THE AMERICAN MINERALOGIST, VOL. 56, MARCH-APRIL, 1971

THE "UNIT PARTICLE" OF ALLOPHANE

YASUO KITAGAWA, *Department of Soils and Fertilizers, National Institute of Agricultural Sciences, Nishigahara Kita-ku Tokyo, Japan*

ABSTRACT

High magnification electron micrographs determination of specific surface area and specific gravity indicate that the microaggregate of allophane consists of 55 Å "unit particles". It is suggested that the unit particle is spherical, and that there is a monolayer of adsorbed water around the particle, as well as a little water in the space among the particles under air-dried condition at room temperature. The unit particles in microaggregates were collapsed and joined to each other by grinding, then mutually joined by heating as the adsorbed water was released. Allophane specimens treated by grinding and heating had a smaller specific surface area than untreated specimens, but no change of phosphorus absorption was observed. Such results suggest that physical, not chemical bonds act among the unit particles of allophane.

INTRODUCTION

Allophane, a dominant clay mineral in volcanic ash soils, is amorphous to X rays, and has large surface area, high water-holding capacity, high phosphorus absorption coefficient, strong affinity with humic substances, and feeble bonding forces between particles. These properties of allophane are also the characteristics of volcanic ash soils.

Mitchel, Farmer, and MacHardy (1964) and Egawa (1967) reviewed in detail the studies on allophane in soils. In spite of numerous studies on allophane, its definition is imperfect, and the conclusion by Ross and Kerr (1934) that "Allophane has no definite atomic structure or chemical composition, and is a mutual solution of silica, alumina, water and minor bases and accessory acid radicals" still prevails.

Recently, Wada (1967) presented a "structural scheme of allophane" deduced from the results of chemical analysis, infrared absorption spectrum, and morphological data of "imogolite." He proposed a fibrous shape for allophane, but it was not based on the observed micromorphology. Iimura (1969) constructed a "structural formula" of allophane on the basis of chemical analysis, thermogravimetry, and its ion exchange property. Birrell and Fieldes (1952) concluded that the allophane particles are less than 100 Å from the fact that allophane is amorphous to X-rays. They also recognized particles of 50 Å in diameter or less in an electron micrograph of an allophane specimen separated from a volcanic ash soil in New Zealand. Egawa and Watanabe (1964), in their electronmicrographic study on allophane, pointed out that allophane exists as microaggregates with numerous fine holes and large specific surface area, and that those characteristics are closely related to the physical and chemical properties of allophane. Watanabe and Sudo (1969) suggested that allophane consists of extremely fine particles of several tens of angstroms judging from the result of small-angle X-ray scattering analysis.

In this paper, I confirm that allophane consists of extremely fine particles from electron micrographs of high magnification. Measurement of specific surface area, specific gravity and phosphorus absorption value, and their changes upon grinding and heating were investigated.

MATERIALS

Allophane samples were separated from five weathered pumice beds in Central and North east Japan, as listed in Table 1. They were prepared by the following method: First the gel film, which is composed of the "imogolite", was removed from weathered pumice with tweezers; then the sample was puddled with distilled water into a paste in a flat-bottom evaporating dish using a rubber-pestle. An acid suspension was formed from the sample (adjusted to pH 3.5 with HCl) and the fraction of particles of less than 2 microns was syphoned, according to Stokes' law, at the required time from a definite depth. Then sufficient NaCl was added to make a 1N solution, and the precipitated particles were separated by decantation and centrifugation. The collected particles were washed with distilled water, ethanol, and acetone successively; then air-dried, carefully pulverized with a rubber-pestle, and sieved. These samples were found to be amorphous by X-ray diffraction.

TABLE 1. ALLOPHANE SAMPLES FROM WEATHERED PUMICE BEDS IN JAPAN

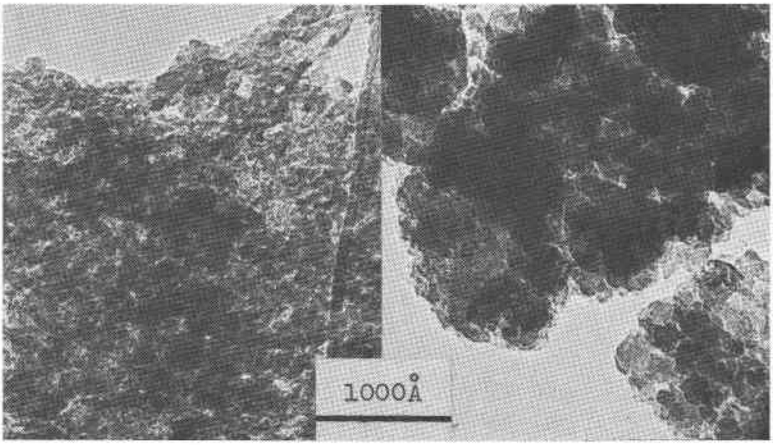
	Location	Original volcano
Kanumatsuchi	Kanuma, Tochigi Pref.	Akagi
Imaichitsuchi	Imaichi, Tochigi Pref.	Nantai
Shichihonzakura	Imaichi, Tochigi Pref.	Nantai
Misotsuchi	Iijima, Nagano Pref.	Ontake or Norikura
Kurosawajiri	Kitakami, Iwate Pref.	Kurikoma ?

An artifically coprecipitated silica-alumina gel prepared as follows was used for comparison with allophane. Silica solution (0.02M) prepared from water-glass, kept alkaline with sodium hydroxide, was mixed with equal volume of 0.02M aluminum chloride solution, and adjusted to pH 7.0. The precipitate formed was washed, air-dried, pulverized, and sieved in the same way as allophane. This gel has a silica/alumina ratio of 1.33, and is amorphous to X rays.

EXPERIMENTAL METHODS

Electron micrographs were taken by direct magnification of 50,000 at 100 kV, using an HU-11E type electron microscope, after the specimens were suspended in distilled water and placed on a microgrid. The actual observation and measurement of specimens were carried out at 200,000× magnification by enlarging the negative to four times the original size.

The grinding treatment was performed for 5 minutes using an automatic agate mortar. Heating was done for 24 hours in an oven at 100°C.

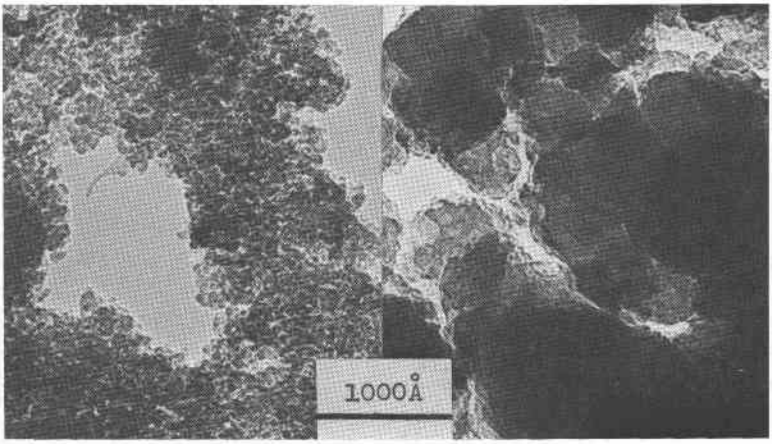


untreated ground

Fig. 1. Electron micrograph of Kanumatsuchi specimen.

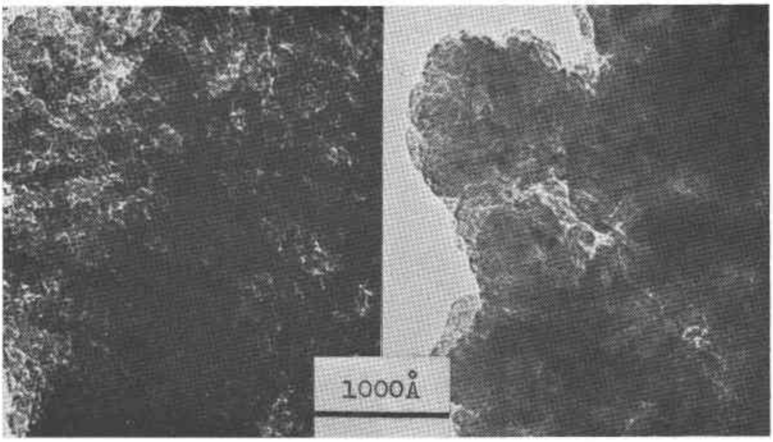
Specific surface areas were determined by the glycerol-retention method of Kinter and Diamond (1958) with some modification. Heating was omitted with untreated and ground specimens before glycerol saturation, because the original method made it difficult to observe the changes during the later heating experiments with the specimens. Instead, another specimen was heated simultaneously with the glycerol saturation of specimens. Other specimens were treated completely by the method of Kinter and Diamond.

Phosphorus absorption value: 0.5g specimen was suspended in 5 ml of 0.274M ammonium phosphate (pH 7.0) at room temperature for 24 hours. The value was calculated from the difference between the initial and final phosphate concentrations in the solution.



untreated ground

Fig. 2. Electron micrograph of Imaichitsuchi specimen.



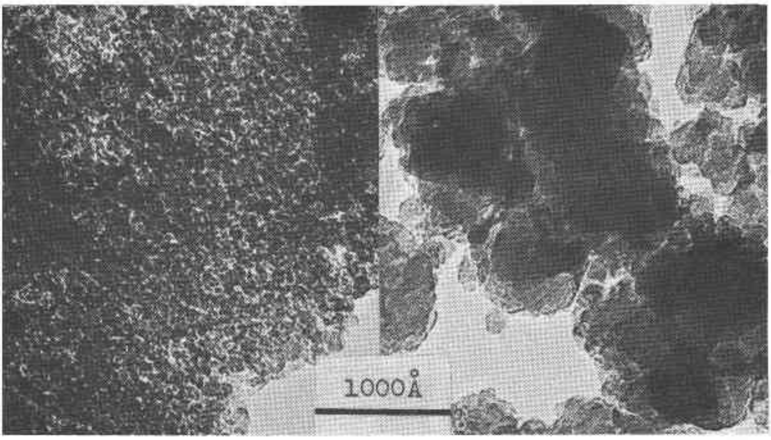
untreated ground

FIG. 3. Electron micrograph of Shichihonzakura specimen.

Specific gravity was determined with a pycnometer. To assure close contact with water, specimens were immersed in water for 24 hours before filling to the volume.

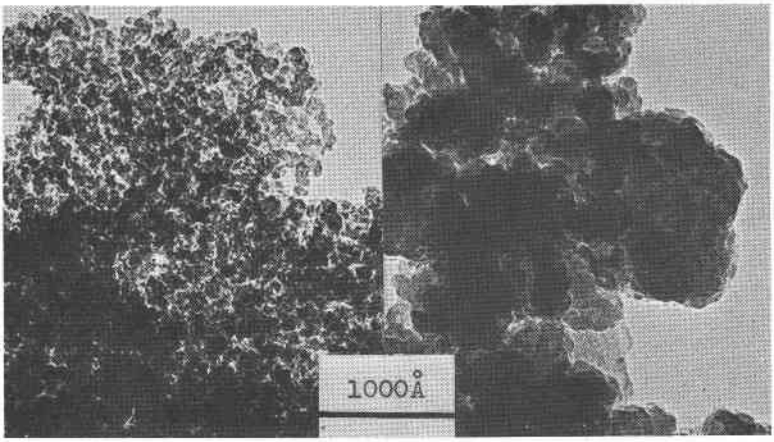
RESULTS AND DISCUSSION

Electron micrographs of high magnification of each allophane are shown in Figures 1–5, and that of coprecipitated silica-alumina gel in Figure 6. In these photographs, the left side represents untreated specimens, while the right side represents ground ones. In the electron micro-



untreated ground

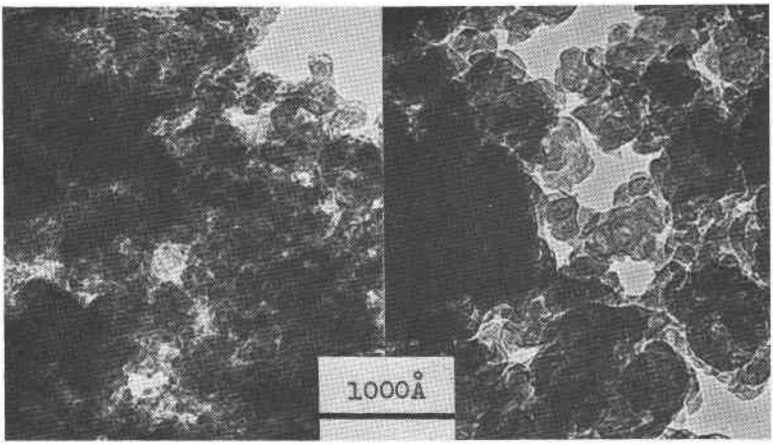
FIG. 4. Electron micrograph of Misotsuchi specimen.



untreated ground

FIG. 5. Electron micrograph of Kurosawajiri specimen.

graphs of untreated allophane specimens, it is clearly seen that allophane is the aggregate of fine particles suggested by Birrell and Fieldes (1952) and Watanabe and Sudo (1969), and it seems that these particles are hollow. Further, the electron micrographs of the ground specimens indicate that when the fine particles of allophane are collapsed, they join together and form thin films. In this respect, Watanabe and Sudo also found in a small-angle X-ray scattering analysis that the size of allophane particles is increased by grinding. Figure 6 shows that coprecipitated



untreated ground

FIG. 6. Electron micrograph of coprecipitated silica-alumina gel.

silica-alumina gel is also composed of fine particles, and, although the particles were joined to each other by grinding, the size of the particles seems to be significantly larger than those of allophane.

Twenty particles of allophane or silica-alumina gel were selected at random from visual fields of electron micrographs of untreated specimens, and their particle sizes were measured individually (Table 2). In allophane, the maximum was 58 Å (from Kanumatsuchi); the minimum was 53 Å (from Shichihonzakura and Kurosawajiri); and average value of allophanes was 55 Å. Fairly good agreement was obtained among allophanes. This value also corresponds with the numerical value of several tens of angstroms estimated by Watanabe and Sudo. On the other hand, in the coprecipitated silica-alumina gel, the particle diameter was 107 Å, which is nearly double that of allophane. It appears that the size of gel particle may be affected by the concentration of the solution from which it is prepared, but this point remains unsolved for future investigation. The results of observations by electron micrography correspond fairly well with the estimations from specific surface area and specific gravity determinations which will now be discussed.

TABLE 2. THE FINE PARTICLE SIZE OF ALLOPHANE AND COPRECIPITATED SILICA-ALUMINA GEL MEASURED FROM ELECTRON MICROGRAPH, AND CALCULATED FROM SPECIFIC SURFACE AREA AND DENSITY

	Measured Å	Calculated Å
Allophane		
Kanumatsuchi	58±4	58
Imaichitsuchi	55±4	53
Shichihonzakura	53±4	52
Misotsuchi	56±4	52
Kurosawajiri	53±4	50
Mean of allophanes	(55)	(53)
Silica-alumina gel	107±19	102

The specific surface areas of allophanes and coprecipitated silica-alumina gel are shown in Table 3. In the table, Kanumatsuchi has the lowest value of 542 m^2/g among allophanes, while Kurosawajiri has the highest of 632 m^2/g, and the average value of allophanes was 598 m^2/g. On the other hand, silica-alumina gel has a value of 287 m^2/g which is only half that of the average value of allophane. When these specimens were ground, the specific surface area of allophane was found to be only about 70 percent of the untreated ones, and, in gel, it decreased to approximately 80 percent. Further, heating at 110°C, the specific surface area of allophanes and gel was decreased to about two thirds of untreated specimens. Decrease of the specific surface area of allophane by these treatments is basically due to the fact that allophane consists of extremely fine particles, which will be discussed later in detail. Kinter and Diamond (1960) reported a value of 424 m^2/g for the specific surface area of allophane separated from a volcanic ash soil in Japan. A little lower value than reported in the present study may be due to the sample preparation in an oven before the glycerol saturation of the specimens. Their value for the specific surface area corresponds fairly well with the value obtained after heating treatment, shown in Table 3. Egawa, Watanabe, and Sato (1955) measured the specific surface area of allophane separated from the Misotsuchi pumice bed by the ethyleneglycol retention method of Dyal and Hendricks, and obtained 828 m^2/g. This value is a little higher than the value in Table 3.

TABLE 3. SPECIFIC SURFACE AREA, PHOSPHORUS ABSORPTION VALUE IN AMMONIUM PHOSPHATE SOLUTION (0.274M, pH 7.0), ADSORBED WATER CONTENT, THEIR CHANGES BY GRINDING AND HEATING, AND SPECIFIC GRAVITY IN ALLOPHANE AND ARTIFICIALLY COPRECIPITATED SILICA-ALUMINA GEL

	Specific surface area[a] m^2/g			Phosphorus absorption value[a] P_2O_5mg/g			Adsorbed water[b] percent		Specific gravity
	Untreated	Ground	Heated	Untreated	Ground	Heated	Untreated	Ground	
Allophane									
Kanumatsuchi	542	390	393	71	75	73	19.1	14.2	1.92
Imaichitsuchi	598	437	388	99	92	91	23.4	16.7	1.90
Shichihonzakura	611	470	348	99	100	77	23.2	19.8	1.89
Misotsuchi	602	430	416	84	84	85	21.9	13.3	1.93
Kurosawajiri	632	485	378	70	74	71	17.8	15.0	1.91
Mean of allophanes	(598)	(443)	(384)	(85)	(85)	(79)	(21.1)	(15.8)	(1.91)
Silica-alumina gel	287	231	164	29	33	26	12.5	10.4	2.05

[a] Oven dry basis (at 110°C).
[b] Air dry basis.

According to the specific gravity of allophanes and coprecipitated silica-alumina gel shown in Table 3, the specific gravity of allophanes was 1.9 or so for all specimens, the average being 1.91; while that of gel was a little larger, 2.05. Birrell and Fieldes reported values of from 1.98 to 2.37 as specific gravity of allophane separated from volcanic ash soils in New Zealand, which are higher than the values obtained in this experiment.

Assuming that the fine particle of allophane referred to above is spherical, we can obtain the following relation between specific surface area, S (m^2/g); diameter of particle, D (Å); and density of particle, d (g/cm^3):

$$S = 6/dD \times 10^4$$

Since density practically agrees with the value of specific gravity, the diameter of fine particle of allophane may be calculated, as shown in Table 2, from the value of specific surface area and specific gravity, using this equation. These values correspond fairly well with those obtained from electron micrographs. The decrease of specific surface area of allophanes and coprecipitated silica-alumina gel by grinding is considered to be due to the fact that each fine particle is collapsed by the grinding pressure and then joined to others as was demonstrated in the electron-micrographic study. The decrease of the specific surface area by heating may be due to: (1) insufficient percolation of glycerol within the particles, where many cavities formed inside by the removal of water, and to (2) mutual joining of particles with others.

However, the values from phosphorus absorption measurements did not differ much between the ground or heated specimens and the untreated ones (Table 3). Consequently, it is suggested that the number of hydroxyl groups reached by phosphoric acid does not change even after grinding and heating. Specifically even when fine particles are joined to each other by grinding and heating, they may be bound by physical, not chemical, force. It should be more difficult for water and glycerol, which are physically adsorbed, to enter the spaces between particles when fine particles of allophane are joined to each other. Actually, the amount of absorbed water released at 110°C was decreased by grinding under the same air-dried condition as the untreated specimens (Table 3). Birrell and Fieldes (1952) pointed out the irreversible drying of volcanic ash soils. Misono, Terasawa, Kishita, and Sudo (1953) perceived the hysteresis between dehydration and rehydration of volcanic ash soils. Miyazawa (1966) studied the dispersion of microaggregates in volcanic ash soils by ultrasonic vibration and found the formation of stable microaggregate is accomplished by dehydration of allophane. These phenomena are thought to be the result of mutual joining of fine particles in the microaggregate of allophane by dehydration.

On the basis of the results discussed so far, I consider this fine particle to be the most fundamental particle in microaggregates of allophane and name it the "unit particle." This unit particle is the basis of my model.

THE MICROMORPHOLOGICAL MODEL OF ALLOPHANE

From the hollow spherical shape of fine particles of allophane in high magnification electron micrographs, it has been assumed that the unit

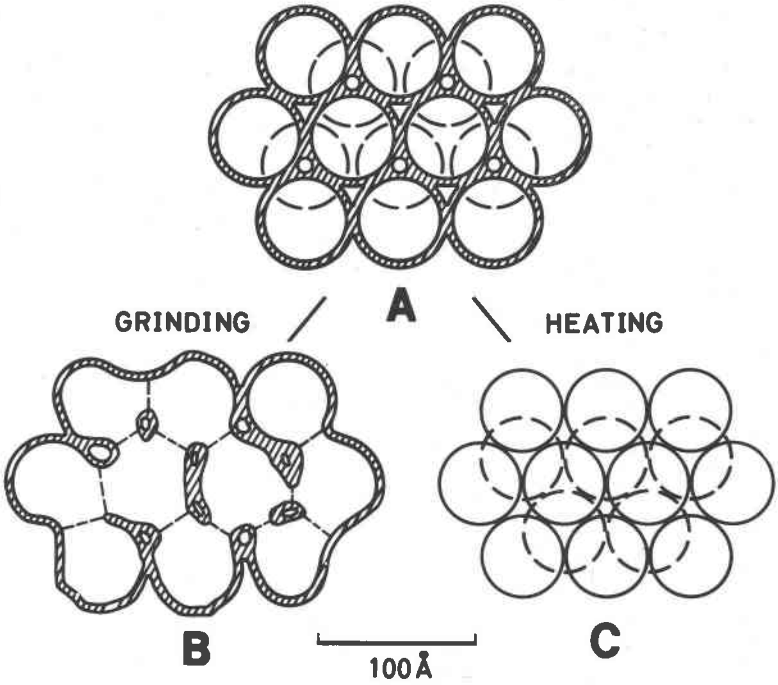


FIG. 7. Micromorphological model of allophane microaggregate. A: untreated, B: ground, c: heated. The oblique lines represent the water layer.

particle is spherical in form and that these spheres are close packed in the microaggregates. On this basis a model of the allophane microaggregate is constructed as illustrated in Figure 7: A shows the normal air-dried state; which undergoes changes, by grinding into B, and by heating into C.

Suppose that the diameter of the unit particle is 55 Å, the density of the particle is 1.9 g/cm^3, the water content of allophane is 20 percent, and that the unit particles have a close packed, adsorbed monolayer of water around them; then 13 percent of water in allophane is directly absorbed around the particles and the remaining approximate 7 percent fills the space existing among the particles under the air-dried condition at room temperature. However, since this water content is not enough to fill entirely the space among the close packed particles, bubbles will be formed there. In the case of close packing, two kinds of space, large *R* space and small *T* space, must be formed, and there must be large and small bubbles correspondingly, as shown in A of Figure 1. When moisture increases further than this air-dried level, there is more absorbed water, and the bubbles will disappear.

On grinding, the unit particle is collapsed by pressure, the water between particles is partially exuded, and the particles are mutually joined; that is, the bond is considered to be physical and not chemical. The exudation of water was observed by naked eye during the grinding of allophane specimens. Actually, this can be inferred also from the fact that the water contents of ground specimens are less than that of untreated specimens, as shown in Table 3.

The heating at 110°C released the absorbed water from the unit particle and the particles joined to each other as in C (This state is the same as observed in electron micrograph). It is supposed, however, that a little of the water remains in the space among the particles after they are joined. So far many investigators have observed by thermogravimetry that the water in allophane is released continually until considerably high temperature are reached. It is reasonable to consider that such a phenomenon is caused by the relative difficulty in removal of the adsorbed water from the particles and the concurrent release of structural hydroxyl groups of the particles.

Iimura (1970) pointed out, after determination of water content in allophane by the Karl-Fischer method, that the value obtained by this method show higher water content than the value obtained by the oven drying method at 110°C. This fact indicates that the water among the particles of an allophane microaggregate is not released efficiently on heating to 110°C.

In the present study, the micromorphological model of allophane was presented hypothetically. A more refined model may be obtained in the future by confirming the details of the size and shape of this particle with observations by electron micrography, studies on the surface properties by means of various adsorption technique, and especially by small-angle X-ray scattering.

ACKNOWLEDGMENTS

I wish to express gratitude to Prof. Toshio Sudo, Faculty of Science, Tokyo University of Education, for his helpful suggestions and critical reading of the manuscript; to Dr. Yutaka Watanabe, National Institute of Agricultural Sciences, who spared no trouble offering valuable advice; to Dr. Shingo Iwata and Mr. Toru Kubota, National Institute of Agricultural Sciences, for their kind discussions; and to Dr. Takashi Watanabe, Faculty of Science, Tokyo University of Education. Further, I wish to thank Mr. Masao Wada, Application Laboratory, Naka Works, Hitachi Ltd., for taking high magnification electron micrographs.

REFERENCES

BIRRELL, K. S., AND M. FIELDES (1952) Allophane in volcanic ash soils. *J. Soil Sci.* **3**, 156–166.

EGAWA, T. (1967) Progress in studies on allophane. *Nendo Kagaku* (*J. Clay Sci. Soc., Japan*) **6**, 13–19 [In Japanese].

———, AND Y. WATANABE (1964) Electronmicrographs of the clay minerals in Japanese soils. *Bull. Nat. Inst. Agric. Sci., Tokyo, Japan* **B14,** 173–182.

———, ———, AND A. SATO (1955) Studies on the clay minerals of some upland soils in Japan. *Bull. Nat. Inst. Agric. Sci., Tokyo, Japan* **B5,** 39–107. [In Japanese].

IIMURA, K. (1969) The chemical bonding of atoms in allophane, the "structural formula" of allophane. *Proc. Int. Clay Conf., Tokyo, 1969* **I,** 161–172.

——— (1970) An aspect on the water in allophane. *Abs. Ann. Meet. Soc. Sci. Soil Manure, Japan* **16,** 149 [In Japanese].

KINTER, E. B., AND S. DIAMOND (1958) Gravimetric determination of monolayer glycerol complexes of clay minerals. *Proc. Nat. Conf. Clays Clay Minerals* **5,** 318–333.

———, AND ——— (1960) Pretreatment of soils and clays for measurement of external surface area by glycerol retention. *Proc. Nat. Conf. Clays Clay Minerals* **7,** 125–134.

MISONO, S., S. TERASAWA, A. KISHITA, AND S. SUDO (1953) Studies on the soil water system of volcanic ash soils in Japan. *Bull. Nat. Inst. Agric. Sci., Tokyo, Japan* **B2,** 95–124 [In Japanese].

MITCHELL, B. D., V. C. FARMER, AND W. J. MACHARDY (1964) Amorphous inorganic material in soils. *Adv. Agron.* **16,** 327–383.

MIYAZAWA, K. (1966) Clay mineral composition of andosols in Japan, with reference to their classification. *Bull. Nat. Inst. Agric. Sci., Tokyo, Japan* **B17,** 1–100 [In Japanese].

ROSS, C. S., AND P. F. KERR (1934) Halloysite and allophane. *U.S. Geol. Surv. Prof. Pap.* **185G,** 135–148.

WADA, K. (1967) A structural scheme of soil allophane. *Amer. Mineral.* **52,** 690–708.

WATANABE, T., AND T. SUDO (1969) Study on small-angle scattering of some clay minerals. *Proc. Int. Clay Conf., Tokyo, 1969* **I,** 173–181.

Manuscript received, July 21, 1970; accepted for publication, November 23, 1970.