Structural Variations of Kaolin Minerals

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Kaolin minerals are made of stacking of aluminosilicate unit layers in their crystal structure. However, there are a continuous gradation in the manner of stacking from kaolinite which has a perfectly ordered sequence of layers to halloysite which has a throughly disordered sequence of layers.[1]

In the results given by Murray, the degree of crystallinity determined by using the X-ray powder diffraction data does not agree with that based on the differential thermal analysis curve of halloysite.[2] When one say the degree of crystallinity, however, there are two kinds of structural imperfection. One is the imperfections within the crystallographic unit layer and the other is the stacking disorder of the unit layers. As the definition of the crystallinity, both kinds of imperfection should be considered.

The purpose of this study is to determine the degree of crystallinity for all kaolin minerals through X-ray, thermal and other experimental methods, and to get some fundamental information for the relationship between structural characteristics and physico-chemical properties.

Results and Discussion

Samples.—The following kaolin minerals were investigated: Kaolinite from Mesa Alta, N.M., U.S.A., Kaolinite from Drybranch, Geor., U.S.A. The both materials are the API Standard Clay Minerals. Kibushi-clay from Shidare, Gifu, Japan which is a kaolin of fireclay type. Halloysite from Spruce Pine, N.C., U.S.A. which is the API Standard Clay Mineral and is considered to have the highest degree of crystallinity from the result of study through electron diffraction[3]. Halloysite from Bedford, Ind., U.S.A. which is the API Standard Clay Mineral. Halloysite from Tintic, Utah, U.S.A. which is the API Standard Clay Mineral. Shichinoe-clay from Shichinoe, Aomori, Japan which is known to have a considerably low degree of crystallinity among halloysites[4].

X-Ray Diffraction Studies.—From the investigation made by Brindley and Robinson, it was clarified that kaolin minerals are characterized by the stacking randomness in their structure. Their X-ray diagrams indicate the structural variations in kaolin minerals. To determine the relative degreee of crystallinity of kaolin minerals, in the present study, the criteria used by Brindley and Robinson, and some additional features found by Murray were used.

X-ray powder diffraction diagrams of kaolin minerals were obtained by X-ray diffractometer (Geigerflex). Halloysites were treated at 110°C in order to dry up the inter-layer water, this might result to have approximately the same basal spacing as in kaolinites. All specimens were ground, dried, and then sieved through 300 mesh. Experimental conditions were as follows: Filtered Cu radiation (Cu $K\alpha$: 1.5418 Å) is used at 35 kV and 15 mA, scanning speed is 1° or 1/4° 2θ per minute, time constant is 4 seconds, receiving slit is 0.2 mm or 0.1 mm, angular aperture is 1° or 1/2°.

To determine the degree of crystallinity in the X-ray diagram, the following major differences were used as criteria.

(1) Sharpness of the reflections.
(2) Number of reflections.
(3) Slight change in the basal spacing.
(4) Resolution between closely spaced reflections.
(5) Absence of certain reflections.

X-ray diffractometer traces of kaolin minerals are shown in Fig. 1. The X-ray reflections of kaolinites are sharp and distinct, and those of Spruce Pine halloysite are considerably sharp. For all other kaolin minerals, X-ray reflections are relatively broad and diffuse. These diffractometer records were made carefully by repeating the X-ray traces of specimens. It is also observable that the sharpness of reflections is dependent on particle size and orientation.

In the experiments, the specimens were prepared not to be oriented and particles of almost the same size were used, accordingly the effects of these factors might be

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[1] G. W. Brindley and K. Robinson, *Trans. Farad. Soc.*, **42B**, 198 (1946); S. Iwai, *Min. J.*, **1**, 233 (1955).

[2] H. H. Murray, *Am. Mineral.*, **39**, 97 (1954).

[3] G. Honjo and K. Mihama, *Acta Cryst.*, **7**, 511 (1954).

[4] T. Sudo and H. Takahashi, "Proc. Fourth Conference on Clay and Clay Minerals", National Academy of Science-National Research Council, 1956, p, 67.

TABLE I

POWDER DATA OF KAOLIN MINERALS (in Å)

Brindley and Robinson			Kaolinite				Kibushi-Clay		Halloysite							
			Mesa Alta, N.M.		Drybranch, Geor.		Shidare, Gifu		Spruce Pine, N.C.		Bedford, Ind		Tintic, Utah		Shichinoe, Aomori	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
7.15	10+	001	7.14	VS	7.15	VS	7.20	S	7.15	VS	7.25	S	7.30	S	7.40	M
4.45	4	020	4.46	M	4.45	S	4.45	MS br	4.44	S	4.45	S	4.46	S	4.47	S
4.35	6	$1\bar{1}0$	4.35	S	4.36	M	4.33	W								
4.17	6	$11\bar{1}$	4.18	S	4.17	M										
4.12	3	$1\bar{1}\bar{1}$	4.13	W												
3.837	4	$0\bar{2}1$	3.84	M	3.86	W										
3.734	2	021	3.73	W	3.74	WV										
3.566	10+	002	3.57	VS	3.58	VS	3.58	S	3.57	VS	3.63	MS	3.64	MS	3.66	M
3.365	4	111	3.37	M	3.37	. W										
3.138	2	$11\bar{2}$	3.14	W												
3.091	2	$1\bar{1}\bar{2}$	3.09	W												
2.748	2	022	2.75	W	2.74	W										
2.553	8	$20\bar{1}, 1\bar{3}0, 130$	2.55	MS	2.56	MS	2.56	M br	2.56	M	2.57	W br	2.57	W br	2.57	W br
2.521	4	$13\bar{1}, 1\bar{1}2$	2.53	M	2.53	W	2.53	W br	2.53	W						
2.486	9	$1\bar{3}\bar{1}, 200, 112$	2.49	S	2.49	MS	2.50	VW br	2.49	M						
2.374	7	003	2.37	M	2.38	M	2.38	M br	2.38	M						
2.331	10	$20\bar{2}, 1\bar{3}1, 11\bar{3}$	2.33	S	2.34	S	2.34	VW br	2.33	M	(2.37	W br)	(2.37	W br)	(2.38	W br)
2.284	9	$1\bar{1}\bar{3}, 131$	2.29	MS	2.29	M			2.29	W						
2.243	1	$13\bar{2}, 040$	2.24	W	2.24	VW										
2.182	3	$13\bar{2}, 220$	2.18	W	2.18	W	2.20	VW	2.20	W						
2.127	2	$02\bar{3}, 041$	2.13	W												
2.057	1	$2\bar{2}\bar{2}$	2.06	W												
1.985	7	$20\bar{3}, 1\bar{3}2$	1.992	S	1.990	S	1.992	M	1.997	MS						
1.935	4	132, 221	1.941	M	1.936	M	1.90	W br								
1.892	2	$13\bar{3}$	1.902	W	1.898	W										
1.865	1	042	1.862	W												
1.835	4	$1\bar{3}\bar{3}, 202, 22\bar{3}$	1.840	M	1.840	W										
1.805	1	$11\bar{4}, 2\bar{2}\bar{3}$	1.810	W												
1.778	5	004	1.782	M	1.790	M	1.79	W br			1.80	W br			1.78	W br
1.704	1	$2\bar{2}2$	1.702	W												
1.682	2	$1\bar{5}0, 24\bar{1}, 31\bar{1}, 3\bar{1}\bar{1}, 222$	1.684	W	1.688	W										
1.659	8	$2\bar{4}0, 15\bar{1}, 20\bar{4}, 1\bar{3}3$	1.664	S	1.668	S	1.65	M br	1.670	MS	1.68	W br	1.68	W br	1.67	W br

Key to abbreviation: VS: very strong, S: strong, MS: medium strong, M: medium, W: weak, br: broad.

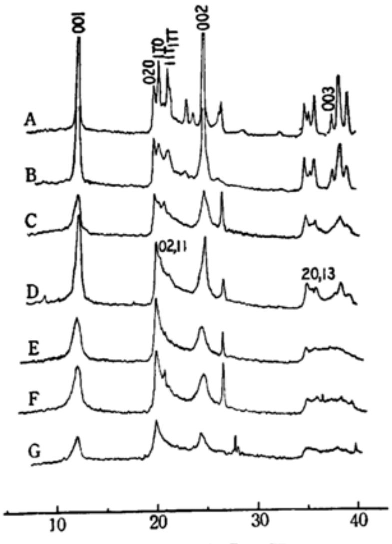

Fig. 1. X-ray diffractometer traces of kaolin minerals.
A, kaolinite, Mesa Alta, N.M., U.S.A.
B, kaolinite, Drybranch, Geor., U.S.A.
C, Kibushi-clay, Shidare, Gifu, Japan
D, halloysite, Spruce Pine, N.C., U.S.A.
E, halloysite, Bedford, Ind., U.S.A.
F, halloysite, Tintic, Utah, U.S.A.
G, halloysite, Shichinoe, Aomori, Japan

little. Among the specimens of halloysite, Spruce Pine halloysite has the largest number of reflections. The number of X-ray reflections which appear in the diagram indicates the relative degree of crystallinity.

Table I shows powder data for the kaolin minerals used in this study obtained from the X-ray diagram in Fig. 1.

The basal spacings were measured precisely. Slight changes of the basal spacings were detected for samples from Mesa Alta kaolinite to Shichinoe-clay. The basal spacing indicates a measure for the relative degree of crystallinity. The basal spacing in halloysite with lower degree of crystallinity is generally greater than that in kaolinite with higher degree of crystallinity. The slight change in the basal spacing can be attributed to the following reasons: (a) the presence of water layer between neighboring unit layers in kaolin minerals with lower degree of crystallinity, and/or (b) the disorderliness in the unit layer and looseness of the packing or stacking variations of the kaolin unit layers which should be greater in the specimens with lower degree of crystallinity.

The resolution between the closely spaced reflections in an X-ray diagram can be used as an indicator of the relative degree of crystallinity. The closely spaced reflections in an X-ray diagram of kaolinite with a considerable high degree of crystallinity are well resolved as exemplified by the reflections adjacent to the (020) and the (003) reflections of Fig. 1. These closely spaced reflections become hazy and indistinct in the diagrams of Kibushi-clay and Spruce Pine halloysite, and are completely merged in the diagrams of Bedford halloysite, Tintic halloysite and Shichinoe-clay.

The number of reflections closely related to the randomness of the stacking of kaolin unit layers. Reflections are not so many in the X-ray diagrams of kaolin minerals with lower degree of crystallinity. It is well known that the (OH) groups in the kaolin layers are arranged regular intervals along the b-axis, this distance being equall to $b_0/3$. This means that if one of two adjacent layers is displaced along the b-axis by an integral multiple of $b_0/3$, the two sheets will still be each oriented with same relationship to each other. If the displacement is not an integral multiple of $b_0/3$, then all reflections are cut out except those with a k index of $0, 3, 6, \cdots\cdots$. And if one of two adjacent layers is rotated by $n2\pi/3$, that is, random displacement is taken, all reflections indexed as (hkl) completely disappear. As the displacement in the kaolin layer remarkably increases and becomes irregular, the total number of reflections decreases and reflections become broad and diffuse.

As shown in Fig. 1 and Table I, Mesa Alta kaolinite has the highest degree of crystallinity and Shichinoe-clay has the lowest degree of crystallinity among the samples in this study.

Differential Thermal Analysis.—The crystallinity of kaolinite is indicated by differential thermal analysis curves..[5] Differential thermal analysis curves were made by using the same kaolin minerals as were used in the X-ray studies. The results obtained by using the differential thermal analysis curves are compared with the results of the X-ray data.

The specimens is the same as that described by Sudo et al[6]. Care was taken to place the sample into the sample block

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[5] R. E. Grim and W.F. Bradley, *Am, Mineral.*, **32**, 493 (1947).

[6] T. Sudo et al., *J. Geol. Soc. Japan*, (*Chishitsu Gaku Zasshi*) **58**, 115 (1952).

as being packed homogeneously and keeping nearly constant weight. The mean heating rate was 12.5° per minute. It is known that the temperature of the peak of the endothermic reaction is correlated with the degree of crystallinity of kaolin minerals. However, general criteria based on differential thermal analysis curves which can be used for all kaolin minerals to determine the relative degree of crystallinity are yet to be found. In this study, the criteria used by Murray and some additional features were used to determine the relative degrees of crystallinity of the kaolin minerals.

The following measurements can be used as criteria to determine the relative degree of crystallinity:

(1) The peak temperature, the peak height and the area of the first endothermic reaction (E_{n1}) associated with the loss of the adsorbed or inter-layer water. The area is measured by a planimeter from the basal line.

(2) The peak temperature, the peak height and the area of the second endothermic reaction (E_{n2}) associated with the loss of the lattice water.

(3) The peak temperature, the peak height, the area and the breadth of the exothermic reaction (E_x) associated with the transformation to the new phase from the original mineral. The breadth is measured at the half value of the exothermic peak.

Differential thermal analysis cuves and data are shown in Fig. 2 and Table II respectively. The peak temperature of the second endothermic reaction indicates the degree of crystallinity, as the lattice water should be more tightly bonded in the kaolin with higher degree of crystallinity than the one with lower degree of crystallinity. As a large amount of energy is needed to break the bonds holding the lattice water, the peak temperature, and its peak height become higher and its area becomes larger as the degree of crystallinity becomes higher. From the data of Table II, it is clearly seen that the peak temperature, the peak height and the area of the reaction are correlated to the relative degree of crystallinity of kaolinite group based on X-ray data. This relation is also maintained in the halloysite group. However, as shown in Table II, the peak temperature, the peak height and the area of halloysite with higher degree of crystallinity are greater than those of Kibushi-clay. The data in Table II show that in addition to those values the breadth of the exothermic reaction is also correlated to the relative degree of crystallinity. The breadth of peak of the exothermic reaction is expressed as the breadth at a half of peak height, since the expression of the breadth as the difference in temperature between the points at which the reaction begins and ends is indistinct in the measurement of those points. In Mesa Alta kaolinite and Drybranch kaolinite, the peak breadths are small, the peak temperatures are high and the heights are large. In spite of the degree of crystallinity based on X-ray data for Spruce Pine halloysite being low as compared with that of kaolinite, a higher degree of crystallinity is suggested from the character of the exothermic peak. In Kibushi-clay and halloysite excepting Spruce Pine halloysite, the degree of crystallinity is lower than that of kaolinite and Spruce Pine halloysite in the data of the final exothermic reaction. The smallness of the value of breadth of a kaolin mineral with a high degree of crystallinity confirms that the structure of the new phase

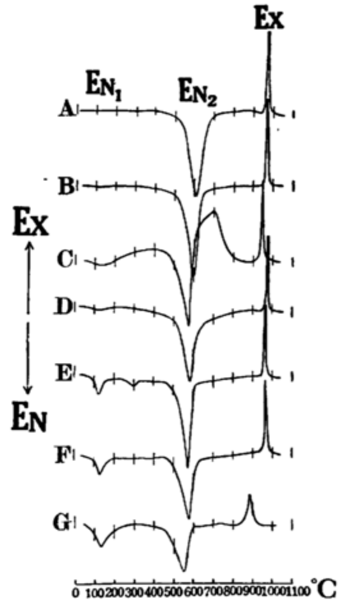

Fig. 2. Differential thermal analysis curves of kaolin minerals.

A, kaolinite, Mesa Alta, N.M., U.S.A.
B, kaolinite, Drybranch, Geor., U.S.A.
C, Kibushi-clay, Shidare, Gifu, Japan
D, halloysite, Spruce Pine, N.C, U.S.A.
E, halloysite, Bedford, Ind., U.S.A.
F, halloysite, Tintic, Utah, U.S.A.
G, halloysite, Shichinoe, Aomori, Japan

formed by exothermic reaction is correlated to the structure of original kaolin mineral, and that the more regular is the original structure, the faster is the transformation of the kaolin structure. In general, the peak temperature of the exothermic reaction of the kaolinites with a high degree of crystallinity is high, for more energy is needed in transformation to a new phase when the mother structure is stronger.

It is proved by the differential thermal analysis that Mesa Alta kaolinite, Drybranch kaolinite and Spruce Pine halloysite among the halloysite group have higher degree of crystallinity and that their crystallinity is higher than that of a kaolin of fireclay type like Kibushi-clay. Therefore, it is noteworthy that the degree of crystallinity of kaolinite determined by using a differential thermal analysis has the different meaning from that of halloysite determined by the same method.

Relationship between X-Ray and Thermal Data—The degree of crystallinity determined from the X-ray diffraction data is consistent with that from the thermal data in the series from kaolinite to kaolin of fireclay type, but not in the halloysite series.

When the inter-layer water is removed from the hydrated halloysite, it is considered that the unit layer which is structurally similar to the kaolinite layer may be the same as in a well-crystallized kaolinite. But the configuration of aluminum atoms may not be in the same manner as they are in a well-crystallized kaolinite. The possible variation in the configuration of aluminum atoms in each succesive layer is considered as a cause of broad reflections which are characteristic of the X-ray pattern of halloysite.

From the data of the X-ray diffraction, it seems that there is a continuous gradation of the structure from a kaolinite with a high degree of crystallinity to a halloysite with a low degree of crystallinity such as Shichinoe-clay. The differential thermal analysis made it clear that Spruce Pine halloysite has a high degree of crystallinity. This fact gives a valuable suggestion to the definition of the degree of crystallinity of kaolin minerals. This means that the degree of crystallinity of kaolin minerals involves two elements, that is, internal orderliness and stacking orderliness. The X-ray and thermal data suggest that X-ray reflections reveal both internal structural disorder and random stacking of the unit layers, whereas differential thermal analysis curves indicate internal structural disorder of the unit layers. Differential thermal analysis curves indicate the energy changes which a structure breaks down or a new phase forms. As shown by the thermal data, Spruce Pine halloysite has considerably perfect unit layers, however, as shown by X-ray data, the unit layers orientate with each other in a completely random manner with respect to to the *a*- and *b*-axis. In Kibushi-clay which is in a considerably low degree of crystallinity, there is a random displacement of $nb_0/3$ in different layers but not in a random orientation.

From these facts, it is considered that there are four typical variations in kaolin minerals when crystallinity is concerned.

(I) The mineral with the highest degree of crystallinity is estimated by using both X-ray and thermal method.

(II) The kaolin mineral with the lowest degree of crystallinity, estimated by using both methods.

(III) The kaolin mineral with the highest degree of crystallinity which is estimated by using X-ray method, but with the lowest degree of crystallinity by using thermal method.

(IV) The kaolin mineral with the highest degree of crystallinity estimated by using thermal method, but with lowest degree of crystallinity by using X-ray method.

These four ideal forms are related to the sizes and shapes of crystallites, physico-chemical properties and other forms.

Base Exchange Capacity.—A comparison of the relative degree of crystallinity of kaolin mineral used in this study with their base exchange capacity was made. It is well known that the base exchange capacity in kaolin mineral is attributed primarily to broken bonds7), and possibly to negative charges of the lattice due to vacancies of alumina or silica positions in kaolin with the lower degree of crystallinity.

The base exchange capacity was determined by the titration method. The clay was treated with hydrochloric acid, to convert it into " hydrogen clay ", then it was washed with water and titrated with sodium hydroxide solution. The base capacity was expressed as the number of

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7) S. Speil, *J. Am. Ceram. Soc.*, **23**, 33 (1940).

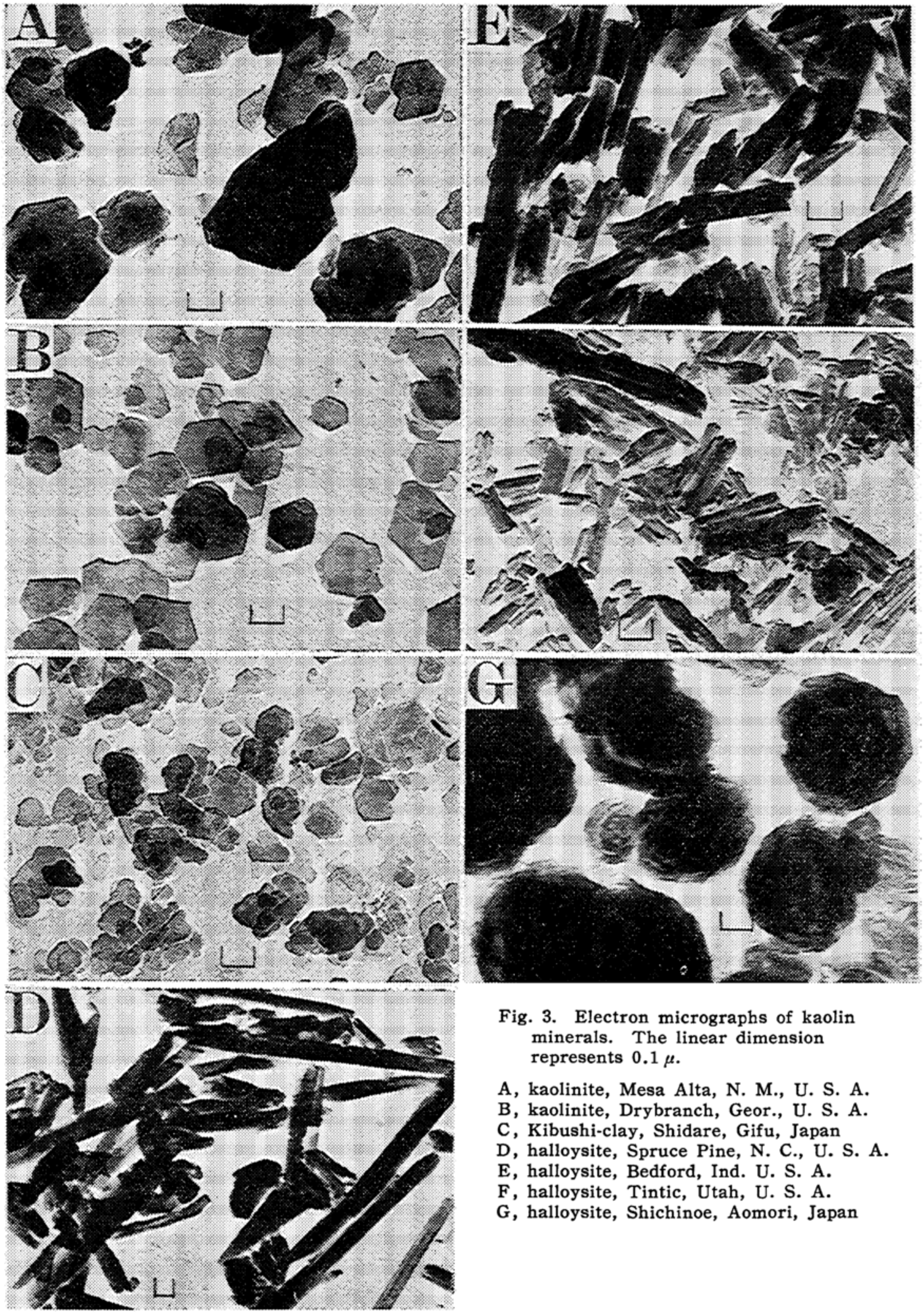

Fig. 3. Electron micrographs of kaolin minerals. The linear dimension represents 0.1 μ.

A, kaolinite, Mesa Alta, N. M., U. S. A.
B, kaolinite, Drybranch, Geor., U. S. A.
C, Kibushi-clay, Shidare, Gifu, Japan
D, halloysite, Spruce Pine, N. C., U. S. A.
E, halloysite, Bedford, Ind. U. S. A.
F, halloysite, Tintic, Utah, U. S. A.
G, halloysite, Shichinoe, Aomori, Japan

TABLE II

THERMAL DATA OF KAOLIN MINERALS

(all temp. are degrees centigrade)

Specimen	E_{n1}			E_{n2}			E_x			
	Temp.	Height	Area	Temp.	Height	Area	Temp.	Height	Area	Breadth
Kaolinite (Mesa Alta, N.M.)	—	—	—	604°	16	1080	966°	39	220	5.1°
Kaolinite (Drybranch, Geor.)	—	—	—	592	20	1280	964	41	250	4.8
Kibushi-Clay (Shidare, Gifu)	130°	1	140	574	14	740	945	13	140	10.5
Halloysite (Spruce Pine, N.C.)	125	1	70	583	17	1380	973	41	220	4.0
Halloysite (Bedford, Ind.)	125	2	110	574	16	720	970	34	170	4.5
Halloysite Tintic, Utah)	130	4	170	571	12	680	999	16	170	9.4
Halloysite (Shichinoe, Aomori)	129	6	480	550	12	660	885	7	130	23.4

TABLE III

BASE EXCHANGE CAPACITY OF KAOLIN MINERALS AT THE DRIED STATE

Specimen		Base exchange capacity (meq./100 g.)
Kaolinite	Mesa Alta, N.M., U.S.A.	1.0
	Drybranch, Geor., U.S.A.	1.4
Kibushi-clay (fireclay type)	Shidare, Gifu, Japan	7.3
Halloysite	Spruce Pine, N.C., U.S.A.	0.8
	Bedford, Ind., U.S.A.	4.0
	Tintic, Utah, U.S.A.	6.0
	Shichinoe, Aomori, Japan	12.5

TABLE IV

DENSITY OF KAOLIN MINERALS AT THE DRIED STATE

Specimen		Density (g./cc)
Kaolinite	Mesa Alta, N.M., U.S.A.	2.622
	Drybranch, Geor., U.S.A.	2.606
Kibushi-clay (fireclay type)	Shidare, Gifu, Japan	2.489
Halloysite	Spruce Pine, N.C., U.S.A.	2.561
	Bedford, Ind., U.S.A.	2.516
	Tintic, Utah, U.S.A.	2.464
	Shichinoe, Aomori, Japan	2.339

milli-equivalents of cations, per 100 g. of clay, required to bring the pH to 7.

Table III shows the base exchange capacity of kaolin samples. These results indicate that kaolin mineral with a lower degree of crystallinity has a higher base exchange capacity. Consequently, it can be concluded that the base exchange capacity is correlated to the internal randomness of structure.

Density—Another property which is considered to indicate the degree of crystallinity of kaolin minerals is their density. The density was determined with a pycnometer in carbon tetrachloride. The density of kaolin minerals used in this study are shown in Table IV. These values indicate that the density is correlated to the relative degree of crystallinity in the internal and stacking variations. The kaolinite with a higher degree of crystallinity has a larger density, and halloysite with a lower degree of crystallinity has a smaller density, with the exception of Kibushi-clay which contains organic matter as seen in the differential thermal analysis curve.

Electron Microscopic Studies.—Electron micrographs were obtained by the Hitachi HU-10A Type Electron Microscope.

Electron micrographs of kaolin minerals used in this study are shown in Fig. 3. The two kaolinites have platty particles, and the particles of Mesa Alta kaolinite has a sharp but irregular shape and the particles of Drybranch kaolinite has a hexagonal shape. The electron micrographs of halloysite samples with the exception of Shichinoe-clay have tubular particle. Bates et al. have indicated a structure that explains the tubular arrangement of halloysite.[8] That is, when the bonding forces of atoms in kaolin unit layer are very much stronger than the inter-layer forces, a particle takes tubular shape due to the characteristic of the unit layer lattice of the kaolin mineral. This means that the shape of the particle of the kaolin mineral is correlated to the disorderliness of the crystallographic unit layer and the disorderliness of the stacking of kaolin unit layer.

The X-ray data indicate that the degree of crystallinity of the Kibushi-clay is higher than that of the Spruce Pine halloysite while the thermal data indicate the opposite. This means that the kaolin layers in Kibushi-clay orient with respect to each other in relatively regular manner, but the layers themselves are less perfect than in Spruce Pine halloysite. As shown in the micrograph of Kibushi-clay, its crystal has a far finer size than the two kaolinites. The shape of Kibushi-clay is hexagonal and platty. This leads to assumption that the degree of crystallinity is the higher, the larger is the size of a crystal whose shape is platty.

Shichinoe-clay has the lowest degree of crystallinity among kaolin minerals used in this study by X-ray, thermal and other methods. As shown in a micrograph (Fig. 3-G), the shape of Shichinoe-clay is a round grain, which is well-defined and many of the grains have polyhedral outlines. The interiors of the polyhedral grains were observed in detail. It was found then that polyhedral grains are composed entirely of polyhedral crust like a cabbage. As to the shape of halloysite like the Shichinoe-clay, they were reported in previous papers.[4,9]

It is supposed that a schematic diagram for all the shapes of kaolin minerals could be drawn with respect to the degree of crystallinity in the internal randomness of the unit layer and the degree of crystallinity in the stacking randomness of kaolin layers. An ideal schematic diagram is shown in Fig. 4.

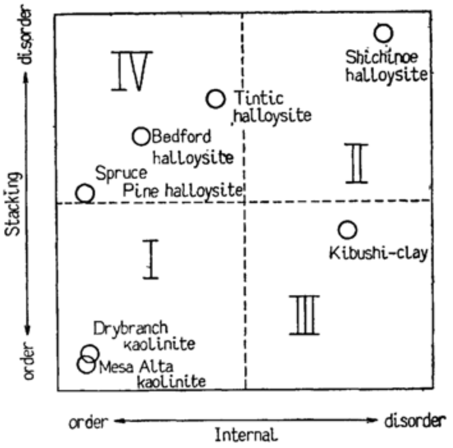

Fig. 4. A schematic diagram for the shapes of kaolin minerals with respect to two elements of the degree of crystallinity.

I : hexagonal, platty and large particle
II : fibrous, lath, cabbage like particle or rounded grain composed of fiber and lath
III : hexagonal, platty and fine particle
IV : tubular particle

All kaolin minerals are composed of kaolin unit layers, and kaolin minerals have various shapes. These facts are particularly remarkable in the hydrated halloysite clays altered from Japanese glassy tuff in the course of weathering. But the various shapes of kaolin minerals as above-mentioned can be readily understood by reference to the two elements of the randomness.

Summary

(1) The degree of crystallinity of kaolin minerals must be defined in relation to the degree of crystallinity in the internal randomness of the kaolin unit layer and that of the stacking randomness of kaolin unit layers. The X-ray diffraction data seem to reflect both internal and stacking variations.

(2) The relative degrees of crystallinity determined by the X-ray data and thermal data are consistent with each other in the series from kaolinite to fireclay. This holds also in the halloysite series. There is a continuous variation in the series from kaolinite to fireclay and also in the

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[8] T. F. Bates, F. A. Hildebrand and A. Swineford, *Am. Mineral.*, **35**, 463 (1950).

[9] H. Takahashi, *J. Electron Microscopy, (Denshi-Kenbikyo)*, **4**, 269 (1955).

halloysite series. The X-ray data indicate that some of halloysites have a low degree of crystallinity, but the thermal data show a high degree of crystallinity. This means that in most cases the displacement in the series from kaolinite to fireclay is a one-dimensional displacement with respect to the *b*-axis, while the displacement in halloysite is a rotational displacement, that is, a two-dimensional displacement.

(3) The values of the base exchange capacity of kaolinite, fireclay and halloysite are correlated to the internal disorderliness of kaolin structure.

(4) The values of density of kaolin mineral samples nearly correspond to the degrees of the crystallinity with the exception of Kibushi-clay.

(5) The variety of shapes of kaolin minerals are determined in the relation of the two elements of the internal variation and the stacking variation.

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