# *Effects of Dry Grinding on Kaolin Minerals. II. Kibushi-clay*

By Hiroshi TAKAHASHI

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In the preceding part of this series, the effect of dry grinding of kaolinite was discussed.[1] From these results, it was ascertained that the dry grinding by a mechanical-mortar is more effective than that by ball-milling in its structural change, and the mechanism of the process of dry grinding of kaolinite was found. There are two sorts of change in structure. That is, one is the production of a non-crystalline substance resulting from the disordering of a crystalline part. The other is the process of reaggregation. In a certain stage of grinding, a zeolitic structure is formed and it changes finally into an amorphous structure.

A considerable amount of work was done on the grinding effect of kaolinite, but the grinding effects of kaolin minerals with the exception of kaolinite were not studied much. The disordering of kaolinite in the process of dry grinding follows each of the structural variations as reported by Brindley and Robinson[2]. From these facts, the effects of dry grinding of fireclay type kaolin mineral were studied with respect to the degree of crystallinity of the original structure.

## Experimental

The sample used in this study is Kibushi-clay from Shidare, Gifu, Japan. This clay is a kaolin mineral of fireclay type and contains a little organic substance[2,3]. The structural characteristics of this clay were discussed in the previous paper[4]. The grinding conditions were the same as those of kaolinite described in the preceding part. The experimental specimens were examined by X-ray diffraction, differential thermal, electron microscopic and other methods. All experimental conditions were the same as those of kaolinite.

## Results and Discussion

**X-Ray Diffraction Studies.**—X-ray diffractometer traces in the process of dry grinding of Kibushi-clay are shown in Fig. 1, and X-ray powder data observed from the X-ray traces are given in Table I. As shown in the X-ray diagram of the original sample, the structure of Kibushi-clay is similar to that of fireclay. That is, in the X-ray diagram, 020 and $1\bar{1}0$ reflections are not resolved to each other and become a wedge-like band, 001 reflection is considerably broad and weak, $13\bar{1}, 1\bar{1}2$ reflections are weak and $20\bar{1}, 130$ reflections are broad.

1) H. Takahashi, This Bulletin, **32**, 235 (1959).
2) G. W. Brindley and K. Robinson, *Trans. Faraday Soc.*, **42B**, 198 (1946).
3) G. W. Brindley and K. Robinson, *Trans. Brit. Ceram. Soc.*, **46**, 49 (1947).
4) H. Takahashi, This Bulletin, **31**, 275 (1958).

TABLE I
POWDER DATA OF GROUND KIBUSHI-CLAY IN ANGSTROM UNITS

| Fireclay from Brindley and Robinson | | | Original clay | Ground 48 hr. | Ground 96 hr. | Ground 144 hr. | Ground 144 hr. treated with 0.1 N HCl after 0.1 N NaOH | Ground 192 hr. | Ground 384 hr. |
|---|---|---|---|---|---|---|---|---|---|
| *d* | *I* | *hkl* | *d* *I* | *d* *I* | *d* *I* | *d* *I* | *d* *I* | *d* *I* | *d* *I* |
| 7.15 | 10 | 001 | 7.20 S | 7.20 S | 7.3 M br | 7.7 M br | | 8.0 W vbr | |
| 4.45 | 8 | 02,11 | 4.45 S | 4.45 S | 4.44 M br | | | | |
| 4.36 | 2 | 110 | 4.33 VW | | | | | | |
| 4.14 | 2 | 11$\bar{1}$ | | | | | | | |
| 3.57 | 10 | 002 | 3.58 S | 3.58 S | 3.57 M br | 3.6 M br | 3.7 M vbr | 3.5 M vbr | 3.6 W vbr |
| 2.55 | 7 | 20$\bar{1}$, 130 | 2.56 M | 2.57 M | 2.57 W br | | | | |
| | | | 2.53 W | 2.55 VW | | | | | |
| 2.50 | 7 | 13$\bar{1}$, 200 | 2.50 M | 2.50 M | | | | | |
| 2.375 | 7 | 003 | 2.38 W | 2.38 VW | | | | | |
| 2.325 | 8b | 20$\bar{2}$, 131 | 2.34 M | 2.34 M | 2.35 W br | | | | |

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

When Kibushi-clay is ground, its structure gradually becomes more and more disordered. That is, the background increases as the intensity of the reflection weakens. In the X-ray diagrams of the ground specimens during the early stage of grinding, a lowering in the intensity of 001 reflections is remarkable, and the 131, 112, 200 reflections are very indistinct in the ground specimen after 72 hours.

In the X-ray diagrams of the ground specimens after 96 hours, only 02, 11$\bar{1}$ and 20, 13 bands are observable. When the 144-hour-ground specimen which has an amorphous structure is treated with a weak alkaline solution, it changes into a permutite-like substance. In the next place, it is treated with a weak acid solution to dissolve the amorphous substance produced by dry grinding. The X-ray diagram of the residual part produced by the above treatments is shown in Fig. 1-b-B

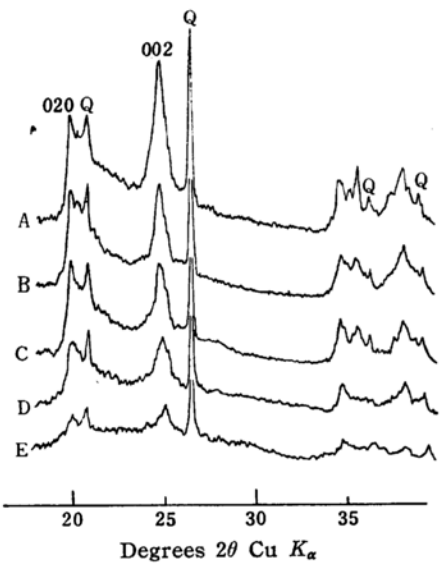



Fig. 1-a. X-ray diffractometer traces of Kibushi-clay. (I)
A, original Kibushi-clay
B, ground 24 hours
C, ground 48 hours
D, ground 72 hours
E, ground 96 hours

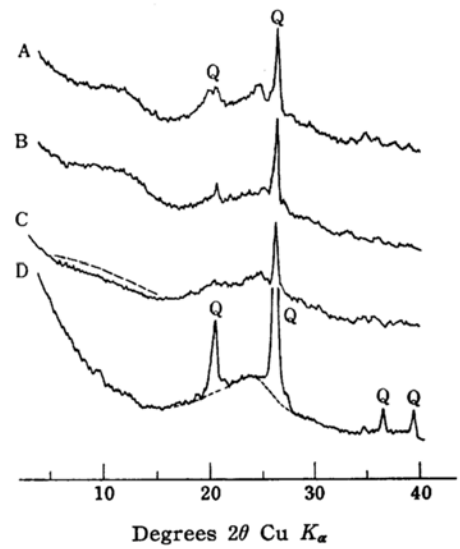



Fig. 1-b. X-ray diffractometer traces of ground Kibushi-clay. (II)
A, ground 144 hours
B, 144-hour-ground Kibushi-clay treated with 0.1 N HCl after 0.1 N NaOH.
C, ground 192 hours
D, 192-hour-ground Kibushi-clay treated with 0.1 N HCl after 0.1 N NaOH.

and its electron micrograph is shown in Fig. 6-F. The above-mentioned alkali-acid treatment was done for the 192-hour-ground specimen, too. The X-ray diagram of the residual part is shown in Fig. 1-b-D. As shown in this trace, the X-ray diagram is closely similar to that of the silica gel. This fact indicates that the crystalline part is absent in this specimen and it has changed into a gel-like substance. The specimen of Kibushi-clay ground after this stage gives a perfectly amorphous pattern in its X-ray diagram. The above-mentioned alkali-acid treatment of this specimen leaves only the impurities such as quartz.

When the result of X-ray study in Kibushi-clay is compared with that of kaolinite, it is clear that Kibushi-clay takes to become amorphous in far shorter than grinding time the case of kaolinite. On the basis of the X-ray data in the various stages of grinding of Kibushi-clay, it can be concluded that the effects of dry grinding of kaolinite and Kibushi-clay depend on the perfectness of kaolin unit layer, that is, the internal degree of crystallinity.

**Differential Thermal Analysis.**—Differential thermal analysis curves and data of ground specimens of Kibushi-clay are shown in Fig. 2 and Table II.

The tendency observed from the differential thermal analysis curves are similar to those in the kaolin specimens, but the only difference observable is that all of them have a broad exothermic reaction at about 600°C caused by the presence of some organic substances.

The first endothermic reaction ($E_{n1}$) associated with the loss of adsorbed or inter-layer water, which is not so remarkable in the original sample, becomes apparent and its height and area grow as the grinding progresses. These phenomena mean that the substance produced by the grinding adsorbs water vapor and its quantity increases with grinding. The peak temperature of this reaction rises slightly. This fact suggests that the substance produced by the grinding adsorbs more and more strongly the water vapor as the grinding progresses.

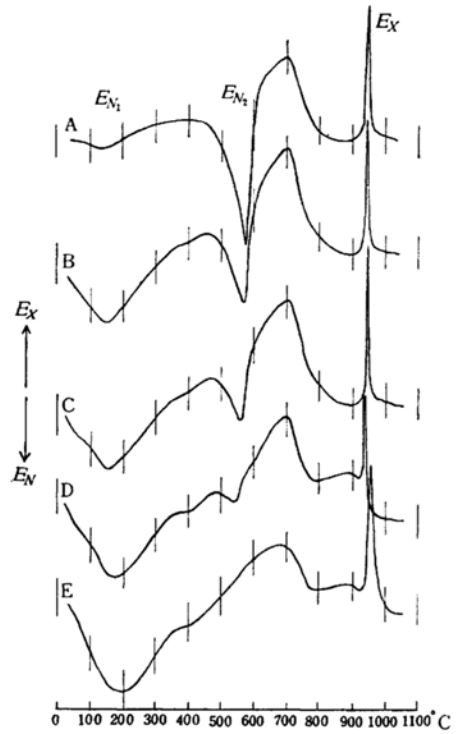



Fig. 2. Differential thermal analysis curves of ground Kibushi-clay.
A, original Kibushi-clay
B, ground 48 hours
C, ground 96 hours
D, ground 192 hours
E, ground 384 hours

In the second endothermic reaction ($E_{n2}$) associated with the loss of lattice water, a lowering in its peak temperature, and a reduction in the peak height and area

TABLE II
THERMAL DATA OF GROUND KIBUSHI-CLAY
(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 | 130° | 1 | 140 | 574°C | 14 | 740 | 945°C | 13 | 140 | 10.5°C |
| 48 | —140— | 12 | 1320 | 563 | 12 | 480 | 941 | 28 | 160 | 6.4 |
| 96 | —145— | 10 | 1410 | 551 | 7 | 260 | 941 | 36 | 180 | 4.6 |
| 192 | —160— | 10 | 1830 | 534 | 1 | 30 | 940 | 53 | 220 | 3.9 |
| 384 | —180— | 10 | 1780 | — | — | — | 960 | 15 | 200 | 14.0 |

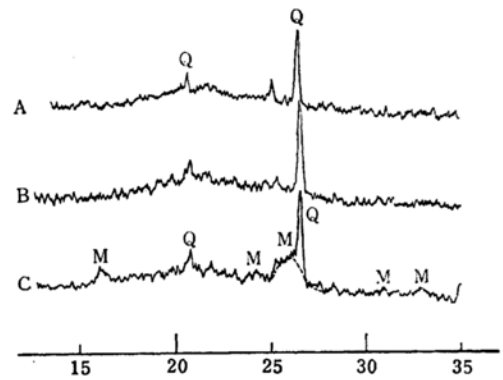
are observable. Finally, this reaction disappears completely. This leads to the disintegration of kaolin structure while it is being ground for long periods.

The final exothermic reaction ($E_x$) which corresponds to the mullite nucleation, is somewhat different from that of kaolinite. The peak temperature tends to fall, though very slightly, up to 192 hours of grinding. Except for the 384-hour-ground specimen, the peak height and area of the other specimens increase and the peak breadth is reduced. For the 240-hour-ground specimen, the peak temperature is almost the same as that of the 192-hour-ground specimen but the breadth is broader. In the 384-hour-ground specimen, the peak temperature rises above that of all other ground specimens, and the height and the area are smaller than those of the 192-hour-ground or the 240-hour-ground specimens. These facts mean that the structure of a non-crystalline substance produced by dry grinding changes into a more disordered structure as the grinding progresses. In the early stage of grinding, the strcture of a non-crystalline substance becomes to some extent a regular structure which is related to the original kaolin structure, but the structure of the 384-hour-ground specimen is not regular, it is an entirely disordered gel-like substance. From these facts, it might be seen that the temperature for the transformation of kaolin into mullite is high.

As shown in Figs. 2-D and -E, the slight endothermic reaction is observable just before the exothermic reaction. It has been known that the presence of this slight endothermic reaction is observable on the thermal curve of kaolin mineral with the highest degree of crystallinity[6]. The 192-hour-ground specimen of Kibushi-clay has a non-crystalline structure according to the X-ray and other data. Why does this slight exothermic reaction exist in this specimen? It is difficult to draw a conclusion as yet. But it is supposed that this fact is related to the considerable sharpness of the peak of the exothermic reaction and its remarkable height. There are two interpretations of this fact. One is that the way of transformation of kaolin into mullite is different from that of the original sample, and the other is that the tranformation of kaolin into mullite becomes more liable to grow than in the case of the original sample.

5) H. H. Murray, *Am. Mineal.*, **39**, 27 (1954).

To ascertain the character of the final exothermic reaction, X-ray diagrams were taken of some specimens after the exothermic reaction on the differential thermal analysis curve. Their traces are shown in Fig. 3.




Degrees $2\theta$ Cu $K_\alpha$
M: Mullite, Q: Quartz

Fig. 3. X-ray diffractometer traces of ground Kibushi-clay obtained just after the final exothermic reaction ($E_x$) on the differential thermal analysis curve.
A, original Kibushi-clay
B, ground 96 hours
C, ground 192 hours

In this case, too, it is indicated that as the grinding progresses, the reflection line of mullite crystal becomes clear. The final exothermic reaction has two elements, that is, the nucleation of mullite from the original kaolin mineral and the growth of mullite crystal from the mullite nuclei.

This is true because the presence of this weak endothermic reaction in the kaolin mineral with the highest degree of crystallinity corresponds to the nucleation of mullite. In the case of this ground specimen, it is clear that the nucleation of mullite from the kaolin mineral is easy, but the crystal growth of mullite nuclei is hard. But in the case of the ground specimen such as the 192-hour-ground Kibushi-clay, the presence of its endothermic reaction corresponds to the crystal growth of mullite nuclei. That is in the 192-hour-ground specimen or the 384-hour-ground specimen of Kibushi-clay, though the nucleation of mullite from the kaolin mineral is hard, the crystal growth of mullite nuclei is easy. Consequently, in the specimen of Kibushi-clay which is ground for a long period, the temperature of the transformation into mullite rises, because the nucleation of mullite is hard.

But, as the crystal growth of mullite nuclei is easy and rapid, the reflection of mullite is distinctly detected in its X-ray diagram, and so the height of the exothermic peak increases.

**Base Exchange Capacity and Density.**— In Fig. 4 are shown the changes of the base exchange capacity with the grinding time. Measurements were made on the dried specimens.

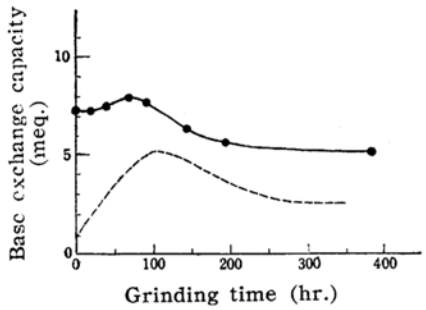



Fig. 4. Curve showing the change of base exchange capacity with the time of grinding.
------: The change in the grinding process of Mesa Alta kaolinite.

In this figure, the change in the grinding process of Mesa Alta kaolinite is drawn for reference.

The features obtained from the curve of base exchange capacity are slightly different from those of kaolinite. The maximum point is observable on the base exchange capacity curve of the grinding process of kaolinite, but it is not distinct on this curve. As shown in the micrograph of the original clay to be noted in the following section, the particle size of the original Kibushi-clay is very fine as compared with that of other kaolin minerals. Therefore, the fracturing into crystallites from the original crystal during the early stage of grinding is not so remarkable as that of kaolinite. In this clay, an increase in the broken bond which results in an increase of the capacity is not remarkable. As the result, it seems that the maximum point on the base exchange capacity curve is unobservable. In this case, the change of the base exchange capacity depends mainly on the production of a non-crystalline substance by dry grinding. This tendency also supports the thought shown by Laws and Page in the explanation for the change of the base exchange capacity due to dry grinding[6].

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

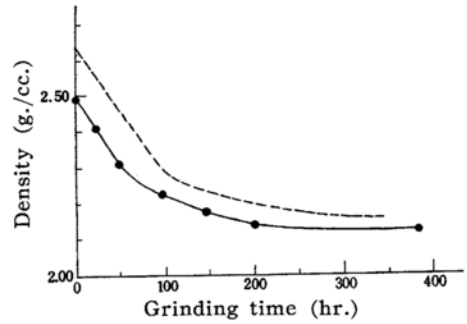



Fig. 5. Curve showing the change of density with the time of grinding.
------: The change in the grinding process of Mesa Alta kaolinite.

In Fig. 5 are shown the changes of the density with the grinding time. Measurements were made on the dried specimens.

In this figure, the change of density in the process of grinding of Mesa Alta kaolinite is drawn for reference. As the original sample of Kibushi-clay contains only a little organic substance, its density value is small.

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

**Electron Microscopic Studies.** — Fig. 6 shows the electron micrographs in the various periods of grinding of Kibushi-clay. The original clay is very fine and hexagonal platty, and the particle has a considerably sharp edge. In the early stage of grinding, fine crystallites separated from the original crystal are observable. These fine crystallites are nearly hexagonal and platty. As the grinding progresses, the fine crystallites promptly reaggregate, and reaggregated particles become spherical and the particle size increases gradually. As the grinding further progresses, the irregular growth of particles is observable. On the basis of the results obtained through the X-ray and other methods, it is understood that this irregular growth of reaggregated particles indicates that an amorphous substance is produced by dry grinding. The same thing is also found in halloysite as shown latter.

If the mean sizes of the fine particles which are produced through dry grinding and the particles which are produced by

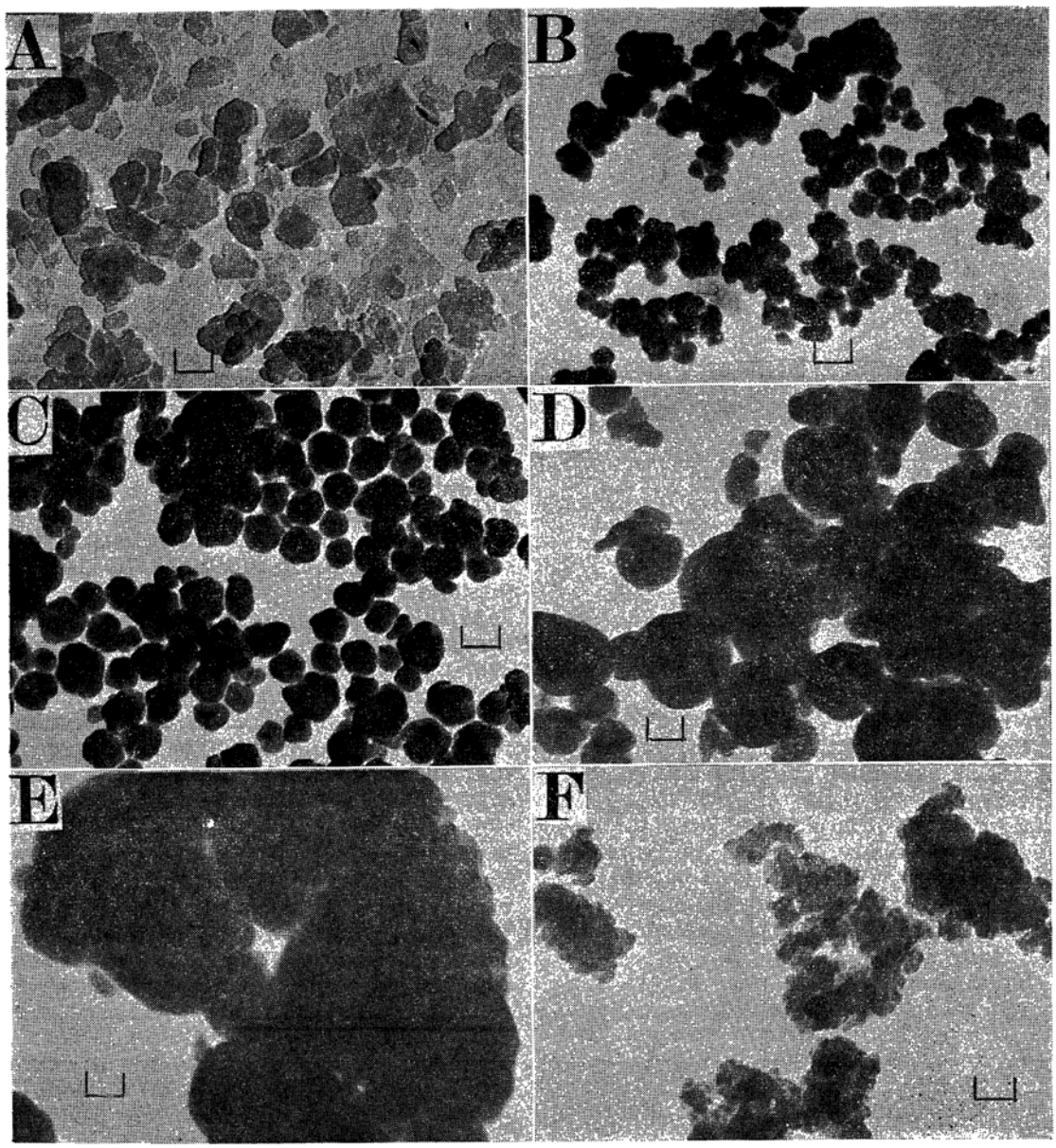



Fig. 6. Electron micrographs of ground Kibushi-clay. The linear dimension on the micrographs represents 0.1 $\mu$.

A, original Kibushi-clay
B, ground 48 hours
C, ground 96 hours
D, ground 192 hours
E, ground 384 hours
F, 144-hour-ground Kibushi-clay treated with 0.1 N HCl after 0.1 N NaOH.

the reaggregation of such particles are plotted against the grinding time, the results are as shown in Fig. 7.

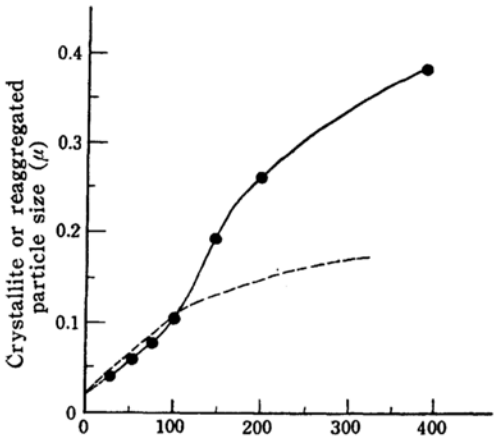



Fig. 7. Crystallite or reaggregated particle size of ground Kibushi-clay plotted against the time of grinding.
------: The change in the grinding process of Mesa Alta kaolinite.

In this figure, the curve showing the change of the crystallite or reaggregated particle with the grinding time in Alta kaolinite is drawn for reference. The curve, if extrapolated to zero time, indicates the value of about 200 Å. This value is the same as that in the case of kaolinite. As in kaolinite, in Kibushi-clay, too, the crystallites produced in the early stage of grinding seem to have about 200 Å in size. It is supposed that the time when the irregular growth begins is related to the degree of crystallinity of the original sample. This tendency is found also in halloysite. That is, the lower the crystallinity, the faster the irregular growth.

## Summary

The effects of several-hundred-hour mechanical-mortar dry grinding of Kibushi-clay which is a kaolin mineral of fireclay type were studied by X-ray diffraction, thermal, electron microscopic and other methods and compared with those of kaolinite. It has been found that the process of a production of a non-crystalline substance attended with a disordering of a crystalline part and the process of a reaggregation are present in the dry grinding of Kibushi-clay as in kaolinite. Finally, Kibushi-clay changes into an amorphous substance as the result of dry grinding. In a certain stage of grinding, a zeolitic structure is formed. As the grinding progresses, the particle size increases owing to reaggregation. When an amorphous substance like silica-alumina mixed gel is produced, the particle size grows irregularly. In Kibushi-clay, the time it takes to become amorphous by dry grinding is shorter than in the case of kaolinite. Consequently, the effects of dry grinding of kaolinite and kaolin mineral of fireclay type depend on the structural perfection of unit layers of the original kaolin minerals.

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