Clays and Clay Minerals, Vol. 37, No. 3, 203–210, 1989.

STACKING FAULTS IN THE KAOLIN-GROUP MINERALS: DEFECT STRUCTURES OF KAOLINITE

A. PLANÇON,[1] R. F. GIESE, JR.,[2] R. SNYDER,[3]
V. A. DRITS,[4] AND A. S. BOOKIN[4]

[1] Centre de Recherche sur les Solides à Organisation Cristalline Imparfaite and Université d'Orléans, 45100 Orléans, France

[2] Department of Geology, State University of New York at Buffalo 4240 Ridge Lea Road, Amherst, New York 14226

[3] New York State College of Ceramics, Alfred University, Alfred, New York 14802

[4] Geological Institute, Academy of Sciences of the U.S.S.R., Pyzevsky 7, Moscow, U.S.S.R.

Abstract—Previous studies of the defect structure of kaolinite have examined samples having a restricted level of defects. This study examined nine kaolinite samples having a large diversity of defect contents, as indicated by Hinckley indexes ranging from 1.44 to 0.18. The samples were chosen so as to cover this range in as regular a manner as possible. The types and abundances of the defects were determined by examining the X-ray powder diffraction profiles for the 02,11 and 20,13 bands. The diffraction intensities were measured by counting for a fixed time in steps of 0.01°2θ. Analysis of these diffraction profiles indicated that (1) the major defect is the existence of a translation between adjacent layers, which is not the usual $\vec{t}_1$ (approximately $a/3$), but is related to that translation by the pseudo-mirror plane coincident with the long diagonal of the unit cell; (2) the existence of a few C layers among the B layer stacking is a minor defect; (3) many of the samples could be accurately modeled only by assuming the existence of two kaolinite phases; (4) the existence of only a few C layers in some samples does not support the idea of a continuous series from kaolinite to dickite through disordered intermediates; and (5) the Hinckley indexes of several samples depend on the relative proportions of the two types of kaolinite in the mixture.

The nine kaolinite samples fall into three groups: those having a low to moderate abundance of defects (Hinckley index > 0.43) are mixtures of two types of kaolinite (one almost free of defects, the other richer in defects); those having low Hinckley indexes (0.43 to 0.18) are single phases with different proportions of defects; and those which contain a single type of kaolinite, unlike the others in the nature of the interlayer translations and the greater abundance of C layers. The agreement between calculated and observed X-ray diffraction profiles is excellent for all specimens, except one sample (from Charentes) for which the fit is acceptable but not perfect.

Key Words—Crystallinity, Defect structure, Hinckley index, Kaolinite, Stacking faults, X-ray powder diffraction.

Resumé—Les précédentes études des défauts structuraux de la kaolinite ont porté sur des échantillonnages restreints. Dans cette étude, ont été examinés neuf échantillons de kaolinite présentant une large diversité dans l'abondance des défauts, et choisis de façon à couvrir, de manière aussi régulière que possible, le domaine de variation de l'indice d'Hinckley (de 1,44 à 0,18). Les types et abondances des défauts ont été déterminés à partir des bandes 02,11 et 20,13 d'enregistrements de diffraction X de poudres. Les intensités ont été enregistrées en pas à pas, avec un pas de 0,01°Θ, et un comptage à durée constante. L'analyse des profils de diffraction indique que: (1) le principal défaut est l'existence d'une translation entre feuillets adjacents qui n'est pas la translation habituelle (approximativement $-a/3$), mais celle qui s'en déduit par le pseudo miroir passant par la grande diagonale de la maille élémentaire; (2) l'existence de feuillets C, au sein des empilements majoritairement composés de feuillets B, est um défault mineur; (3) la plupart des écantillons ne peuvent être correctement modélisés que si l'on suppose l'existence de échantillons ne conforte pas l'idée d'une série continue allant de la kaolinite à la dickite, via les intermédiaires que seraient les kaolinites désordonnées; et (5) l'indice d'Hinckley de plusieurs échantillons dépend de la proportion des deux types de kaolinites dans les mélanges.

Les neuf échantillons de kaolinite se répartissent en trois groupes: ceux du premier groupe, qui ont une faible ou moyenne abondance de défauts (indice d'Hinckley >0,43), sont des mélanges de deux types de kaolinites (l'une presque sans défauts, l'autre riche en défauts); ceux du second groupe, qui ont un faible indice d'Hinckley (0,43 à 0,18), sont monophasés avec différentes proportions de défauts; le troisième groupe contient un seul echantillon, qui se distingue des autres par la nature de la translation entre feuillets et par la plus grande abondance en feuillets C. L'accord entre les intensités de diffraction expérimentales et calculées est exellent pour tous les énchantillons, excepté celui du troisième groupe, pour lequel l'accord est acceptable, mais non parfait

INTRODUCTION

The determination of structural defects in kaolinite samples from X-ray powder diffraction (XRD) data has been the object of numerous qualitative studies, such as those of Brindley and Robinson (1946), Murray (1954), and Brindley (1961). Several quantitative studies have since appeared, notably by Mitra (1963), Mitra

Copyright © 1989, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1989.0370302 Published online by Cambridge University Press

and Bhattacherjee (1969a, 1969b, 1970) and Noble (1971). One of the most recent examinations of this problem (Plançon and Tchoubar, 1977) suggested the existence of several types of layers in disorderd kaolinite samples and, thus, the existence in these samples of dickite sequences. In other words, if a pure kaolinite consists of the sequence –BBBB–, in the terminology of Bailey (1963), a disordered kaolinite would contain the sequence –BCBCB–. This idea was reconsidered by Brindley *et al.* (1986), who suggested, based on electron paramagnetic resonance, infrared spectroscopy, and XRD, that a continuous series exists between defect-free kaolinite and dickite by way of disordered structures.

The model proposed by Plançon and Tchoubar (1977), while generally considered to be the best model of the defect structure of kaolinite, is not completely satisfactory because of (1) crystal chemical arguments, and (2) the fact that some features of the observed XRD profiles are not accurately reproduced by the model. As pointed out by Bookin *et al.* (1989), some of the defects introduced by Plançon and Tchoubar have a high energy (distortions of the layers, unfavorable stacking sequence, etc.) and therefore are unlikely in the low-energy environments where kaolinite typically forms. To remedy this weakness, Bookin *et al.* (1989) proposed that the defects in kaolinite arise from (1) the coexistence in crystals of structural fragments (B layers only) of right- and left-handed kaolinite each generated by different interlayer vectors; and (2) the presence of some C layers in a predominantly B-layer structure.

XRD profiles calculated by Plançon and Tchoubar (1977) were in good agreement with their observed diffraction patterns near the major peaks, but the calculated background between peaks was systematically weaker than observed. This discrepancy existed for the 02,11 reflections of well-crystallized kaolinite and for the 20,13 reflections of poorly crystallized kaolinite. Their work was based on only a few kaolinite samples; e.g., three of the four samples came from the same region of Charentes, France, and all were relatively rich in defects. Subsequent studies of kaolinite samples having a wider range of defect contents indicated that the model was unsatisfactory.

To resolve this problem, the defect structure of kaolinite was re-examined using highly accurate XRD intensity data that were collected from a suite of clays that sampled systematically, to the extent possible, the total range of defect structures as estimated by the Hinckley index (Hinckley, 1963). Such a collection was characterized by Brindley *et al.* (1986), and the samples for the present study were chosen from this collection. In addition, one kaolinite, from Charentes, of a type not represented in the Brindley *et al.* collection, was examined. The defect model used was that described by Bookin *et al.* (1989), and the goal of the present study was to reproduce the entire X-ray diffraction profile, including interpeak background as well as peak heights and shapes.

EXPERIMENTAL

An examination of the suite of samples described by Brindley *et al.* (1986) showed that many of the samples had similar Hinckley indexes, chiefly because in the Brindley *et al.* collection many of the samples were actually different size fractions of the same sample. Inasmuch as the purpose of the present work was to sample the variety of defect structures represented in the collection, only a subset of the entire collection was examined.

The kaolinite samples were used as supplied and were fabricated into small spheres using the spray-drying technique of Cline and Snyder (1983). This method produced a sample which had no preferred orientation, simplifying the interpretation of the XRD intensities. The XRD intensities were measured with a Siemens D500 diffractometer using CuKα radiation and a graphite monochromator. The intensities were measured every 0.01°2θ and recorded as counts/5 seconds. The XRD pattern was recorded under these conditions between 5.0° and 50.0°2θ. From these data, intensities from the regions of interest for the analysis of the defect structure, the 02,11 (9° to 13°) and 20,13 (17° to 21°) bands, were extracted. The 001 reflection was used to estimate the average number of layers in the diffracting domains. All samples were examined under the same experimental conditions, thereby removing the possibility of artifacts due to changes in the diffractometer. Because the analysis examined the intensities over a limited region of 2θ, the intensities required no correction for Lorentz and polarization effects.

CHARACTERISTICS OF THE DEFECT MODEL

Interpeak background

Kaolinite samples having high to medium Hinckley indexes (1.50–0.50) show sharp 02,11 reflections and clearly visible separations of the $\bar{1}\bar{1}1$ and $\bar{1}11$ reflections. The $0\bar{2}1$ and 021 reflections have non-negligible intensities, and, at the same time, the interpeak background is very high.

We were unable to reproduce the totality of the observed XRD using the defect model of Plançon and Tchoubar (1977) or the model of Bookin *et al.* (1989). This lack of success in reproducing the observed profiles using a single kaolinite sample is understandable inasmuch as the introduction of any type of defect softens the modulation of the XRD profile, i.e., the reflections broaden and the peak intensity weakens. For this reason, neighboring reflections, such as $\bar{1}\bar{1}1$ and $\bar{1}11$, which are well separated in kaolinite samples having few defects, rapidly become indistinguishable as the level of defects rises. At the same time, low intensity

https://doi.org/10.1346/CCMN.1989.0370302 Published online by Cambridge University Press

reflections having large Miller indexes, such as $02\bar{1}$, tend to disappear in the background. Given the difficulty of reproducing sharp, well-separated peaks (as in a low-defect kaolinite) with a relatively high background between the peaks (as in a high-defect kaolinite), a model consisting of a mixture of two kinds of kaolinite was tried, one kaolinite nearly free of defects and the other rich in defects and having a 02,11 band with practically no modulation. Details of the development of the two-phase model were presented in Plançon *et al.* (1989). Such a model, as will be seen, reproduces very well the experimental XRD profiles of kaolinite samples having medium- to high-Hinckley indexes examined in this study.

Peak positions in the 20,13 band

The XRD patterns of kaolinite samples having small values of the Hinckley index differ in two important ways from kaolinite samples having larger Hinckley indexes: the distance between the $1\bar{3}1$ and 131 reflections is smaller for the disordered kaolinite samples than for the low-defect samples, and the $\bar{1}\bar{3}1$ reflection is shifted toward the $\bar{1}31$ reflection. Previously Plançon and Tchoubar (1977) accounted for this shift by introducing a special parameter describing the so-called monoclinic character of the sample. This parameter was an artificial construction which is not necessary if the defect model allows the existence of C layers among a matrix of B layers. As the proportion of C layers increases, the ensemble of layers in the crystal must approach a monoclinic symmetry.

Modulation of the 02,11 band

A second problem arises with the recognition that the existence of C layers is not sufficient to explain the observation that the 02,11 reflections for the most disordered kaolinite samples appear as an almost unmodulated band. Following Bookin *et al.* (1989), however, the translations between adjacent layers should be not only $\vec{t}_1$, which is characteristic of a perfectly ordered kaolinite ($\sim a/3$) but also $\vec{t}_2$, related to $\vec{t}_1$ by the mirror plane m that passes through the long diagonal of the unit cell. These two translations correspond to right-handed and left-handed kaolinite. Because of the approximately trigonal symmetry of the basic kaolinite layer, a third vector, $\vec{t}_0$, exists which corresponds to monoclinic kaolinite. A crystal chemically accurate model of the defect structure should allow the existence of these three translations; the probabilities of each are variable parameters that must be determined by fitting the calculated diffraction profile to the observed profile.

The lengths and directions of these three vectors are fixed by the structure of the kaolinite layer; however, each translation may be perturbed slightly both in direction and magnitude. This possibility follows from the observation that the stable stacking of one kaolinite layer on another is characterized by a rather broad potential energy minimum (Giese, 1982). In this situation, small displacements of one layer with respect to the adjacent layer result in negligible changes in the interlayer hydrogen bond distances. The perturbation of the three translations can be incorporated in the defect model in the form of a Gaussian distribution whose width is related to the extent of perturbation, i.e., a very narrow distribution corresponds to a very small perturbation.

PARAMETERS OF THE INTENSITY CALCULATION

The theoretical diffraction intensity was calculated using the formalism proposed by Plançon (1981). This approach is based on the representation of the diffraction intensity as the product of matrices. The distribution of the structural defects, as suggested by the potential energy calculations of Giese (1982), must be considered as involving interactions between nearest neighbor layers; that is, a Reichweite of 1. For such a distribution, the matrices have dimensions equal to the number of different types of layers present in an individual crystal. In the present study, the calculation involves 2 × 2 matrices.

The average intensity diffracted by a stacking of layers is given by

$$I(\vec{s}) = M \,\text{Spur}\, \mathscr{R}(A \cdot W \cdot R), \qquad (1)$$

where

$$R = I + 2 \sum_{n=1}^{M} \frac{M - n}{M} Q^n, \text{ and}$$

M is the number of layers in the crystal, A is the matrix of amplitudes, W is the matrix of abundances, and Q is the matrix of phases.

The A matrix depends only on the atomic arrangement (the crystal structure) of the different layers in the stacking. In the following discussion, the B layers (in the Bailey notation) are referred to as type-1 layers, and C layers are referred to as type-2 layers. The general term for the matrix describing this structure has terms of the type:

$$A_{ij} = F^*_i(\vec{s}) F_j(\vec{s}),$$

where F_i is the structure for layer i taking the center of the ditrigonal hole as the origin. The coordinates of the C layers are then obtained from those of a B layer by a simple inversion of the y coordinates. The calculations reported here are based on the atomic coordinates of Drits and Kashaev (1960), with a change in the tetrahedral rotation by 2° or 4°. For all calculations, the parameters of the unit cell in the a,b plane are those of Goodyear and Duffin (1961), with $a = 5.155$, $b = 8.959$ Å, and $\gamma = 89.94°$.

https://doi.org/10.1346/CCMN.1989.0370302 Published online by Cambridge University Press

In Eq. (1), W is a diagonal matrix whose terms, W_{ii}, represent the proportions of the ith layer in the stacking. For a defect-free kaolinite, W_{11} (= W_B) = 1 (only B layers) and W_{22} (= W_{CC}) = 0 (no C-layers). Values of W_C that differ from 0 represent the monoclinic character of the sample. The Q matrix depends only on the displacements between layers. Its terms are a function of the amplitudes and the probabilities of the translations between layers. The first translation between B layers, $(\vec{t}_1)_{BB}$, is that of the unit cell determined by Goodyear and Duffin (*1961*), with slight modifications.

$$(\vec{t}_1)_{BB} = -0.3689\,\vec{a} - 0.0223\,\vec{b} + 7.155\,\vec{n},$$

where $\vec{n}$ is a unit vector perpendicular to the a,b plane. The second translation, $(\vec{t}_2)_{BB}$, is obtained from $(\vec{t}_1)_{BB}$ by symmetry with reference to the pseudo-mirror plane that passes through the centers of the vacant octahedral sites. Taking into account the fact that the unit cell is C-centered, the value for the translation is

$$(\vec{t}_2)_{BB} = -0.3488\,\vec{a} + 0.3051\,\vec{b} + 7.155\,\vec{n}.$$

The third translation, $(\vec{t}_0)_{BB}$, lies in the a,b plane coincident with the pseudo-mirror plane and has a modulus equal to that of $\vec{t}_1$ and $\vec{t}_2$, as follows:

$$(\vec{t}_0)_{BB} = -0.3151\,\vec{a} - 0.3151\,\vec{b} + 7.155\,\vec{n}.$$

The translations $(\vec{t}_k)_{BC}$ are the same as the translations $(\vec{t}_k)_{BB}$, and the translations $(\vec{t}_k)_{CC} = (\vec{t}_k)_{CB}$ are obtained starting with the translations $(\vec{t}_k)_{BB}$ by inversion of the y coordinates.

Related to each translation $(\vec{t}_k)_{ij}$ is a probability $(\vec{p}_k)_{ij}$. Because of the symmetry between the B and C layers, the ratio between the probabilities is assumed to be independent of the type of layer in question; that is, $(p_2)_{ij}/(p_1)_{ij}$ and $(p_0)_{ij}/(p_1)_{ij}$ do not depend on i or j. With this assumption, the specification of the defects due to translations is determined by giving values to p_1, p_2, and p_0.

For stackings made up only of these translations, the ij term of matrix Q is given by:

$$Q_{ij} = \sum_{k=0}^{2} (p_k)_{ij} e^{(2\pi i \vec{s}\cdot(\vec{t}_k)_{ij})}. \qquad (2)$$

If the translations between layers are not absolutely fixed in direction and length, the variation about the average values can be described by a Gaussian distribution. To accommodate this distribution, matrix Q is multiplied by:

$$e^{[-\pi^2(h^2\delta_x^2 + k^2\delta_y^2)]},$$

where δ_x and δ_y are, respectively, the characteristic widths (in fractions of the unit cell) of the distribution along a and b. The kaolinite samples examined in this study were adequately modeled by a single parameter, δ (i.e., $\delta_x = \delta_y$).

RESULTS

The defect structure of each of the samples was determined by trial and error by varying the types of defects as discussed above and the frequency of each. The correct specification of the defect structure was taken to be that which gave a good fit between experimental and calculated profiles for the 02,11 and 20,13 bands, including peak heights, widths, and the interpeak backgrounds. Any examination of the fit between the experimental intensities and the calculated profiles should consider that the calculated diffraction profiles do not contain the 002 and 003 peaks, which are part of the experimentally recorded data. In addition, some of the kaolinite samples contained small amounts of impurities, mainly quartz (sample C3) and mica (sample III-MP). The impurity peaks are indicated in the profiles. The values of the parameters used in the calculations for all the kaolinite samples are presented in Table 1.

The results indicated that the samples can be grouped into three broad categories. The first consists of samples (III-I, IV-L, and V-G) that (1) are monomineralic, (2) do not have well-defined 021 and $0\bar{2}1$ reflections, and (3) have reflections $\bar{1}10$ and $\bar{1}\bar{1}1$ that can be considered as simple modulations in the 02,11 region. The agreement between observed and calculated profiles for the kaolinite samples in category 1 is shown in Figure 1. These samples are not very different from each other, and this group is referred to below as the MD (for medium crystallinity) group. For the MD kaolinite samples, the proportion of C layers (i.e., the monoclinic character) is not very important, comprising only 6–7% of the layers.

Category 2 samples (I-A, E-I, II-D, II-MP, and III-MP) can only be described as a mixture of two types of kaolinite, one containing relatively few defects (designated BC) and the other (designated MC) having a defect structure similar to the MD kaolinite samples (Plançon *et al.*, 1989). This group is referred to as the TP kaolinite group (for two phase). The experimental and observed XRD profiles are shown in Figure 2, and the relative proportions of the two types of kaolinite in each of the samples are given in Table 2.

The third category consists of a single sample, C3 from Charentes. Any kaolinite sample in this group is highly disordered, as shown by the observation that not only is there almost no modulation to the 02,11 band, but also the 20,13 band differs greatly from those of the other two groups. The monoclinic character of sample C3 is obvious, and the background between the $\bar{1}31$ and $1\bar{3}1$ reflections is abnormally intense. Although the agreement between the experimental and calculated intensities (Figure 3) is not as good as for the other two groups, sample C3 appears to be a mixture of two phases, ~5% of the low-defect type kaolinite seen in the TP kaolinite samples and ~95% of

https://doi.org/10.1346/CCMN.1989.0370302 Published online by Cambridge University Press

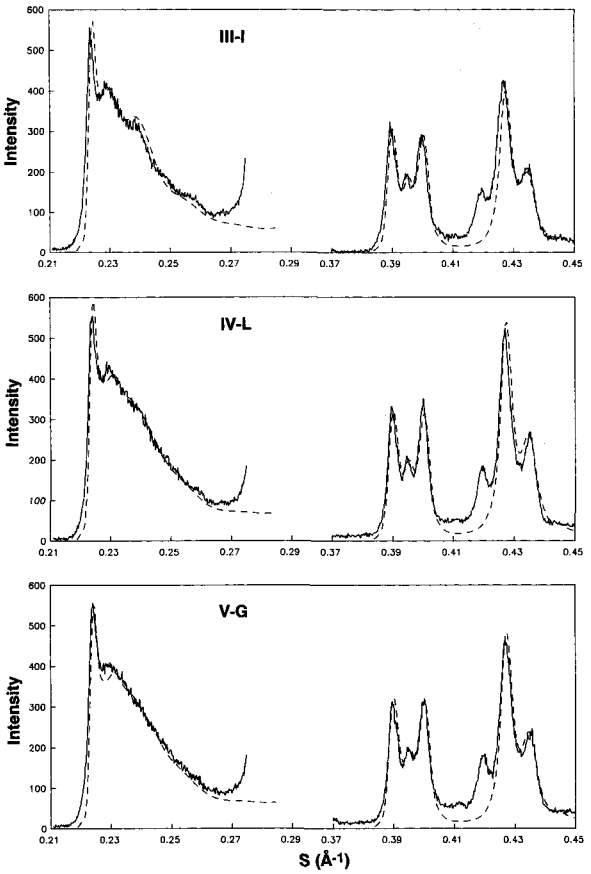


Figure 1. Experimental X-ray powder diffraction profiles (solid line) for the 02,11 and 20,13 bands of the MD-type kaolinite samples (III-I, IV-L, and V-G) and calculated profiles (dashed line). Intensities are total counts per 5-s interval. Defects present in these samples are enumerated in Table 1.

a highly disordered type of kaolinite (referred to as $C3_{pc}$ in Table 1). The monoclinic character of the $C3_{pc}$-type kaolinite is due to the relatively high proportion of C layers (85%), and the high background between the $\bar{1}31$ and $1\bar{3}1$ reflections can be explained by the greater variation in the direction and lengths of the interlayer translations ($\delta = 0.08$) for this sample, compared with the other kaolinite samples in this study.

Table 2. Relative proportions of low defect kaolinite (BC of Table 1) in the nine kaolinite samples of this study.[1]

Sample	Hinckley index	Proportion of BC-type kaolinite
I-A	1.44	0.60
E1	1.14	0.45
II-D	1.00	0.30
II-MP	0.81	0.15
III-MP	0.57	0.10
III-I	0.43	0.0
IV-L	0.32	0.0
C3	0.25	0.05
V-G	0.18	0.0

Sample notation and Hinckley indexes were taken from Brindley *et al.* (1986), except for sample C3, which was taken from Plançon and Tchoubar (1977).

[1] Samples I-A, E1, II-D, II-MP, and III-MP are binary mixtures of the BC-type kaolinite, in the proportion indicated, and the remainder is MC-type kaolinite; samples III-I, IV-L, and V-G are single phase (no BC-type kaolinite) having a defect structure described in Table 1; sample C3 is a mixture of the BC-type kaolinite, as indicated, the remainder being the $C3_{pc}$ kaolinite described in Table 1.

DISCUSSION

On the basis of the defect structures that were determined for the collection of kaolinite samples in this study, several observations can be made. Perhaps the most unexpected is that kaolinite samples which might normally be classed as medium to well-crystallized (according to their Hinckley index) are mixtures of two types of kaolinite, one being nearly defect free. In fact, for those kaolinite samples that are mixtures, the Hinckley index is directly related to the relative proportion of the high-defect component (Plançon *et al.*, 1989). This conclusion is based on intensity data from *hk* bands and should not be confused with the results

Table 1. Parameters describing the defect structure of the different types of kaolinite samples.[1]

Material	δ	W_C	p_1	p_2	p_0	$\Delta\alpha°$	M	R_{02}	R_{20}
III-I	0.04	0.07	0.60	0.28	0.05	0	40	225	175
IV-L	0.04	0.06	0.58	0.32	0.04	−4	40	225	175
V-G	0.04	0.07	0.57	0.33	0.03	−2	40	225	175
BC phase	0.02	0.00	0.98	0.02	0.00	0	40	225	175
MC phase	0.02	0.03	0.60	0.32	0.05	0	40	225	175
$C3_{pc}$ phase	0.08	0.15	0.55	0.25	0.05	−4	30	200	200

δ = the parameter describing the uncertainty in direction and distance of the interlayer translation vectors; W_C = the proportion of C layers; p_i = the probability of the occurrence of t_i; $\Delta\alpha°$ = the change in tetrahedral rotation for the Drits and Kashaev (1960) kaolinite structure; M = the average number of kaolinite layers in the coherent diffraction domain; R_{02} = the radius (in Å) of the diffraction domain in the 001 plane; this is assumed to be cylindrical; the value is for the 02,11 band; R_{20} = the radius (in Å) of the diffraction domain for the 20,13 band.

[1] Samples III-I, IV-L, and V-G are kaolinite samples of type MD; the BC and MC are the two kaolinites which mix to form the TP-type kaolinite samples (see Table 2); and the C_{3p} mixes with the BC-type kaolinite to form the C3 kaolinite sample (see Table 2).

https://doi.org/10.1346/CCMN.1989.0370302 Published online by Cambridge University Press

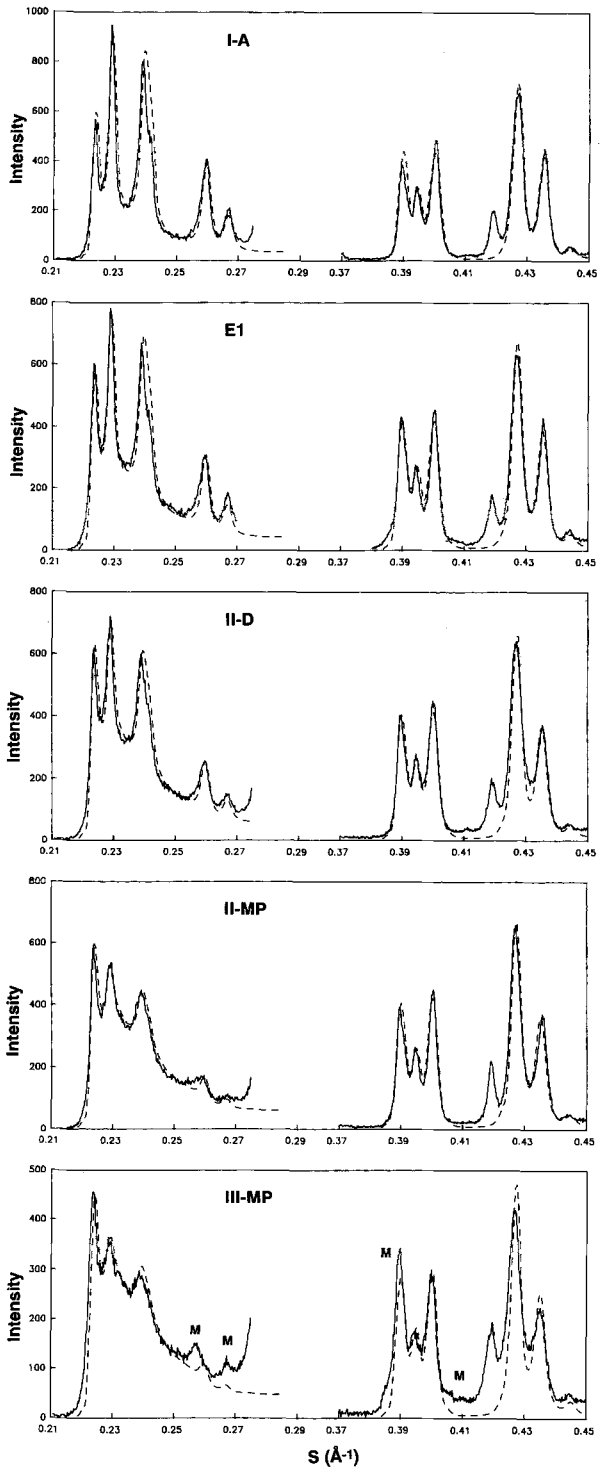


Figure 2. Experimental X-ray powder diffraction profiles (solid line) for the 02,11 and 20,13 bands of the TP-type kaolinite samples (I-A, E1, II-D, II-MP, and III-MP) and calculated profiles (dashed line). Intensities are total counts per 5-s interval. Calculated profiles are based on a mixture of two kaolinite phases: one having few defects (BC kaolinite) and the other having a moderate amount of defects (MC kaolinite). Defect structures of both components are described

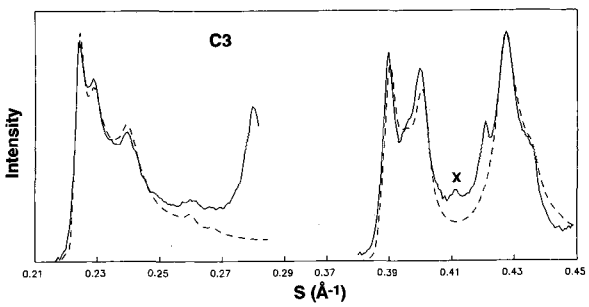


Figure 3. Experimental and observed X-ray powder diffraction profiles for C3 kaolinite. Intensity scale is in arbitrary units; observed data were taken from Plançon and Tchoubar (1977). Peak marked X is due to an impurity (probably quartz).

of the study of Deluca and Slaughter (1985), who used only the 001 reflection of the Keokuk kaolinite, a material having a high Hinckley index. The two types of kaolinite in the TP kaolinite samples of this study have identical d(001) values, whereas Deluca and Slaughter proposed that the Keokuk kaolinite is a mixture of structures having different d(001) values. The present study was not designed to test their proposal, and the *hk* reflections are probably relatively insensitive to the presence of materials having slightly different values of d(001).

The results of the calculations for the TP group of kaolinite underline the danger in using the Hinckley index as a measure of the "crystallinity" of a kaolinite. The present study and that of Plançon *et al.* (1989) demonstrate that a difference in the Hinckley index of two kaolinite samples could be due either to a real difference in the defect structure of the two or simply to a difference in the proportions of the two types of kaolinite present as a mixture.

The presence of two phases in many of the kaolinite samples of this study also suggests a possible explanation for the greater degree of structural order seen in oblique electron diffraction images of a given kaolinite than seen in the XRD profile. It is quite possible that in the preparation of the sample for electron diffraction, the higher defect component is eliminated from the mixture. Such a physical separation was reported by Tettenhorst and Corbató (1986) for a kaolinite from Lewistown, Montana. Interestingly, the high-defect size fraction (<0.5 μm) of the Lewistown kaolinite has a X-ray powder diffraction (XRD) pattern that closely resembles the MC-type kaolinite of this study, and, similarly, the Lewistown low-defect size fraction (2–15 μm) has an XRD pattern analogous to

←

in Table 1; relative proportions of the two components in each kaolinite are given in Table 2. Peaks marked M in the III-MP sample are contributed by a 10-Å mica-like impurity.

https://doi.org/10.1346/CCMN.1989.0370302 Published online by Cambridge University Press

that of the BC-type kaolinite. Based on the present study, the coarse fraction of the Lewistown kaolinite is probably a mixture of the BC and MC kaolinite fractions, because the Hinckley index of the Lewistown kaolinite is 1.3 (Tettenhorst and Corbató, 1986), whereas the index for the pure BC kaolinite is 1.76. In the Lewistown kaolinite, the coarse fraction contains predominantly platy particles, whereas the fine fraction is rich in elongate particles, supporting Keller's idea that elongate particles and plates are different kinds of kaolinite (Keller and Haenni, 1978).

Subtle changes exist in the structure of the individual layers of kaolinite samples in groups MD and C3, which are apparently a result of the layer stacking. As pointed out above, even the regular alternation of B and C layers in a disordered kaolinite does not lead to the dickite structure, inasmuch as the location of the vacancy at the corner of the cell having $\gamma = 90°$ makes the C layer a defect layer (in dickite, $\gamma = 90°$ and both layer cells are equivalent). Moreover, rotation angles for the tetrahedra and octahedra differ for the B layers of dickite (Bookin *et al.*, 1989). The occurrence of C layers among B layers probably induces a distortion of the layer structures so that they are more similar. The different tetrahedral and octahedral rotations required by the observed XRD profiles strongly supports the idea of real variations in the atomic coordinates of different defect-rich kaolinite samples.

The aim of this study was to determine which defects are present and to what degree in the suite of kaolinite samples examined. Good agreement between the observed and calculated XRD profiles was the criterion for accepting the correctness of the defect model. For the defects used in these calculations, the principal defect in disordered kaolinite samples (the groups C3 and MD) appears to be the stacking of the layers according to $\vec{t}_2$ rather than the usual $\vec{t}_1$.

All samples except one contain <8% C layers. For these samples, a reasonable fit may also be achieved between observed and calculated XRD profiles by assuming that the inter-layer vector is a variable parameter. Thus, whether and to what extent C layers are present cannot be established unambiguously. For the samples examined here, the main stacking sequence for adjacent layers is that of the right-hand and left-hand kaolinite in a ratio of 2:1 and a random alternation of $\vec{t}_1$ and $\vec{t}_2$. Monoclinic, kaolinite-like stackings exist in <5% of the samples; however, demonstrating the existence of this stacking is beyond the present accuracy of the present calculations. Using the potential energy calculations for different stackings of kaolinite layers (Giese, 1982) and the relation

$$\frac{p_0}{p_1 + p_2} = e^{(-\Delta E/kT)},$$

the difference between the cohesion energy for triclinic and monoclinic polytypes can be readily evaluated. For T = 300–400 K, the triclinic stacking has an advantage of $\Delta E = 2$ kcal/mole over the monoclinic stacking.

The 15% of C layers which were found in sample C3 supports the existence of dickite-like layers in some disordered kaolinite samples; for this sample the observed and calculated XRD patterns were in poor agreement if the content of C layers was set to zero, regardless of the types or abundances of the other defects introduced into the calculation.

In view of these results, the suggestion of Brindley *et al.* (1986) that a continuous series of structures exists between kaolinite and dickite in the form of defect-rich intermediates seems doubtful. The chief difficulty is that Brindley *et al.* (1986) assumed the Hinckley index to be proportional to the position and width of the hydroxyl infrared bands for kaolinite and dickite. The present results clearly indicate that the magnitude of the Hinckley index is not related to the C layer content of the kaolinite. Moreover, according to the calculations of the present study, C layers are randomly distributed among the B layers. A continuous series between kaolinite and dickite requires a regular alternation of B and C layers, i.e., the sequence CC is forbidden for $W_C < 0.5$. Thus, an extrapolation of the amount of defects by increasing W_C to 0.5 leads to a defect structure having a diffraction profile containing no reflections characteristic of the two-layer structure of dickite. Values of W_C of 20–25%, in fact, produce diffraction profiles which have not been reported for natural kaolinite samples; $W_C = 0.15$ must therefore be the upper limit for this type of defect.

ACKNOWLEDGMENTS

The research was partially funded by the National Science Foundation through grant EAR8414337. In addition, the authors thank Schlumberger-Doll Research for their interest and support and M. Lipsicas, M. Herron, and P. Costanzo for helpful discussions. The samples were provided by J. L. Harrison of Georgia Kaolin Research.

REFERENCES

Bailey, S. W. (1963) Polymorphism of the kaolin minerals: *Amer. Mineral.* **48,** 1196–1209.

Bookin, A. S., Drits, V. A., Plançon, A., and Tchoubar, C. (1989) Stacking faults in kaolin minerals in the light of real structural features: *Clays & Clay Minerals* **37,** (in press).

Brindley, G. W. (1961) Order-disorder in clay mineral structures: in *The X-ray Identification and Crystal Structures of Clay Minerals,* G. Brown, ed., The Mineralogical Society, London, 51–131.

Brindley, G. W., Kao, Chih-Chun, Harrison, J. L., Lipsicas, M. L., and Raythatha, R. (1986) Relation between structural disorder and other characteristics of kaolinites and dickites: *Clays & Clay Minerals* **34,** 239–249.

Brindley, G. W. and Robinson, K. (1946) Randomness in the structures of kaolinitic clay minerals: *Trans. Faraday Soc.* **42B,** 198–205.

https://doi.org/10.1346/CCMN.1989.0370302 Published online by Cambridge University Press

Cline, J. and Snyder, R. L. (1983) The dramatic effect of crystallite size on X-ray diffraction intensities: *Adv. X-ray Anal.* **26,** 111–118.

DeLuca, S. and Slaughter, M. (1985) Existence of multiple kaolinite phases and their relationship to disorder in kaolin minerals: *Amer. Mineral.* **70,** 149–158.

Drits, V. A. and Kashaev, A. A. (1960) An X-ray study of a kaolinite single crystal: *Kristallogr.* 5, 207–210.

Giese, R. F. (1982) Theoretical studies of the kaolin minerals: Electrostatic calculations: *Bull. Mineral.* **105,** 417–424.

Goodyear, B. and Duffin, M. A. (1961) An X-ray examination of an exceptionally well crystallized kaolinite: *Mineral. Mag.* **32,** 902–907.

Hinckley, D. N. (1963) Variability in "crystallinity" values among the kaolin deposits of the coastal plain of Georgia and South Carolina: in *Clays and Clay Minerals, Proc. 11th Natl. Conf., Ottawa, Ontario, 1962,* Ada Swineford, ed., Pergamon Press, New York, 229–235.

Keller, W. D. and Haenni, R. P. (1978) Effects of micro-sized mixtures of kaolin minerals on properties of kaolinites: *Clays & Clay Minerals* **26,** 384–396.

Mitra, G. B. (1963) Structure defects in kaolinite: *Z. Kristallogr.* **119,** 161–175.

Mitra, G. B. and Bhattacherjee, S. (1969a) Layer disorders in kaolinite during dehydration: *Acta Crystallogr.* **B25,** 1668–1669.

Mitra, G. B. and Bhattacherjee, S. (1969b) X-ray diffraction studies on the transformation of kaolinite into metakaolin—I. Variability of the interlayer spacings: *Amer. Mineral.* **54,** 1409–1418.

Mitra, G. B. and Bhattacherjee, S. (1970) X-ray diffraction studies on the transformation of kaolinite into metakaolin: Study of layer shift: *Acta Crystallogr.* **B26,** 2124–2128.

Murray, H. H. (1954) Structural variations of some kaolinites in relation to dehydrated halloysite: *Amer. Mineral.* **39,** 97–108.

Noble, F. R. (1971) A study of disorder in kaolinite: *Clay Miner.* **9,** 71–80.

Plançon, A. (1981) Diffraction by layer structures containing different kinds of layers and stacking faults: *J. Appl. Crystallogr.* **14,** 300–304.

Plançon, A., Giese, R. F., and Snyder, R. (1989) The Hinckley index for kaolinite: *Clay Miner.* **24,** 249–260.

Plançon, A. and Tchoubar, C. (1977) Determination of structural defects in phyllosilicates by X-ray diffraction. II. Nature and proportion of defects in natural kaolinites: *Clays & Clay Minerals* **25,** 436–450.

Tettenhorst, R. T. and Corbató, C. E. (1986) Properties of a sized and ground kaolinite: *Clay Miner.* **21,** 971–976.

(Received 11 February 1988; accepted 26 September 1988; Ms. 1736)

https://doi.org/10.1346/CCMN.1989.0370302 Published online by Cambridge University Press