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PROTOTROPY IN KAOLINITE DURING PERCUSSIVE GRINDING

JOHN G. MILLER

Department of Chemistry, University of Pennsylvania, Philadelphia 4, Pa. 19104, U.S.A.

and

T. DIXON OULTON

Engelhard Minerals & Chemicals Corp., Menlo Park, Edison, New Jersey 08817, U.S.A.

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Abstract—When kaolinite undergoes percussive grinding, pronounced changes take place in its i.r. absorption spectrum even in the earliest stages of the grinding when the lattice is not yet destroyed. In this report, attention is directed to the change in the stretching bands of the hydroxyl ions. A remarkably rapid effect on the band of the intralayer hydroxyl ions has been observed and is attributed to a permanent removal of the protons from these ions. Auxiliary measurements of X-ray diffraction, thermal water loss, and DTA were used to corroborate the spectroscopic evidence for this ready prototropy.

INTRODUCTION

BY USE of i.r. absorption spectroscopy, we have discovered that a remarkably rapid prototropy, i.e., transfer of protons from one place to another within the structure, takes place in kaolinite when that substance is subjected to percussive grinding. In the earliest stage of the prototropy the protons move away from the intralayer hydroxyl ions, i.e., away from the hydroxyl ions located in the plane shared by the octahedral and tetrahedral sheets of the kaolinite. Later on, the other (basal) hydroxyl ions also lose their protons and the new sites of attachment of the migrated protons appear to be scattered randomly about the structure where, for the most part, they are more weakly attached.

The kaolinite was dry-ground in a small cylindrical container with two steel balls, the container being put through an oscillatory motion resembling that of an inverted, high-speed pendulum (a "Wig-L-Bug" mixer was used for this purpose). The measurement of the proton transfer was carried out by i.r. absorption spectrometry, with auxiliary measurements of thermal dehydroxylation, differential thermal analysis and X-ray diffraction.

This prototropy due to percussion appears to be quite different from the proton delocalization that occurs when kaolinite is subjected to heating short of dehydroxylation.

EXPERIMENTAL

Materials

Although other varieties of kaolinite produced similar results, the work described here was carried out with a water-washed kaolinite of 5·5 μ average particle size and with 80 per cent of the particles lying between 2 and 8 μ in equivalent spherical diameter.

The potassium bromide was Harshaw Infrared Quality powdered material (IR No. G-715). It was dried for seventeen hours at 100°C and was then stored in a desiccator over Indicating Drierite.

Apparatus

A Perkin Elmer Model 521 i.r. recording spectrophotometer was used to obtain all of the i.r. absorption spectra. The extended range interchange was employed in the linear mode since our chief interest was in the high-frequency range. A small wooden holder was machined to hold the KBr disks of the samples at an angle of 45° to the measuring beam for studies of pleochroism.

The Wig-L-Bug mixer used for the grinding was produced by the Crescent Dental Manufacturing Co. (Serial No. W-94258). Its steel vial was a right cylinder, 0·5 in. in diameter, and 1 in. long. Two 0·25-in. diameter spherical steel balls were used in it to cause the percussion.

The differential thermal analyses (DTA) were made with instrumentation supplied by the R. L. Stone Company, essentially as described by Smothers and Chiang (1966). The DTA runs were made at a constant heating rate of 10°C per min in a dynamic nitrogen atmosphere flowing at an equal balanced rate through both the sample and the calcined alumina used as the reference material.

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The samples were compacted as uniformly as possible and with nearly equal sample weight into a solid inconel block of the type supplied with the R. L. Stone apparatus.

Equilibrium weight loss determinations were made after drying and calcining in a standard laboratory drying oven and in a high temperature muffle, both controlled to very close temperature limits at the indicated temperatures.

X-ray diffraction measurements were made using nickel filtered CuKα radiation (at 20 mA and 35 kV) and a Philips Norelco high angle diffractometer with chart recording and with a scanning speed of $(\frac{1}{4})^\circ$ 2 θ per min. The sample was mounted as a pressed powder in the standard Philips sample holder.

Preparation of samples

The kaolinite was ground in the Wig-L-Bug in batches of 300 mg each. Four of these batches were prepared for each grinding time and these batches were mixed together thoroughly to form the stock sample for that time. For the i.r. spectroscopy, 13 mm-diameter KBr disks were prepared, 0·7 mg of the kaolinite being mixed with 300 mg of KBr for each disk. After measurement, the disks were wrapped in tissue paper and kept in a desiccator for study of relaxation of the grinding effect.

In the preparation of the disks, the samples were mixed with the KBr by hand because it was found that Wig-L-Bug mixing, as is commonly used in preparing such disks, produced serious grinding effects itself. The effect of KBr on kaolinite in mixing the two together in a Wig-L-Bug will be described in another publication. In our procedure the mixing and pressing caused no appreciable adsorption of water by the kaolinite.

RESULTS

Brief discussion of some aspects of the structure and the i.r. spectrum of normal kaolinite is needed for description of the results of the percussive grinding. Figure 1 shows the unit layers and their stacking along the *a* and *b* axes according to Brindley and Robinson (1946). The hydroxyl ions or groups lying in the basal plane (marked A) will be called *basal hydroxyls* and the oxygen atoms in the basal plane (marked C) immediately adjacent will be called basal oxygens. The hydroxyl ions in the intralayer plane (marked B) common to the octahedral and tetrahedral sheets will be called *inner hydroxyls*.

Figure 2 gives the normal projection onto (001), the *Z* values being measured perpendicular to that plane. This figure and its *Z* values are based on a figure constructed by Bailey (1963) and may be regarded as the structure of an undistorted unit layer. It also includes the projection of the basal oxygens of the next layer above, which has been shifted by the amount $\frac{1}{3}a_o$ along the *a* axis. The Si—O bonds are shown as solid lines, the Al—O and Al—OH linkages and the hydrogen bondings as dotted lines, to emphasize the fact that the Si—O bondings are more highly covalent, and hence more definitely directed and stronger, than the other bonding attachments.

Figure 3 pictures the i.r. absorption spectrum of

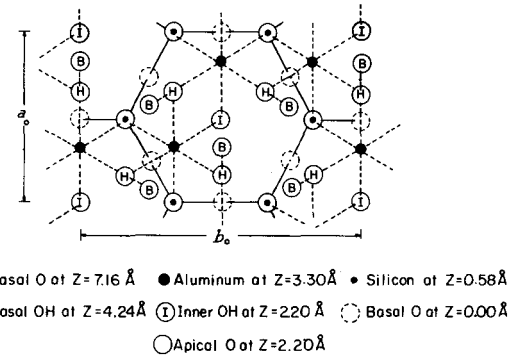


Fig. 2. The normal projection onto (001) according to Bailey.

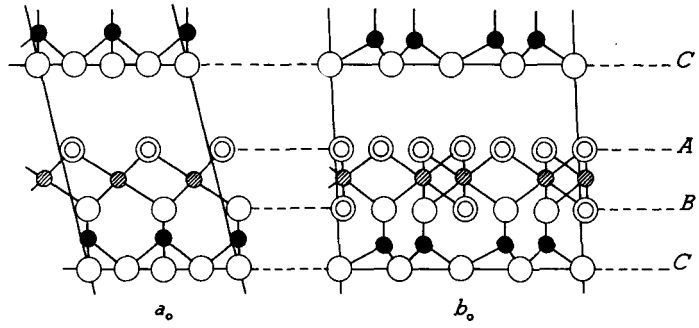


Fig. 1. The unit layers of kaolinite along the *a* and *b* axes and the stacking of the layers. ○ – oxygen; ◎ – OH; ◍ – Al; ● – Si.

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kaolinite over the frequency range studied here. The solid line shows the absorption of dry and unground kaolinite. Extra bands that appear when adsorbed water is present (N and O) and on grinding (P) are shown by dashed lines. The following positions for the different bands are average values (in cm^{-1}): A, 3692, B, 3670; C, 3650; D, 3620; E, 1110; F, 1027; G, 1002; H, 930; I, 908; J, 786; K, 750; L, 686; M, 534; N, 3440; O, 1625; P, 1090.

The O—H stretching bands are of primary interest to this work. The assignment of the first three (A, B, and C) to the basal hydroxyls has been confirmed by many studies, especially those of Ledoux and White (1964, 1966) on intercalation and deuteration. It is also well agreed that band D is due to the stretchings of the inner hydroxyls. Its remarkable sharpness reveals a rather close equivalence for all of these inner hydroxyls.

The only other O—H stretching band that occurs for the unworked kaolinite is the broad one, N, centered close to 3440 cm^{-1}. This band is due to adsorbed water molecules and when it appears, so also does the water-molecule bending vibration band, O, at 1625 cm^{-1}. These two bands are not shown by normal, dry kaolinite. It should be noted that heating (Stubican, 1959; Miller, 1961; and De Keyser, Wollast, and De Laet, 1963) and grinding (Perkins *et al.*, 1955) cause the appearance of a broad band located similarly to N, but this must be due to randomly attached hydroxyl ions rather than water molecules as is revealed by the complete lack of an accompanying bending band (at O in Fig. 3) for water molecules. It is also of interest that the protons of some of the OH groups formed at high temperature are very strongly attached (Stubican, 1959; Miller, 1961; De Keyser, 1965).

Other bands in the kaolinite spectrum are due fully or in part to hydroxyls, the remaining being caused by Si—O linkage vibrations. Of those in which hydroxyls appear to participate, bands H and I (at 930 and 908 cm^{-1}) are the most certainly assigned. One of the principal pieces of evidence for the assignment of these bands to hydroxyls has been provided by the finding that both of them are shifted greatly in frequency on deuteration of kaolinite (Stubican and Roy, 1961). The vibrations involved are probably libratory oscillations of the hydroxyls. It has been found (Miller, 1961) that the I band decays regularly on the dehydroxylation of the kaolinite and we have discovered that the hydroxyl ions involved are probably basal since intercalation of kaolin with such hydrogen-bonding substances as ammonium acetate causes the I band to shift to longer wave lengths.

The J, K, L, and M bands also appear to have contrbutions from hydroxyl vibrations (Farmer and Russell, 1964 and 1966) but are less certainly assigned. While these bands, especially K and L, are affected by the percussive grinding, we regret that the knowledge of the cause of these absorption bands is insufficient to aid in interpretation of the prototropy at present.

Bands, E, F, and G are caused by Si—O stretching. For the first of these, and O atoms are apical oxygen atoms and the vibrations are perpendicular to (001) and are affected by the attachment of those apical oxygen atoms to the aluminum ions (Farmer and Russell, 1964). The pair, F and G, at 1027 and 1002 cm^{-1} are the most intense in the whole spectrum. They are caused by in-plane Si—O vibrations, the O atoms being basal (Saksena, 1961; Farmer and Russell, 1964). Since they involve the basal part of the relatively stable sheet, they should be the least sensitive to grinding. Farmer and Russell (1966) have demonstrated that particle size has little effect on such bands.

As noted above, we have observed a band at 1090 cm^{-1} (P) that appears on grinding the kaolinite used in this study. Earlier study (Miller, 1961) has shown that it is present in some specimens of unground kaolinite. Farmer and Russell (1964) found that dickite, nacrite, and kaolinite of large

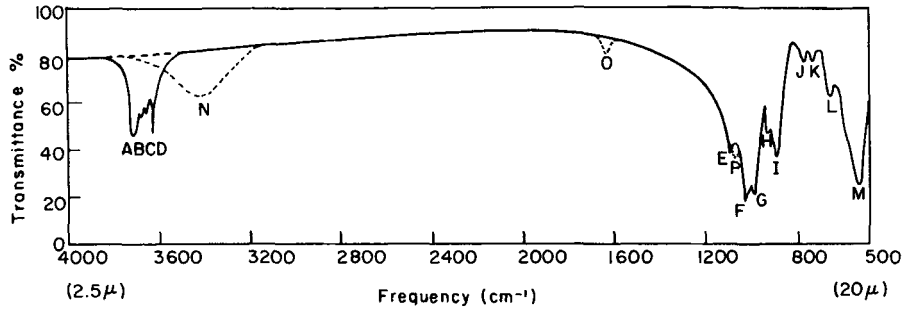


Fig. 3. The i.r. absorption spectrum of kaolinite from 4000 cm^{-1} to 500 cm^{-1}.

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particle size exhibit this band instead of the E band and they believed that it is caused by the same perpendicular apical oxygen vibration as the E band. They also found (1964, 1966, and 1967) that this perpendicular mode is sensitive to factors other that particle size. In view of the complexity of these factors and the broadness of the P band in our samples, we have not studied this band in detail and will not treat its behavior further here.

The i.r. spectral effects of the grinding

The effects of the grinding can be shown by the relative changes in the intensities of the different bands. These intensities will be expressed as base-line absorbance values, A, calculated by $A = \log (T_0/T)$, where T and T_0 are the per cent transmission values at the band peak and at the base line at the same frequency.

In order to view the relative changes in the intensities of the bands, preliminary calculations based on the Bouguer–Beer Law were made by evaluating the quantity C, representing the per cent change in functional group concentration by the equation $C = 100(I-M)/M$, where, for a given ground specimen, I is equal to the absorbance ratio, A_i/A_0 for the band for which C is calculated, A_i being the absorbance at the frequency for the specimen, and A_0 being the value at that same frequency for the parent, unground material, and where M is the average of the A_i/A_0 values for all of the bands in the spectrum of the specimen under study. Twelve bands were used for most of the calculations: A, D, E, F, G, H, I, J, K, L, M, and P; the B and C (and occasionally E and P) bands were not used because of their relatively poor resolution. Very little adsorbed water was shown in the spectra of any of the samples.

The preliminary calculations showed that up to 5 min of grinding only the D, K, and L bands showed steady and large changes, the C values for the others scattering about zero or showing only small changes. Beyond 5 min, the grinding affected all of the bands and the spectra showed that a broad O—H stretching band appeared at 8 min and grew in width and intensity as the grinding proceeded until in the 15 min sample it extended from 2750 to 3900 cm^{-1}. This band was not due to adsorbed water molecules since the H_2O-bending band although present was little different in intensity than before this O—H stretching band became apparent. Wholesale destruction of the kaolinite structure was also obvious in the spectra of samples ground longer than 5 min. A broadening of the longer-wavelength bands, including those due to vibrations in the tetrahedral sheet, occurred.

Because of the multifarious nature of the effects caused by longer grinding and the uncertainty of the nature of the contributions of the hydroxyls to some of the bands, attention will be focused on the effects of the early stages of grinding and on the O—H stretching bands.

In order to treat the band intensity changes more quantitatively, a more absolute method of calculation was formulated. This method was based on the stability expected for the bands, F and G, assigned to the in-plane Si—O stretchings. This expected stability was confirmed by the C values and the G band was chosen as a standard of reference to be used as follows. For each sample, the quantity $N_i = A_i/A_G$ was calculated for each band, A_i being the absorbance of that band in the given sample and A_G the absorbance of the G band in that same sample. If the value of N_i for the unground, parent material is designated as N_{i0}, the percentage change in the band intensity, P, is then given by the equation $P = 100(N_i - N_{i0})/N_{i0}$. The values of P so obtained are plotted as functions of the grinding time in Fig. 4. These plots do not differ much from those obtained for the C values, especially in the initial stages of grinding. The curves are dashed in for times longer than 5 min to emphasize the large-scale decay of structure, and indeed, the failure of the standard of reference in that region.

A scattering of points in any of these plots should be expected in view of the difficulty of obtaining reproducible absorption measurements with fine solid particles. It should also be expected that the shortest periods of grinding would produce the least uniform products and the greatest random error, as was observed in general.

Despite these difficulties, the results show clearly that the D band falls off sharply and the K and L bands rise sharply in the first 5 min of grinding. Tests with other varities of kaolinite and with other grinding procedures confirmed these effects. Less severe grinding, such as air milling or wet grinding caused much less change of these band intensities.

The datum points shown in Fig. 4(a) for 1, 3, and 5 min are the arithmetic mean values for several measurements and for these points the arithmetic mean deviations from the mean are indicated. The 1-min point is the mean for five measurements made on two samples ground separately. The first sample was ground for the 1-min period and was then disked with the KBr and measured within 15 min after grinding. The disk was then stored in a desiccator for 10 days and was then remeasured, and finally it was kept in the desiccator for 21 more days before remeasuring. The second sample was let stand for 24 days after grinding before it was put into a disk and measured. Its disk was then stored in a desiccator for 144 days before remeasurement.

For the 3 and 5 min values, the same procedure

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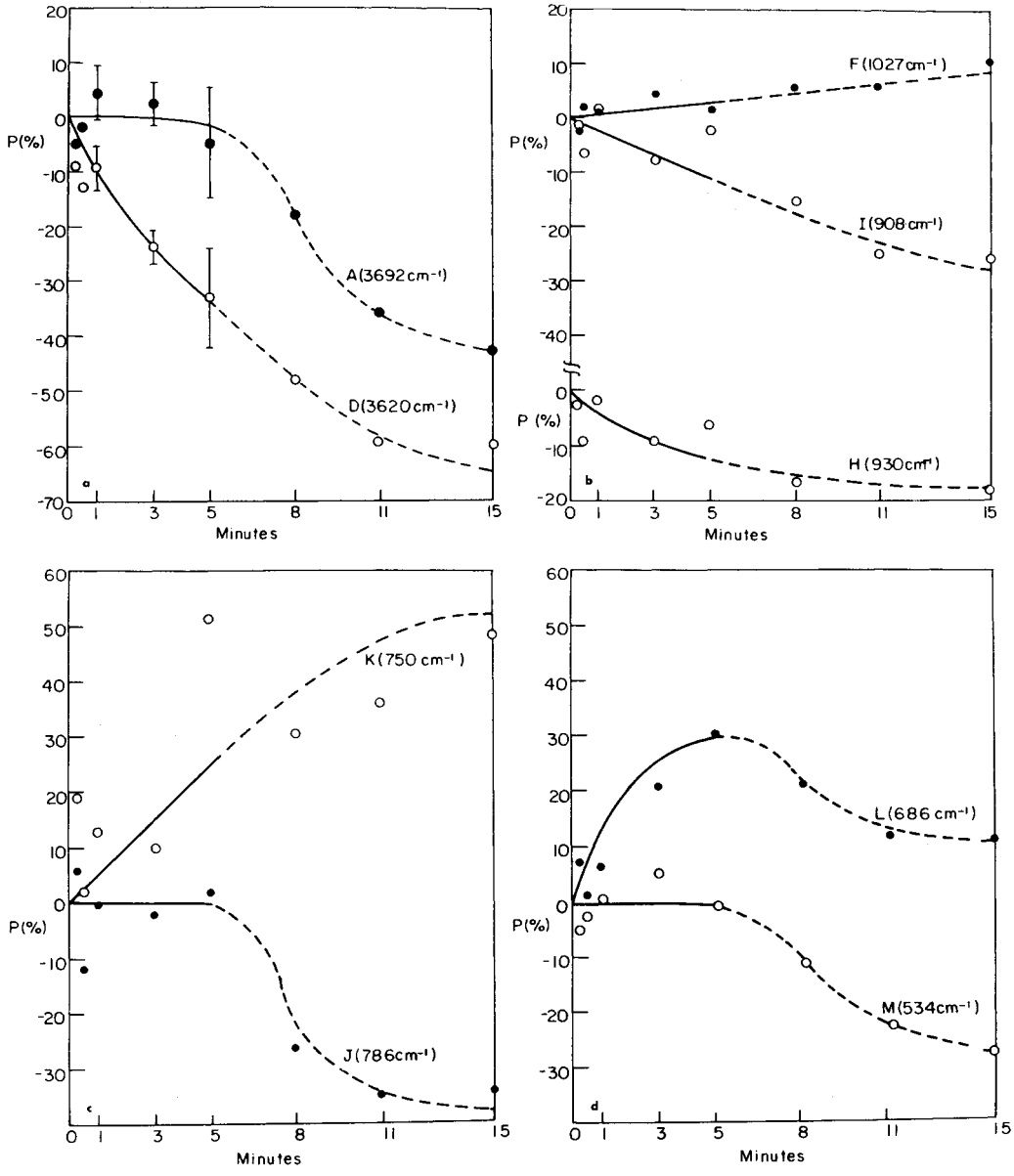


Fig. 4. Percentage change (P) in absorbance as a function of grinding time for bands A and D (upper left, *a*), bands F, H, and I (upper right, *b*), bands J and K (lower left, *c*), and bands L and M (lower right, *d*).

of grinding and measurement was followed with the two samples and, in addition, the disks were stored for four more months and then heated at 100°C for three days and remeasured to see if such an annealing would produce a relaxation of the effect of grinding. Some of the undisked kaolinite that had been stored for 284 days after grinding for 3 or 5 min was also heated for three days at 100°C and was then made into disks and measured. The points shown in Fig. 4(a) at 3 and 5 min are in each case the arithmetic mean values for all of the eleven measurements just described. The greater spread of the 5 min sample values may be the result of the incipient structure breakdown at that point. Neither storage nor heating at 100°C appeared to cause relaxation of the effects of 1, 3, or 5 min

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of grinding. The remainder of the points shown in Fig. 4 were determined by single measurements of samples that had been let stand for periods of 24–42 days between grinding and measurement.

No pleochroism was found for the A and D bands for any of the samples, no matter what the grinding time, showing that the particles were at random orientation in the disks. The spectra of the 8, 11 and 15 min samples showed the broad O—H stretching band caused by randomly attached hydroxyls. This band overlapped both the A and D bands and the absorbances of those two bands were corrected for the overlap.

The effect of grinding on the thermal water loss

The weight loss, assumed to be due entirely to loss of water, on heating to constant weight in an oven at different temperatures is given in Table 1 for different periods of grinding. The values of per cent loss above 105°C given in the last column were not measured separately, but were calculated from the other values by excluding the per cent free moisture from the reference base. It is seen that the grinding increases what is generally regarded as "free moisture" (i.e., weight loss on heating at 105°C). It also increases the loss between 105° and 250°C and lowers the loss of structural hydroxyl groups in the normal region of thermal dehydroxylation, 250°–600°C. For the purpose of this discussion we assume that the total equilibrium weight loss between 105° and 600°C represents substantially all of the structural hydroxyl groups present and is also substantially the same as the free-moisture-free loss on ignition (LOI) more conventionally reported after ignition at 1000°C and which amounts to 13·98 per cent for kaolinite with ideal composition $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.

It is clear that the grinding makes dehydroxylation occur at lower temperatures, as would be expected from the i.r. spectroscopic observation that the protons move from their original positions of stable attachment to oxygen ions. The steady increase in free moisture and the initial decrease in LOI followed by an increase in LOI after 1 min of grinding indicates that probably some dehydroxylation occurs even during initial grinding but that as grinding proceeds a compensatory hydroxylation takes place by reaction of the kaolinite with atmospheric water molecules. This would further suggest that the FM values for the ground samples are not due entirely to loss of adsorbed water molecules but are at least in part due to dehydroxylation of extremely weakly bound hydroxyl groups.

These results are similar to those reported by Kelley, Jenny, and Brown (1936) and by Laws and Page (1946), although in the more detailed study made by Laws and Page their ball-mill grinding was so prolonged that it caused appreciable destruction of the lattice in all of their samples. Thus, the water-loss values reported for their shortest period of ball-mill grinding (24 hr) are about the same as we have observed for 8–11 min of the percussive grinding where it is certain that large decay of even the tetrahedral sheet has occurred.

Differential thermal analyses

The differential thermal analysis (DTA) curves of the kaolinite after grinding are shown in Fig. 5. The broad shoulder on the low-temperature side of the principal endotherm increases in intensity and the principal endotherm diminishes in intensity and moves to lower temperatures as grinding continues. The changes are most pronounced in the samples ground longer than 5 min, but all are in accord with the more ready dehydroxylation expected by the prototropy observed spectroscopically. The other workers who have noted changes in the DTA of kaolinite on grinding have ground their samples to a state of greater destruction of the lattice before making the DTA measurements. Laws and Page (1946) ball milled their sample for no less than 24 hr and the DTA curve for their sample of minimum grinding corresponds, like the water-loss values, to those of our 8 or 11 min samples. The shortest time used by Takahashi (1959) was 48 hr

Table 1. The water losses at different temperatures as a function of grinding time

Grinding time (min)	% Free moisture (loss to 105°C)	% Weight loss (105°–250°C)	% Weight loss (250°–600°C)	Total weight loss,% Including % FM	Total weight loss,% Excluding % FM
0	0·5	0·1	13·9	14·5	14·1
1	0·6	0·1	12·6	13·3	12·8
3	1·4	0·6	12·2	14·2	13·0
5	2·0	1·1	11·7	14·8	13·1
8	2·4	2·6	10·6	15·6	13·5
11	3·6	3·1	10·8	17·5	14·4
30	4·4	4·2	9·3	17·9	14·1

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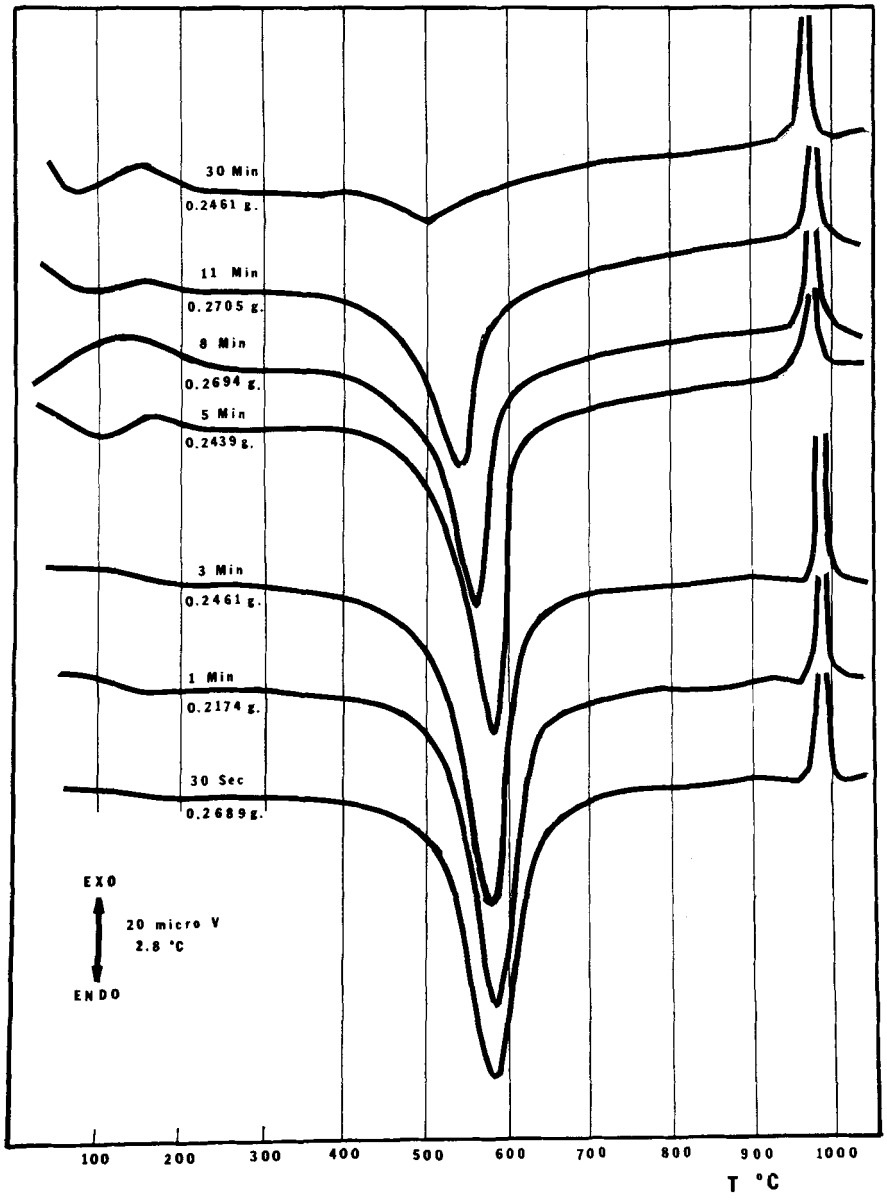


Fig. 5. The differential thermal analysis curves of the kaolinite after grinding.

in a mechanical mortar and his DTA curve for the sample resembles that of our 8-min sample.

X-ray diffraction

Structural degeneration resulting from percussive grinding is also revealed by systematic changes in the X-ray diffraction patterns. Estimates of the relative degree of such structural degeneration expressed as "Crystallinity Index" values are given in Table 2. Since preliminary measurement had revealed that the shortest periods of grinding caused extensive change in the X-ray diffraction of the kaolinite, the measurements were extended to include samples ground for even shorter periods than were used for the spectroscopic studies.

Two different but somewhat related criteria for relative crystallinity are given as Index I, which is simply the ratio of the peak height of the (002)

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Table 2. Crystallinity index values as a function of grinding time

Grinding time (sec)	Index I		Index II	
	I/I_0^*	B, °2θ†	C.I. Crystallinity index	B.I. Banding index
0	1·00	0·24	0·73	1·05
2·5	1·03	0·23	0·69	0·72
5·0	1·03	0·22	0·56	0·66
10	1·01	0·24	0·45	0·53
20	1·01	0·23	0·44	0·53
30	0·76	0·24	0·37	0·42
60	0·67	0·25	0·22	0·23
300	0·37	0·23	0·07	0·08
600	0·19	0·24		

*Intensity of (002) peak height relative to that of unground material.

†Line breadth at ½ peak height.

basal reflection of the ground material to that of the unground material and as Index II, which is a slightly modified form of the "Crystallinity index" as defined and determined by Bates and Hinckley (1958). In this work, the preparative precautions followed by Bates and Hinckley to eliminate the type of preferred orientation typically encountered when platelet-shaped particles are pressed against a smooth surface were not observed; instead, preferred orientation was minimized by production of a matte sample surface realized by pressing against hard blotter paper. Under Index II we have entered the two alternate crystallinity criteria suggested by Bates and Hinckley, namely: the crystallinity index and the banding index. We make no particular argument in favor of these criteria as anything more significant than a practical relative indication of increasing disorder in the *a*, *b* unit cell dimensions.

A feature of the (002) diffraction angle data (Index I) was that while peak intensity remained constant for an apparent induction period of more than 20 seconds and then declined regularly, the diffraction line breadth (peak width at one-half peak height) remained essentially constant until virtual disappearance of this peak.

It has been suggested by both Van der Marel (1960) and Brindley and Kurtossi (1961) that reflected intensities are diminished by lattice disorder and that the angular widths are related to the number of coherently reflecting planes, i.e., to the effective crystallite size. The virtual absence of peak broadening or developing dissymmetry is taken to be evidence for minimal change in the *c* dimension of the lattice and only indicates a decrease in the number of crystallite domains containing a sufficient number of ordered parallel unit cell layers per particle necessary for *c* direction reflection reinforcement. On the other hand, disordering in the *a*, *b* direction is immediately evident even after as little as 2·5 sec of percussive grinding.

These results confirm that profound distortion of the crystal lattice has taken place on grinding up to only 5 min, in accord with the i.r. spectroscopic, water-loss, and DTA measurements. But more important, these other measurement techniques reveal the persistence of some degree of short-range ordered structure long after the X-ray diffraction patterns have indicated loss of long-range order.

DISCUSSION

Grim (1968, p. 469) has reviewed some of the other studies of changes taking place in kaolinite due to grinding. Most of these investigations have correlated the changes of the properties in which they were interested with changes in the X-ray diffraction of the kaolinites, although, as cited above, some studies have based their correlations also on water-loss and DTA values, and Perkins *et al.*(1955) made a few rough measurements of the i.r. spectra of kaolin that had been dry-ground. Our investigation appears to be the only one to date in which the effect of grinding has been studied extensively by i.r. spectroscopy.

Although the previous studies of the dry-grinding of kaolin have not examined the extremely early stages of the grinding in detail, they agree that lattice distortion and some particle size reduction takes place before destruction of the lattice occurs in dry-grinding. Legrand and Nicolas (1959) stressed their observation that the early displacement of the layers with respect to each other is a transformation very closely followed by disruption of the lattice.

The experience of others also shows that the

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mode of grinding has an effect on the rapidity of the changes. Wet grinding produces the slowest change, and percussive dry grinding the most rapid. The grinding used in our investigation appears to be the most drastic on record in the rapidity of its effects.

Earlier studies mentioned in the presentation of our results for the water-loss values and the DTA curves have agreed with our evidence for an increase in the total number of hydroxyl groups because of reaction with moisture in the atmosphere during grinding. In addition, it has been suggested that the more ready thermal dehydroxylation caused by grinding may be due in part to bringing hydroxyl groups to the surface by cleavages. It is not likely that cleavages bringing inner hydroxyls to surface positions where they would have different stretching frequency can account for the rapid decrease observed for the D band. Calculation shows that large-sized kaolinite particles, e.g., 5 μ in diameter and 0·1 μ thick, much like those of the parent material studied here, can have not more than about 0·02 per cent of their inner hydroxyl groups at the surface. If these particles were cleaved and delaminated into particles 0·25 μ in diameter and 0·05 μ thick, the percentage would rise to only 0·4 per cent. Both percentages are so low that this simple geometric change for the inner hydroxyls cannot explain the observed decrease in the D band. In any case, such an affect would also call for a proportionate increase in the A band intensity, which was not observed.

Two observations account amply for the observed decrease in the number of inner hydroxyls by prototropy. These are the water-loss values observed at low temperature and the recorded occurrence and growth of a broad O—H stretching band due to hydroxyl groups of widely distributed nature, some with protons more strongly bound, most with protons more weakly attached than in the inner hydroxyl ions of normal kaolinite. The broad band probably starts in the shortest periods of grinding but is not observable until later because of its overlap with other O—H stretching bands and its early weak intensity, especially due to its broadness.

The observed decrease in the amount of water lost in the range 250°–600°C is alone more than sufficient to account for the diminution of the number of inner hydroxyl groups. For example, Fig. 4 shows that the D band decreases about 10 per cent in intensity in 1 min of grinding, 24 per cent in 3 min, and 33 per cent in 5 min. As recorded in Table 1, the observed decrease in the water-loss in the range 250°–600°C, where normally structured hydroxyl groups are lost, is from 13·9 per cent down to 12·6 per cent for 1 min of grinding. If this were attributed entirely to loss of inner hydroxyl groups during grinding, it would call for a 34·4 per cent decrease in intensity of the D band. The corresponding percentage changes for the 3 and 5 min samples would be 43·0 and 57·3 per cent according to Table 1. Apparently, the changes in the several water-loss values are due to a variety of happenings, not all of them simply related to prototropy, as explained above. These happenings include the formation of new hydroxyl groups some of which are resistant to dehydroxylation.

Our principal finding is the relatively rapid migration of protons away from the inner hydroxyl groups. The i.r. absorption band for the proton vibration along the line connecting the proton to the nucleus of the oxygen atom of an inner hydroxyl ion remains sharp while it decreases greatly in intensity during the shortest periods of grinding, thus indicating the complete loss of protons rather than a change in the strength of attachment to the original oxygen atoms. A gradual modification in the strength of binding of the protons would cause a broadening of the band.

Each inner hydroxyl ion is located in the center of a hexagon of surrounding apical oxygen atoms coplanar with it (see Fig. 2). The arrangement of all of its nearest neighbors about it is symmetric except for the two aluminum ions and these two ions must cause a strong net field to act on the inner hydroxyl ion in such manner as to direct its O—H axis so that the proton points away from the aluminum ions and toward the apical oxygen atoms on the other side of the hexagon beyond the vacant site, an orientation suggested by Radoslovich (1963) in considering the inner hydroxyl ions of dickite. The uniformity of the orientation and environment of the inner hydroxyl groups in kaolinite is shown by the sharpness of the D band. In addition, the frequency of that band relative to the frequency of the A band indicates that the protons of the inner hydroxyls are attracted more strongly to their neighboring apical oxygen atoms than the protons of the basal hydroxyls are to their neighboring basal oxygen atoms. This suggests that the transfer of the proton from an inner hydroxyl would take place more readily than from a basal hydroxyl ion as the grinding stresses are first imposed on the crystals. Little more can be said of the mechanism of the prototropy at the present state of our knowledge. No doubt further study of the large effects taking place simultaneously for the K and L bands will be helpful in explaining our observations, but this must await further knowledge of the vibrations causing those bands.

The effects cannot be ascribed principally to temperature changes resulting during the grinding.

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Other studies, particularly the work of Toussaint, Fripiat and Gastuche (1963) and Fripiat and Toussaint (1963) have shown that the predehydroxylation effects caused solely by raising the temperature of the kaolinite are different from those observed here. The i.r. spectroscopic measurements they made show that the relative intensities of the O—H stretching bands are not much affected during the heating preceding dehydroxylation as compared with the changes we have found in grinding the kaolinite. The proton delocalization that they discovered in their studies of the thermal effects does not involve a net loss of protons from the inner hydroxyl groups but, rather, an exchange of protons from one set of hydroxyl groups to another (See also, White, 1968).

Furthermore, they found that the A band shifted slightly downward in frequency while the D band increased in frequency, the shifts coming to a halt when the temperature reached the point at which dehydroxylation proceeds at appreciable speed. Fripiat and Toussaint explained their spectroscopic observations of the thermal predehydroxylation as probably due to the lattice distortion caused by the rise in temperature. The known thermal distortion is probably sufficient to account for the slight changes in the different O—H···O lengths in which the protons are involved and thereby the observed frequency shifts of the O—H stretching bands. The distortion of the crystals taking place during percussive dry-grinding causes much greater stresses than does the thermal distortion.

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Résumé – Quand la kaolinite subit un broyage par percussion, des changements prononcés se produisent dans son spectre d'absorption de l'infra-rouge, même dès les premiers stades du broyage, quand l'édifice cristallin n'est pas encore détruit. Dans cet exposé l'attention est orientée au changement des ions hydroxyles dans les bandes d'allongement. Un effet extrêmement rapide sur la bande des ions hydroxyles entre les couches intermédiaires a été observé et est attribué à un enlèvement permanent des protons de ces ions. Les mesures auxiliaires de la diffraction des ryons X, de la perte d'eau thermique et des analyses thermiques différentielles ont été utilisées afin de corroborer l'évidence spectroscopique pour cette prototropie.

Kurzreferat – Wenn Kaolinit in der Schlagmühle zerkleinert wird, treten deutliche Veränderungen im ultraroten Absorptionsspektrum auf, und zwar in den Frühstadien der Zerkleinerung, ehe noch das Kristallgitter zerstört worden ist. Im gegenwärtigen Bericht wird auf die Veränderung in den sich dehnenden Banden der Hydroxylionen hingewiesen. Es wurde ein bemerkenswert prompter Effekt auf die Bande der Zwischenschicht-Hydroxylionen beobachtet, der einer bleibenden Entfernung der Protonen von diesen Ionen zugeschrieben wird. Zur Bekraftigung der spektroskopischen Bejundung dieser schnellen Prototropie wurden Hilfsmessungen der Röntgenbeugung, des thermischen Wasserverlustes und der differentiellen thermischen Analyse (DTA) durchgeführt.

Резюме — Если каолинит подвергается ударному размалыванию, то в его инфракрасных спектрах поглощения даже на ранних стадиях, когда решетка еще не разрушена, обнаруживаются заметные изменения. Наблюдалось весьма быстрое изменение полос межслоевых гидроксилов, которое, очевидно, обусловлено непрерывным удалением из них протонов. Для подтверждения этого процесса переноса протонов в структуре каолинита использованы рентгенографическое исследование, определение потери воды при нагревании и диференциально-термический анализ.

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