

INTERRELATED FEATURES OF STRUCTURE AND STACKING OF KAOLIN MINERAL LAYERS

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Abstract—Layer stackings in the ideal and real kaolinite structures are considered in terms of layer orientations $i = 1, 2, \dots, 6$, intra- and interlayer displacements of adjacent O- and T-sheets, s_i and t_k , distortions of these displacements δ_1 and δ_2 , deviations of unit cell parameters $\eta_i = b^2/a_i^2 - 3$, $\epsilon_i = \gamma_i - \pi/2$, and normal projections c_n of the axis vector c on the ab plane.

The ideal monoclinic angle of dickite ($c_{\text{ax}} = -1/3$) and the deviation $\alpha - \pi/2 \neq 0$ for kaolinite are explained by combinations of the δ_1 and δ_2 values in the sequence of symbols s_i and t_k defining the corresponding structures. Twenty stacking variants in the 3 successive layers of the kaolinite structure are derived, incorporating layer orientations of the same parity, displacements $t_{+,-} = [0, \pm 1/2]$ and reflection operations in planes normal to the axis b_2 . Two deformation mechanisms are proposed for the accommodation of successive layer unit cells adjusting either angular or linear parameters at the agreement of either linear or angular parameters corresponding.

Key Words—Dickite, Halloysite, Kaolinite, Polytypism, Stacking faults.

SYMBOLS USED IN THE PAPER

$i = 1, 2, \dots, 6$ —layer orientations defined by layer axes a_i, b_i which are parallel to the common axes a, b of the structure (Figure 1).

s_i, t_k —projections of the adjacent intra- and interlayer sheet displacements respectively on the ab plane measured in units a, b_i (Figures 2 and 3).

δ_1 and δ_2 —deviations of the real values of s_i and t_k from the ideal values which have components along the axes a and b $0, \pm 1/3, \pm 1/6$; δ_1 and δ_2 concern the first and second component respectively.

η_i —distortion of the ideal ratio $b_i/a_i = \sqrt{3}$ to a value $\sqrt{3 + \eta_i}$.

ϵ_i —deviation from orthogonality of the unit cell a_i, b_i in the form $\gamma_i = 90^\circ + \epsilon_i$.

c_n —normal projection of the axis c on the ab plane directly related to the orthogonal, monoclinic or triclinic shape of the unit cell.

INTRODUCTION

The general features of the kaolin mineral layers were originally deduced by Pauling (1929, 1930) according to the crystallochemical principles formulated by him for the association of coordination polyhedra into crystal structures. A kaolin layer is composed of one octahedral (O) and one tetrahedral (T) sheet similar to those that form the structures of gibbsite and tridimite-crystoballite, but without reversion of tetrahedra relative to the common plane of their bases. Sheets of both kinds having similar dimensions are linked into a valency-balanced layer OT (or 1:1) of the composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Figures 1 and 2). The

layer stacking is defined by the condition of formation of hydrogen bonds between adjacent layers. Therefore, all the layers have the same polarity (OT or TO) and the O-atoms of the T-bases of one of the layers approach to the OH-groups of the bases of the adjacent layer at nearly equal distances (Brindley 1951).

It is appropriate to reveal the mean features of crystal structures that can be formed from the given layers according to the rules of their stacking using ideal models. Such models do not require detailed structural studies, and it is easier to construct them and to operate with them. Their features are general and it is convenient to consider the actual deviations of particular structures in relation to them by estimating the degree and character of these deviations. The ideal models built of regular octahedra and tetrahedra show the existence of several variants for the mutual positions of adjacent layers, which is a reason for polytypism and stacking faults. Ideal structures can be derived theoretically with lattice and symmetry characteristics provided. Distortions of layers and their stacking may result from interaction of atoms not only from the same, but also from different layers depending on the relative atomic positions and crystallization processes. Some of the distortions may be explained or even predicted from crystallochemical considerations while others are established experimentally. Therefore, deviations of real structures from ideal models may be both a consequence and a precondition for the formation of different layer stackings and polytypes, in particular, affecting the relative abundance of polytypes (Zvyagin et al. 1979).

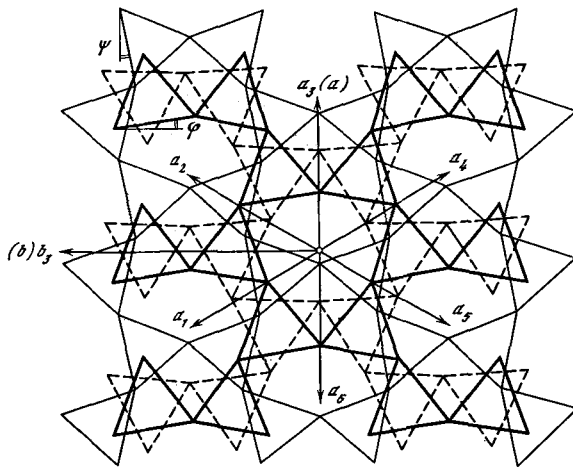


Figure 1. Scheme of a kaolin OT (1:1) layer in a normal projection on the *ab* plane, displaying six possible choices of unit cells: *i* = 1, 2, . . . 6, lower O-bases are outlined with a dashed line, upper O-bases with a solid line, T-bases with a thin line; φ and Ψ are angles of ditrigonal rotation of the O- and T-bases.

The distortions affecting the equivalence of different layer unit cells and, hence, the possibility and/or probability of stacking faults were considered by Bookin et al. (1989b). A detailed analysis of real structural features of kaolinite and dickite has permitted them to reveal the existence of stacking variants involving completely or almost completely equivalent unit cells defining the most probable stacking faults as confirmed by comparison of experimental and simulated diffraction effects (Plançon et al. 1989).

The analysis of the relationship between the structure and stacking of layers allows a refinement and a better understanding of the mechanism of kaolin layer stacking variations.

GENERAL FEATURES OF KAOLIN STRUCTURAL MODELS

Although the ideal 1:1 layer inherits only one mirror plane, the high symmetry of the elementary O- and T-sheets (hexagonal-trigonal) is the reason for the existence of 6 equal hexagonal or base centered orthogonal unit cells $a_i, b_i, \gamma_i = 90^\circ, b_i/a_i = \sqrt{3}$ ($i = 1, 2, \dots 6$) related by rotations through multiples of 60° . Such layers may have 6 orientations $i = 1, 2, \dots 6$ compatible with the common unit cell *a, b* of the whole structure. Each orientation *i*, at which axes a_i, b_i are parallel to *a, b*, is characterized by the projection s_i of the relative displacement of the intralayer sheets on the *ab* plane (Figures 2 and 3), measured in a_i, b_i units between their origins in the centers of vacant octahedra and centers of T-hexagons from the lowest to the upper sheet. For the sake of accuracy, one may accept the sequence order OT, as was shown by Pauling (1930), from below upwards, expressed by sym-

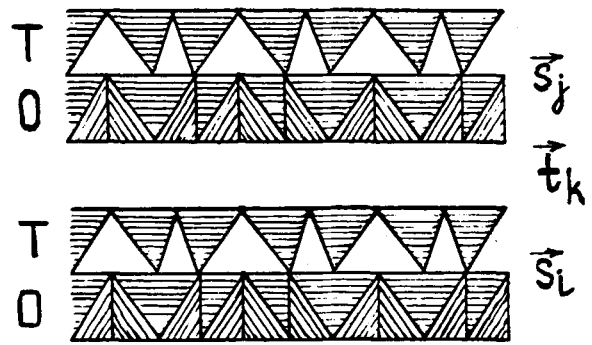


Figure 2. Two adjacent OT-layers viewed along the axis a_3 described by symbols as s_i, t_k, s_j or i_k, j , values *i, j* being the same both for the intralayer displacement subscripts and layer orientations. Letters O, T and vectors s_i, s_j, t_k are indicated at levels corresponding to the sheet locations and displacement action.

bols from left to right. The vector $s_3 = [1/3, 0]$, whereas s_i are related to s_3 by rotations $(i - 3)60^\circ$ (Figure 3).

Because of the high symmetry of the adjacent atomic planes of a layer pair (O- and OH), hydrogen bonds (O-OH) may be realized with six relative positions of these planes. Three of them are related by displacement projections t_k ($k = 1, 2, \dots 6$) and have the same values as s_i at $i = k$, but the parity of *k* should be opposite to the orientation *i* parity of the displaced (upper) layer; whereas 3 such interlayer sheet T-O displacement projections are expressed by vectors $t_0 = [0, 0], t_+ = [0, 1/3],$ and $t_- = [0, -1/3]$ (Figure 3). Any sequence of OT layers satisfying the above stacking rules may be analytically described as a sequence of symbols $i_k \dots$ where *i* may be related both to the layer orientations and to intralayer sheet displacements s_i ; whereas *k* indicates interlayer sheet displacements t_k . Periodical sequences of layers are described by repeated links of symbols in the structure notations (Zvyagin 1962). The analysis of the sequences permits description of the unit cell shape, choice of the most

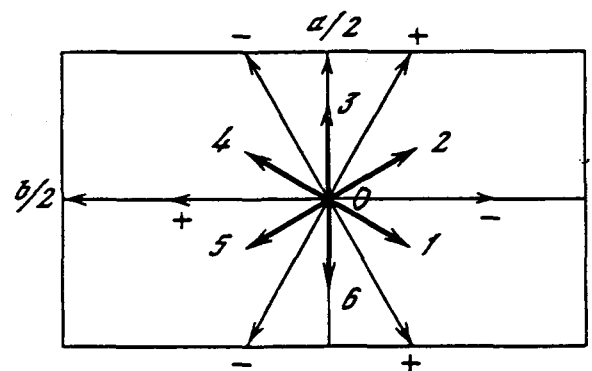


Figure 3. Normal projections on the *ab* plane of the intra- and interlayer displacements of successive OT and TO sheets s_i ($i = 1, 2, \dots 6$) and t_k ($k = 0, +, -, 1, 2, \dots 6$).

suitable setting of coordinate axes, presents of symmetry elements and their positions, atomic coordinates and calculation of structure amplitudes $F(hkl)$. By using these symbols, it is easy to describe stacking defects by changes of a definite alternation order of permitted orientation and displacement symbols (Zvyagin 1967).

The interlayer displacements of v_{ij} , depending upon the choice of layer origins either at the vacant octahedra centers or at the T-hexagon centers are expressed as sums of consecutive elementary sheet displacements either $s_i + t_k$ or $t_k + s_j$ respectively. According to the recommendations of nomenclature committees, the structural notations that involve orientations and interlayer displacement symbols are of the form $i_{ikj} \dots$ or $i_{kij} \dots$ (Bailey 1977; Guinier 1984). Both single relative sheet displacements and their sums may have components $n/3$ ($n = 0, \pm 1$) of their normal projections on the ab plane along the axes a and b of the base-centered lattice. If both components of the sheet displacement sums per repeat are non-zero, a rotation of the structure around the normal to the layers by an angle multiple of 60° will bring the structure to an orientation in which $c_n = [-\frac{1}{2}, 0]$ or $c_n = [0, -\frac{1}{2}]$. Therefore ideal models may be characterized either by orthogonal or monoclinic unit cells with an ideal angle β or α satisfying one of the relationships $\cos \beta/a = -\frac{1}{2}$ or $\cos \alpha/b = -\frac{1}{2}$ (Zvyagin 1962; 1967).

CONSEQUENCES OF DISTORTIONS THAT DO NOT AFFECT THE TWO DIMENSIONAL LATTICE OF KAOLINITE LAYERS

General crystallochemical considerations indicate that ideal models built of regular polyhedra cannot be realized. According to the rules of Pauling (1929), shared edges of octahedra should be shortened in order to screen mutual repulsion of cations. In dioctahedral layers the oxygen atoms are displaced leading to ditrigonal rotation of octahedral bases (Figure 1). Such distortions being equal for different edges (although in actuality, they are not equal) retain the three-fold axes of both sheets, and the cells a_i, b_i remain rotationally equivalent. However, the displacements of oxygen atoms shared by T- and O-sheets affect the interlayer displacements of the sheets, so that $s_3 = [\frac{1}{2} - 2\delta_1, 0]$. According to structural data, for example dickite has $\delta_1 \approx 0.01$ (Rozhdestvenskaya et al. 1982).

With ideal values of $s_3 = [\frac{1}{2}, 0]$, the monoclinic unit cell shape for the triclinic structure of kaolinite is realized for two variants 2_- and 4_+ related by a mirror plane. The normal projections c_n of the vectors c on the ab plane are: $s_2 + t_- = [\frac{1}{6}, -\frac{1}{6}] + [0, -\frac{1}{2}] = [\frac{1}{6}, -\frac{1}{2}]$ and $s_4 + t_+ = [\frac{1}{6}, \frac{1}{6}] + [0, \frac{1}{2}] = [\frac{1}{6}, \frac{1}{2}]$. In both cases under the condition of a base-centered unit cell, there is an equivalent value $c_n = [-\frac{1}{2}, 0]$ correspond-

ing to a monoclinic unit cell shape with an obtuse ideal angle β_{id} . According to the linear transformations of axes a_i, b_i the ditrigonal rotation of octahedral and tetrahedral bases results in the values $s_2 = [\frac{1}{6} - \delta_1, -\frac{1}{6} + \delta_1]$, $s_4 = [\frac{1}{6} - \delta_1, \frac{1}{6} - \delta_1]$, so that $c_{n2} = [-\frac{1}{2} - \delta_1, \delta_1]$, $c_{n4} = [-\frac{1}{2} - \delta_1, -\delta_1]$. Thus only the ditrigonal rotation alone leading to $\delta_1 \neq 0$ gives an automatic increase in the angle β and a deviation of the angle α from 90° , that is in a triclinic unit cell shape. Both the distortion of β_{id} and the deviation $\alpha - 90^\circ$ are related to the same value for $\delta_1 > 0$, so that for right-handed unit cells, the angle α is acute for the structure 2_- and it is obtuse for the structure 4_+ .

The atomic coordinates for the dickite structure show that the interlayer displacements of consecutive sheets t_+, t_- also deviate from ideal values $[0, \pm\frac{1}{2}]$ because of an additional shift $2\delta_2 a$ of the T-sheet in the direction of the vector $s_i + t_k$ projected on the ab plane between the origins of octahedral sheets of the adjacent layers. In the case of dickite $1,5_-1$, this gives $c_n = [-\frac{1}{6} + \delta_1, -\frac{1}{6} + \delta_1] + [-\delta_2, \frac{1}{2} + \delta_2] + [-\frac{1}{6} + \delta_1, \frac{1}{6} - \delta_1] + [-\delta_2, -\frac{1}{2} - \delta_2] = [-\frac{1}{6} + \delta_1 - \delta_2, \frac{1}{6} + \delta_1 + \delta_2] + [-\frac{1}{6} + \delta_1 - \delta_2, -\frac{1}{6} - \delta_1 - \delta_2] = [-\frac{1}{2} + 2(\delta_1 - \delta_2), 0]$. Since $\delta_1 \approx \delta_2 = \delta$, $c_n = [-\frac{1}{2}, 0]$ for dickite. Thus, it becomes clear why this mineral has an ideal value for the angle β as displayed by coincidence of reflections $\bar{2}.0.l+1$ and $\bar{1}\bar{3}l, 20l$ and $\bar{1}\bar{3}.l \pm 1$ in diffraction patterns. Under similar conditions, kaolinite would have $c_n = [-\frac{1}{2} - \delta_1 - 2\delta_2, \pm\delta_1] = [-\frac{1}{2} - 3\delta, \pm\delta]$. However, the actual value is $c_n = [-\frac{1}{2} - 3\delta, \pm 2\delta]$. It seems that whereas the distortions of the intralayer displacements of the sheets are the same both for dickite and kaolinite, they are different for the interlayer displacements t in kaolinite (instead of $[-2\delta_2, 0]$, they are $[-2\delta_2, \pm\delta_2]$).

These features are best displayed in oblique-texture electron diffraction patterns. The reflections there are distributed over ellipses corresponding to constant hk values. The reflection positions along the ellipses are defined by distances from the line of small axes that are proportional to the distances of the reciprocal lattice nodes from the plane normal to c^* and passing through the origin $D = (ha^* \cos \beta^*/c^* + kb^* \cos \alpha^*/c^* + l)c^*$, whereas the projections of the axes a^*, b^* on the axis c^* satisfy the equations $a^* \cos \beta^*/c^* = -c_{nx}$, $b^* \cos \alpha^*/c^* = -c_{ny}$ (Zvyagin et al. 1979). Figure 4 shows that for the ideal $c_n = [-\frac{1}{2}, 0]$, as in dickite, the coincident reflections occupy the levels $\frac{1}{2}$ and $\frac{3}{2}$ between the levels 0 and 1 of consecutive reflections $(00l)$ and $(0.0.l+1)$. The kaolinite projection $c_n = [-\frac{1}{2} - 3\delta, -2\delta]$ defines a sequence of 6 reflections $(\bar{2}.0.l+1), (\bar{1}\bar{3}l), (13l), (\bar{1}\bar{3}.l+1), (\bar{1}.3.l+1)$ and $(20l)$ at the levels $\frac{1}{2} - 6\delta, \frac{1}{2} - 3\delta, \frac{1}{2} + 9\delta, \frac{3}{2} - 9\delta, \frac{3}{2} + 3\delta, \frac{3}{2} + 6\delta$. In fractions of c^* for $\delta = 0.011$ the consecutive levels of a reflection sextuple are 0.267, 0.300, 0.432, 0.568, 0.700, 0.733. The next sextuple

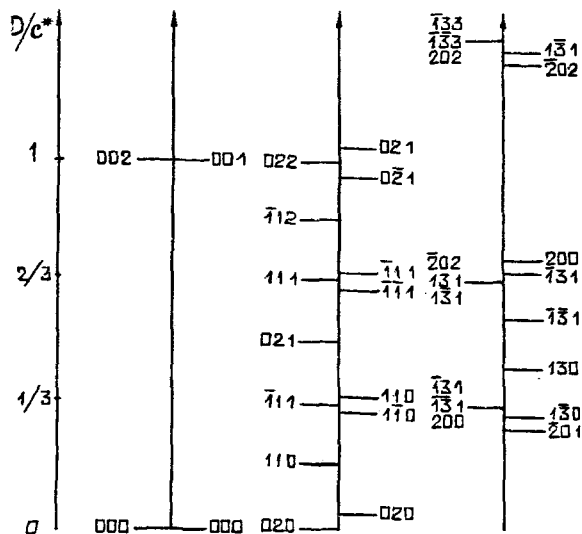


Figure 4. Level positions of reciprocal lattice nodes along the c^* -direction representing at some scale reflection positions along ellipses in oblique-texture electron diffraction patterns indicated by straight segments normal to the vertical lines: to the left for dickite and to the right for kaolinite.

begins at 1.267. Actually the outer reflection pairs of the sextuples are not resolved, and quadruples of reflections are observed on the second ellipsis corresponding to hk absolute values 13, and 20. The separations between reflections inside the quadruples seem to be the same (of the order 0.135) with the gaps between consecutive quadruples at approximately 0.534 (Figure 4).

The c_{ny} value is directly measured from the difference $\Delta D_1/c^*$ between the D/c^* -values for the first ellipsis reflections ($0\bar{2}1$) and (021), since $\Delta D_1/c^* = 4b^*\cos\alpha^*/c^* = -4c_{ny}$. The half-sum of these values defines c^* . After this, the c_{nx} value is obtained from the interval $\Delta D_2/c^*$ between the internal single reflections of the quadruples of the second ellipsis (reflections (13 l) and ($\bar{1}$ 3. l +1), $\Delta D_2/c^* = 1 - 2a^*\cos\beta^*/c^* - 6b^*\cos\alpha^*/c^* = 1 + 2c_{nx} + 6c_{ny}$. As mentioned above $c_{nx} \approx -\frac{1}{2} - 3\delta$, $c_{ny} \approx -2\delta$, so that $\Delta D_1/c^* \approx 8\delta$ and $\Delta D_2/c^* \approx \frac{1}{3} - 18\delta$ are very sensitive to the real values of δ . Careful measurements performed recently for the most perfect kaolinite samples (Bookin et al. 1989b) have revealed a good agreement between the electron and XRD data.

CONSEQUENCES OF THE TWO-DIMENSIONAL LAYER-LATTICE DISTORTIONS

The kaolin layers, as well as other phyllosilicate layers have lower symmetry than the O- and T-sheets that compose them. This implies the possibility of distortions that are compatible with the layer symmetry. If the reflection plane normal to the b_3 axis is retained,

then the right angles $\gamma_{3,6}$ are also retained. However, the axis ratios may be distorted, so that $\sqrt{3} \neq b_3/a_3 = \sqrt{3} + \eta_3$. This distortion alone is sufficient for the other unit cells to become non-orthogonal, so that $\gamma_i = 90^\circ + \epsilon_i$ for $i \neq 3, 6$. This is to be expected, and was observed, for all dioctahedral layer silicates because of the different length of shared octahedral edges OH-OH and OH-O in kaolins or O-O in micas.

Additional freedom for layer distortion appears under the influence of layer stacking differences. The interaction between atoms belonging to different layers and depending on their relative positions, although weaker than intralayer bonds, may influence the structure of the layers. In particular, the mirror plane m , normal to the axis b_3 may become a pseudo-plane "m", whereas the angle γ_3 may remain equal to or deviate from 90° .

Thus, the layers of different kaolin polytypes are not strictly identical. The kaolinite angles $\gamma_{2,4} \neq 90^\circ$, and their deviations from 90° are related to a distortion of the ratio $b_3/a_3 < \sqrt{3}$, whereas γ_3 remains equal to 90° (Bookin et al. 1989b). The same layers having $\gamma_3 = 90^\circ$ are expected for halloysite (Chukhrov and Zvyagin 1966). The dickite structure is formed by alternation of two mirror-related layers having successive orientations either $i = 1$ or 5 and $\gamma_{1,4}$ or $\gamma_{5,2} = 90^\circ$. The other cells i (and always with $i = 3$) are not orthogonal. Two mirror-related layers having orientations either $i = 1$ or 2 and the same $\gamma_{1,4}$ or $\gamma_{2,5} = 90^\circ$ also alternate in the structure of nacrite, $1_3 2_6 \dots$.

According to high-energy electron data, the nacrite layers differ by having smaller angles of ditrigonal rotation of tetrahedral bases ($\approx 3^\circ$ instead of $\approx 8^\circ$), which agrees with other combinations of atomic interactions affecting the positions of basal oxygen atoms (Zvyagin et al. 1972). Although the new high-precision refinement of the nacrite structure by single-crystal XRD (Zheng and Bailey 1994) has revealed a close similarity of the tetrahedra rotation angles in the nacrite and dickite layers, the electron diffraction indications should not be neglected. They were obtained by an independent method of structure analysis for the best nacrite sample and from the very best oblique-texture electron diffraction patterns ever obtained in the study of minerals. In any case, layers of different kaolin polytypes are not identical. Nevertheless, one may expect that for all such cases the lattice distortions are rather small and are described by minor η and ϵ values.

The values of η_i , ϵ_i for different unit cells of a cyclic succession $i = 1, 2, \dots, 6, \dots$ are interrelated according to the linear equations of the axis transformations that always have the same form which is independent of the layer distortions. Transformation equations for one pair of unit cells $(\mathbf{a}_{i+1}, \mathbf{b}_{i+1}) = (\frac{1}{2} - \frac{1}{2}\beta_2 \frac{1}{2}) (\mathbf{a}_i, \mathbf{b}_i)$ define the transformation of all other unit cells, because the reverse transformation of axes $i + 1$ into axes i is the same as for those expressing the axes i

- 1 through axes *i*. Then $\mathbf{a}_{i\pm 2}, \mathbf{b}_{i\pm 2} = -\mathbf{a}_{i\pm 1}, -\mathbf{b}_{i\pm 1}$; $\mathbf{a}_{i\pm 3}, \mathbf{b}_{i\pm 3} = -\mathbf{a}_i, -\mathbf{b}_i$. The reverse-transposed matrices, that is matrices of reverse axes transformations with interchanged lines and columns, relate the components of the vectors $\mathbf{c}_n, 2\delta_1, 2\delta_2$, in different coordinate systems.

The vector equations are easily transformed into algebraic ones of the type given by Bookin et al. (1989a) but concerning right-handed unit cells. Thus from

$$\begin{aligned} \mathbf{a}_{i+1} &= (\mathbf{a}_i - \mathbf{b}_i)/2, & \mathbf{b}_{i+1} &= (3\mathbf{a}_i + \mathbf{b}_i)/2; \\ \mathbf{a}_{i-1} &= (\mathbf{a}_i + \mathbf{b}_i)/2, & \mathbf{b}_{i-1} &= (-3\mathbf{a}_i + \mathbf{b}_i)/2 \end{aligned}$$

one obtains

$$\begin{aligned} 4a_{i\pm 1}^2 &= a_i^2 + b_i^2 \mp 2a_i b_i \cos \gamma_i, \\ 4b_{i\pm 1}^2 &= 9a_i^2 + b_i^2 \pm 6a_i b_i \cos \gamma_i, \\ 4a_{i\pm 1} b_{i\pm 1} \cos \gamma_{i\pm 1} &= \pm(3a_i^2 - b_i^2) - 2a_i b_i \cos \gamma_i, \\ 4a_i b_i \cos \gamma_i &= 3a_{i-1}^2 - b_{i-1}^2 - 2a_{i-1} b_{i-1} \cos \gamma_{i-1} \\ &= -3a_{i+1}^2 + b_{i+1}^2 - 2a_{i+1} b_{i+1} \cos \gamma_{i+1}. \end{aligned}$$

The last equation shows that $\cos \gamma_i = 0$ when $2 \cos \gamma_{i\pm 1} = \mp(3a_{i\pm 1}/b_{i\pm 1} - b_{i\pm 1}/a_{i\pm 1})$. Thus, Bookin et al. (1989b) found for kaolinite that $\gamma_3 = 90^\circ$, $(b_3/a_3)^2 = 2.978$ in accordance with the precise parameters $(b/a)^2 = 3.010$, $\epsilon = \pm 0.18^\circ$ of unit cells $i = 2$ and 4 .

Under such conditions, the unit cells $i + 1$ and $i - 1$ are mirror-equivalent because $\mathbf{a}_{i+1} = \mathbf{a}_{i-1}, \mathbf{b}_{i+1} = \mathbf{b}_{i-1}$ whereas the deviations of the angles γ_{i+1} and γ_{i-1} from 90° are equal by absolute value but opposite in sign, only if $\sqrt{3}a_i \neq b_i$, which is obvious, since the lattice of the kaolinite layer has a reflection plane *m*.

If $(b/a)_i^2 = 3 + \eta_i$, $\gamma_i = \pi/2 + \epsilon_i$, the following approximate expressions are valid at sufficiently small values of η_i, ϵ_i :

$$\begin{aligned} a_{i\pm 1} &\approx a_i(4 + \eta_i \pm 2\sqrt{3}\epsilon_i)^{1/2}/2, \\ b_{i\pm 1} &\approx a_i(12 + \eta_i \mp 6\sqrt{3}\epsilon_i)^{1/2}/2, \\ \eta_{i\pm 1} &\approx -\eta_i/2 \mp 3\sqrt{3}\epsilon_i, \\ \epsilon_{i\pm 1} &\approx (\pm\eta_i - 2\sqrt{3}\epsilon_i)/4\sqrt{3}. \end{aligned}$$

It follows from these equations that if $\eta_i = \pm 2\sqrt{3}\epsilon_i$ (ϵ_i is here measured in radians), then $\epsilon_{i+1} = 0, \eta_{i\pm 1} = -2\eta_i$ and $\epsilon_{i-1} = -\epsilon_i$. This simple relationship for a cell *i* is thus a condition for the existence of orthogonal unit cells $i \pm 1, i \mp 2$ and mirror-equivalent unit cells $i \mp 1, i \pm 2$ adjacent to the orthogonal ones. On the other hand, if $\epsilon_i = 0$ and $\eta_i < 0$, then $\epsilon_{i-1} > 0, \epsilon_{i+1} < 0$, the deviations from 90° having equal absolute values, whereas $\eta_{i+1} = \eta_{i-1} > 0$. As mentioned above, this is the case for both enantiomorphic modifications of kaolinite, $2_-. \dots$ and $4_+. \dots$ (Bookin et al. 1989b). In the monoclinic dickite structure having $(b/a)^2 \approx 3.014$, $\gamma = 90^\circ$ layers of orientations 1 and 5 alternate. The first layers have angles $\gamma_{1,4} = 90^\circ; \gamma_{2,5} > 90^\circ, \gamma_{3,6} < 90^\circ$; and the second layers have $\gamma_{5,2} = 90^\circ, \gamma_{4,1} < 90^\circ, \gamma_{3,6} > 90^\circ$. Thus, the alternating layers of dickite cannot be transferred one into another by any coincidental

operation. They are only mirror-equivalent, related by glide operations in a plane normal to their axes b_1 or b_5 , respectively. Thus it can be seen that the kaolin layers do not retain a fixed structure, as they should for the formal definition of polytypes which may differ only in the stacking of layers. A particular structure built of real layers provides no strict reasons to expect other polytypes built of the same layers but with different stackings, if these are not completely equivalent. Such reasons are provided by idealizations, which neglect the detailed variations of real structures of the layers. It is against the background of the structural diversity of ideal models that one can imagine real polytypes and refine the mechanism of their formation.

VARIANTS AND FAULTS IN THE KAOLIN LAYERS STACKING

There are 36 variants for the stacking of two adjacent kaolin layers, which may have 6 orientations and 6 relative displacements. However, for the kaolinite structures $2_-. \dots$ and $4_+. \dots$ it is reasonable to restrict the consideration to the use of orientations of the same parity and displacements t_+, t_- . Such features are characteristic also for the structures of dickite $1_+5_-. \dots$ and halloysite $3_+3_-. \dots$ (Chukhrov and Zvyagin 1966; Zvyagin 1964; Zvyagin et al. 1979). As indicated above, the successive layers of dickite, although having different orientations, are not rotationally identical and are related not by rotations $\pm 120^\circ$ accompanied by displacements $+, -$ but by operations of a glide reflection. Hence a reflection operation *m* should also be taken into account, and the orientation symbol supplied with a dash (*i'*) will indicate the action of such an operation. Its repeated operation eliminates the dash, so that the correct notation of dickite is $1_+5'_-1_-. \dots$. Although the lattice of the kaolinite layer has a mirror plane ($\gamma_3 = 90^\circ$), it is only a pseudo-plane "m" for the layer structure. Thus, the *m*-related atoms may differ, for example, in their *z*-coordinates. Therefore, if one of the kaolinite enantiomorphs is described as $2_-. \dots$, the other is $4'_+. \dots$. For the same reasons halloysite should be described as $3_+3'_-. \dots$.

Another problem to be considered is the accommodation of layer lattices at different stacking variations. The existence of a symmetry plane in the lattice of the kaolinite layer makes interchanges of intersheet and interlayer displacements related to this plane quite probable for layers of the same orientation as shown by Bookin et al. (1989b). As a result of careful analysis of experimental data, Bookin et al. (1989a) found that kaolinite and dickite have equal *a* and *b* periods and differ slightly in the angles γ . This supports layer orientation changes adjusting a_1, b_1 of one layer and a_5, b_5 of the adjacent layer. However, when the ratios $b_{1,5}/a_{1,5} > 3$ are in agreement, the discrepancy of $\gamma_5 > 90^\circ$ and $\gamma_1 < 90^\circ$ of the unit cells superimposed along the *c* axis should be resolved. The preceding layer may

Table 1. Layer triples (T1-T12) expected in the structure of kaolinite.

1. 3 ₊ 3 ₊ 3	5a. 3 ₊ 3 ₊ 1	7a. 3 ₊ 3 ₊ 1'	9a. 3 ₊ 3 ₋ 1	11a. 3 ₊ 3 ₋ 1'
2. 3 ₊ 3 ₋ 3	5b. 1 ₊ 1 ₊ 5	7b. 1 ₊ 1 ₊ 5'	9b. 1 ₊ 1 ₋ 5	11b. 1 ₊ 1 ₋ 5'
3. 3 ₊ 3 ₋ 3'	6a. 3 ₊ 3 ₋ 5	8a. 3 ₊ 3 ₋ 5'	10a. 3 ₊ 3 ₊ 5	12a. 3 ₊ 3 ₊ 5'
4. 3 ₊ 3 ₊ 3'	6b. 5 ₋ 5 ₋ 1	8b. 5 ₋ 5 ₋ 1'	10b. 5 ₊ 5 ₋ 1	12b. 5 ₊ 5 ₋ 1'

force the succeeding layer growing over it to obtain improper angles $\gamma_5 < 90^\circ$ or $\gamma_1 > 90^\circ$ as it would be in two enantiomorphic pseudomonoclinic "dickites" whose lattices are distorted by small deviations $\pm \epsilon$ of γ from 90° .

Bish and von Dreele (1989) succeeded in refining the structure of kaolinite in the presence of an admixture of dickite. It is easy to see from the published unit cell data that there is an opposite deviation $b/a < \sqrt{3}$ for the dickite studied in comparison with that of dickite single crystals (Rozhdestvenskaya et al. 1982). This result inspires an idea of special growth conditions when layers in orientation $i = 1$ or 5 are adjusted to layers in orientation $i = 3$. The growing layer inherits the features of the preceding kaolinite layer, that is γ_1 or $\gamma_5 = \gamma_3 = 90^\circ$ and b_1/a_1 or $b_5/a_5 = b_3/a_3 < \sqrt{3}$, whereas usual dickites have b_1/a_1 or $b_5/a_5 > \sqrt{3}$. Such a layer deformation is further transferred to the next layer alternating in a dickite sequence. This idea is in quantitative agreement with the unit cells published by Bish and von Dreele (1989). Thus, according to the experimental values $\eta_4 = 0.010$ and $\epsilon_4 = -0.003$ of the kaolinite unit cell, the values $\eta_3 = -0.020_5$, $\epsilon_3 = 0$ and $\epsilon_5 = 0.003$ calculated by means of the above formula exactly correspond to the experimental values $\eta_{1,5} = -0.020$, $\gamma = 90^\circ$ of dickite.

Although there is no direct evidence of such an effect (Bish personal communication), the indicated cell unit relationships deserve to be noted for the case if in the event future evidences are shown. Thus, layer differences of polytypes and probably the unit cell measurements by Bish and von Dreele (1989) indicate the possibility of layer deformations adjusting layers in different orientations, comprising the agreement of either linear or angular unit cell parameters and changing either their angular or linear parameters. Layer deformations were incorporated in an indirect form when Plançon and Tchoubar (1977) simulated kaolinite stacking faults compatible with diffraction data. For layer rotations $\pm 120^\circ$ having been found unsuitable, vacant octahedra were assigned to positions A, B, C. Actually this meant a change in the layer azimuthal orientation. However, by keeping the unit cell dimensions unchanged, the authors at the same time, unconsciously deformed the layers forcing a priori different unit cells to be equal.

Taking account of layer deformations necessary for the accommodation of their lattices in different azimuthal orientations and the possibility of m-related layers, a list of stacking variants may be compiled for

three successive layers, the first two of which are stacked in one of the regular kaolinite structures (2... in the setting 3...) and the third displays all the stacking variants. The layer triples are presented in orientations that indicate which unit cells i, i' of the second and third layers are to be accommodated by means of deformations (if necessary).

In comparison with the regular triple 1 (T1), Bookin et al. (1989a) qualified T2 as a shift stacking fault and T3 as a growth fault that replaces the "kaolinite" stacking by the "halloysite" stacking relating the adjacent layers by a glide operation. T4 may be considered as a combination of growth and shift faults. T5a-T8b expresses a replacement of a "kaolinite" vicinity of adjacent layers by a "dickite" one incorporating layer deformations of either the angle γ or the ratio b/a , with and without reflection operations in the planes normal to the axis b_3 . In a similar way, the triples T9a-T12b contain layer pairs similar to those forming the structure of the theoretical polytype 2M described as 1_5... , which differs from dickite in relative sheet displacements O-O and T-T according to the sums $s_i + t_k$ and $t_k + s_i$. These stacking faults, if present in the crystals, may either be single or divide zones of different polytypes, for example, regular layer sequences of the left-handed and right-handed kaolinite, kaolinite and halloysite, kaolinite and dickite.

Plançon et al. (1989) simulated diffraction effects for models of the kaolinite structure containing layer stacking faults described by Bookin et al. (1989a). The comparison of calculated and experimental profiles of reflections (02l), (11l), (13l) and (20l) has shown that the most frequent stacking faults in the samples studied are those of the type T3 representing "halloysite" intrusions leading to random alternation of right-hand and left-hand kaolinite fragments. Many samples were found to be mixtures of two kaolinite phases having either high or low concentration of such stacking faults. The Hinkley-index usually accepted as a measure of the crystallinity degree actually corresponded to the relative content of these kaolinite phases.

According to Plançon et al. (1989) the concentration of the "dickite"-type faults did not exceed 5%, so that a possibility of a continuous series between kaolinite and dickite seems hardly probable. Drits (1987) arrived at the same conclusion by considering calculated diffraction patterns corresponding to the whole range of random alternation of kaolinite and dickite stackings. Bookin et al. (1989a) found that the T2- and T3-stacking faults resulted in qualitatively similar dif-

fractional effects. It is especially difficult to distinguish between them if they alternate in the same crystal.

CONCLUSION

Admission of layer deformations in addition to displacements, rotations and reflection operations is of key importance not only for understanding, but also for explanation of the formation of different polytypes and stacking faults in the kaolin structures. It also solves the problem of modeling of some polytype structures according to the atomic coordinates of other polytypes in estimation of their relative stability as for the study of polytype transitions 1M-2M₁ of micas and 1TC-2M of pyrophyllites. In general, module deformations are an important feature of modular structures being related to the problem of commensurability-incommensurability and phenomena of structure modulations and superperiodicities. It is the task of further studies to obtain a more detailed pattern of realization of stacking variations both in kaolin and other modular structures.

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