

AN X-RAY STUDY OF THE DECOMPOSITION
OF KAOLINITE

by

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INTRODUCTION

Many of the physical and chemical properties of soils have been found to depend on the crystalline nature of the constituent minerals. Soils consist essentially of mixtures of clay minerals whose crystallinity is in general very well developed. The important soil clay minerals have been divided into three groups, the Illites, the Montmorillonites, and the Kaolins. The Illites (6,9) are clays having many properties of the micas, differing in some details of atomic structure (20). The Montmorillonites are a group best characterized by an expanding lattice, that is, the crystal structure expands in one direction as additional water molecules are added to it (25). The Kaolin group is a group of clays that has been widely studied because of some properties markedly different from those of other clays, and because of the importance of the mineral kaolinite, which gives the group its name, in industry (23).

The Kaolin group consists of four principal minerals, nacrite, dickite, kaolinite, and halloysite (6,23). All members of the group have the same chemical formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, with the exception of halloysite, which has two additional H_2O per formula unit (24). Halloysite loses this additional water when subjected to very gentle dehydration and gives approximately the same formula upon analysis as the other members of the group (4). An irregular form, anauxite, containing an excessive amount of SiO_2 , is recognized (23).

The arrangement of atoms in the crystal lattice of the kaolin

minerals was not determined until Pauling completed his study of the principles of ionic crystals (19) and applied the results of the study to silicate minerals (21). The structure proposed by Pauling was shortly afterward verified by x-ray methods by Gruner (8) and others (1,10,14). It was found, as suggested by Pauling, that the forms nacrite, dickite, and kaolinite differed only in the placement of layers, the atomic arrangement within the layers being identical for all three minerals. Nacrite, an extremely rare mineral, was found to have the layer pattern repeated every six layers, dickite repeated the layer pattern every two layers, and Gruner found the kaolinite layer pattern repeated every two layers. Later, in 1945, Brindley and Robinson (3) showed that a slight change in the structure proposed by Gruner was necessary to account for all the lines observed with diffraction equipment of higher resolving power. Gruner had proposed a unit cell of monoclinic symmetry containing two layers. Brindley and Robinson suggested the existence of a unit cell of triclinic symmetry containing only one layer. The structure proposed by Brindley and Robinson is the one presently accepted, and is shown in Plate I. The unit cell dimensions are:

$$\begin{array}{ll}
 a = 5.14 \text{ \AA.} & \alpha = 91.8^\circ \\
 b = 8.93 \text{ \AA.} & \beta = 104.5^\circ \\
 c = 7.37 \text{ \AA.} & \gamma = 90^\circ
 \end{array}$$

Halleysite is considered to be made up of layers identical to those of the other members of the group, but interleaved with layers of H_2O molecules (4). Upon dehydration the water layers are removed, and the remaining mineral has a structure similar to that of kaolinite.

A property of interest in the study of clays is their base-exchange capacity. The base-exchange capacity of a clay is the ability of the clay to retain cations, and to exchange these cations for cations of another type when present in solution, without altering the crystal structure of the mineral. This property is a measure of the ability of a soil to support plant life, and has a very low value for kaolinite (9). Work by many investigators has shown that base-exchange capacity in kaolinite increases with decreasing particle size. This has led to numerous investigations of change in base-exchange capacity with grinding, a few of them being Jackson and Troug (13), Laws and Page (15), Marshall (16), Perkins (22), and Parkert (18).

X-ray diffraction patterns made by Parkert of the ground samples showed marked changes as the grinding progressed. Since the material being ground was assumed to change only in particle size, it was expected that the x-ray patterns would show little more than the effect of diminishing particle size with increasing grinding time. The changes observed in the x-ray patterns then suggested a more thorough study by x-ray methods be made to substantiate the chemical and thermal data gathered by Parkert. Parkert's samples were made available for this study.

PRELIMINARY STUDY

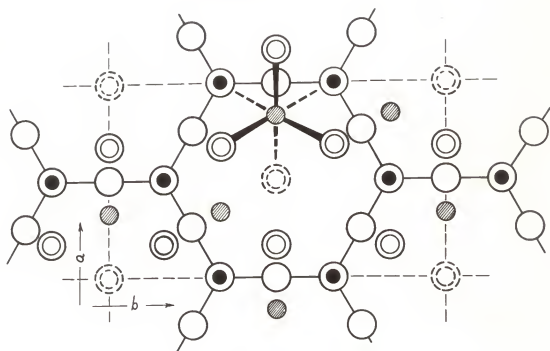
The unit cell structure of kaolinite shown in Plate I assigns the aluminum atoms to definite positions in the lattice. It should be noted that only one-third of the available positions are occupied by aluminum atoms. Brindley and Robinson (2) have shown

EXPLANATION OF PLATE I

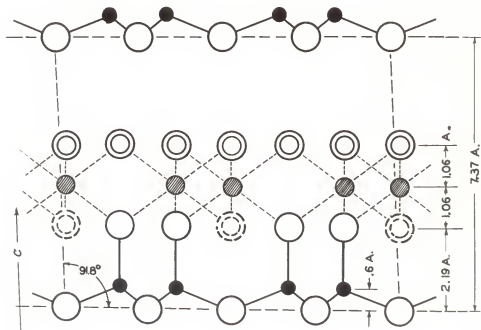
Top view. The crystal structure of kaolinite projected on (001), or the a-b plane. For simplicity, the octohedral bonds for only one Al-O(OH) group are shown.

Bottom view. The structure of kaolinite projected on (100), the b-c plane.

PLATE I



- OXYGEN ● SILICON ◐ ALUMINUM
 ◑ HYDROXYL GROUP AT 2.19 Å.
 ◒ HYDROXYL GROUP AT 4.31 Å.



that the aluminum atoms may occupy any one of three sets of positions without disturbing the layer structure or the interlayer bonds. These three arrangements are shown in Plate II, Fig. 1, where only the outline of the unit cell, the hexagonal pattern formed by the Si atoms, and the Al positions are shown. Plate II, Fig. 2, shows how the three different unit cells in Fig. 1 may be represented as identical unit cells arranged at 120° to each other in the a-b plane. The remaining atoms of the structure form identical patterns when the unit cell borders are turned through 120° .

Brindley and Robinson (2) assumed that the triclinic symmetry of the unit cell is due to the triclinic distribution of Al atoms in the lattice. If layers containing each of the three arrangements shown are distributed randomly in the crystallite, the small displacements responsible for the triclinic unit cell will add vectorially and yield a zero resultant. The effective unit cell will then be one of pseudo-monoclinic symmetry, and lines appearing on a powder pattern of sample containing this type of disorder could be assigned indices based on a monoclinic unit cell. The dimensions of the monoclinic cell would be the same as the triclinic cell, except for the angle α which would become 90° . Randomness of this type has been commonly observed by Brindley and Robinson in naturally occurring kaolinitic clays.

A second form of disorder in kaolinite, noted by Hendricks (11), arises from the fact that the pattern of the uppermost hydroxyl groups is repeated at intervals of $b/3$ in the b direction. The interlayer bonding results from the H atoms associated with

EXPLANATION OF PLATE II

Fig. 1. The three possible arrangements of aluminum atoms in the unit cell of kaolinite. Only aluminum and silicon atoms are shown, together with the hexagonal pattern formed by the silicon atoms.

Fig. 2. The three different unit cells shown in the top view represented as identical unit cells at 120° to each other.

PLATE II

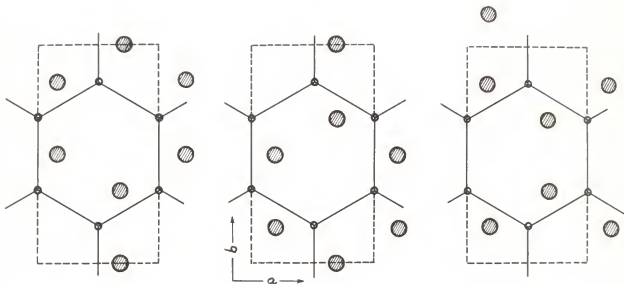


Fig. 1

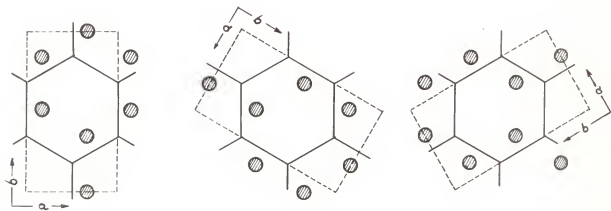


Fig. 2

these hydroxyls, and the weak bonds permit displacements of adjacent layers in multiples of $1/3$ of the b axis length in the b direction. Displacements in the a direction probably can occur also but because the pattern of atomic arrangement is not repeated in the a direction cannot be observed by x-ray techniques.

Displacements in the b direction produce diffraction patterns in which the lines formed by reflections from planes whose k indices are integers other than zero or multiples of 3 are missing or diminished in intensity. For lines whose k indices are not zero or some multiple of 3, the layers become effectively random two-dimensional lattices of the type studied by Warren (32) and Wilson (33), where the interlayer spacing is maintained but the layers are not otherwise oriented. The lines having a k index equal to zero arise from planes parallel to the b axis, and of course are not affected. Lines whose k indices are 3 arise from planes whose intercepts on the b axis are $b/3$, and likewise are not affected by disorders of this type. This type of disorder is often found in kaolinites occurring naturally, as well as in other minerals of layer structure (12).

Shaw and Humbert (28) and Shaw (27) have studied, by means of the electron microscope, the mechanical effect of grinding clay particles. The crystals of kaolinite before grinding were revealed as plates or tablets, of more or less regular hexagonal outline, and of thickness small compared to other dimensions. The size of the particles ranged from 0.5 micron to 2 microns across the plates, and from 0.005 micron to about 0.1 micron in thickness. Part of the clay sample consisted of particles of no

regular outline, believed to be clumps of amorphous material about a kaolinite crystallite as a nucleus. Dry grinding was found to fracture the kaolinite plates across their faces with only minor diminution in thickness. Wet grinding, on the other hand, removed layers from the plates without appreciably decreasing their area.

The samples studied by Parkert (18) were dry ground, so the initial rapid decrease in particle size was evidently due to fracture of the plates perpendicular to their area, perhaps accompanied by some reduction in thickness by removing layers. The particle size reached a minimum at about ten weeks grinding, and thereafter increased very slightly until 25 weeks, when the grinding process was stopped.

Differential thermal analysis of the ground samples showed a characteristic kaolinite (29) endothermic reaction at about 500 C. and exothermic reaction at about 930 C. The endothermic peak results from the loss of water of crystallization and subsequent disintegration of the kaolinite lattice. This reaction is irreversible, the mineral after this treatment being known as metakaolin or anhydro-kaolin and is amorphous to x-rays (7,17). The exothermic peak results from the transition of the amorphous Al_2O_3 in the metakaolin to a crystalline form. Mellor (17) has shown that the crystallization occurs in two steps, first the alpha crystalline form followed by the gamma form. This exothermic peak is very sharp in kaolinite, while for amorphous Al_2O_3 alone it is quite broad. Evidently the amorphous silica has some effect on the activity of the amorphous alumina in metakaolin. Mellor

believes that metakaolin is a structural remanant of kaolinite, not truly crystalline, but sufficiently so that the alumina is restrained by rigid SiO_2 bonds.

The thermal curves observed by Parkert showed a decrease in the area of the endothermic peak at 500° with increasing grinding time. Grim (5) observed endothermic peaks of varying area in naturally occurring kaolinites, and attributed the decrease in area to imperfections or disorder in the kaolinite crystal structure. Speil (29) however showed that decreasing the particle size decreased the area of the endothermic peak.

Parkert found that the sample of kaolinite ground 25 weeks showed no endothermic peak, indicating that the crystal structure had been completely destroyed. Samples of muscovite mica and montmorillonite clay ground 25 weeks yielded thermal curves almost identical with that of kaolinite ground for the same period of time. The exothermic peak in the kaolinite sample was much sharper than for the other two minerals. All three showed evidences of a large amount of water given off as adsorbed water at about 130°C . This effect increased considerably at 25 weeks over that noted at 10 weeks, although the average particle size changed only slightly.

Laws and Page (15), in an investigation very similar in many respects, found that about one-half the exchange positions in their sample of kaolinite were occupied by sodium or calcium ions before grinding was begun. The number of exchangeable cations decreased with grinding, which appeared to indicate the Na and Ca ions formed a compound or compounds with the amorphous products of

grinding. Marshall (16) has found that such compounds have many properties of permutites.

The amount of exchangeable cations present in the samples used in this investigation was not determined. Since the samples were given no chemical treatment prior to grinding, there was no reason to consider the kaolinite entirely free of exchangeable cations.

PROCEDURE

In order to secure optimum resolution in the x-ray diffraction patterns, a Phragmen-type focusing camera was designed and built. The camera, shown in Plate III, was constructed with three separate slit systems, the beam through any one slit system falling on the same specimen position. In this manner the camera could be made to cover any one of three ranges of diffraction angles. The body of the camera was made of 8 inch diameter brass tubing with wall thickness of $3/16$ inch. The end plates were made of $1/8$ inch sheet brass. The slits, also of brass, were made adjustable both in position and in width of slit opening. Lead shields were placed inside the camera body to properly direct the beam and to protect the film from radiation scattered from the slit edges. A cut out portion extending slightly less than 180 degrees around the circumference from the specimen position was provided, through which the film could be exposed to the diffracted radiation. The film, enclosed in a black paper envelope, was pressed tightly against the outer surface of the film position by a cover secured to the camera body at one end by hinges and at the

EXPLANATION OF PLATE III

Two views of the focusing x-ray camera used in this study.

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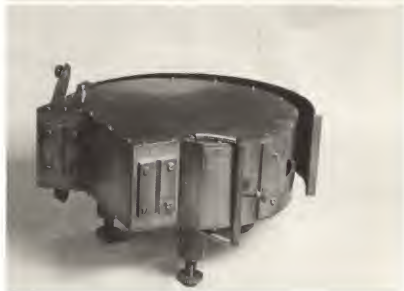
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PLATE III



other by a spring latch. The sample holder was made of a portion of the 8 inch tubing, finished with emery paper to fit exactly the outer surface of the sample position, and provided with rectangular opening into which the powdered mineral sample could be packed. To guarantee proper focusing conditions a form was made to insure that the radius of curvature of the sample surface was equal to the radius of the camera body. A narrow strip of metal was placed in the film opening to provide an index mark on the film when exposed.

The camera was calibrated by determining the Bragg angle corresponding to the line on the film formed by the index marker. This was done by using as a calibrating substance magnesium oxide, a material having a f. c. cubic structure. Since the interplanar spacings of the magnesium oxide and the wave length of the radiation are accurately known, the angles of reflection producing the lines on the film can be calculated from the Bragg equation $n\lambda = 2d \sin \theta$. In this equation θ is the angle of reflection, d is the interplanar spacing, and λ is the wave length of the radiation. N is the order of the reflection and was unity for the MgO reflections.

The Bragg angle θ of any line, in degrees, is given by $\theta_x = \theta_0 - kS$, where θ_0 is the angle in degrees corresponding to the position of the index mark, S is the distance on the film from the index mark to the line in question, and k is a constant of proper value. Both k and θ_0 were determined by the use of the calibrating substance MgO , k being found to have the value 1.4096 degrees per centimeter and θ_0 the value 44.515 degrees. S was

considered positive for lines on the low angle side of θ_0 , and negative for those on the high angle side,

This camera resolved the closely spaced lines of the kaolinite pattern very well, but its usefulness was found to be somewhat limited by the fact that lines corresponding to Bragg angles of less than about 17 degrees were not registered on the film. Typical patterns are shown in Plate IV.

To study the range of diffraction angles below the range of the focusing camera, a General Electric Circular camera of 143.3 mm. diameter was used. The sample holder was of the oscillating wedge type. Well resolved patterns were obtained with this apparatus. Most of the few cases of doubtful resolution fell within the range of the focusing camera. Patterns made with the circular camera are shown in Plate V.

Due to the formation of amorphous material and decrease in particle size with grinding, the exposure times could not be kept constant for all samples. To resolve the weaker lines in the patterns it was necessary to expose the stronger lines to a point not in the linear range of the film used. For these reasons a careful photometric determination of scattered intensities was not attempted. Aided by semi-quantitative measurements on microphotometer tracings of the patterns, intensities were estimated visually. The observed intensities were transformed to the diagrammatic representation shown in Plate VI, where the height of each line represents the intensity of the corresponding line in the diffraction pattern.

The film used was Eastman No-Screen X-ray film. A develop-

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EXPLANATION OF PLATE IV

Representative patterns made with the focusing camera.

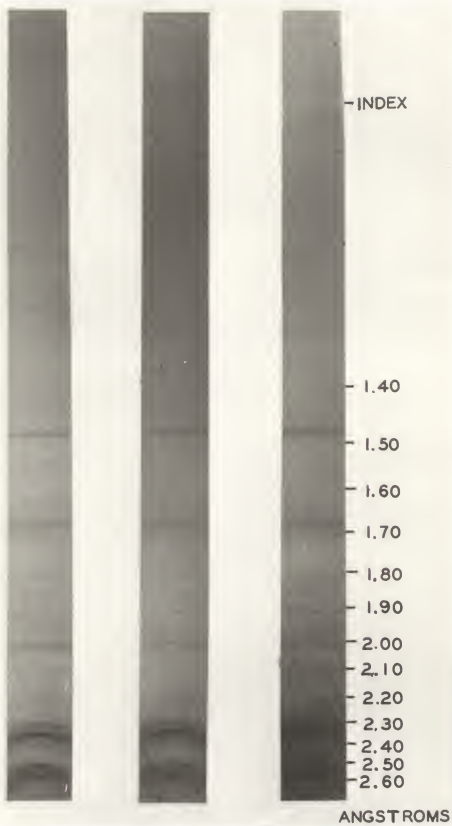
Left. Pattern of unground kaolinite.

Center. Pattern of kaolinite ground four weeks.

Right. Pattern of kaolinite ground ten weeks.

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VALLEY PHOTO CO
U.S.A.

PLATE IV



EXPLANATION OF PLATE V

Patterns made with circular x-ray powder camera.

Pattern 1. Unground kaolinite.

Pattern 2. Kaolinite ground four weeks.

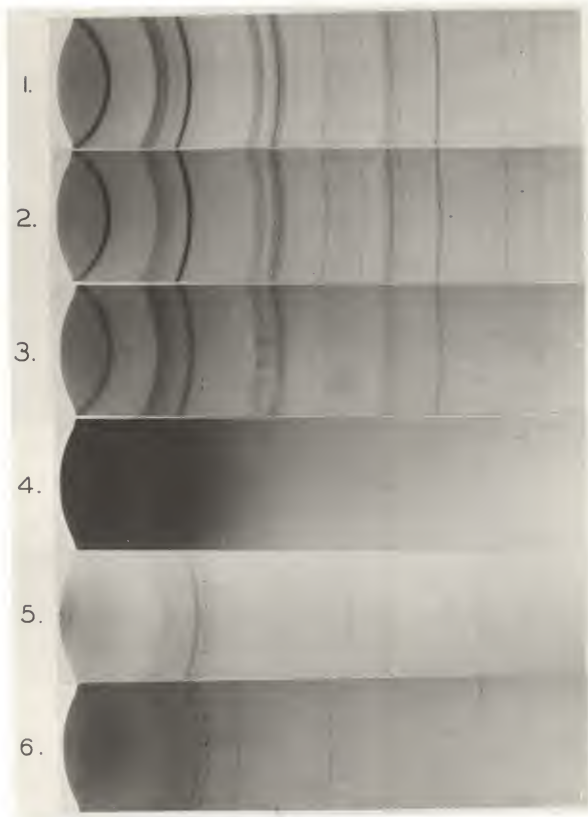
Pattern 3. Kaolinite ground ten weeks.

Pattern 4. Kaolinite ground 25 weeks.

Pattern 5. Kaolinite ground 25 weeks, treated with NaOH and HCl.

Pattern 6. Kaolinite ground 25 weeks, treated with NaOH and HCl in an excess of MgO.

PLATE V



EXPLANATION OF PLATE VI

Diagrammetric representation of lines found in x-ray patterns.

Pattern 1. Lines in pattern of unground kaolinite, with indices based on triclinic unit cell.

Pattern 2. Lines in pattern of kaolinite ground four weeks.

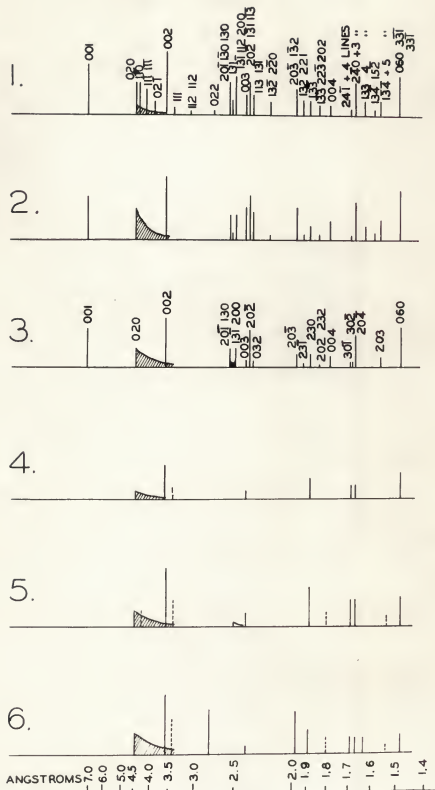
Pattern 3. Lines in pattern of kaolinite ground ten weeks, with indices based on monoclinic unit cell.

Pattern 4. Lines appearing in pattern of kaolinite ground 25 weeks. The intensities shown are only approximate, as the lines were too faint to be microphotomered.

Pattern 5. Lines after treatment with NaOH and HCl. Dotted lines represent spotted lines on pattern due to quartz.

Pattern 6. Lines after treatment with NaOH and HCl in an excess of MgO.

PLATE VI



ment time of 5 1/2 minutes in standard x-ray developer was found to give high contrast with no appreciable fogging. In general, the patterns were microphotomered with a Leeds and Northrup Recording Densitometer. Lines on the patterns produced by samples ground 25 weeks were too faint to produce a satisfactory trace.

X-RAY STUDY OF STAGES OF GRINDING

Diffraction Pattern of Unground Kaolinite

The kaolinite used by Parkert was a type collected at Langley, North Carolina. Preliminary treatment consisted of mortar grinding to pass a 100-mesh screen. This tended to break up large clumps and aggregates and produce particles consisting of but one crystallite. This is the form of the mineral referred to as unground kaolinite, the term unground signifying that ball mill treatment had not yet begun.

The diffraction pattern produced by the mineral in this form was a well resolved pattern in which the background scattering due to amorphous material was very low. The pattern is shown in Plates IV and V, and a diagrammatic representation is shown in Plate VI.

The pattern showed certain features specified by Brindley and Robinson (2) as characteristic of slightly disordered kaolinites. These features were the absence of several lines which are to be found in patterns of perfectly ordered samples, and the wedge background in the region of the (020) line. The possibility that the initial mortar grinding was responsible for this disorder

was immediately suggested, but unfortunately could not be investigated since all of the original material had been given the preliminary mortar grinding. A sample of kaolinite from Georgia, with no treatment other than water washing, gave a pattern identical in all respects to the pattern described above. Apparently the kaolinites occurring naturally in this general region are not perfectly ordered, and the initial mortar grinding introduced little if any disorder in the crystal structure.

The average particle size at this stage was 1.51 microns. This is in agreement with values of particle size for typical natural kaolinites given by Ross and Kerr (23), and Hendricks (9). There is no evidence to indicate that this sample of kaolinite has any properties not common to kaolinites in general, except for the degree of order.

Diffraction Pattern of Kaolinite Ground Four Weeks

After grinding in the ball mill for a period of four weeks, the kaolinite sample produced an x-ray diffraction pattern different in important features from that of the unground sample. The average particle size at this stage was about 0.95 micron, as determined by Parkert.

The x-ray pattern (Plates IV, V and VI) was notable in that almost every line having k indices different from zero or a multiple of 3 has disappeared, and some lines remaining are altered in intensity. The lines that did not appear, listed in order of decreasing interplanar spacing, were the $(1\bar{1}0)$, $(11\bar{1})(\bar{1}\bar{1}\bar{1})$, $(02\bar{1})$, (111) , $(11\bar{2})(\bar{1}\bar{1}\bar{2})$, and (022) . Indices not separated by commas in

this list indicate multiple reflections, that is, several sets of reflecting planes have the same spacing and are responsible for one line on the film. The following multiple reflections appeared to be diminished in intensity relative to neighboring lines: (131) ($1\bar{1}2$), $(13\bar{1})(112)(200)$, $(113)(131)$, $(13\bar{2})(2\bar{2}0)$, $(132)(221)$, and $(1\bar{3}\bar{3})(22\bar{3})(202)$. This appeared to indicate that those sets of planes having k indices not equal to zero or 3 did not contribute to the diffracted intensity responsible for the line, or was much diminished.

The higher angle portion of the film contained several lines resulting from multiple reflections of four and five different sets of planes. The indices of the planes are given in Plate VI. The relative intensity of these lines did not appear to change appreciably. It was assumed that each line was diminished in intensity approximately equal amounts due to loss of some reflections from the multiplicity. This result was then consistent with the conclusion that reflections from planes having k indices not equal to 0 or multiples of 3 did not appear in the pattern of the kaolinite ground four weeks, with the exception of the (020) reflection.

The (020) reflection did not disappear from the pattern, however it was greatly changed in appearance. Instead of the sharp line appearing in the pattern of unground kaolinite, the intensity was spread over a large region of the film and appeared to tail off in the higher angle direction. This is the profile discussed by Warren (32), characteristic of random two dimensional lattices.

Diffraction Pattern of Kaolinite Ground Ten Weeks

After ten weeks grinding the average particle size was 0.60 microns. The diffraction pattern showed a large amount of amorphous material was present in the sample, the background scattering being quite intense. The lines were quite faint and were superimposed on the dense background making measurement difficult. Except for the less distinct lines, the pattern was quite similar to the pattern of the sample ground four weeks. The important changes noted were the disappearance of the lines corresponding to d spacings of 1.581 A. and 2.184 A., and the appearance of a line which presumably had been masked by adjacent lines in previous patterns. This line corresponded to a d spacing of 1.703 A.

The particle size broadening of the lines made it impossible to resolve the weak ($1\bar{3}1$) line, occurring as it does between two much stronger lines.

The monoclinic unit cell described by Brindley and Robinson (2) in their discussion of randomness accounted for all observed lines. The comparison between observed and calculated d values, together with the monoclinic indices, is given in Table 1. The monoclinic indices also were found to be restricted to those having k equal to zero or a multiple of 3.

X-RAY STUDY OF PRODUCTS OF GRINDING

The amount of amorphous material in the sample ground 25 weeks did not appear to increase appreciably, since the background scattering by amorphous material did not become more in-

tense. The lines became much weaker than those appearing in the pattern of the ten week ground sample but did not appear to become more diffuse. However, only seven of the lines remained in the pattern. These were in the same positions in which they occurred in other kaolinite patterns. The (020) line retained its tailed profile. Lines in the positions of the (002), (003), ($13\bar{3}$), ($24\bar{1}$), ($2\bar{4}0$), and (060) lines of unground kaolinite remained but all others were missing. In addition, a new line consisting of quite large distinct spots appeared at 3.25 A.

Attempts to find a compound or mineral structure which could produce such a pattern were unsuccessful. Any crystalline substance present was present either in very small amounts or was very poorly crystallized. To more closely study the x-ray data an attempt was made to remove a part of the amorphous material from the sample. Following a procedure of Laws and Page (15), a one-gram sample was digested for three days in 0.5 N NaOH at 65° C., then washed with 0.1 N HCl. Additional samples were given the NaOH treatment alone, the HCl wash alone, and the NaOH - HCl treatment in an excess of MgO.

No changes were observed in the diffraction patterns after this treatment for the samples treated with NaOH alone and with HCl alone. The treatment in an excess of MgO decreased the background slightly and produced three additional lines. Treatment with NaOH and HCl gave a very clear, well defined pattern of the same type as that of the untreated material after 25 weeks grinding.

Several features of the pattern either became visible with

Table 1. Comparison of observed spacings and spacings calculated on the basis of a monoclinic unit cell, for kaolinite ground ten weeks.

Observed spacing	Calculated spacing	Indices
1.485 A.	1.485 A.	060
1.537	1.538	203
1.662	1.659	204
1.684	1.681	302
1.703	1.713	301
1.788	1.783	004
1.838	1.835	202, 232
1.891	1.907	230
1.939	1.938	231
1.994	1.985	203
2.284	2.283	032
2.332	2.553	202
2.378	2.378	003
2.492	2.488	200
	2.505	131
2.567	2.550	130
	2.556	201
3.550	3.567	002
4.431 banded	4.455	020
7.155	7.135	001

The spacings were calculated by means of the formula:

$$\frac{1}{d^2} = \frac{h^2}{(a \sin \beta)^2} + \frac{l^2}{(c \sin \beta)^2} - \frac{2hl \cos \beta}{ac \sin^2 \beta} + \frac{k^2}{b^2}$$

where

$$a = 5.14 \text{ \AA.}$$

$$b = 8.91 \text{ \AA.}$$

$$c = 7.37 \text{ \AA.}$$

$$\beta = 104.5^\circ$$

the removal of the amorphous material or were produced by the treatment given. Additional lines of the spotted character became visible, at 4.25 Å., 1.82 Å., and 1.53 Å., in both the NaOH-HCl and NaOH-HCl-MgO treated samples. These lines, together with the line noted previously at 3.25 Å., corresponded to the four strongest lines of alpha-quartz, SiO₂, with an apparent particle size of the order of 0.001 cm.

A weak band was noted at about 2.54 Å. The remainder of the lines occupied the same positions as before treatment.

DISCUSSION OF EXPERIMENTAL RESULTS

Lattice Disorders Produced by Grinding

In the sample of kaolinite ground four weeks, the experimental evidence pointed conclusively to the presence of disordered crystallites of the type discussed in general by Hendricks (12). Successive layers were displaced multiples of $b/3$ in the direction of the b axis. Since the uppermost surface of the unit layers contains an atomic arrangement repeated three times in the length of the unit cell, displacement and subsequent rearrangement of the interlayer bonds, produced the randomness.

After ten weeks grinding the randomness became more pronounced. In addition to randomness in the stacking of layers discussed above, the Al atoms occupied all positions in the layer at random, with resultant pseudo-monoclinic symmetry. The satisfactory agreement between spacings calculated from a monoclinic unit cell and those actually observed was considered sufficient

evidence of such randomness. A comparison of calculated and observed intensities was not attempted, as calculation of structure factors would have involved separate summations over the coordinates of each of the 26 atoms in the unit cell for each combination (hkl). The time allotted to this study was not sufficient to complete such a comparison.

The presence of disorders in the kaolinite lattice after grinding was correlated by Parkert's thermal data. Grim (5) found that increased disorder decreased the area of the endothermic peak at 525°. Although Speil, et al. (29) found that decreasing the particle size also decreased the area of the endothermic peak, his samples were obtained by grinding and fractionating, and no measurements of degree of order were made. The exothermic peak remained unchanged. After heating to the dehydration temperature the kaolinite is converted to amorphous metakaolin, so the exothermic peak would be expected not to depend on particle size or degree of order.

Nature of the Products of Grinding

Various types of lattice disorders were considered in an attempt to explain the x-ray pattern after 25 weeks grinding. Disorders of the halloysite type, in which the layers are stacked along the c axis but not otherwise oriented, did not account for the disappearance of the (001) reflection with the (002) and (003) yet remaining. The montmorillonite structure, in which the layers are separated variable distances, accounted for the absence of the (001) line but did not account for the presence of the (002) and

(003). In addition, thermal data tended to rule out the possibility of any kaolinite remaining, since the endothermic peak had completely disappeared. The exothermic peak, also, became very much sharper in the 25 week ground sample while remaining unchanged for the other samples ground four and ten weeks. In the face of this evidence, it was concluded that the material remaining was no longer kaolinite, but some other compound of very closely related structure.

Laws and Page (15) noted a decrease in exchangeable cations with grinding, and concluded that a compound with the grinding products was being formed. This compound was called a permutite by Laws and Page, since it had many of the properties of this group, especially base exchange. Marshall (16) described a similar product.

Although the number of exchangeable cations present was not known for the samples used in this study, it was assumed that at least part of the exchange positions held cations. In that case, only a small part of the amorphous or partially crystalline products of grinding could combine with the cations present to form the new compound.

Schwarz (26) has shown that kaolinites may be converted to zeolites in very alkaline agents under pressure, and to feldspars in weakly alkaline agents. It is quite possible that very fine grinding had much the same effect as pressure on the reaction, the exchangeable Na and Ca ions furnishing the alkaline conditions. Digestion in NaOH, instead of dissolving amorphous material, may have provided additional alkaline surroundings for the reaction.

The amount of amorphous material was not reduced until the sample was washed with HCl. This is possibly related to Stout's findings on phosphated kaolinite (30) that kaolinite dephosphated in strongly alkaline solutions did not give an x-ray pattern until washed with HCl. Stout noted that dephosphated kaolinite re-crystallized to form kaolinite and dephosphated halloysite re-crystallized to form halloysite.

A more likely possibility is that the finely ground material formed an amorphous permutite or zeolite as a result of the NaOH treatment. Permutites are very easily decomposed by acids (1), leaving a residue of silica. HCl washing then removed most of the amorphous material leaving the SiO_2 in the sample as crystalline quartz.

Sveshnikova and Kuznetsov (31) have shown a close similarity between some of the zeolites and kaolinite. X-ray study showed that many lines of a crystalline zeolite with the formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ also appeared on the kaolinite pattern. The thermal curves of the zeolite described above were identical with those of the 25 week ground sample studied, with an endothermal effect between 100° and 350° , and an exothermic effect at 960° .

Other properties of zeolites and permutites are high base-exchange capacity, an open but strongly linked crystal structure, and a great affinity for water. The water may be driven off by heat and replaced by exposing the material to a moist atmosphere, without change in the crystal structure (1). Some zeolites expand visibly as excessive water is absorbed, a property exhibited by the treated grinding product. The terms zeolite and permutite

are used interchangeably.

Feldspars have many properties in common with zeolites, such as similar chemical formulas, thermal properties, and structural features. The division between the zeolites and feldspars is not well defined (1).

Parkert found that grinding 25 weeks increased the base exchange capacity approximately eight-fold. Laws and Page (15) found that treatment with 0.5N NaOH raised the base exchange capacity to much higher values than for the grinding product before treatment. Washing with HCl then reduced the base exchange capacity to a value lower than after NaOH treatment but higher than for the grinding product before treatment. However, electron diffraction showed that the material present after this treatment was kaolinite. Since their grinding was not carried to the point where the endothermic peak of kaolinite disappeared from the thermal curves, it was concluded that the mineral predominant in the grinding product was kaolinite. The high base exchange capacity following NaOH treatment was considered by Laws and Page to be due to the formation of an amorphous permutite.

The presence of quartz in the samples ground 25 weeks was concluded to be a result of partial disintegration of the kaolinite structure. Perkins (22) has suggested that one form of break-down of the kaolinite lattice would result in the formation of silicic acid, H_2SiO_4 , which is easily dehydrated to yield the oxide, SiO_2 . The most stable crystalline structure for the SiO_2 would probably be the alpha phase of quartz. Contamination by quartz particles was suggested, but no source of such contamina-

tion could be found. The ball mill consisted entirely of porcelain and would not produce quartz contamination. After NaOH-HCl treatment, quartz resulted from the decomposition of the amorphous permutites by the acid.

On the basis of the evidence revealed by this study, it was concluded that the product of grinding kaolinite in a ball mill for long periods of time resulted in the formation of a compound not kaolinite but of related structure. The properties of the grinding product were similar to those of feldspars and seclites. The presence of large amounts of loosely held water, a structure similar to that described for zeolites, a great affinity for water, and the property of expanding or swelling noticeably when additional water was taken up tended to support this conclusion.

Treatment with an excess of Mg ions gave a diffraction pattern in which the lines appearing before treatment were not altered, and several additional lines were observed, apparently indicating a closely related crystalline substance in which Mg ions replaced Na in some positions. There is also a possibility that the additional lines resulted from a separate compound of Mg, mixed with the material already present. Reference to published data failed to identify any such compound.

Studies of the dehydration and rehydration properties of the product, determination of exchangeable cations present as the grinding progressed, and determination of crystal structure and atomic arrangement were not attempted due to time limitations. Studies of these properties will add greatly to the understanding of the physical changes occurring in the grinding operation.

SUMMARY

X-ray studies of samples of kaolinite ground up to 25 weeks in a ball mill revealed that in addition to the reduction of particle size by fracturing of individual crystallites, pronounced disorders in the crystal lattice structure were introduced. Initial periods of grinding produced disorders in the stacking of component layers. Repetition of atomic arrangement in the b direction allowed displacements in the b direction in amounts equal to multiples of $b/3$. Such disorders were responsible for the almost complete absence of all reflections from planes having k indices not equal to zero or 3. The lines remaining having such indices were radically altered in intensity distribution. All other lines were unchanged except for the effect of particle size.

After further grinding, randomness of a second type was found to be present. The four Al atoms per unit cell occupy only one-third of the positions available, and in ordered kaolinite the Al atoms occupy the same positions in all unit cells. The triclinic symmetry of the unit cell is assumed to be due to the triclinic distribution of Al atoms. If the Al atoms occupy all positions at random, the pattern resulting is the pattern of a monoclinic cell. The triclinic displacements of the unit cells, occurring at random in three directions at 120° to each other produce an effective monoclinic cell. After ten weeks grinding the lines observed corresponded to spacings calculated on the basis of such a monoclinic cell, and randomness of this type was established.

After 25 weeks grinding thermal evidence indicated that the

ground material no longer had the kaolinite crystal structure. The complete disappearance of the endothermic peak at about 525° showed that no endothermic reaction resulting from loss of bound hydroxyl groups and resultant disintegration of the kaolinite lattice occurred. Also the exothermic peak at 930° was much sharpened. Dehydration at 525° results in the formation of amorphous metakaolin, and the crystalline form before dehydration should not have any effect on the exothermic reaction resulting in the transition of the amorphous alumina in the metakaolin to the crystalline form. Since the peak was changed markedly, it was concluded that a compound of silica and alumina different from metakaolin was present before the reaction occurred.

The resulting x-ray pattern was intensified by treating the ground material with NaOH and HCl. Treatment with NaOH or HCl separately had no effect. Evidently the finely ground material combined with the Na ions to produce a permutite, easily decomposed by the acid. Such compounds have been prepared from kaolinite in alkaline agents and under pressure. The very fine grinding performed much the same function as pressure in assisting the formation of an amorphous permutite or zeolite. The ability to absorb large amounts of water, characteristic of some permutites, was demonstrated by the treated grinding product.

The material remaining after removal of amorphous material was concluded to be a compound of the exchangeable alkali ions present in the kaolinite with some part of the grinding product. It was evident that the final product was a mineral form distinct from, although structurally related to, the original kaolinite.

All lines of the final pattern, except for four lines of quartz, were present in the pattern of the unground kaolinite. The atomic arrangement and chemical formula of this final product of grinding were not determined.

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