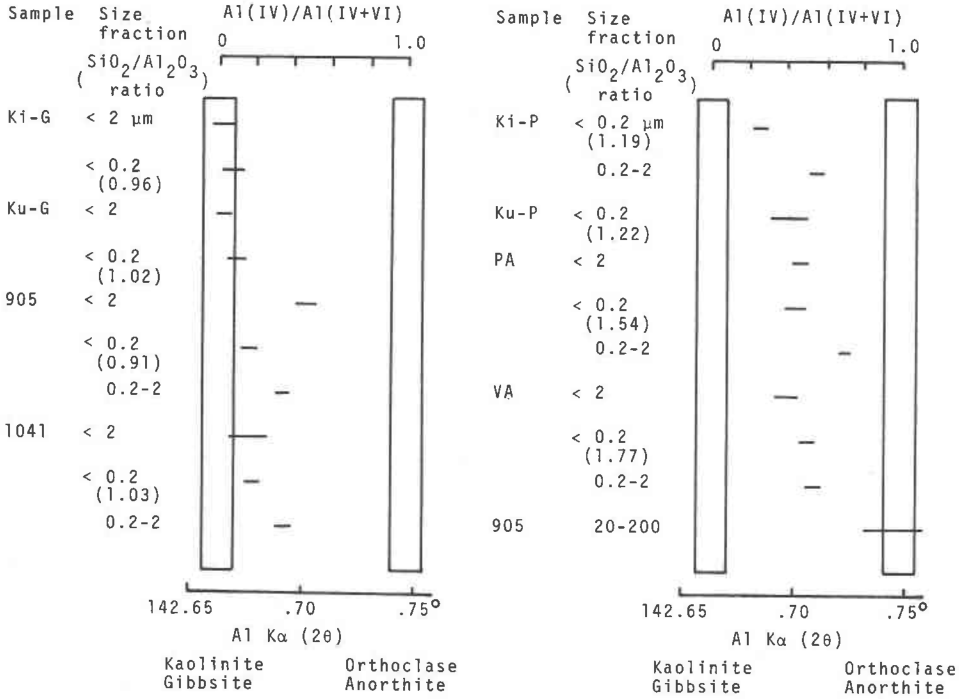

FIG. 8. The 2θ position of Al$K\alpha$ and the relative content of Al(IV) for samples differing in particle size and mineral composition. All <2 μm but no other samples were subjected to dithionite-citrate and Na_2CO_3 treatments. Horizontal bars and rectangles show the range of the 2θ positions of Al$K\alpha$ for the samples and the reference minerals, respectively.

logically similar particles. This suggests that certain allophanes must have definite structural arrangements and therefore can not be considered "amorphous." According to the literature, the size and shape of allophane particles are indefinite and variable. It is now apparent that this is true for aggregates which allophane particles form with themselves and with other soil constituents, but not for allophane particles themselves. These particles appear as rings in the electron micrograph, and three-dimensionally may be hollow spherules or polyhedrons, with outside diameter of 35–50 Å and wall thickness of 10 Å or less. Allophane and allophane-like constituents are differentiated by their dissolution characteristics, but not by their morphology. They vary in chemical composition; their SiO_2/Al_2O_3 ratio ranges at least from 0.4 to 2.0. X-ray fluorescence spectroscopy indicated that nearly all aluminum in volcanic glass and imogolite is in 4- and 6-fold coordinations respectively, while aluminum in allophane is both in 4- and 6-fold coordinations. High-resolution electron micrographs indicated formation of the allophane "spherules" in weathered glass shards. Allophane probably inherits aluminum in 4-fold coordination from volcanic glass.

The resolution of the electron micrographs does not permit one to obtain direct information about the internal structure of the allophane spherules. The instability of the material to the electron beam hampers observation at higher electron optical magnifications. The chemical analyses also do not give the content of hydroxyl groups, which have a vital importance in elucidating the atomic arrangement in allophane. Nevertheless, the data obtained have some implications on the structure and charge characteristics of allophane.

That allophane has a sheet structure related to kaolinite has been proposed on several grounds by Udagawa *et al.* (1969), Brindley and Fancher (1969) and Okada *et al.* (1975). Although these investigators did not discuss the structural and morphological relationships, it does not seem difficult to reconcile their proposal with the observed morphology of allophane. The assumption that allophane is built from three sheets like kaolinite, *i.e.* oxygen, oxygen-hydroxyl, and hydroxyl sheets, is at least consistent with the estimated wall thickness of the "spherules." The curvature may arise from the internal strains due to either geometrical misfits between the respective sheets or some unbalanced growth of them. There should be some differences between kaolinite and allophane in the packing of oxygen atoms and hydroxyl groups on these sheets. This is illustrated by the difference in the ease and completeness with which deuterium exchange takes place with the hydroxyl groups in these minerals, even after the interlayer space of kaolinite has been opened up by some intercalation treatments (Ledoux and White, 1964; Wada, 1966; 1967; Russell *et al.*, 1969). The wall of the allophane spherules may have many openings which admit free entry of water molecules.

Table 2 shows the result of allocation of the analyses to the Si and Al(IV) atoms in the tetrahedral spaces between the oxygen and oxygen-hydroxyl sheets and to the Al(VI) atoms in the octahedral spaces between the oxygen-hydroxyl sheets described above. In this allocation, either the sum of the Si and Al(IV) atoms or that of the Al(VI) atoms is arbitrarily fixed at 4.0. The result shows that a high proportion of the Al(IV) atoms in the tetrahedral spaces would be a key structural feature of allophane, irrespective of its SiO_2/Al_2O_3 ratio and the presence or absence of vacant sites. Of the investigators mentioned above, Okada *et al.* (1975) made a similar allocation of aluminum to the tetrahedral and octahedral spaces in propounding their structure models, but did not consider balancing the excess negative charge which would arise from the presence of the Al(IV) atom in the oxygen tetrahedron. In layer silicates such as montmorillonite and vermiculite, this excess of negative charge is balanced by retention of exchangeable cations. The development of this surface charge is independent of the pH of an ambient solution. On the other hand, the development of negative surface charge on allophane is known to be very pH-dependent (Wada and Ataka, 1958; Iimura, 1966; Harada and Wada, 1973). The available data indicate that the cation-exchange capacity (CEC) value of allophane would not exceed 50 me per 100 g clay when the sample is subjected to such washing with water or an aqueous salt solution at about pH 5 or less, as has been used for the preparation of the fine clay in the present study. As shown in Table 2, this value is far smaller than the potential CEC values of the fine clays calculated from their Al(IV) content (Table 2).

Cloos *et al.* (1969) found that the CEC values of synthetic silico-aluminas at pH 7 were lower than the potential CEC values computed from their Al(IV) content. They interpreted this discrepancy as an indication that the negative charge of the central core of the silicoaluminas might partly be balanced by a complex form of hydroxy-aluminum cations. The central core was considered to be made from a tetrahedral network in which silicon was partly substituted by aluminum producing the net negative charge. As shown in Table 2, however, the relative contents of Si, Al(IV) and Al(VI) in allophane suggest that the formation of polymeric hydroxy-aluminum cations may be limited by the Al(VI) content, particularly in allophane with a lower Al content. The negative charge due to the Al(IV) atoms in allophane is therefore considered to be internally balanced, most simply by the adsorption of protons within the structure. In the three sheet structure described above, the apical oxygen of a tetrahedron containing an Al(IV) atom may be substituted by a hydroxyl group, or may coordinate to an Al(VI) atom in the nearest octahedral space. The proton may be adsorbed by such apical hydroxyl group or oxygen. The easy access of these groups to protons in an aqueous solution has been substantiated by the ease and completeness with which deuterium exchange takes place with all the hydroxyl groups present in allophane (Wada, 1966; Russell *et al.*, 1969). Dissociation of a proton from such sites would be restrained by interaction with the negative charge, but would increase with increasing pH.

TABLE 2. The number of Si and Al atoms allocated to the kaolin layer structure and the calculated value of the potential CEC of imogolite and allophane

Sample	Tetrahedral spaces		Octahedral spaces	Potential* CEC (me/100g)
	Si	Al	Al	
Ki-G	1.92	0.00	4.00	0
905	2.14	0.71	4.00	150
1041	2.48	0.82	4.00	163
Ki-P	2.82	1.18	3.55	225
Ku-P	2.42	1.58	2.38	362
PA	2.52	1.48	1.81	376
VA	2.56	1.44	1.44	393

* The potential CEC value was calculated by using an average value of the molar $H_2O(+)/Al_2O_3$ ratio of 2.5 for allophane and imogolite (Wada and Yoshinaga, 1969) and by assuming one unit of the negative charge being created by every Al(IV) atom.

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