

# SHAPES OF HALLOYSITE PARTICLES IN JAPANESE CLAYS

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## ABSTRACT

Hydrated halloysite clays altered from glassy tuff during weathering were examined in detail by x-ray, thermal, and electron micrographic methods. The electron micrographs show fibrous crystals of hydrated halloysite associated with many rounded grains, the former frequently jutting out from the latter. X-ray powder diffraction data and thermal curves show clearly the presence of hydrated halloysite, and on closer examination dehydrated halloysite and a small amount of montmorillonite can be detected. The presence of allophane as an accessory mineral is suggested in certain specimens. Furthermore the degree of crystallinity of hydrated halloysite varies slightly from specimen to specimen. The variation of the degree of crystallinity of the hydrated halloysite and of the kinds and amounts of accessory clay minerals, and the variation of the shapes of the particles observed in the electron micrographs are generally related to each other. Hydrated halloysite of a relatively well-crystallized sort generally co-exists with halloysite (dehydrated) and consists of elongated crystals having sharp edges; rounded grains are composed entirely of these fibrous crystals. On the other hand, a poorly crystallized sort tends to be associated with allophane and to show extremely fine hairlike, twisted fibers; these are associated with well-defined rounded grains. A genetic process of clay-mineral formation from volcanic glass is considered.

## INTRODUCTION

In several earlier papers (Sudo, Minato, and Nagasawa, 1951; Sudo and Otsuka, 1952; Sudo, 1953, 1954) it has been shown that white clays largely composed of hydrated halloysite are frequently found as alteration products from Japanese vitric tuffaceous rocks. These clays show noteworthy properties in the electron microscope (Sudo, 1953). The writers studied these clays mineralogically by means of x-ray diffraction and, more recently, electron micrographs. The variations of the thermal, x-ray and electron micrographic properties are considered to be related to the degree of crystallinity of hydrated halloysite and also to the kind and amount of impurities (accessory clay minerals); furthermore they seem to suggest the course of crystallization of hydrated halloysite. The present study is related to the problem of the formation of clay minerals.

## EXPERIMENTAL

X-ray powder reflections were recorded by a Philips Geiger-counter x-ray spectrometer. The experimental conditions are as follows: filtered Cu radiation (Cu  $K\alpha$ : 1.5418 Å), 30 kv, 15 ma, scanning speed  $2^\circ 2\theta$  per minute, time con-

stant 4 seconds, receiving slit 0.006 inch, angular aperture  $1^\circ$ , goniometer radius 17 cm. The differential thermal analysis curves were recorded by the apparatus reported in an earlier paper (Sudo, Nagasawa, and others, 1952). The mean heating rate is  $10^\circ$  C per minute.

### REFERENCE SPECIMENS

X-ray diffraction data and differential thermal analysis curves of eight reference specimens are given in Figures 1 and 2 (2)-(9). For comparison, the x-ray spectrogram of hydrated halloysite from Joshin, Gumma Prefecture, is illustrated in (1) in Figure 1. Its mode of occurrence is different from those of the clays now under consideration; that is, it occurs as an alteration product from volcanic rocks and pyroclastics by hot-spring action related to the formation of the sulfur deposits at this locality. Its degree of crystallinity is considered to be higher than those of most of the other specimens. For comparison, the thermogram of allophane from Oya, Tochigi Prefecture, is illustrated in (10) in Figure 2. This specimen is an alteration product from pumice fragments that occur in beds at the earth's surface and/or intercalated in a shallow zone of volcanic ash soil ("Kwanto loam") in the Kwanto area. Its degree of crystallinity is distinctly lower than those of the specimens now under consideration.

### X-RAY AND THERMAL PROPERTIES (Figs. 1 and 2)

The thermal and x-ray data are summarized in Table 1. They are enumerated as follows: (a) Temperature,  $T$  of the second endothermic peak (between  $500^\circ$  and  $600^\circ$  C); (b) the ratio of the area of the second endothermic peak to that of a final exothermic peak ( $A_2/A_3$ ); (c) the ratio of the amplitude of a first endothermic peak to that of a second one ( $a_1/a_2$ ); (d) the ratio of the intensity of the 001 line (10 Å) to that of the 02, 11 line ( $I_{001}/I_{02, 11}$ ); (e) the ratio of the intensity of the 02, 11 line to that of the 13, 20 line ( $I_{02, 11}/I_{13, 20}$ ); and (f) the ratio of the particle size measured from the half-breadth value of the 001 line (10 Å) to that measured from the 02, 11 line ( $L_{001}/L_{02, 11}$ ). Furthermore the ratio of the ignition loss below  $200^\circ$  C to that above  $200^\circ$  C ( $i_1/i_2$ ) was taken into account.

The area of the thermal peaks was measured by a planimeter.  $L_{001}$  was calculated from Jones' (1938) formula, and  $L_{02, 11}$  and  $L_{13, 20}$  from Warren's (1941) formula.

### ACCESSORY CLAY MINERALS

The presence of any clay mineral other than hydrated halloysite is not clearly detected by close examination of the thermograms. However, montmorillonite is faintly suggested in certain specimens (6 and 9), as indicated by a trace of an endothermic peak at about  $700^\circ$  C.

The x-ray powder diagrams confirm the presence of halloysite (dehydrated) in certain specimens, as (1) to (6). Among these, four specimens show the 001 line (about 7 Å) and the 003 line (2.5 Å), although the 002 line is not clearly observed because of the overlapping effect of the quartz line. In the diagrams of the remaining two specimens, (1) and (6), the 003 line can be identified, but the 001 line is not obvious; probably it is concealed by a diffuse back-

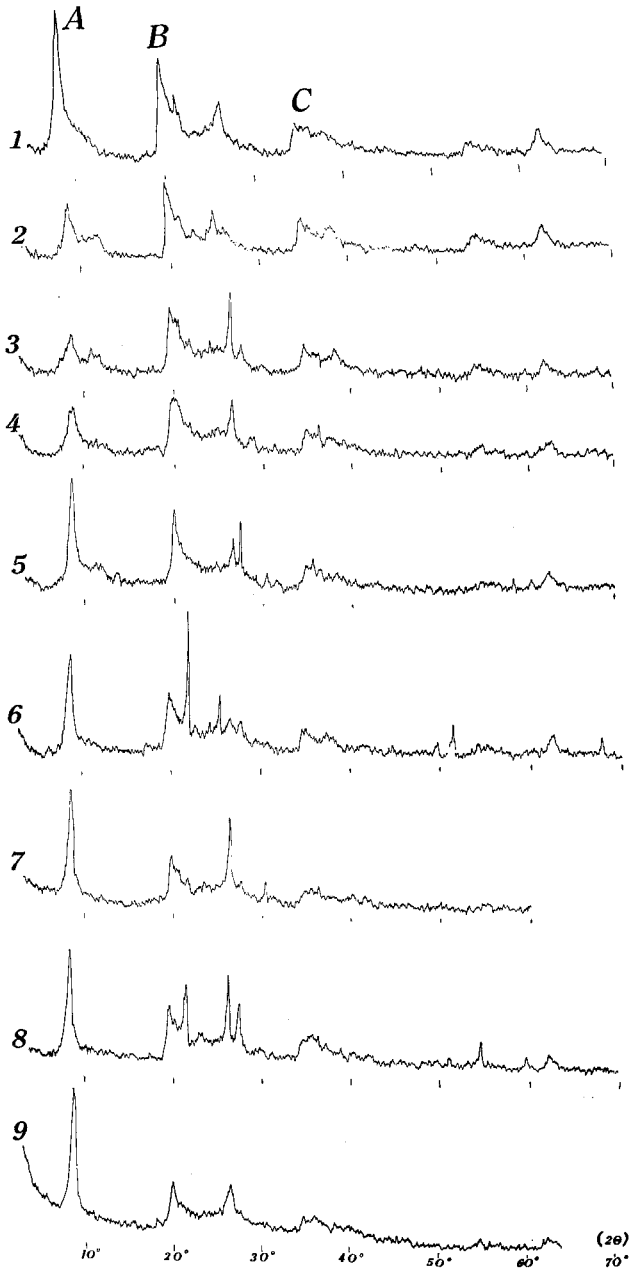


FIGURE 1.—X-ray spectrograms of some hydrated halloysite samples. Each numeral corresponds to that in Table I. A: 001. B: 02, 11. C: 13, 20.

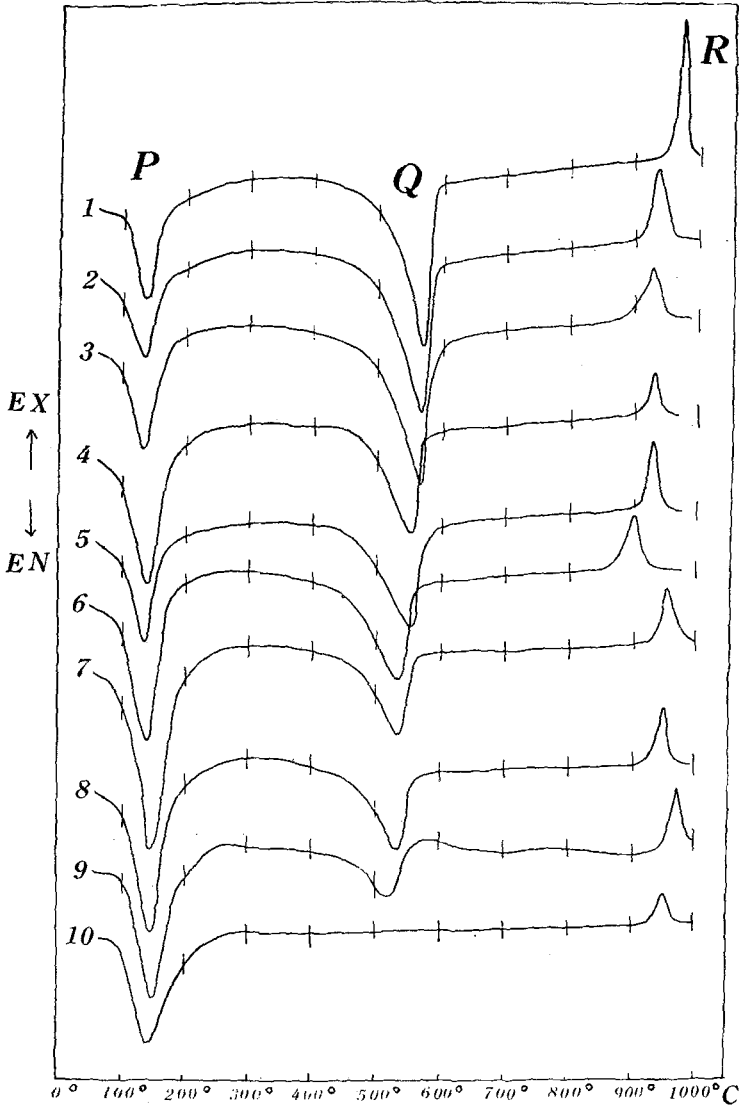


FIGURE 2. — Thermograms of some hydrated halloysite samples and of allophane from Oya. Each numeral corresponds to that in Table 1. P: first endothermic peak. Q: second endothermic peak. R: final exothermic peak.

TABLE I.—X-RAY, THERMAL, AND ELECTRON MICROGRAPHIC PROPERTIES OF HYDRATED HALLOYSITE CLAYS (ARRANGED ACCORDING TO TEMPERATURE OF SECOND ENDOTHERMIC PEAK)

Sample no.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
X-ray properties									
$I_{001}$	107	41	29	37	81	77	80	80	95
$I_{02, 11}$	75	55	48	43	59	48	37	41	38
$I_{13, 20}$	25	26	24	22	20	19	12	20	15
$I_{001}/I_{02, 11}$	1.4	0.7	0.6	0.9	1.4	1.6	2.2	2.0	2.5
$I_{02, 11}/I_{13, 20}$	3.0	2.1	2.0	2.0	2.9	2.5	3.1	2.0	2.5
$L_{001}$	187	82	70	70	128	104	137	134	137
$L_{02, 11}$	123	154	107	90	133	105	142	104	114
$L_{001}/L_{02, 11}$	1.52	0.53	0.72	0.78	0.96	0.99	0.96	1.28	1.20
$I_H$	vw	w	w	vw	vw	vw	0	0	0
$I_M$	—	—	—	—	—	vwv	—	—	vwv
Thermal properties									
$T, ^\circ\text{C}$	571	570	568	558	553	536	536	531	518
$A_2$	6.0	6.0	6.3	3.5	4.1	4.6	3.2	3.2	2.7
$A_3$	1.3	1.3	1.1	0.6	1.0	1.1	1.0	0.9	0.8
$A_2/A_3$	4.6	4.6	5.3	5.8	4.2	4.2	3.2	3.6	3.4
$a_1$	3.0	2.7	3.3	4.2	3.2	4.8	6.0	4.7	4.4
$a_2$	5.3	5.0	4.8	3.2	3.2	3.1	2.6	2.5	1.7
$a_1/a_2$	0.6	0.5	0.7	1.3	1.0	1.6	2.3	1.9	2.6
$i_1$	7.91	9.37	7.64	10.61	9.08	10.54	18.88	12.72	22.26
$i_2$	13.11	12.58	10.95	13.24	10.37	11.12	12.76	9.12	11.30
$i_1/i_2$	0.61	0.78	0.70	0.80	0.87	0.95	1.48	1.39	1.97
Electron micro. prop.									
Diam.	—	0.1-0.2	0.2-0.4	0.1-0.2	0.1-0.3	0.1-0.3	0.1-0.2	0.1-0.2	0.05-0.1
Length	—	0.1-0.2	0.1-0.2	0.1-0.2	0.1	?	0.1	0.1-0.2	0.05-0.1

(1) Joshin clay, Gumma Prefecture; (2) Tsukinokawa clay, Nagasaki Prefecture; (3) Taneichi clay (brown color), Iwate Prefecture; (4) Hachinohe clay, Aomori Prefecture; (5) Yame clay, Fukuoka Prefecture; (6) Shichinohe clay, Aomori Prefecture; (7) Imaichi clay, Tochigi Prefecture; (8) Taneichi clay (white color), Iwate Prefecture; (9) Shizukishi clay, Iwate Prefecture.

Specimens (2) to (9) are alteration products from vitric tuffaceous rocks (mostly by weathering processes) and are the principal subject of the present study. Specimen (1) is considered to be an alteration product from tuffaceous and volcanic rocks, mostly by hot-spring action; the data are included in this table for comparison.

$I_{001}$ : Intensity of the 001 reflection measured from the peak height.

$I_{02, 11}$ : Intensity of the 02, 11 reflection measured from the peak height.

$I_{13, 20}$ : Intensity of the 13, 20 reflection measured from the peak height.

$L_{001}$ : Particle size measured from the half-breadth value of the 001 reflection.

$L_{02, 11}$ : Particle size measured from the half-breadth value of the 02, 11 reflection.

$I_H$ : Intensity of the 001 reflection of halloysite (dehydrated).

$I_M$ : Intensity of the 001 reflection of montmorillonite.

$T, ^\circ\text{C}$ : Temperature of the second endothermic peak.

$A_2, A_3$ : Areas of the second endothermic peak and final exothermic peak respectively.

$a_1, a_2$ : Amplitudes of the first endothermic peak and the second endothermic peak respectively.

$i_1, i_2$ : Ignition losses below  $200^\circ\text{C}$  and above  $200^\circ\text{C}$  respectively.

Diam.: Diameter of rounded grains (in microns).

Length: Length of elongated crystals of halloysite minerals (in microns).

ground developed on the higher-angle side of the 10 Å line. A clear indication of montmorillonite is difficult to obtain from these x-ray spectrograms; however, a very weak reflection at about 14 Å in (6) and (9) may be due to montmorillonite. The thermograms of the specimens treated by piperidine increased the indication of an exothermic peak between 600° and 700° C, which is considered to indicate the presence of montmorillonite (Sudo, 1953a, 1954). These exothermic effects were observed in specimens (4) and (9). However, it is difficult to detect the montmorillonite reflection in the x-ray diagrams of specimen 4.

The shape of the final exothermic peak is rather asymmetric, and in some instances it is double (not illustrated) as in the thermogram of specimen (7), which is considered to be free from halloysite (dehydrated) and montmorillonite. This may suggest the presence of allophane, an amorphous or nearly amorphous material. Its x-ray diffraction pattern shows only a very diffuse band between 3 Å and 4 Å (about 3.7 Å); its thermogram is composed of a strong endothermic peak between 100° and 200° C and a final exothermic peak between 900° and 1000° C; and its electron micrograph shows extremely fine particles (0.02 microns in mean diameter). Allophane as such is commonly associated with the clays now under consideration (Fig. 2, specimen 10).

#### RELATIONS BETWEEN THERMAL AND X-RAY PROPERTIES

Referring to the data listed in Table I, we see that any one of these thermal and x-ray properties maintains correlative relationship with the others.

(a) The ratio  $I_{001}/I_{02, 11}$  gradually increases with decrease of temperature  $T$ , whereas the ratio  $I_{02, 11}/I_{13, 20}$  remains almost constant.

(b) The ratio  $L_{001}/L_{02, 11}$  clearly increases as the temperature  $T$  decreases. This shows that the unit particle of hydrated halloysite varies from nearly flat in the (001) plane, through a cubical shape, toward a relatively elongated form along the  $c$ -axis, with decrease of temperature  $T$ .

(c) The decrease of temperature  $T$  is correlated with the decrease of the ratio of the area of the second endothermic peak to that of the final exothermic peak, ( $A_2/A_3$ ), and also with the increase of the ratio of the amplitude of the first endothermic peak to that of the second endothermic peak, ( $a_1/a_2$ ).

(d) The decrease of temperature  $T$  is also correlated with the increase of the ratio of the ignition loss below 200° C to that above 200° C ( $i_1/i_2$ ).

#### CAUSES OF THE VARIATIONS

These variations are thought to be caused by the kind and amount of impurities, but the writers believe that the variation of the degree of crystallinity of hydrated halloysite also plays an important role.

(1) The variation of the ratio ( $I_{001}/I_{02, 11}$ ) may be caused by the variation in the amount of included halloysite (dehydrated). Specimens (1) to (6), in which the presence of halloysite (dehydrated) is confirmed by x-rays, show a lower ratio than the other specimens. However, the writers consider that the variation of this ratio is caused not only by the presence of halloysite (dehydrated) but also by variation in the structure of the hydrated halloysite itself. The amount of halloysite (dehydrated) is always small, and furthermore it shows

no tendency to increase as the temperature of the second endothermic peak decreases (Table 1 and Figs. 1 and 2). Nevertheless, the ratio ( $I_{001}/I_{02, 11}$ ) clearly increases with decrease in temperature  $T$  in these tables and figures. Particularly, the 02, 11 line is weak in the x-ray spectrograms of (8) and (9). If the increase of the ratio ( $I_{001}/I_{02, 11}$ ) is caused by disorder in the crystal of hydrated halloysite, the following kind could be considered, namely the ratio increases when the periodicities along the  $a$ - and  $b$ -axes are more disordered than along the  $c$ -axis.

(2) The variation in particle size of hydrated halloysite is not affected by the presence of other minerals. Accordingly, this variation is considered to be related to the degree of crystallinity as mentioned above. When the periodicities within the (001) plane are more disordered than that of piling up of layers, the development of crystallites is expected to be more restricted parallel to the (001) plane than along the direction of the  $c$ -axis.

(3) The variation of the thermal curves is caused by the kind and amount of accessory minerals other than hydrated halloysite. The presence of halloysite (dehydrated) along with hydrated halloysite may cause the decrease of the first endothermic peak and increase of the temperature of the second endothermic peak; these facts are clearly observed in the thermogram from the specimen in which the presence of halloysite (dehydrated) was confirmed by x-rays; that is, the first endothermic peak is smaller, and the temperature of the second endothermic peak is higher in specimens (1) to (6). The presence of allophane along with hydrated halloysite may be expected to cause the decrease of the ratio  $A_2/A_3$  and also the increase of the first endothermic peak. The presence of allophane is suggested in (7) from the shape of the last exothermic peak, noted previously.

On the other hand, the variation of the degree of crystallinity of hydrated halloysite may reflect upon the variation of the thermal peaks. The lower degree of crystallinity may cause the following variations: the increase of the first endothermic peak because of the increase of the adsorbed water on minute crystallites, the decrease of sharpness, temperatures, areas, and amplitudes of the second endothermic peak and the final exothermic peak. These features are in harmony with the trend shown from samples (1) to (9) in Table 1 and Figures 1 and 2. In this case, however, it is not certain whether the decrease in degree of crystallinity is the only factor relating to the decrease in  $A_2/A_3$ .

In conclusion it seems that slight variations of x-ray and thermal properties of these clays are related to the kind and amount of accessory clay minerals and also to the variation of degree of crystallinity of hydrated halloysite itself. This conclusion is in harmony with the data from electron micrographs.

## ELECTRON MICROGRAPHS

The electron micrographs of the clays are all similar; that is, rounded grains are closely associated with elongated crystals of halloysite minerals. Generally speaking, elongated crystals of halloysite minerals commonly jut out from a central rounded grain forming a chestnut shell-like shape. The numerical ratio of rounded grains to elongated crystals seems to be greater in the lower-numbered specimens illustrated in Table 1 and Figures 1 and 2. On close examination these micrographs can be classified into the following types:

Type 1: Tsukinokawa clay (Fig. 3, A), Taneichi (brown) clay (Fig. 3, B), and Hachinohe clay (Fig. 3, C). Elongated crystals of halloysite minerals have sharp edges whereas the outlines of the rounded grains are not well defined. In the Taneichi brown clay, radial aggregates of fibrous crystals ((a), in Fig. 3, B) of halloysite seem to predominate over rounded grains. In the Hachinohe clay, most of the rounded grains show collapsed forms (a, b, c, d, in Fig. 3, C), which reveal that these grains are composed entirely of fibrous crystals of halloysite minerals.

Type 2: Yame clay (Fig. 4, D) and Shichinohe clays (Fig. 4, E). Elongated crystals are not so predominant as in Type 1. Rounded grains are commonly well defined and many of them have polyhedral outlines. In the Shichinohe clay, grains commonly have irregular outlines and thin film-like materials are associated with them (a, in Fig. 4, E).

Type 3. Taneichi (white) clay (Fig. 4, F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>) and Imaichi clay (Fig. 5, G). Elongated crystals are associated closely with well-defined rounded grains. Elongated crystals have less sharply defined edges in Type 1; some of them show aggregates of twisted fibers or curled hairs ((a) in Fig. 4, F<sub>3</sub>) and frequently they jut out from a central grain in nearly radial manner. Rounded grains commonly have well-defined outlines, and some of them show a concentric structure suggesting that each is composed of a crust and a core.

Type 4: Shizukuishi clay (Fig. 5, H<sub>1</sub>, H<sub>2</sub>). Elongated crystals and rounded grains are much smaller than in the other types. Elongated crystals appear mostly as twisted fibers or curled hairs; rounded grains having concentric structure, which appears, as in Type 3, as if each grain is composed of a crust and core ((a) (b) (c) in Fig. 5, H<sub>2</sub>). In Type 4 rounded grains reveal their inner textures because of their small size; these textures suggest that each grain is composed of extremely fine, entangled fibrous crystals or of extremely fine dot-like particles.

Summarizing the above descriptions, the following general facts are obvious.

(1) The sizes of rounded grains and of elongated crystals are of similar order of magnitude throughout, except in specimen (9). Furthermore, in each sample, the mean length of elongated crystals is similar in magnitude to the mean diameter of rounded grains; the shorter the length, the smaller the diameter.

(2) Elongated crystals of hydrated halloysite which are considered on the basis of x-ray and thermal data to be relatively well crystallized, have sharp edges, whereas those thought to be relatively poorly crystallized appear as extremely fine twisted fibers or curled hairs. It seems natural to consider that such differences in the shapes of elongated crystals reflect the difference in degree of crystallinity of halloysite minerals in the clays.

(3) Rounded grains associated with sharp-edged elongated crystals commonly show collapsed forms which suggest that they seem to be composed entirely of elongated crystals of halloysite minerals. On the other hand, rounded grains associated with extremely fine fibrous crystals are commonly well defined and have well-defined rounded shapes, polyhedral outlines, or concentric textures.

In the micrographs it is very difficult to identify halloysite (dehydrated) and allophane. It is expected that halloysite (dehydrated) crystals show a similar shape to those of hydrated halloysite excepting that the terminal por-



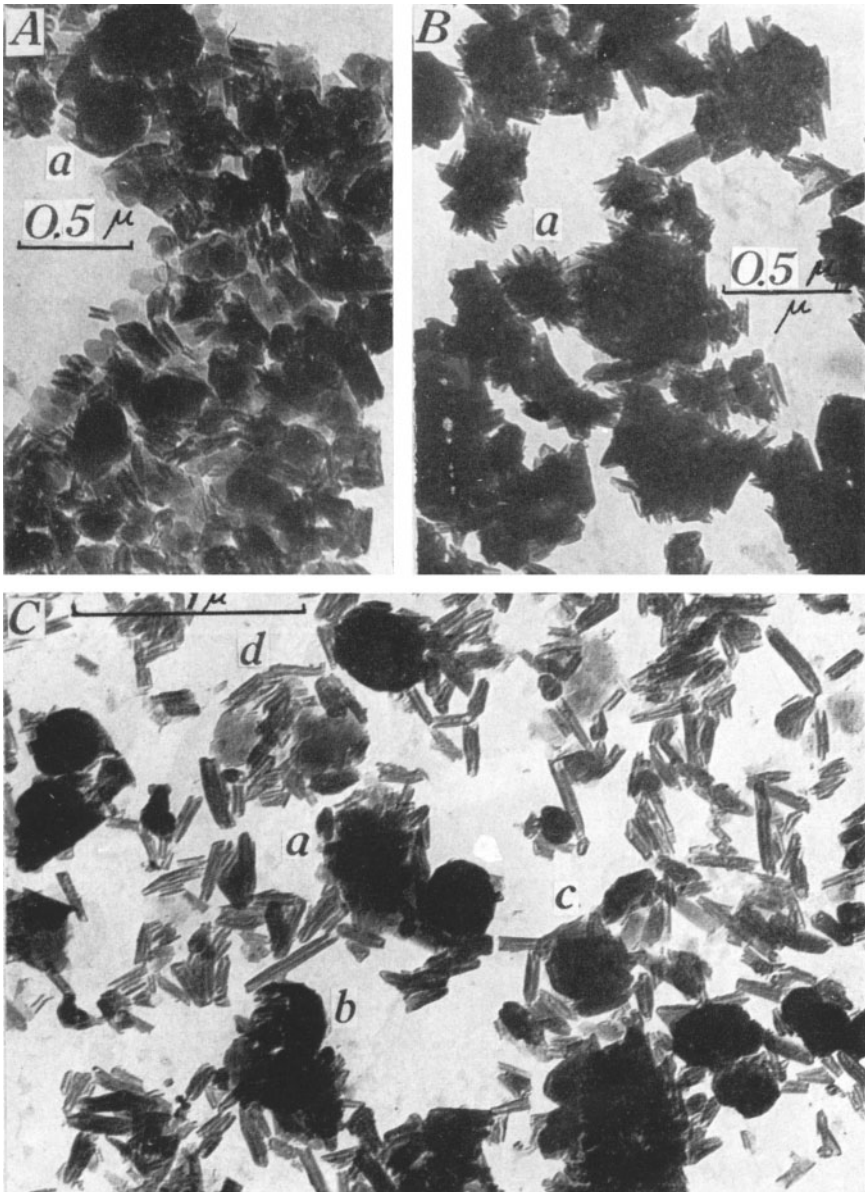


FIGURE 3.— Electron micrographs. A, Tsukinokawa clay. B, Taneichi (brown) clay; a, radial aggregates of elongated crystals. C, Hachinohe clay; a, b, c, d, collapsed form of rounded grains.

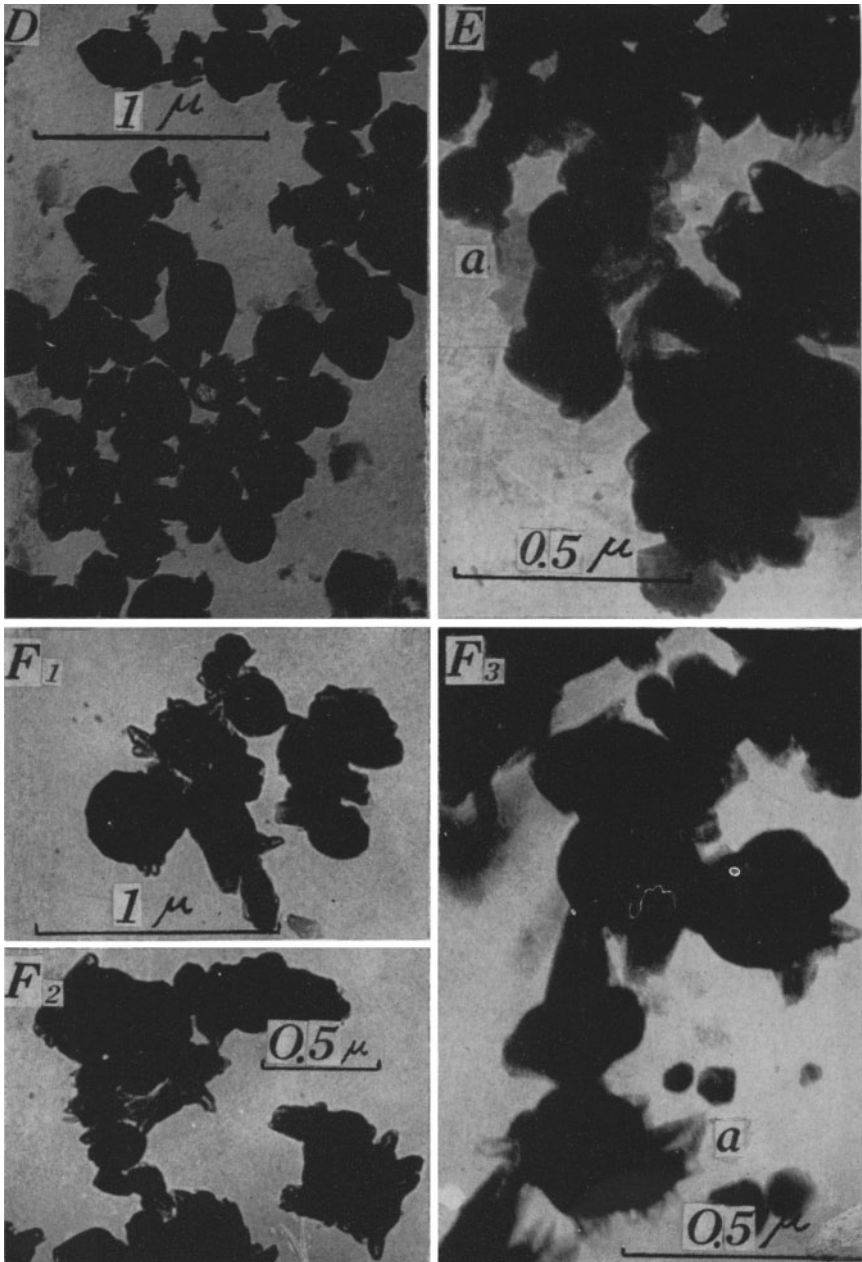


FIGURE 4. — Electron micrographs. D, Yame clay. E, Shichinohe clay; a, material having a thin film-like appearance. F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, Taneichi (white) clay; a, very fine fibrous hairlike crystals.

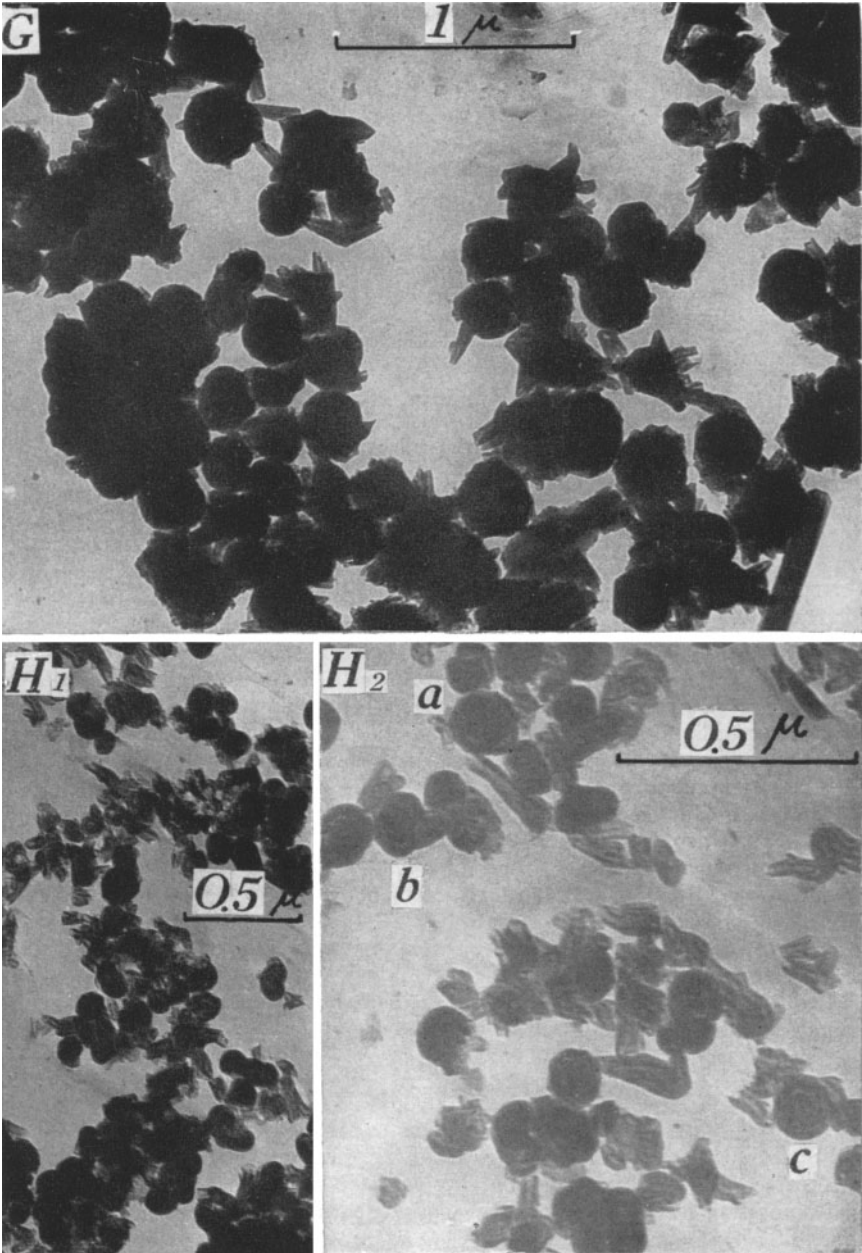


FIGURE 5.— Electron micrographs. G, Imaichi clay. H<sub>1</sub>, H<sub>2</sub>, Shizukuishi clay; a, b, c, rounded grains apparently composed of a crust and a core.

tions of some of the tubular crystals are collapsed. It has been reported that allophane shows rounded shapes. However, in the present study, it is definitely overhasty to conclude that rounded grains are entirely allophane, for the following reasons: the mean size of these rounded grains is considerably greater than that of allophane associated with these clays (Fig. 2 (10)). Most of these rounded grains are clearly at least in part composed of elongated crystals or extremely fine fibrous crystals of halloysite minerals. However, the writers believe that the rounded shape may be genetically related to the presence of an amorphous material such as allophane, which might have existed in the past and might still be intimately mixed with extremely fine fibrous crystals of halloysite mineral in the rounded grains.

#### IMPLICATION CONCERNING FIELD OF FORMATION OR DECOMPOSITION OF CLAY MINERALS

In conclusion, the writers suggest the following concept. It seems likely that the variations in hydrated halloysite (the principal mineral component of the clays) and the variations in kind and amount of accessory clay minerals are not caused by arbitrary, independent, and different factors, but are caused by differences in origin, because the following relationships can be observed: hydrated halloysite of a well-crystallized sort is likely to co-exist with halloysite (dehydrated), and a poorly crystallized sort tends to co-exist with allophane.

The writers suggest the following interpretation: The slightly different mineralogical properties of the clays may represent the different stages of the course of crystallization of volcanic glass to clay minerals, as volcanic glass, allophane, hydrated halloysite, and halloysite (dehydrated). In the initial stage, extremely fine particles of allophane (0.02 microns in mean diameter) will coagulate into rounded grains. Gradually, each of these rounded grains will change into an aggregate of hydrated halloysite with a low degree of crystallinity and having shapes like twisted fibers or curled hairs. With progressive crystallization, extremely fine fibers will have sharp edges and rounded grains will change into aggregates consisting entirely of well-crystallized halloysite minerals. As crystallization advances further, some of the crystals of hydrated halloysite will change into the dehydrated form with an accompanying higher degree of crystallinity.

The writers consider that the electron micrographs may show an initial stage in the formation of clay minerals.

Recently Kinoshita and Muchi (1954) obtained similar data for several clays from Kyushu.

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