Effects of Dry Grinding on Kaolin Minerals. III. Halloysite

By Hiroshi TAKAHASHI

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In the preceding parts of this series, the effects of dry grinding of kaolinite and Kibushi-clay have been studied[1]. From the results, a common mechanism in the structural change of kaolinite and Kibushi-clay by dry grinding was presented. That is, in the process of dry grinding, the separation into unit crystallites from the original crystal, the reaggregation of crystallites, the production of a non-crystalline material, the disordering of the crystallites, the reaggregation of crystallites and a non-crystalline material, the formation of a zeolitic structure in a certain period of grinding and the change into an amorphous substance such as silica-alumina mixed gel are observable. The effects of grinding of halloysite have been little studied so far. In this paper, the effects of dry grinding of halloysite are studied with respect to the degree of crystallinity of kaolin minerals with various degrees of crystallinity.

Experimental

The following samples were used in this study: Halloyste from Spruce Pine, N. C., U. S. A.; Halloysite from Bedford, Ind., U. S. A.; Halloysite from Tintic, Utah, U. S. A. These samples are the API Standard Clay Minerals and their structural characteristics are discussed in the previous paper[2]. As shown in the paper, it is considered that the structural differences among varieties halloysite chiefly depend on the internal variations rather than their stacking variation. Of halloysite, Spruce Pine halloysite has the highest degree of crystallinity. This was ascertained by the electron diffraction method[3]. Bedford halloysite has a lower degree of crystallinity than Spruce Pine halloysite. Tintic hallosite has the lowest degree of crystallinity of all the kinds of halloysite used in this study. Both Bedford and Tintic halloysite are partially hydrated halloysites.

The grinding conditions were the same as for kaolinite described in part I of this series. Experimental specimens were examined by X-ray diffraction, thermal, electron microscopic and other methods. The experimental conditions were the same as for kaolinite. The base exchange capacity and the density in various stages of dry grinding were measured after the specimens had been dried at 110°C in order to avoid the effect of the inter-layer or adsorbed water.

Results and Discussion

X-Ray Diffraction Studies.—X-ray diffractometer traces in the processes of grinding of halloysite are shown in Fig. 1. Figs. 1-a, -b and -c show the X-ray diffractometer traces of Spruce Pine halloysite, Bedford halloysite and Tintic halloysite, respectively. In Tables I-a, -b and -c, the interplanar spacing and the relative intensity measured from their X-ray diagrams are given.

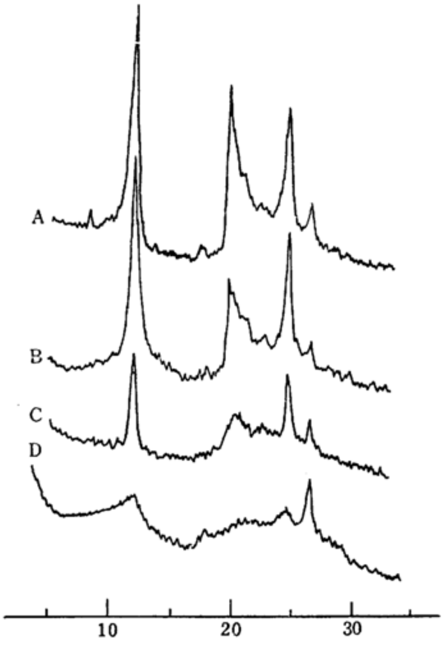

Fig. 1-a X-ray diffractometer traces of ground halloysite (Spruce Pine, N. C.).
A, original halloysite
B, ground 48 hours
C, ground 96 hours
D, ground 192 hours

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[1] H. Tahakashi, This Bulletin, **32**, 235, 245 (1959).
[2] H. Takahashi, ibid. **31**, 275 (1958).
[3] G. Honjo and K. Mihama, *Acta Cryst.*, **7**, 511 (1954).

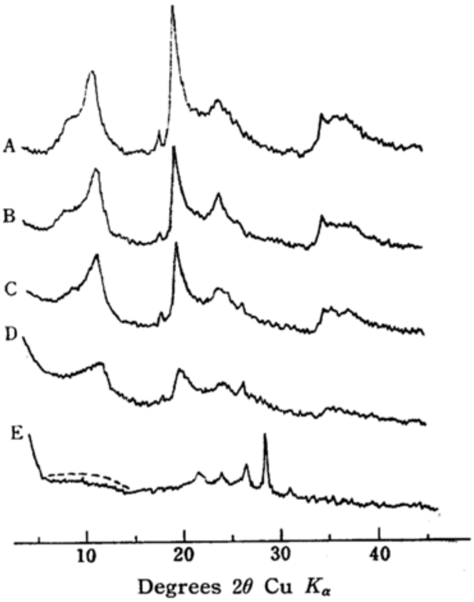

Fig. 1-b. X-ray diffractometer traces of ground halloysite (Bedford, Ind.).

A, original halloysite
B, ground 48 hours
C, ground 96 hours
D, ground 144 hours
E, ground 312 hours

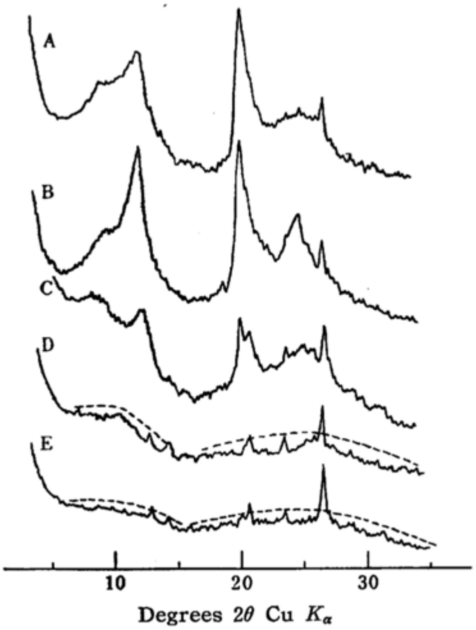

Fig. 1-c. X-ray diffractometer traces of ground halloysite (Tintic, Utah).

A, original halloysite
B, ground 48 hours
B, ground 96 hours
D, ground 144 hours
E, ground 240 hours

When halloysite is ground, it gradually assumes a more and more disordered structure; that is, the background increases as the intensity of the reflection weakens. In the X-ray diagrams of the original samples of Bedford and Tintic halloysite which are partially hydrated halloysites, the reflection of about 10 Å spacing is present in both original samples. It is known that this reflection indicates the presence of a hydrated halloysite in these samples. This reflection is observable even in the 96-hour-ground specimen of Tintic halloysite and the 144-hour-ground specimen of Bedford halloysite. This fact indicates that the loss of the inter-layer water due to the heat caused by dry grinding does not occur in these specimens. This leads to the theory that the dry grinding does not produce so much local heat. The intensity of all the reflections apparent in the X-ray diagrams decreases as the grinding progresses. The manner of the disappearance of the reflections depends on the degree of crystallinity of original halloysite samples. In the X-ray diagram of the 144-hour-ground specimen of Tintic halloysite which has the lowest degree of crystallinity in the original state, 02, 11 bands are not distinct and very diffuse. Whereas, in the X-ray diagram of the 144-hour-ground specimen of Bedford halloysite, the reflection is considerably distinct though its intensity lowers. As the grinding progresses further, the X-ray diagram of this specimen comes to correspond to the amorphous pattern. In Spruce Pine halloysite, which has the highest degree of crystallinity of all the kinds of halloysite, all reflections in the X-ray diagram are considerably distinct even with a 192-hour-ground specimen.

In the early stage of grinding of all halloysite, the lines of basal reflections become sharp as compared with those of the original samples. This tendency is observable also in the case of kaolinite. The structure of halloysite is pseudohexagonal in symmetry, and is nearly two-dimensional[4]. The structure of halloysite is not precisely two-dimensional; however, if it is supposed that the theory of the reflection of the two-dimensional lattice is applicable to the structure of halloysite, the crystallite dimension in the process of grinding can be calculated from the breadths of reflection lines[5]. It is

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[4] G. W. Brindley and K. Robinson, *Min. Mag.*, **28**, 393 (1948).

[5] B. E. Warren, *Phys. Rev.*, **59**, 693 (1941).

TABLE I-a

POWDER DATA OF GROUND HALLOYSITE (SPRUCE PINE, N. C.) IN ANGSTROM UNITS

Brindley and Robinson			Original Halloysite		Ground 48 hr.		Ground 96 hr.		Ground 192 hr.	
d	*I*	$00l$ or hk	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
7.2∼7.5	8	001	7.15	VS	7.15	VS	7.20	S	7.3	M
4.422	10+	02, 11	4.44	S	4.44	S	4.43	M br	4.3	M vbr
3.578	8	002	3.57	S	3.58	S	3.59	M	3.5	W br
2.559	7	13, 20	2.56	M	2.57	M	2.57	W br	2.57	W vbr
			2.53	W						
(2.48)			2.49	M	2.49	W	2.49	VW		
2.403	2	003	2.38	W	2.39	W	2.36	VW		
(2.33)	2		2.33	M	2.33	W	2.30	VW		
2.218	1	04, 22	2.29	W						
			1.997	MW	1.994	W				
1.800	1	004								
1.678	5	31, 15, 24	1.670	MW	1.67	W br	1.68	VW br		
1.481	8	06, 33	1.488	M	1.49	MW br	1.49	VW br		

Key to Abbreviation: VS: very strong, S: strong, M: medium, MW: medium weak, W: weak, VW: very weak, br: broad, vbr: very broad.

TABLE I-b

POWDER DATA OF GROUND HALLOYSITE (BEDFORD, IND.) IN ANGSTROM UNITS

Original halloysite		Ground 48 hr.		Ground 96 hr.		Ground 144 hr.		Ground 312 hr.	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
9.6	W br	9.8	W br	9.8	VW br			8.5	VW vbr
7.3	S	7.5	S	7.5	S br	7.5	M vbr		
4.45	VS	4.45	S	4.45	S	4.44	M		
3.63	M br	3.67	M	3.69	M	3.65	W br	4.0	W vbr
2.57	M br	2.57	M br	2.57	M br	2.56	W vbr		
1.80	W								
1.68	M br	1.68	W br						
1.48	M br	1.48	W br	1.48	W br				

Key to Abbreviation: VS: very strong, S: strong, M: medium, W: weak, VW: very weak, br: broad, vbr: very broad.

TABLE I-c

POWDER DATA OF GROUND HALLOYSITE (TINTIC, UTAH) IN ANGSTROM UNITS

Original halloysite		Ground 48 hr.		Ground 96 hr.		Ground 144 hr.		Ground 240 hr.	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
10.1	M	10.0	M	10.0	M br	8.2	M vbr	8.1	W vbr
7.37	S	7.36	S	7.3	M br				
4.44	VS	4.44	VS	4.44	M				
3.66	M br	3.61	M	3.54	M br	3.6	M vbr	3.5	M vbr
2.56	M br	2.56	M br	2.56	W br				
1.68	M br	1.68	W br						
1.48	M br	1.48	M br	1.48	W br				

Key to Abbreviation: VS: very strong, S: strong, M: medium, W: weak, br: broad, vbr: very broad.

known that the breadth of a reflection line is determined by two factors, that is, the particle size and the distortion of lattice. These factors must be separated for the precise measurement of crystallite dimension[6]. However, the broadening of the line breadth is due to a reduction in crystallite size or a remarkable distortion of lattice. These two elements which correspond to the broadening in the line breadth are related to a lowering in the degree of crystallinity. Therefore, the crystallite dimensions obtained from the line breadth seem to be terms which re-

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[6] C. R. Houska and B. E. Warren, *J. Appl. Phys.*, **25**, 1503 (1954).

present the relative degree of crystallinity of the specimens rather than the real crystallite sizes. To calculate the crystallite dimension from the line breadth, Bragg's equation was used for the dimension along the *c*-axis (L_c) from 001 reflection[7], and Warren's equation was used for the dimension of the broadening, parallel to the layer plane of crystallite (L_a) from 02,11 band[5]. Fig. 2 shows the changes of the crystallite dimensions with the grinding time.

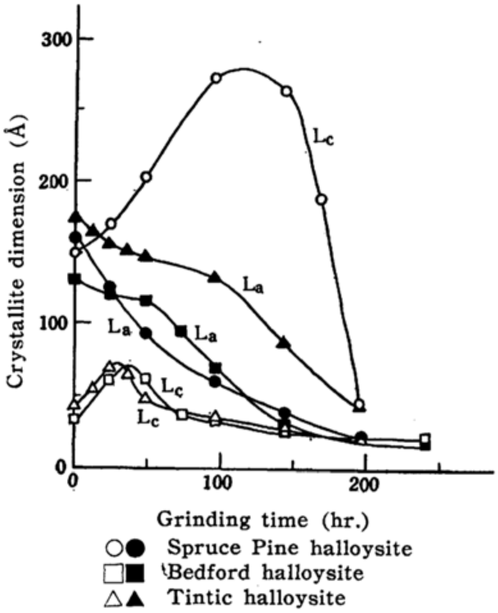

Fig. 2. Curves showing the changes of crystallite dimensions with the time of grinding.

From the curve shown in this figure, it is observable that the breadth of the basal reflection becomes sharper in the early stage of grinding. Of these curves, some features are observable; that is, the maximum point on L_c-dimension curve of Spruce Pine halloysite with the highest degree of crystallinity is apparent when ground for a considerably long time. For the crystallite dimension of Spruce Pine halloysite along *a*-axis (L_a), it decreases quickly with the grinding, whereas, it does not change in Bedford halloysite and Tintic halloysite up to some extent of grinding. When the grinding passes this stage, the L_a-dimensions of Bedford halloysite and Tintic halloysite decrease as that of Spruce Pine halloysite does. This fact means that Bedford halloysite and Tintic halloysite are more resistant to dry grinding than Spruce Pine halloysite, presumably because of the lubricating action of the water layers between the kaolin layers. This resistant action of the interlayer water is also found in vermiculite[8]. The quick decrease in the L_a-dimension is correlated to the fracturing of the kaolin layer.

The increase of the background in the X-ray diagram of halloysite is similar to those of kaolinite or Kibushi-clay, and is correlated to the production of a non-crystalline material. It is considered that the structure of non-crystalline materials produced by dry grinding of halloysite with lower crystallinity is considerably disordered and is similar to a gel-like structure.

For some ground specimens, the alkali-acid treatment noted in the case of kaolinite was made to ascertain the disordering of the crystallite. Throughout all these specimens, the same tendency is observable as that of kaolinite. The 240-

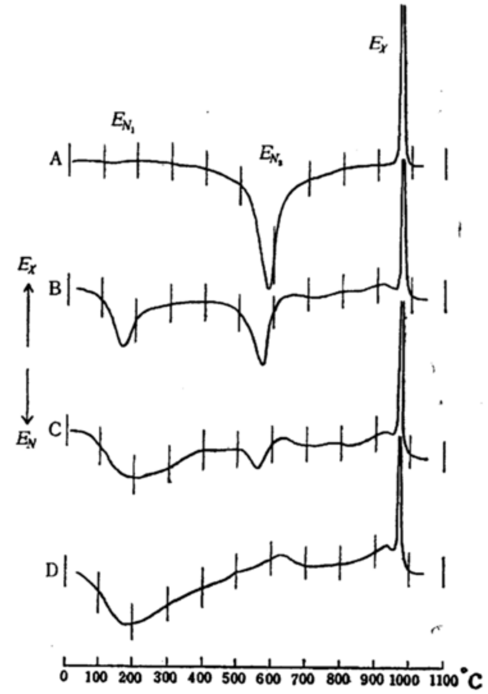

Fig. 3-a. Differential thermal analysis curves of ground halloysite (Spruce Pine, N. C.).

A, original halloysite
B, ground 48 hours
C, ground 96 hours
D, ground 192 hours

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[7] W. L. Bragg, "The Crystalline State", Vol. I, 189 (1933).

[8] R. C. Mackenzie and A. A. Milne, *Clay Min. Bull.*, 2, 57 (1953).

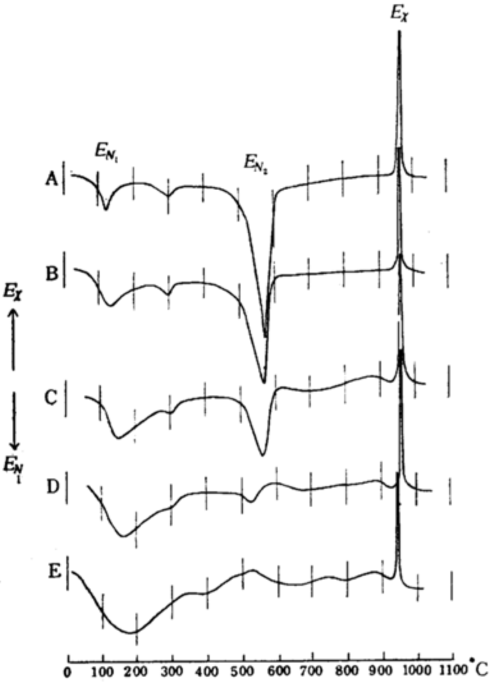

Fig. 3-b. Differential thermal analysis curves of ground halloysite (Bedford, Ind.).
A, original halloysite
B, ground 48 hours
C, ground 96 hours
D, ground 144 hours
E, ground 312 hours

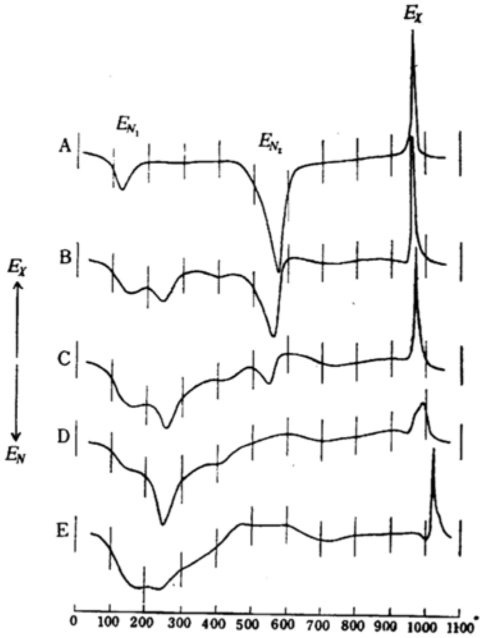

Fig. 3-c. Differential thermal analysis curves of ground halloysite (Tintic, Utah).
A, original halloysite
B, ground 48 hours
C, ground 96 hours
D, ground 144 hours
E, ground 240 hours

TABLE II-a
THERMAL DATA OF GROUND HALLOYSITE (SPRUCE PINE, N. C.).
(ALL TEMPERATURES ARE DEGREES CENTIGRADE)

Grinding time (hr.)	E_{n1}			E_{n2}			E_x			
	Temp. at peak	Height of peak	Area of peak	Temp. at peak	Height of peak	Area of peak	Temp. at peak	Height of peak	Area of peak	Breadth (half value of breadth)
0	125°C	1	70	583°C	17	1380	973°C	45	220	4.0°
48	—130—	5	640	568	10	560	972	43	220	3.8
96	—160—	6	820	563	5	480	971	48	220	3.7
144	—190—	8	960	555	2	310	971	53	230	3.7
192	—190—	9	1940	—	—	—	970	58	230	3.1

TABLE II-b
THERMAL DATA OF GROUND HALLOYSITE (BEDFORD, IND.).
(ALL TEMPERATURES ARE DEGREES CENTIGRADE)

Grinding time (hr.)	E_{n1}			E_{n2}			E_x			
	Temp. at peak	Height of peak	Area of peak	Temp. at peak	Height of peak	Area of peak	Temp. at peak	Height of peak	Area of peak	Breadth (half value of breadth)
0	125°C	2	110	574°C	16	720	970°C	34	170	4.5°
48	—128—	4	410	569	15	590	968	34	180	4.5
96	—150—	6	630	566	9	450	968	43	200	3.3
144	—160—	6	790	535	2	60	967	50	200	2.7
312	—190—	6	1090	—	—	—	951	68	200	3.0

TABLE II-c
THERMAL DATA OF GROUND HALLOYSITE (TINTIC, UTAH).
(ALL TEMPERATURES ARE DEGREES CENTIGRADE)

	E_{n1}			E_{n2}			E_x			
Grinding time (hr.)	Temp. at peak	Height of peak	Area of peak	Temp. at peak	Height of peak	Area of peak	Temp. at peak	Height of peak	Area of peak	Breadth (half value of breadth)
0	130°C	4	170	571°C	12	680	969°C	16	170	9.4°
48	—155— —240—	5 6	350	562	10	480	966	30	200	3.6
96	—165— —260—	5 9	790	548	3	100	967	19	150	7.5
144	—250—	11	1120	—	—	—	994	5	140	39.2
240	—170— —260—	8	1340	—	—	—	1023	15	130	7.3

hour-ground specimen of Tintic halloysite which has an amorphous pattern in its X-ray diagram dissolved completely through the alkali-acid treatment and leaves only the impurities such as quartz, felspars and others. When the X-ray diagram of the ground specimen of halloysite is compared with those of kaolinite and Kibushi-clay, it is clear that the dry grinding is not so effective on kaolinite and Spruce Pine halloysite in the structural change, but is most effective on Kibushi-clay and Tintic halloysite. From the X-ray data, it is concluded that the effects of dry grinding of kaolin minerals in the structural change depend on the perfectness of kaolin unit layers, that is, the internal degree of crystallinity.

Differential Thermal Analysis. — Differential thermal analysis curves and data of the grinding process of halloysite are shown in Fig. 3 and Table II.

The first endothermic reaction (E_{n1}) associated with the loss of the inter-layer or adsorbed water, is not present in the original sample of Spruce Pine halloysite, but is present in the original samples of Bedford and Tintic halloysite. It is natural that this reaction is apparent in the original sample of Bedford and Tintic halloysite, because they are partially hydrated halloysite. As the grinding progresses, this reaction appears and its height and area increase. These facts mean that the substance produced by dry grinding adsorbs water vapor and its quantity increases as the grinding progresses. The peak temperature of this reaction gradually rises. This leads to the water adsorbed by the ground substance being combined more strongly as the grinding progresses. In the original sample of Bedford halloysite, a weak endothermic reaction is apparent at about 300°C, probably due to the presence of gibbsite as impurity. This reaction is wholy apparent in the process of grinding. The rates of change in the first endothermic reaction are the same as those in the cases of Spruce Pine and Bedford halloysite. But, in the grinding process of Tintic halloysite, this reaction is slightly different from those of Bedford and Spruce Pine halloysite. On the differential thermal analysis curves of the ground specimens of Tintic halloysite after 48 hours of grinding, the second maximum is apparent in this reaction, and the height and area increase, and the peak temperature gradually rises. In the 240-hour-ground specimen of Tintic halloysite, this reaction increases more, and the second maximum becomes indistinct.

In the second endothermic reaction (E_{n2}) associated with the loss of the lattice water, it is observable that the features of this reaction are similar to those of kaolinite. That is, a lowering in the peak temperature, and a reduction in the peak height and area are observable. When the grinding progresses for a long time, in such specimens as the 144-hour-ground specimen of Tintic halloysite, the 162-hour-ground specimen of Bedford halloysite and the 192-hour-ground specimen of Spruce Pine halloysite, this reaction is unobservable. This fact indicates that the kaolin structure finally disintegrates due to dry grinding. The grinding time in which this reaction disappears is shorter as the crystallinity of the original sample is lower.

In the exothermic reaction (E_x) are found some interesting phenomena. The exothermic reactions of ground specimens of Bedford halloysite and Spruce Pine halloysite are similar to that of kaolinite. The peak temperatures tend to fall very slightly, and in the specimens ground for a long period, the peak temperature falls remarkably. Except for the 312-hour-ground specimen of Bedford halloysite, the peak height and area of the exothermic reaction increase and the breadth of peak decreases. The exothermic reaction behaves the same as in the case of kaolinite. But, the exothermic reaction of Tintic halloysite behaves very differently from that of kaolinite and the other halloysite. At first the peak temperature tends to be somewhat low, but as the grinding progresses, the temperature rises rapidly. The peak height increases at first, but soon reduces remarkably. The peak height, as the temperature becomes higher, increases again. The peak breadth also becomes narrower at first, but soon increases and then decreases again. To determine whether there is a difference between their exothermic reactions, X-ray diagrams were taken of several specimens just before and after the exothermic reactions on the differential thermal analysis curve. These traces are shown in Fig. 4. It is indicated that as the grinding progresses, the growth of mullite crystal becomes remarkable, but the presence of mullite is unobservable just before the exothermic reaction.

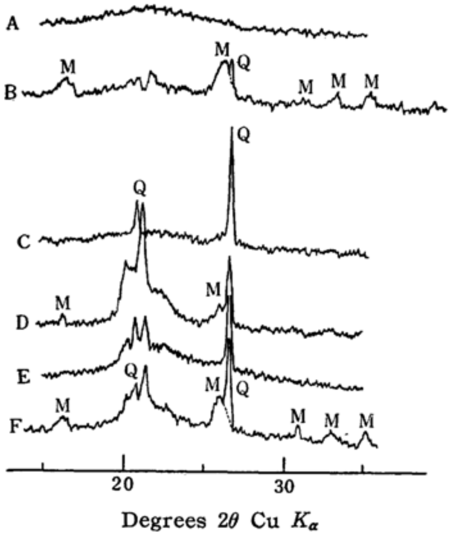

Fig. 4. X-ray diffractometer traces of ground halloysite obtained just before or after the final exothermic reaction (E_x) on the differential thermal analysis curve.

A, original Bedford halloysite just after E_x
B, 312-hour-ground Bedford halloysite just after E_x
C, original Tintic halloysite just after E_x
D, 144-hour-ground Tintic halloysite just after E_x
E, 240-hour-ground Tintic halloysite just before E_x
F, 240-hour-ground Tintic halloysite just after E_x

This tendency was also found in the process of grinding of kaolinite. From this fact, it is certain that the exothermic reaction is attributed to the mullite nucleation in halloysite[9]. It is difficult to draw a conclusion from the character of the exothermic reaction as to the grinding effects of halloysite used in the experiment, but it may be interpreted as follows. When the crystallinity of the halloysite is at a considerably low stage, the non-crystalline material produced by dry grinding has a completely amorphous structure, whereas, when the halloysite with a higher degree of crystallinity is ground, the non-crystalline substance produced by grinding has a structure which is somewhat related to that of the original halloysite; that is, it is not a perfectly amorphous substance. This substance is hard to change into a perfectly amorphous substance. The tranformation of kaolin mineral into mullite is closely related to the original structure. In the case of Tintic halloysite, however, the original structure completely disintegrates by dry grinding. The transformation to mullite from kaolin mineral requires much more energy than that of kaolinite, Spruce Pine halloysite and Bedford halloysite. It is considered that the reaction produces a higher temperature. In kaolinite, Spruce Pine and Bedford halloysite, the non-crystalline substance produced by dry grinding may be an allophanic substance rather than gel-like. In all ground specimens of halloysite, the weak endothermic reaction immediately before the exothermic reaction becomes distinct as the grinding progresses. This fact was also found in kaolinite and Kibushi-clay as discussed above. In the transformation of kaolin into mullite, there are two steps of the structural change. The first step is the nucleation of mullite, and the second step is the crystal growth of mullite nuclei. The dry grinding accelerates the reaction of the second step, that is, the crystal growth of mullite nuclei.

Base Exchange Capacity and Density.—In Fig. 5 are shown the changes of the

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9) R. C. Mackenzie, "Differential Thermal Investigation of Clays", Mineralogical Society (London), (1957), p. 108.

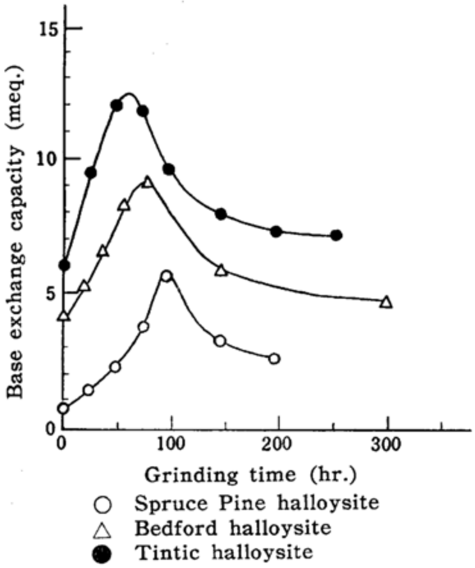

Fig. 5. Curves showing the changes of base exchange capacity with the time of grinding.

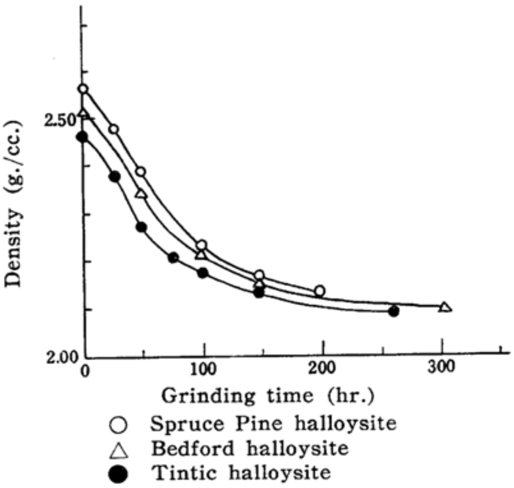

Fig. 6. Curves showing the changes of density with the time of grinding.

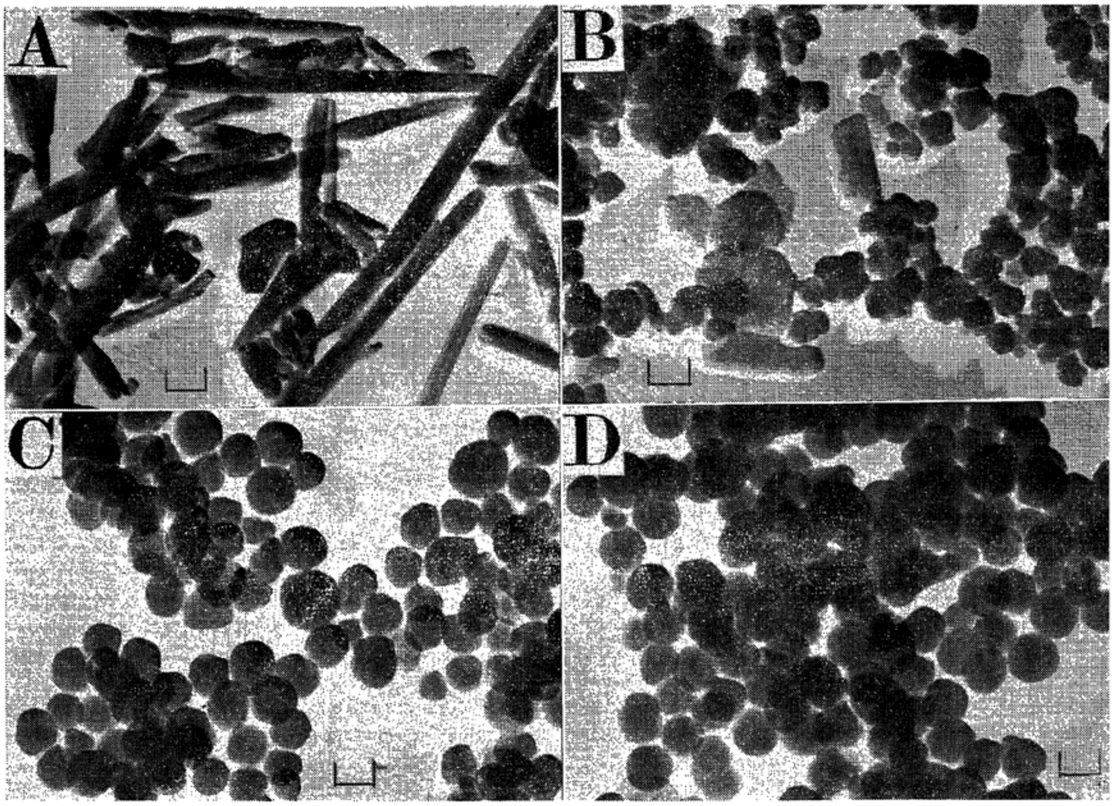

Fig. 7-a. Electron micrographs of ground halloysite (Spruce Pine, N. C.). The linear dimension on the micrographs represents 0.1 μ.

A, original halloysite
B, ground 48 hours
C, ground 96 hours
D, ground 192 hours

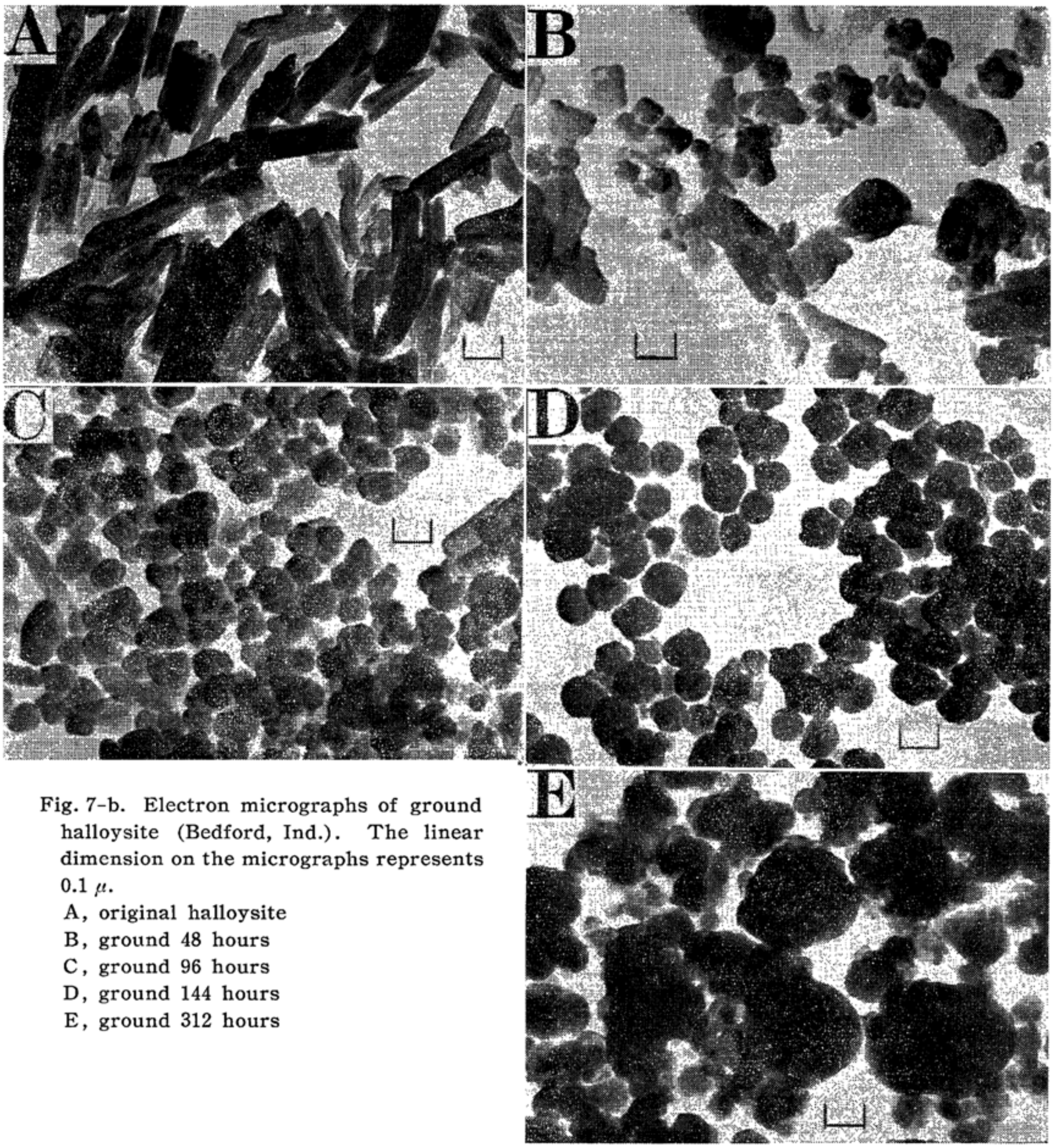

Fig. 7-b. Electron micrographs of ground halloysite (Bedford, Ind.). The linear dimension on the micrographs represents 0.1 μ.

A, original halloysite
B, ground 48 hours
C, ground 96 hours
D, ground 144 hours
E, ground 312 hours

base exchange capacity with the grinding time.

As the grinding progresses, the base exchange capacity at first increases. After reaching a maximum value, it gradually decreases until it attains the constant value. The maximum value and the constant value vary according to the order of the original sample. The lower the crystallinity of the original sample, the shorter the time in which the base exchange capacity attains its maximum point. The rates of change of base exchange capacity against the grinding time are similar to those of kaolinite. As in kaolinite, these results also support the thought of Laws and Page for the explanation of the change on the base exchange capacity through dry grinding[10].

In Fig. 6 are shown the changes of the density with the grinding time.

As the grinding progresses, the density sharply decreases, but after reaching a certain point, it slowly attains a constant value. This constant value is nearly equal to the value of a silica-alumina mixed gel or allophane. These facts mean that halloysite changes into a non-crystalline substance by dry grinding.

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[10] W. D. Laws and J. B. Page, *Soil Sci.*, 62, 319 (1946).

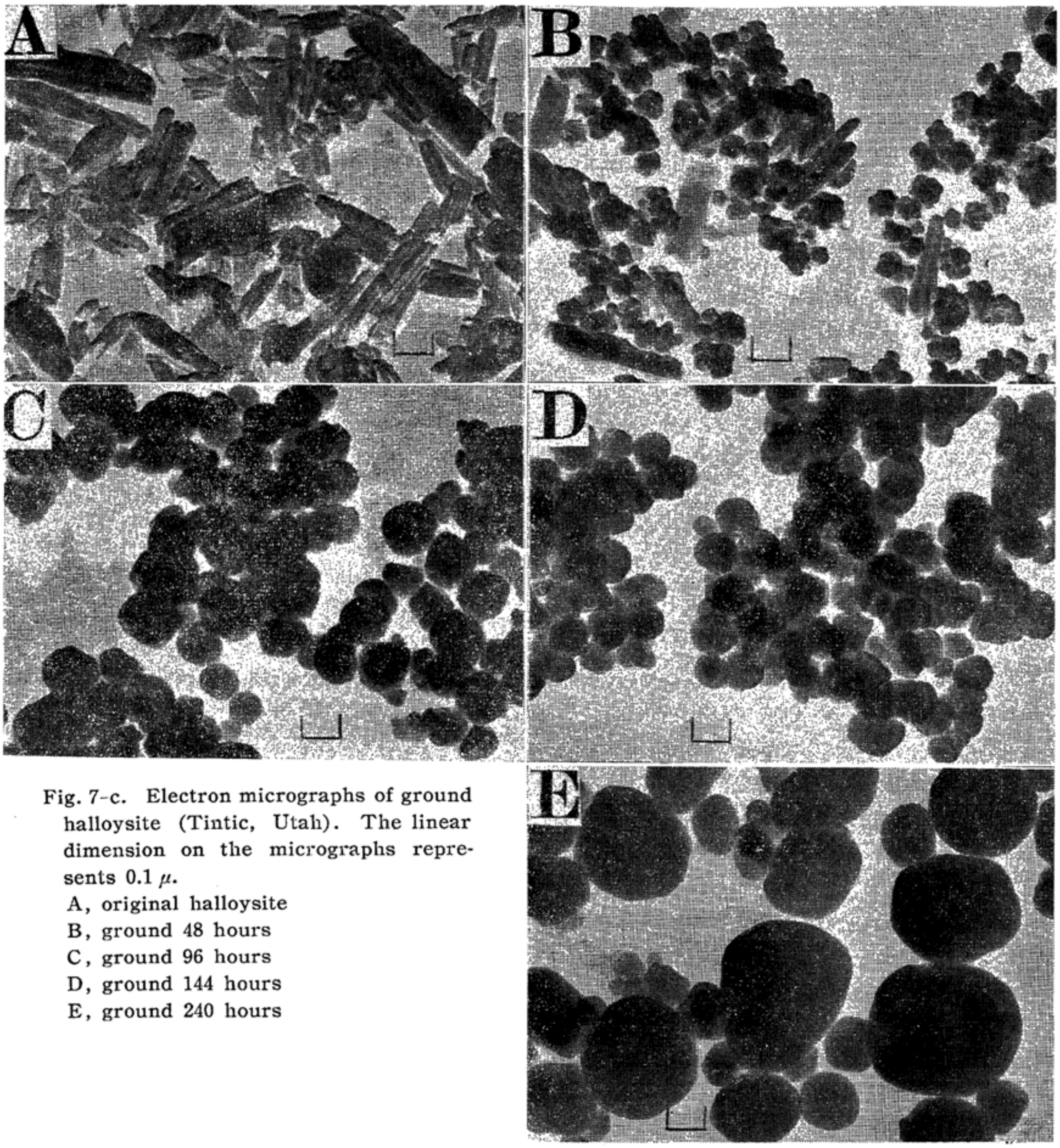

Fig. 7-c. Electron micrographs of ground halloysite (Tintic, Utah). The linear dimension on the micrographs represents 0.1 μ.
A, original halloysite
B, ground 48 hours
C, ground 96 hours
D, ground 144 hours
E, ground 240 hours

The point of the bend in the density curve and the maximum point in the base exchange curve are at nearly identical positions. This phenomenon was also seen in kaolinite. This stage seems to correspond to the point at which the kaolin structure changes to zeolitic.

Electron Microscopic Studies.—Electron micrographs of halloysite in the process of dry grinding are shown in Fig. 7. Figs. 7-a, -b and -c show those of Spruce Pine halloysite, Bedford halloysite and Tintic halloysite, respectively.

The particles of the original halloysite samples have a tubular shape. It is observable that in the early stage of dry grinding, fine crystallite is produced from the original crystal. The shapes of these crystallites are platty with a considerably sharp edge though the shape of the original halloysite is tabular. As the grinding progresses, the fine crystallites reaggregate, and raggregated particles become spherical and the particle size increases, and then the reaggregated particles slowly change into uniformly spherical particles. As the grinding progresses further, for example in the 240-hour-ground specimen of Tintic halloysite or in the 312-hour-ground specimen of Bedford halloysite, the remarkable and irregular growth of particles is observable. In the light of X-ray and thermal data, the irregular growth of reaggregated particles corresponds to the fact that an amorphous substance is produced by dry grinding.

If the mean size of the fine particles which are produced through dry grinding and the particles which are produced by the reaggregation of such fine particles are plotted against the grinding time, the results are as shown in Fig. 8.

The curve, if extrapolated to time zero, indicates the value of about 200 Å in all kinds of halloysite, and this value is the same as that in the case of kaolinite. It seems that the crystallites which separate from the original crystal during the early stage of grinding are about 200 Å in size. As shown on these curves, the time in which the reaggregated particles begin to grow irregularly corresponds to the degree of crystallinity of the original samples. The irregular growth of the reaggregated particles is found also in Kibushi-clay. It is considered that the irregular growth of such particles indicates the change into a perfectly amorphous substance from a non-crystalline substance produced by dry grinding.

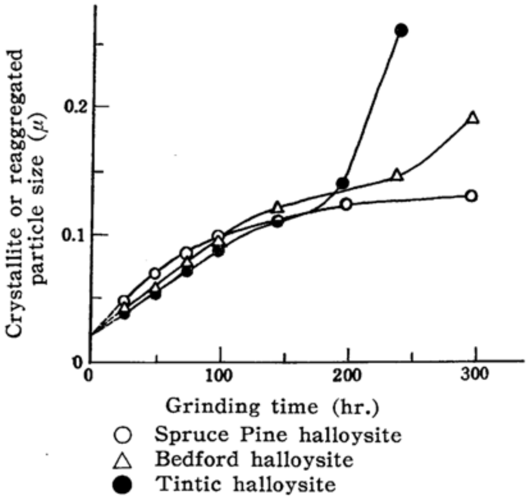

Fig. 8. Crystallite or reaggregated particle size of ground halloysite plotted against the time of grinding.

Mechanism of Change in Halloysite Structure due to Dry Grinding. — When halloysite is ground, halloysite crystals cleave and fracture and then split into fine crystals which are considered unit crystallites. These crystallites are very similar to those in case of kaolinite in shape and size. Groups of several such fine crystallites promptly reaggregate. The reaggregated crystallites change partially or thoroughly into a non-crystalline material. These non-crystalline substances reaggregate with the crystallites. As the grinding progresses, the crystalline part of the reaggregated particle decreases and the size of the reaggregated particle increases gradually. In a certain stage of grinding, a zeolitic structure is formed. The reaggregated particles which have a zeolitic structure become uniformly spherical. This period in grinding corresponds to the maximum point on the base exchange capacity curve and the inflection point on the density curve. The structure, with the progress of grinding, changes finally to the perfectly amorphous structure as silica-alumina mixed gel and the particle size grows irregularly.

The process of the structural change by dry grinding is the same as in the cases of all kinds of halloysite. The only difference is that Spruce Pine halloysite is less easily subject to the effect of the structural change than Tintic halloysite. This means that the effect of dry grinding of halloysite depends on the structural perfectness of the original halloysite. Generally, the effects of dry grinding on kaolin minerals are related to the internal degree of crystallinity of the original kaolin minerals.

Summary

The effects of several-hundred-hour mechanical-mortar dry grinding of halloysite were studied by X-ray diffraction, differential thermal, electron microscopic and other methods and they were compared with those of kaolinite and Kibushi-clay. It has been found that there are two sorts of structural change caused by dry gringing in halloysite as in the case of kaolinite. One is the production of a non-crystalline material attended with disordering of crystallites, and the other is the process of reaggregation. In a certain stage of grinding, the reaggregates come to have a zeolitic structure. This stage of grinding corresponds to the maximum point on the base exchange capacity curve and the inflection point on the density curve. The particle which has a zeolitic structure is uniformly spherical. As the grinding progresses further, halloysite changes into an amorphous substance, and the particle size increases irregularly. In consequence, it

was found that the effects of dry grinding on kaolin minerals depend strikingly on the structural perfectness of unit layers of the original kaolin minerals, that is, the internal degree of crystallinity.

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Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo