STRUCTURAL VARIATIONS OF SOME KAOLINITES IN RELATION TO DEHYDRATED HALLOYSITE

HAYDN H. MURRAY, *Indiana University and Geological Survey.**

ABSTRACT

A selected series of kaolin clay minerals was examined using *x*-ray powder diffraction techniques to show structural variations. Differential thermal analysis curves were run, using these same kaolin clay minerals to see if any relationship could be established between the *x*-ray data and the *DTA* curves. The results show that there is a relationship for all the samples studied with the exception of dehydrated halloysite.

INTRODUCTION

Investigations of the structure of kaolinite have shown that there are structural variations within the kaolinite unit layer and variations in the stacking of these layers, one upon the other (1).

The structural determinations on the kaolin minerals selected for this study were accomplished using *x*-ray powder diffraction data. The kaolin minerals were classed according to their degree of crystallinity. The degree of crystallinity is defined to include the disorder within the crystallographic unit layer and the stacking variations of the unit layers. Differential thermal analysis curves were run using samples which were identical to those used for the *x*-ray powder photographs. The *DTA* curves were then analyzed to see if there were any significant features which could be used to relate these curves to the degree of crystallinity as determined from *x*-ray data.

The following kaolinite clays were investigated: a kaolin from Gordon, Georgia; a flint clay from Montgomery County, Missouri; a flint clay from Soldier, Kentucky; a ball clay from Whitlock, Tennessee; a kaolin clay from Union County, Illinois; a fireclay from Mexico, Missouri; and an underclay from Grundy County, Illinois. In addition to these kaolinite clays, a halloysite clay from Gardner Mine Ridge in Lawrence County, Indiana, was included because it is generally considered to be a member of the kaolin clay mineral group even though it has many different characteristics.

X-RAY DIFFRACTION STUDIES

The most comprehensive study on randomness in the structure of some kaolin clay minerals was that done by Brindley and Robinson (1). They established that differences could be detected on *x*-ray powder photographs, and used to indicate randomness in layer orientation and struc-

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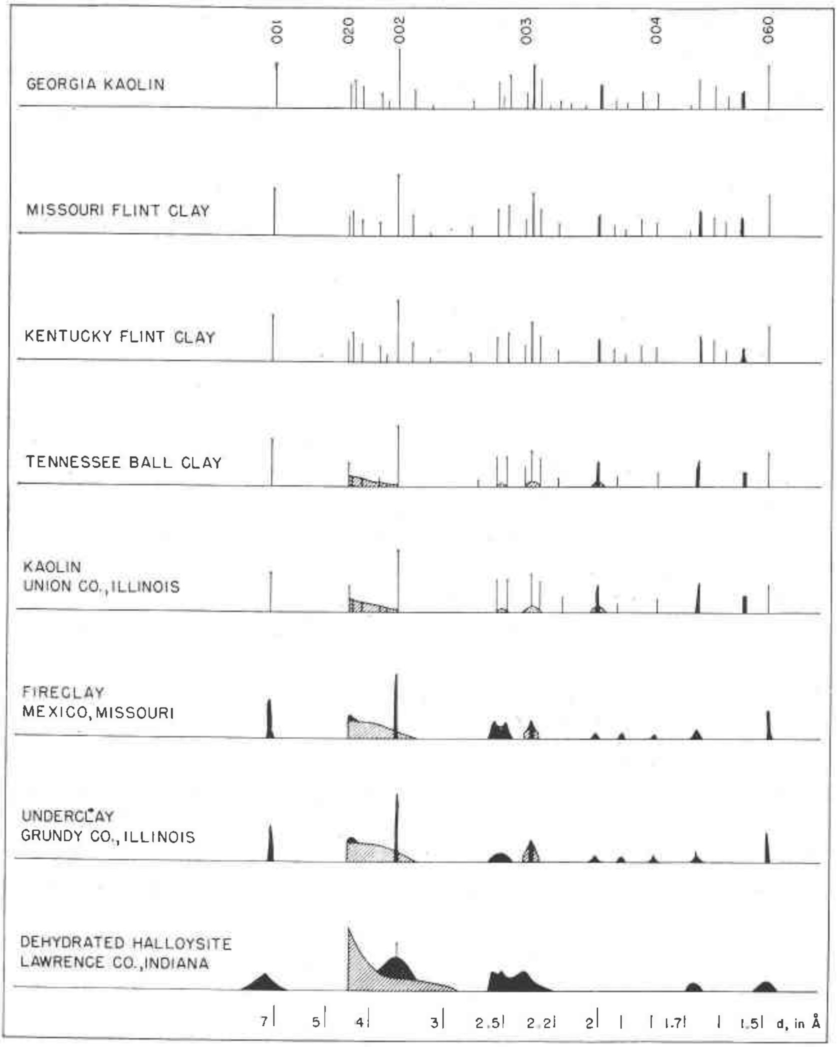

FIG. 1. Diagrammatic representation of x-ray photographs of some kaolin minerals. (Intensities estimated.)

tural variations in kaolin clay minerals. The criteria used by Brindley and Robinson and some additional features found by the author were used to determine the relative degree of crystallinity of the kaolinites and dehydrated halloysite used in this investigation. The halloysite was dehydrated in order that it would have approximately the same basal spacing as kaolinite. The x-ray powder diffraction patterns of the kaolinites and halloysite were obtained with a North American Philips x-ray unit. The samples were ground, dried, and then packed into a wedge-type sample holder. A powder camera with a diameter of 14 cm. was used and the specimens were exposed to nickel filtered Cu radiation for 4.5 hours at 35 KV and 18 ma.

The following major differences, noted on the x-ray powder photographs, were used as criteria to determine the degree of crystallinity:

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

Each of these criteria will be discussed in the following paragraphs.

The x-ray reflections on some of the photographs were very sharp and distinct and on others the reflections were broad, fuzzy bands. The relative sharpness of the reflections from the clays studied are shown diagrammatically in Fig. 1. The x-ray reflections of the three clays at the top of the diagram are sharp and distinct. Some of the reflections of the kaolinite in the Tennessee ball clay and the Union County kaolin become fuzzy and broad. The x-ray reflections on the bottom three photographs of the diagram are all relatively broad and diffuse. It is realized that sharpness of reflections is also dependent on particle size and orientation. The samples were not oriented and the sizes of particles were very similar, so that these factors had little, if any, effect.

The number of x-ray reflections which appear on a photograph serve as an indicator of the degree of crystallinity. The reflections which can be indexed out through the (060) reflection on the x-ray photograph of Georgia kaolin amount to a total of 31. Only 8 reflections appear on the x-ray photograph of the dehydrated halloysite. The other kaolinites have an intermediate number of reflections, the number of reflections decreasing from the top to the bottom photograph shown diagrammatically in Fig. 1.

Slight variations in the basal spacings of the clays used in this study were detected and may indicate to some extent the degree of crystallinity. The (001) spacing for the Georgia kaolinite and the two flint clays was 7.18 Å. The (001) basal spacing of both the Tennessee ball clay kaolinite and the kaolinite in the Union County kaolin was 7.20 Å., and for the kaolinite in the Missouri fireclay and the Grundy County underclay was 7.30 Å. The basal spacing of the dehydrated halloysite was 7.42 Å. This shows that there is a general increase in the (001) basal spacing progressing from the Georgia kaolin to the dehydrated halloysite as shown in Fig. 1 and Table 1. This slight increase in basal spacing could be the

TABLE 1. "*d*" VALUES OF SOME KAOLIN MINERALS IN ANGSTROM UNITS

Brindley and Robinson	*I*	Ga. (soft)	*I*	Flint Mo.	*I*	Flint Ky.	*I*	*hkl*	Tenn. Ball Clay	*I*	Union Co. Kaolin	*I*	Fireclay Mo.	*I*	Grundy Co. Underclay	*I*	Dehy-drated Halloysite	*I*
7.15	10	7.18	VS	7.18	VS	7.18	VS	001	7.20	VS	7.20	VS	7.30	VS	7.30	VS	7.42	VS
4.453	4	4.50	S	4.49	M	4.50	M	020	4.55	S	4.48	S	4.49	S	4.49	S	4.47	VS
4.349	6	4.41	S	4.41	S	4.43	S	$1\bar{1}0$										
4.170	6	4.21	S	4.23	M	4.23	M	$11\bar{1}$										
4.120	3							$1\bar{1}\bar{1}$										
3.837	4	3.87	M	3.87	M	3.91	M	$02\bar{1}$	3.95	W								
3.734	2	3.76	W			3.76	W	021										
3.566	10	3.62	VS	3.61	VS	3.61	VS	002	3.59	VS	3.58	VS	3.58	VS	3.56	VS	3.63	VS
3.365	4	3.42	M	3.43	M	3.41	M	111										
3.138	2	3.13	W	3.13	W	3.15	W	$11\bar{2}$										
3.091	2							$11\bar{2}$	3.09	W								
2.748	2	2.76	W	2.75	W	2.76	W	022										
2.553	8	2.56	S	2.55	S	2.57	S	$20\bar{1}$, $1\bar{3}0$, 130	2.56	S	2.55	S	2.57	M	2.56	M	2.56	M
2.521	4	2.52	M					$13\bar{1}$, $1\bar{1}2$	2.52	S	2.49	S	2.50	M				
2.486	9	2.48	S	2.50	S	2.49	S	$1\bar{3}\bar{1}$, 200, 112									2.48	M
2.374	7	2.38	M	2.42	M	2.41	M	003	2.42	M								
2.331	10	2.36	VS	2.37	VS	2.36	S	$20\bar{2}$, $1\bar{3}1$	2.36	S	2.35	S	2.35	M	2.37	M	2.35	M
2.284	9	2.32	S	2.31	S	2.31	M	$1\bar{1}\bar{3}$, $13\bar{1}$	2.29	S	2.30	S						
2.243	1	2.26	W					$13\bar{2}$, 040										
2.182	3	2.20	W	2.21	M	2.22	W	201, $1\bar{3}\bar{2}$, $2\bar{2}0$	2.21	W	2.20	W	2.21	W				
2.127	2	2.13	W					$02\bar{3}$, 041							2.13	W		
2.057	1	2.08	W	2.01	S	2.05	M	023, $2\bar{2}\bar{2}$										
1.985	7	1.99	S	1.96	W	1.96	W	$20\bar{3}$, $1\bar{3}2$	1.97	S	1.99	S	2.00	W	2.00	W		
1.935	4	1.95	W					221, 132										
1.892	2	1.92	W	1.91	W	1.90	W	113, $13\bar{3}$	1.92	W	1.90	W	1.90	W	1.90	W		
1.865	1							042										
1.836	4	1.86	M	1.86	M	1.85	M	$1\bar{3}\bar{3}$, 202, $22\bar{3}$										
1.805	1							$11\bar{4}$, $2\bar{2}\bar{3}$										
1.778	5	1.79	M	1.80	M	1.80	M	004	1.80	M	1.79	M						
1.704	1							$2\bar{2}2$										
1.682	2	1.68	W	1.69	W			$1\bar{5}0$, $24\bar{1}$, $31\bar{1}$										
1.659	8	1.66	S	1.67	S	1.67	S	$2\bar{4}0$, $20\bar{4}$, $1\bar{3}3$	1.66	S	1.67	S	1.68	M	1.67	W	1.67	W
1.616	6	1.62	M	1.62	M	1.63	M	$24\bar{2}$, 133, 310	1.63	M	1.62	M						
1.581	4	1.58	M	1.58	M	1.58	W	$15\bar{2}$, $13\bar{4}$										
1.539	5	1.52	M	1.54	M	1.54	M	241, $1\bar{1}4$, $1\bar{3}\bar{4}$										
1.486	9	1.48	S	1.49	S	1.49	S	060, $3\bar{3}\bar{1}$, $33\bar{1}$	1.50	S	1.48	S	1.49	S	1.49	S	1.48	M

consequence of : (*a*) the presence of an occasional water layer between the unit layers of the kaolinites with the poorer degrees of crystallinity, and/or (*b*) disorder in the unit layer or stacking variations in the kaolin unit layers which would be expected to be greater in the samples with the lower degree of crystallinity.

The resolution of the closely spaced reflections on an *x*-ray powder photograph of a kaolinite can be used to indicate the degree of crystallinity. The closely spaced reflections on a powder photograph of a kaolinite with a good degree of crystallinity are well resolved as exemplified by the reflections adjacent to the (020) and the (003) reflections on the top three diagrams of Fig. 1. These closely spaced reflections become hazy and indistinct on the diagrams of Tennessee ball clay and the Union County kaolin and are completely merged on the bottom three diagrams of Fig. 1.

Many reflections are absent on the *x*-ray photographs of kaolinites with a poor degree of crystallinity. This criteria is related to the total number of reflections which appear, but there are certain reflections which are cut out by the displacements of the kaolin layers and so need separate discussion. An explanation for the absence of certain reflections has been advanced by Brindley and Robinson (2). The (OH) groups in the kaolin layer are arranged at regular intervals along the *b*-axis, this distance being equal 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 oriented with the 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 · · · . Random displacements result in broad, diffuse reflections (2).

The broad, diffuse reflections may also be explained in a different manner. The hydroxyl groups in the basal plane of the kaolin layer are arranged in three straight lines each trending 120° from the other (Fig. 2). Each hydroxyl group is an equal distance from the adjacent hydroxyl which lies in the same plane and this distance is equal to $b_0/3$. This means that in addition to displacements of $nb_0/3$, some layers may be rotated 120° relative to the adjacent layer without changing the relationships of the hydroxyl groups to the oxygen atoms of the adjacent layer. The positions of the aluminum atoms, however, would be changed, which could cause many reflections to be very diffuse, and the combination of displacement and rotation would cause broad band-like reflections.

The above *x*-ray data indicate that there is considerable structural variation in the kaolinites and dehydrated halloysite. Figure 1 shows the kaolinites and dehydrated halloysite in the relative order of their degree of crystallinity based on *x*-ray data, with Georgia kaolin having the highest degree of crystallinity and dehydrated halloysite the lowest.

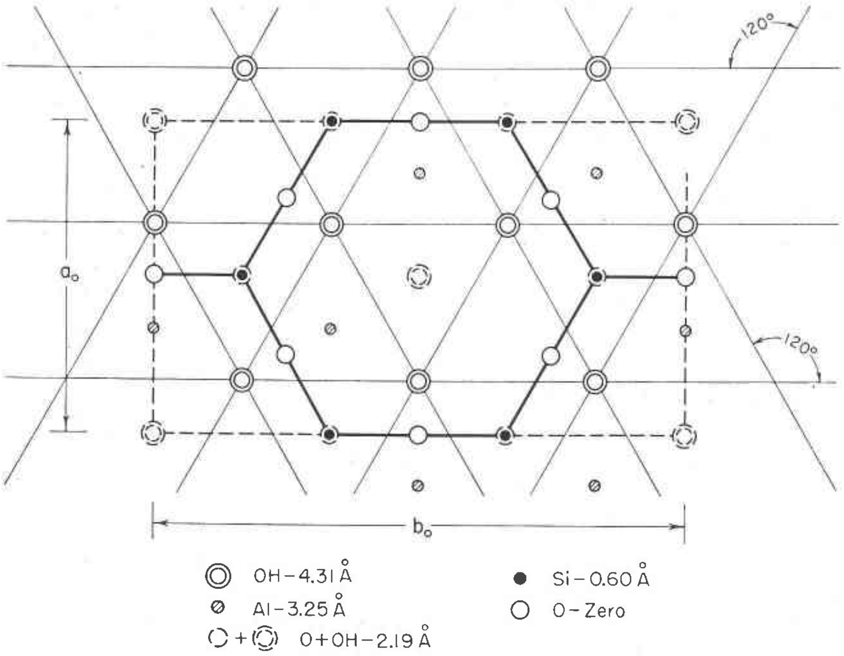

FIG. 2. Diagrammatic representation of the kaolin layer projected on the (001) plane showing the three possible directions along which the O—OH relationship of the adjacent layer could be satisfied.

Dehydrated halloysite, according to *x*-ray data, has the lowest degree of crystallinity of any of the samples studied since the unit layers are randomly oriented with respect to each other. This is significant because the criteria for dehydrated halloysite based on differential thermal analysis do not agree with the *x*-ray data.

DIFFERENTIAL THERMAL ANALYSES

It has been suggested that the crystallinity of a kaolinite is indicated by differential thermal analysis curves (3). In order to further test this suggestion, differential thermal analyses were made using the same kaolin clays as were used in the *x*-ray studies. The results obtained using the differential thermal analysis curves could then be compared with the results of the *x*-ray determinations.

The thermal apparatus used was similar to that described by Grim and Rowland (4). Great care was taken to pack the sample into the sample block in the same manner each time an analysis was run and also to keep the weight of sample constant.

No general criteria based on differential thermal analysis curves which could be used for all kaolinites to determine the relative degree of crystallinity have been indicated previously. Grimshaw et al. (5) have indicated that in kaolins, there is a variation in the temperature of the peak of the endothermic reaction which can be correlated with the degree of crystallinity. Impurities affect the *DTA* curve, as has been shown by Gruver, Henry, and Heystek (6). Recently Bramao et al. (7) have correlated the shape of the main endothermic peak on the *DTA* curve of the kaolin minerals with particle size and degree of crystalline perfection. In addition to the characteristics of the main endothermic peak, other criteria have been used in this study. By recording a variety of measurements and observations, it was hoped that an evaluation of them all would give a relative degree of crystallinity for the kaolins. The measurements and observations which were used are as follows:

(1) The temperature range and the size of the endothermic reaction associated with the loss of the lattice water. Temperature range means the difference in temperature between the points at which the reaction begins and ends. The size refers to the distance of the peak from the base line of the thermal curve.

(2) The peak temperature of the endothermic reaction.

(3) The slope of the curve between the point at which the endothermic reaction ends and the point at which the exothermic reaction begins.

(4) The temperature range between the endothermic peak and the exothermic peak.

(5) The presence of a slight endothermic reaction immediately preceding the exothermic reaction.

(6) The temperature range and size of the exothermic reaction.

(7) The peak temperature of the exothermic reaction.

The temperature range of the endothermic peak should be an indication of the degree of crystallinity, since it would seem that the lattice water would be more tightly bonded in the better crystalline kaolinites than the poorly crystalline ones. More energy would be needed to break the bonds holding the structural water in the lattice and, consequently, the temperature range, temperature, and size of this peak would be greater for the kaolinites with a high degree of crystallinity. The thermal curves (Fig. 3) reveal that the endothermic peak is very useful in determining the crystallinity of a kaolinite. The data in Table 2 show that in general the values for the temperature range, temperature of the peak, and the size of the peak are higher for the kaolinites which are shown to have the higher degrees of crystallinity by *x*-ray data. The major exception is dehydrated halloysite which has higher values than one would expect since *x*-ray data showed it to have a poor degree of crystallinity.

The kaolinites with the highest degree of crystallinity and the dehydrated halloysite reveal an upward sloping curve between the endothermic and the exothermic reactions and also a small endothermic break just before the exothermic peak (Fig. 2 and Table 2). This may mean that all the lattice water has not been ejected and that a structural reorganization is taking place. The final endothermic break may be a breakdown of the newly forming structure. It would seem that an upward sloping curve and a small endothermic break before the exothermic peak is an indication of a high degree of crystallinity. The major exception between the *x*-ray data and the use of this criterion is again dehydrated halloysite.

The values for the temperature range between the endothermic and the exothermic peaks do not appear to give any indication of the degree of crystallinity (Table 2).

TABLE 2. VALUES USED TO CLASSIFY THE KAOLIN MINERALS

(all temperatures are degrees centigrade)

Kaolinite*	Temp. range end. peak	Temp. at peak	Size of peak	Slope (°)	Temp. range between peaks	End. react. before exo.	Range exo. peak	Temp. at peak	Size of peak
1	310	595	4½″	15°	375	strong	30	970	6″
2	290	580	5½″	14	385	strong	40	965	5¼″
3	300	580	3¼″	8	370	none	60	950	6½″
4	270	580	4¼″	7	375	weak	60	955	6¾″
5	170†	570	3½″	0	390	none	60	960	3¼″
6	250	560	4″	7	385	none	70	945	2½″
7	240	560	4″	9	380	none	80	940	5″
8	160†	560	3″	3	380	none	95	940	1¼″
9	260	575	4¼″	12	395	weak	40	970	6″‡

* 1—Georgia Kaolin (soft). 2—Missouri Flint clay. 3—Kentucky Flint clay. 4—Georgia Kaolin (hard). 5—Tennessee Ball Clay. 6—Kaolin (Union Co., Ill.). 7—Missouri Fireclay. 8—Underclay (Grundy Co., Ill.). 9—Dehydrated Halloysite.

† The start of the initial endothermic peak is masked by an exothermic reaction caused by organic material in the clay.

‡ The exothermic peak is actually larger because it went off the record.

The temperature range, temperature, and the size of the exothermic peak can be used to indicate the crystallinity of a kaolinite as is well shown by the values in Table 2. The temperature range is shorter, the temperature at the peak is higher, and the size of the peak is larger for the kaolinites with the higher degrees of crystallinity. The data for dehydrated halloysite again does not agree with the result as determined from *x*-ray data. The temperature range for the kaolinites with a high degree of crystallinity is short because the structure of the new phase formed may be related to the old structure (8). If the kaolinite structure is well ordered then the transformation should take place faster than if the structure were disordered. The peak temperature of the exothermic reaction is higher for the kaolinites with a high degree of crystallinity because more energy is needed to transform to a new phase since the old structure is stronger. The size variation of the peak is probably due to a greater energy release by the kaolinites with a high degree of crystallinity. Another possibility is that the new phase which forms is different in the kaolinite with a poor degree of crystallinity than that which forms from one with a high degree of crystallinity.

The measured values and observations which were taken from the original curves are listed in Table 2. The thermal curves in Fig. 3 are shown in the order of their relative degree of crystallinity.

Comparison of *X*-Ray and Thermal Data

A comparison of the relative degree of crystallinity of the kaolinites (Figs. 1 and 3) determined by using *x*-ray powder diffraction data and differential thermal criteria shows that the two methods compare favorably with the major exception of dehydrated halloysite. Dehydrated halloysite has a low degree of crystallinity according to *x*-ray data and a high degree of crystallinity according to differential thermal data.

The detailed structural characteristics of halloysite cannot be considered as established. Bates et al. (9) have proposed a structure that explains the tubular arrangement of hydrated halloysite but the relation of this concept to *x*-ray diffraction data is not clear. When the interlayer water is removed from hydrated halloysite, it is possible that the unit layers, which are structurally similar to the kaolinite layer, come together so that the O—OH relationship between the uppermost hydroxyls on one layer and the oxygens on the base of adjacent layer is satisfied in substantially the same manner as in well crystallized kaolinite. This directional relationship can be satisfied by any of the three hydroxyl strings (Fig. 2). However, the aluminum atoms may not be oriented in the same way as they are in well crystallized kaolinite since the aluminum atoms can have three possible orientations with respect to the hydroxyls, depending on the orientation of the hydroxyl strings. The possibility that the aluminum atoms are not oriented in the same manner in each successive layer could cause the broad diffuse reflections which are characteristic of the *x*-ray pattern of dehydrated halloysite.

On the basis of *x*-ray diffraction data, it seems that there is a gradation between the structure of a kaolin with a good degree of crystallinity to one with poor degree of crystallinity such as dehydrated halloysite. On the basis of the differential thermal analyses, dehydrated halloysite has a high degree of crystallinity. This suggests that *x*-ray reflections reveal both internal structural disorder and random stacking of the unit layers, whereas differential thermal analysis curves indicate only the orderliness of the internal structure of the unit layers. Differential thermal analysis curves do not reflect random stacking of the unit layers but only reflect

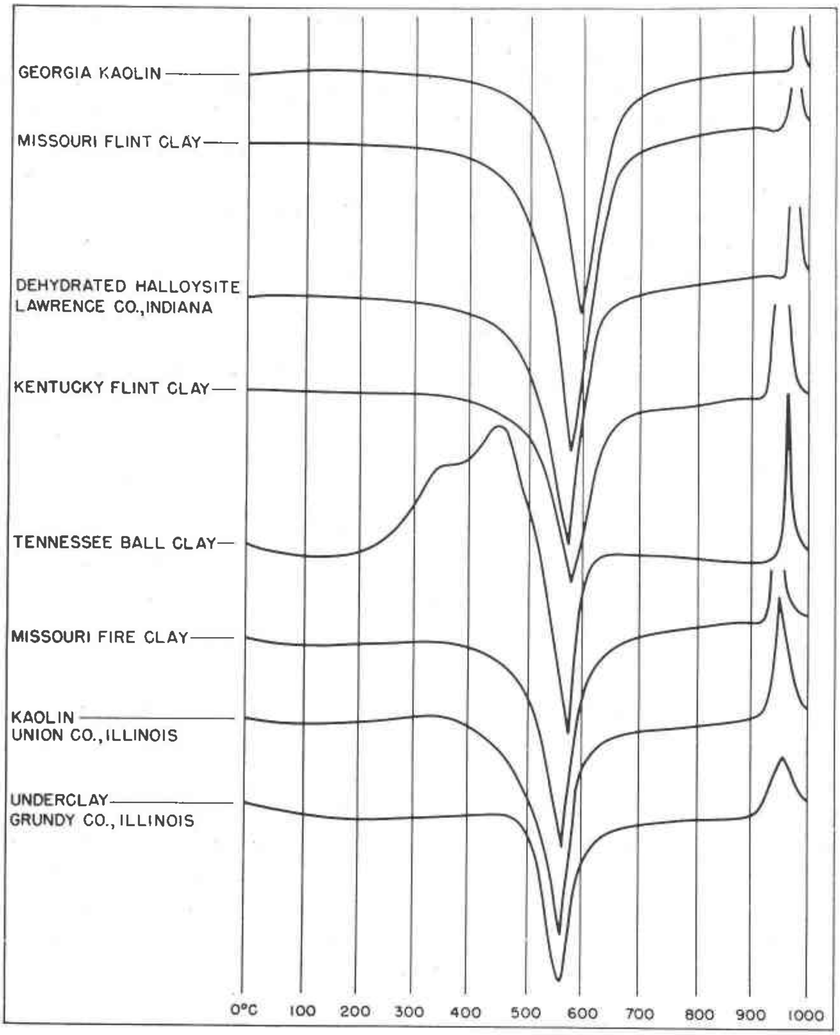

FIG. 3. Differential thermal analysis curves of some kaolin minerals.

the energy changes which occur when a structure breaks down or a new phase forms. This indicates that dehydrated halloysite has a relatively ordered unit layer, as indicated by thermal data, which is stacked upon the next unit layer with complete randomness with respect to the *a* and *b* axes, as indicated by *x*-ray data. The kaolinites, such as the Missouri fireclay, with a poor degree of crystallinity may have random displacements of $nb_0/3$ in different layers but in all probability are not rotated $n\ 2\pi/3$ as are the layers in the dehydrated halloysite. As a consequence, unit layers are oriented slightly better with respect to the *a* and *b* axes, and therefore, a few more reflections appear on the *x*-ray pattern.

A minor discrepancy is observed in the comparative position of Missouri fireclay and Union County kaolin. The differential thermal analysis curve indicates a higher degree of crystallinity for the Missouri fireclay while the *x*-ray data indicates the opposite. The explanation for this is probably that the kaolin layers of Missouri fireclay have a relatively more random orientation with respect to each other but each individual layer is more ordered than those of the Union County kaolin.

BASE EXCHANGE CAPACITY

Another property which might indicate the degree of crystallinity of kaolinites is their base exchange capacity. Base exchange capacity in kaolinite is due primarily to broken bonds (10), and possibly to negative charges on the lattice due to vacancies of alumina or silica positions in the poorly crystalline kaolinites.

The base exchange capacity was determined by the ammonium acetate procedure widely used in agricultural studies (11). The following are the base exchange capacities as determined on five of the kaolin samples.

	meq/100 gms.
Georgia kaolin	3
Kentucky flint clay	6
Kaolin (Union Co., Illinois)	11
Fireclay	18
Dehydrated halloysite	5

These values suggest that the kaolinites with the lower degrees of crystallinity have a higher base exchange capacity, with the exception of dehydrated halloysite. The kaolinite with the lower degree of crystallinity would have larger surface areas exposed due to random stacking, and relatively more broken bonds would be expected. This data again suggests that dehydrated halloysite is not as poorly crystalline as *x*-ray data would seem to indicate.

SUMMARY

1. *X*-ray analysis indicates that dehydrated halloysite has a poor degree of crystallinity and that some kaolinites have a good degree of crystallinity while others have a poor degree of crystallinity. There appears to be a continuous variation in the crystallinity of kaolinites rather than a step-wise gradation.

2. Differential thermal analysis curves indicate the same results as were obtained using *x*-ray data with the major exception of dehydrated halloysite which was indicated to have a high degree of crystallinity.

3. *X*-ray diffraction data seems to reflect both internal and stacking

variations whereas differential thermal analyses indicate only internal variations.

4. It is possible that the structural layers which make up dehydrated halloysite may be oriented in a manner which is different from that of kaolinite and, for that reason, appear to have a poor degree of crystallinity on the basis of x-ray diffraction data.
5. Base exchange data may be used to indicate degree of crystallinity of kaolinites. Dehydrated halloysite has a low base exchange capacity rather than a relatively high capacity as would be predicted on the basis of x-ray data.
6. Differential thermal analysis curves can be used to determine the degree of crystallinity of kaolinites.

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