REFINEMENT OF THE CRYSTAL STRUCTURE OF NACRITE

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Abstract – The crystal structure of nacrite from Pike's Peak district, Colorado, has been refined by least squares and electron density difference maps utilizing ten levels of data. Complete refinement was inhibited by thick domains involving $a/3$ interlayer shifts in the "wrong direction". The ideal structure is based on a 6R stacking sequence of kaolin layers, in which each successive layer is shifted relative to the layer below by $-\frac{1}{3}$ of the 8·9 Å lateral repeat. This direction is X in nacrite, contrary to the usual convention for layer silicates, because of the positioning of the (010) symmetry planes normal to the 5·1 Å repeat direction. Alternate layers are also rotated by 180°. The pattern of vacant octahedral sites reduces the symmetry to Cc and permits description of the structure as a 2-layer form with an inclined Z axis.

Adjacent tetrahedra are twisted by 7·3° in opposite directions so that the basal oxygens approach more closely both the Al cations in the same layer and the surface hydroxyls of the layer below. Interlocking corrugations in the oxygen and hydroxyl surfaces of adjacent layers run alternately parallel to the $[1\bar{1}0]$ and $[1\bar{1}0]$ zones in successive layers. The upper and lower anion triads in each Al-octahedron are rotated by 5·4° and 7·0° in opposite directions as a result of shared edge shortening. Nacrite has a greater interlayer separation and smaller lateral dimensions than dickite and kaolinite, and the observed β angle deviates by $1\frac{1}{2}°$ from the ideal value. These features, as well as its overall lesser stability, are believed due to the less favorable positioning in nacrite of the basal oxygens relative to the directed interlayer hydrogen bonds.

INTRODUCTION

DETERMINATION of the crystal structure of nacrite, the rarest polymorph of the kaolin group, was first attempted by Gruner (1933). On the basis of X-ray powder data from material near Brand, Saxony, Gruner proposed a monoclinic structure of space group Cc, in which four kaolin layers are superposed on (001) to give a $c \sin \beta$ repeat dimension of $4 \times 7 \cdot 16 = 28 \cdot 64$ Å. A β angle of 91°43' was determined by trial and error to give the best fit between observed and calculated d-values and intensities.

Hendricks (1939) next proposed a 6-layer monoclinic structure on the basis of a more detailed single crystal X-ray study of well crystallized nacrite from St. Peter's Dome of the Pike's Peak district, Colorado. In this structure the 6 kaolin layers are superimposed according to the requirements of the rhombohedral space group $R3c$. The 12 Al atoms and 6 vacant octahedral sites in the unit cell, however, are distributed

in such a way as to destroy the 3-fold axes and to reduce the overall symmetry to the monoclinic subgroup Cc. The geometric distortion from a rhombohedral- or trigonal-shaped unit cell is very slight, however, as judged by the proposed β angle of 90°20' + 10'. An unusual feature of the Hendricks' structure, and different from the Gruner structure, is the interchange of the X- and Y-axes that is required by the orientation of the (010) symmetry planes normal to the 5·14 Å repeat direction.

Bailey (1963) confirmed the Hendricks' structure on the basis of additional single crystal X-ray study, but pointed out that the pattern of vacant octahedral sites in the structure permits the selection of two alternate Z-axes, both of which have true two-layer periodicity. The preferred 2-layer unit cell, in which the Z-axis is inclined in the direction of structural layer shift, has a β angle $\cong 114°$. A 2-layer cell with $\beta \cong 100°$ is obtained if Z is inclined in the opposite direction. An entirely different 2-layer structure, based on a sequence of interlayer vector shifts like that in the $2M_2$ mica structure and having the same space group and unit cell shape as observed for nacrite, was

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specifically excluded as the correct structure for nacrite on the basis of comparison of observed and calculated intensities. The present paper reports a 3-dimensional refinement of the nacrite structure.

EXPERIMENTAL

Nacrite, believed to have been formed by the hydrothermal alteration of microcline (Cross and Hillebrand, 1885) in a large vein from the Eureka Tunnel. St. Peter's Dome. Pike's Peak. Colorado. was obtained from the U.S. National Museum (cat. no. 83593) through the courtesy of Dr. George Switzer and Dr. Paul E. Desautels. All the experimental data were obtained from two platy crystals about $0.70 \times 0.50 \times 0.02$ mm and $0.35 \times 0.35 \times 0.02$ mm in size. These were the best of a large number of crystals examined. Cell parameters obtained from the second crystal by the θ method of Weisz, Cochran. and Cole (1948) are $a = 8.909 \pm 2$. $b = 5.146 \pm 1$. $c = 15.697 \pm 2$ Å. and $\beta = 113°42' \pm 5'$.

Chemical analysis of the Eureka Tunnel nacrite (originally called kaolinite) by Cross and Hillebrand (1885). after subtraction of 0.68 per cent CaF_2, gives SiO_2 46.22%. Al_2O_3 39.92%. and H_2O 13.86%. These values compare very favorably with the theoretical composition for nacrite of SiO_2 46.55%, Al_2O_3 39.49%, and H_2O 13.96%.

Intensity data from crystal No. 1 were obtained for six levels along Z by use of anti-equi-inclination and equi-inclination Weissenberg techniques. Multiple film packs were used with MoKα radiation. After loss of crystal No. 1, zero- and first-level data were obtained along X and along Y from crystal No. 2 with multiple film packs and CuKα radiation. The intensities were measured visually by comparison with multiple film pack intensity scales prepared from each crystal for the radiation involved. All intensities were corrected for Lorentz-polarization effects. The data from crystal No. 2 were also corrected for absorption.

The quality of the intensity data is not as high as for other layer silicate structures reported from this laboratory. Although crystal No. 1 gave reasonably sharp spots, it was twinned in such a manner that overlap was a problem for the general reflections. Crystal No. 2 was apparently untwinned but considerably less perfect. The elongate, streaked reflections deteriorated rapidly in quality for higher levels so that only the zero- and first-level data were usable. Although a total of 714 non-equivalent reflections of measurable intensity were recorded from the two crystals combined, the data are not of equal quality and were not all used in all stages of the refinement.

REFINEMENT

The first stage of refinement utilized only the data obtained from crystal No. 1. A total of 454 reflections. including 57 unobserved values. was used in a full matrix least squares refinement test of the two most probable structures. The x and z parameters of one Si atom were held constant in order to fix the origin within the acentric space group Cc. Scattering factors appropriate for 50 per cent ionization were used, and the temperature factors found by Newnham (1961) for the dickite structure were inserted as non-variant values. After four cycles for each structure it was apparent that there was good agreement between observed and calculated structure amplitudes for the Hendricks' model, treated as a 2-layer structure, and much poorer agreement for the $2M_2$ polytype. Further refinement of the latter structure was discontinued.

After several additional cycles, in which the reflections were weighted according to the estimated reliability of the intensity measurements, the Hendricks' structure converged to a reliability factor of 10 per cent compared to its initial value of 29 per cent. Attempts to refine the temperature factors were unsuccessful because several values tended to become negative.

Despite the favorable reliability factor at this point, bond length calculations suggested additional refinement was desirable. It was at this point that the data for 360 more reflections from crystal No. 2 were collected and used in additional least squares cycles, both as a separate set of data and as combined with the data from crystal No. 1. Several weighting schemes were used, including that of Cruickshank (1965). The best results in this second stage of refinement were obtained with the combined data, for which a final reliability factor of 10 per cent was achieved. Bond length calculations, however, again showed more internal inconsistency than should be obtained with the number of reflections used. Three-dimensional electron density XY sections showed the presence of extra electron density peaks displaced from the peaks of the true atomic positions by shifts of $a/3$ (along the 8.9 Å repeat direction). The extra peaks are approximately $\frac{1}{3}$ the height of those of the regular atoms. The net effect is the creation of ridges of undulating but continuous electron density parallel to true X within those sections in which the atoms do not already repeat at intervals of $a/3$. This has apparently biased the least square refinement by displacing the atomic positions along X toward the extra peaks.

Final refinement of the structure was accomplished by a series of three-dimensional electron density difference maps, from which the visible

satellite peaks were subtracted. The resulting bond lengths are internally consistent and compare well with those of other layer silicates. The final atomic positions are listed in Table 1 and the resulting bond lengths and angles in Table 2. It is difficult to assign accuracy values to the final atomic positions and bond lengths because of the unknown influence of the extra electron density peaks that could not be subtracted from the

Table 1. Refined atomic coordinates of nacrite

Atom	x	y	z
Al_1	0·1582	0·3389	0·2202
Al_2	0·5004	0·3248	0·2199
Si_1	0·2022	0·4789	0·0311
Si_2	0·3699	−0·0139	0·0310
O_1	0·2411	0·7499	−0·0041
O_2	0·2765	0·2559	−0·0152
O_3	0·0042	0·4569	−0·0148
O_4	0·2780	0·4360	0·1431
O_5	0·4570	0·0158	0·1422
$(OH)_1$	0·0953	0·0201	0·1488
$(OH)_2$	0·5585	0·6398	0·2882
$(OH)_3$	0·1873	0·6289	0·2850
$(OH)_4$	0·3728	0·1845	0·2842

difference maps because of superposition on regular atoms. By comparison with other layer silicate structures, it is estimated that the accuracy of the bond lengths is approximately ±0·02 Å. Thus, all except minor features of the structure can be considered to be essentially correct.

DISCUSSION

Domain structure

The extra electron density peaks are not diffraction ripples, because they do not appear along the two pseudo X-axes that have atomic sequences nearly equivalent to that along true X. Also, the peaks disappear in difference maps in which $\frac{1}{3}$ atoms are assumed to lie at the satellite positions. The extra peaks are interpreted as evidence for the presence of domains in the crystal in which there are regular interlayer shifts of $a/3$ along true X in the "wrong direction", i.e. along +X. In this sequence of layers, shifts of $a/3$ along both −X and +X are feasible because they both lead to pairing of O and OH across the interlayer space. The domains cannot be thin units randomly interstratified within the normal stacking sequence because there is no preferred broadening or streaking of $k \neq 3n$ reflections. It is probable that the boundaries between domains can be considered as twin planes, but no definite proof of this is available.

The evidence requires superposition of two incoherent sets of diffraction data, perhaps accounting in part for the poor quality of the observed reflections. In the rest of the discussion, only the details of the normal structure will be mentioned.

Stacking sequence of layers

The nacrite structure is based on a 6R stacking sequence of kaolin layers, in which each successive layer is shifted relative to the layer below by $\frac{1}{3}$ of the 8·9 Å lateral repeat along the −X direction of the resultant unit cell. Alternate layers are also rotated by 190° (Fig. 1). This is an entirely different
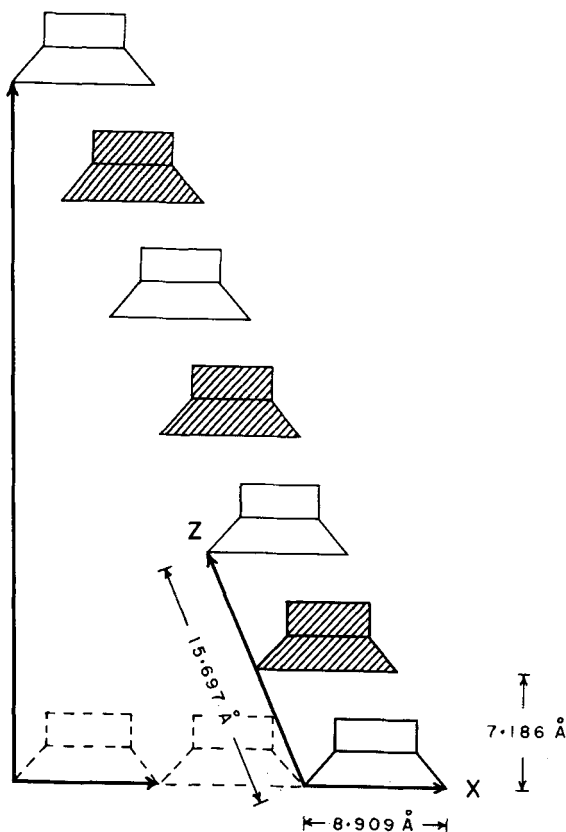

Fig. 1. Layer sequence in nacrite. Each layer is shifted $\frac{1}{3}$ of the 8·9 Å lateral repeat relative to the layer below. Alternate layers (hatched) are rotated 180°. Axes for 6-layer cell of Hendricks are at left, those of present paper for 2-layer cell with $\beta \cong 114°$ are at right.

layer sequence from that found in kaolinite and dickite, for both of which the layer shifts are $\frac{1}{3}$ of the 5·1 Å lateral repeat and in which the layers are not rotated. If nacrite were trioctahedral, it would belong to space group $R3c$ and would have 6-layer periodicity. Because the individual nacrite

Table 2. Final interatomic bond lengths and angles

Si₁—O₁	1·59 Å	Si₂—O₁	1·61 Å	Al₁—O₄	1·97 Å	Al₂—O₄	1·95 Å
O₂	1·63	O₂	1·63	O₅	1·94	O₅	1·95
O₃	1·62	O₃	1·63	(OH)₁	1·94	(OH)₁	1·93
O₄	1·63	O₅	1·61	(OH)₂	1·93	(OH)₂	1·90
Mean*	1·618 Å			(OH)₃	1·77	(OH)₃	1·86
				(OH)₄	1·94	(OH)₄	1·94

Mean　　1·918 Å

Around Si₁　　　　*Around Si₂*

O₁—O₂	2·58 Å	O₁—O₂	2·64 Å
O₃	2·54	O₃	2·64
O₄	2·73	O₅	2·70
O₂—O₃	2·64	O₂—O₃	2·54
O₄	2·65	O₅	2·65
O₃—O₄	2·69	O₃—O₅	2·68
Mean	2·640 Å		

Lateral edges

	Around Al₁	*Around Al₂*	*Around Vacancy*
O₄—O₅	2·88 Å	2·69 Å	3·39 Å
(OH)₁	2·71	2·83	3·44
O₅—(OH)₁	2·82	2·86	3·27
(OH)₂—(OH)₃	2·77	2·88	3·29
(OH)₄	2·84	2·85	3·24
(OH)₃—(OH)₄	2·82	2·81	3·30
Mean	2·813 Å		3·321 Å

Diagonal edges — Shared

	Around Al₁	*Around Al₂*
O₄—(OH)₄	2·41	2·41
O₅—(OH)₃	2·42	2·42
(OH)₁—(OH)₂	2·42	2·42
Mean	2·416 Å	

Diagonal edges — Unshared

	Around Al₁	*Around Al₂*	*Around Vacancy*
O₄—(OH)₃	2·84	2·82	O₄—(OH)₂
O₅—(OH)₂	2·85	2·76	O₅—(OH)₄
(OH)₁—(OH)₄	2·67	2·81	(OH)₁—(OH)₃
Mean	2·792 Å		

Interlayer bonds

O₁—(OH)₂	3·06 Å
O₂—(OH)₃	2·97
O₃—(OH)₄	2·98
Mean	3·002 Å

Tetrahedral angles

O₁—Si₁—O₂	106·1°	O₁—Si₂—O₂	108·9°
O₃	104·9	O₃	109·1
O₄	116·2	O₅	114·2
O₂—Si₁—O₃	108·5	O₂—Si₂—O₃	102·5
O₄	108·6	O₅	109·8
O₃—Si₁—O₄	112·1	O₃—Si₂—O₅	111·6
Mean	109·39°		

Si₁—O₁—Si₂	140·3	O₂—O₁—O₃	{104·9° / 134·3}
O₂	128·7	O₁—O₂—O₃	{104·6 / 135·7}
O₃	131·2		
Mean	133·39°	O₁—O₃—O₂	{106·3 / 133·0}

Mean tetrahedral twist = 7·27°

Octahedral angles

(OH)₁—O₄—O₅	{162·9° / 74·4}	
(OH)₁—O₅—O₄	{168·3 / 73·5}	lower triad (7·01°)
O₄—(OH)₁—O₅	{166·3 / 73·8}	
(OH)₃—(OH)₂—(OH)₄	{169·9 / 70·7}	
(OH)₂—(OH)₃—(OH)₄	{168·0 / 71·0}	upper triad (5·43°)
(OH)₂—(OH)₄—(OH)₃	{169·4 / 70·7}	

Mean octahedral twist = 6·22°

*All mean values calculated using one decimal place more than quoted for individual values.

layers are distorted so that they are only pseudo-ditrigonal (e.g. compare any of several pseudo-symmetric angles in Table 2, such as the basal oxygen interangles of 104·9°, 104·6°, and 106·3°), it can be verified that the hexagonal rings of alternate layers are rotated 180° rather than ±60°. The vacant octahedral sites are not in the same positions in each layer, however, and they can be described as rotating ±60° between layers. It is the pattern of vacant sites in successive layers (Fig. 2) that reduces the symmetry to Cc and permits description of the structure as a 2-layer form with an
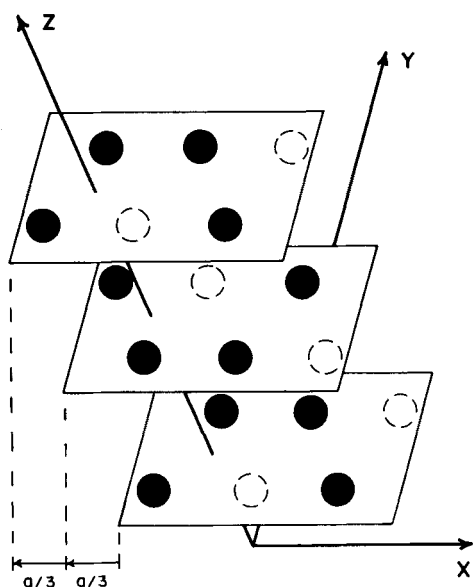
Fig. 2. Pattern of vacant octahedral sites in successive nacrite layers. The second layer is rotated 180° relative to the layers above and below. The vacant site (dashed open circle) changes position within each group of three octahedral sites so that it can be described as rotating ±60° between layers. This creates true 2-layer periodicity along the inclined Z-axis.

Fig. 3. Relative sizes of occupied (shaded) and vacant (open) octahedra in nacrite.

inclined Z-axis. A similar deviation of the observed symmetry from that of the parent trioctahedral layer sequence (1 M) is also found for both kaolinite and dickite as a consequence of the patterns of vacancy ordering adopted in these minerals (Bailey, 1963). The directions usually designated X and Y in layer silicates ($a = 5\cdot1$, $b = 8\cdot9$ Å) are reversed in nacrite ($a = 8\cdot9$, $b = 5\cdot1$ Å) because the (010) symmetry planes are positioned normal to the $5\cdot1$ Å repeat direction.

Structure of layer

The structural features within each nacrite layer are similar to those found in other dioctahedral layer silicates. The mean Si—O bond length is $1\cdot618$ Å and the mean Al—O, OH bond is $1\cdot918$ Å. Shared edges between octahedra are appreciably shortened so that the octahedral sheet is thinned and the vacant octahedral site is enlarged (Fig. 3, Table 2). The upper and lower anion triads in each Al-octahedron are rotated by $5\cdot4°$ and $7\cdot0°$ in opposite directions as a result of shared edge shortening so that the arrangement of oxygens at the octahedral-tetrahedral interface is distorted as shown in Fig. 4.

Each distorted oxygen hexagon in Fig. 4 contains 4 shortened and twisted edges that belong to
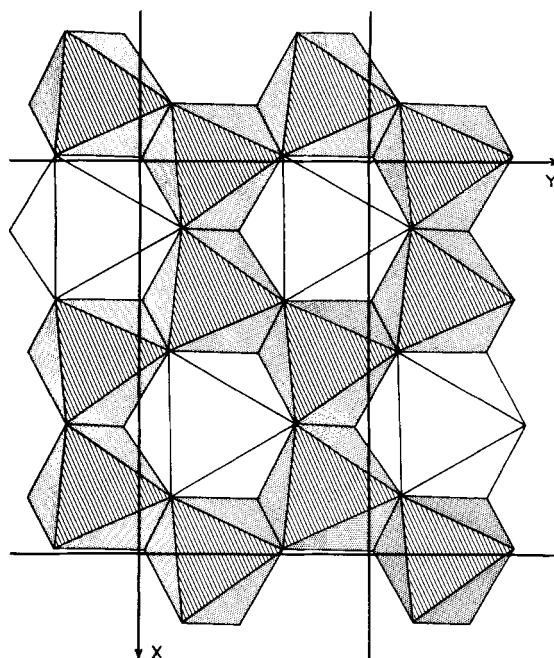
occupied Al-octahedra and two elongate edges that belong to vacant octahedra. Each oxygen shown must also serve as an apical oxygen in the tetrahedral sheet below. Ideally the distance between adjacent apical oxygens should be about $3\cdot1$ Å for a tetrahedral sheet containing only Si atoms. The tetrahedral sheet can compress its lateral dimensions readily to fit the shorter ($2\cdot8$ Å) octahedral edges by the mechanism of tetrahedral rotation (Radoslovich and Norrish, 1962). In nacrite adjacent tetrahedra have rotated in opposite directions by an average angle of $7\cdot3°$ (Fig. 5). The tetrahedra can adjust to the longer ($3\cdot3$ Å) edges around the vacant sites only by a tilting mechanism in which two apical oxygens (O_4 and O_5) move apart and the bridging basal oxygen (O_1) between the two tetrahedra involved buckles upwards by about $0\cdot2$ Å. Radoslovich (1963) has pointed out that the direction of movement of the buckled basal oxygen is also a direction of easy relief from the compressional forces due to tetrahedral twist, as it is toward the vacant octahedral site. In Fig. 4 an upward-buckled basal oxygen (O_1) lies under the mid-point of each elongate octahedral edge so that parallel, linear corrugations are formed in the basal oxygen surface. These corrugations run alternately parallel to the [110] and [1$\bar{1}$0] zones in successive nacrite layers.
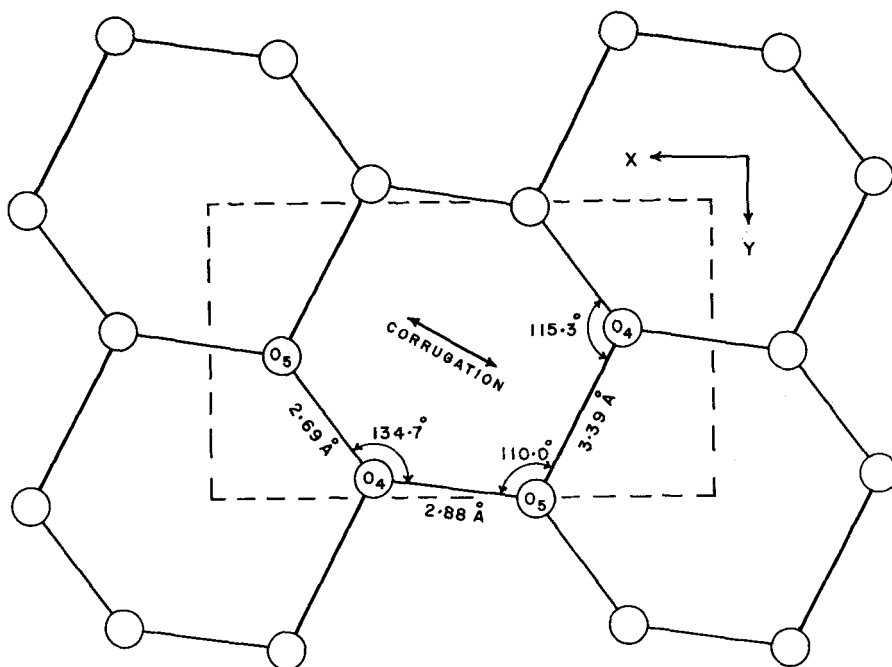
Fig. 4. Distorted apical oxygen network at the tetrahedral-octahedral interface in nacrite. Corrugations in the basal oxygen surface run perpendicular to the elongate vacant site edge (3·39 Å) shown in heavy line.

In addition to the basal oxygen surface, the uppermost hydroxyl surface is also corrugated due to the elevation of $(OH)_2$ above the level of $(OH)_3$ and $(OH)_4$. This corrugation has a different origin. It represents a tendency to minimize the length of the long hydrogen bond across the interlayer by fitting $(OH)_2$ to the buckled basal oxygen O_1. Elevation of $(OH)_2$ is opposed by the tendency to shorten the diagonal shared edge $(OH)_1$—$(OH)_2$ between Al_1 and Al_2. Because $(OH)_1$ is not anchored as tightly as its neighbors, the result is a compromise small elevation of the entire shared edge $(OH)_1$—$(OH)_2$. $(OH)_2$ is elevated only one-third the amount of the buckling of basal oxygen O_1 so that the interlayer bond O_1—$(OH)_2$ between corrugations is still slightly longer (3·06 Å) than the other two interlayer bonds ($2·97_5$ Å ave.). This situation is also found in kaolinite and dickite.

Tetrahedral twist

Bailey (1966) has analyzed the direction of tetrahedral twist in layer silicates in terms of the effective forces acting on the basal oxygens. For $2:1$ micas there is only one effective force, so that the basal oxygens in both tetrahedral sheets always rotate laterally toward the positions of the nearest octahedral cations within the layer. In $2:1:1$

chlorites and vermiculites, where long hydrogen bonds to the basal oxygens from adjacent interlayer OH and H_2O surfaces provide a second influencing factor, the basal oxygens rotate to shorten these interlayer bonds. This direction may be toward or away from the octahedral cations in the $2:1$ silicate layer or in the interlayer sheet for different types of layer sequences, indicating that the interlayer bond is the dominant factor. In $1:1$ layer structures the octahedral cation in the next layer, here considered to be below the basal oxygen surface, provides a third factor that proves to be the dominant force for trioctahedral species.

In the three dioctahedral kaolin minerals the Al cations in one layer are vertically superimposed over the surface hydroxyl groups of the layer below. The basal oxygens of the upper layer, which are at an intermediate z elevation, rotate laterally to approach more closely both the Al cations in the same layer and the surface hydroxyl groups of the layer below. For kaolinite and dickite these are the only two attractive forces operative, and they pull the basal oxygens in the same direction. Rotation toward the Al cations in the layer below is physically impossible because the stacking sequence of layers positions the tetrahedral cations in the upper
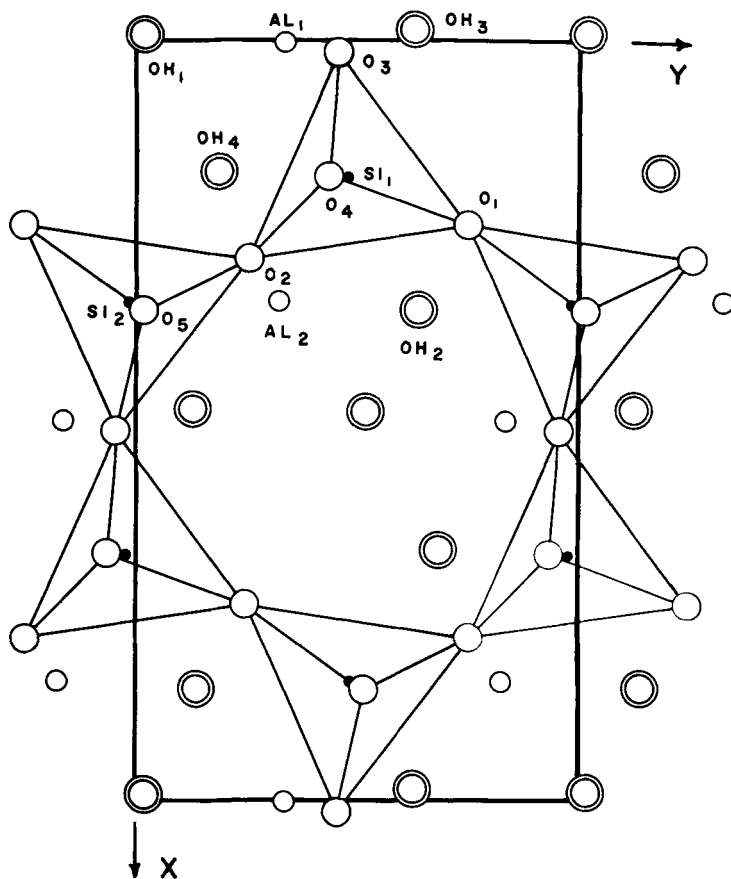
Fig. 5. Atomic positions in first layer of nacrite unit cell. Adjacent tetra-hedra have rotated in opposite directions by 7·3° to allow the basal oxygens (O_1, O_2, O_3) to approach more closely both the Al cations in the same layer (Fig. 5) and the surface hydroxyls of the layer below (Fig. 6).

layer directly over the octahedral cations of the layer below. This is not the case in nacrite, however, and the basal oxygens deviate from the rule observed in trioctahedral species by moving laterally *away* from the octahedral cations in the layer below. Three cooperative reasons can be cited for this behaviour, all related to the diocta-hedral composition.

(1) The direction of easy relief from the lateral compression resulting from tetrahedral tilt and twist buckles the bridging oxygen O_1 up and towards the vacant octahedral site, thereby fixing the direction in which the other basal oxygens must move (towards the occupied octahedral sites).

(2) The torque on the tetrahedral apical oxygens

as a result of shortening of shared edges between occupied octahedra is in the right direction to twist the tetrahedra towards these same octahedral cations. It is assumed that torque on an apical oxygen can twist an entire tetrahedron because of the directed nature of the hybrid sp^3 bond involved.

(3) The interlayer hydrogen bonds are presum-ably stronger in dioctahedral kaolins than in trioctahedral species because of (a) the stronger polarization of the hydroxyls by Al, and (b) the more directed nature of the hydrogen bonds, in which ideally they extend up and out from the hydroxyls to be coplanar with the bonds to the two coordinating Al cations below (Fig. 6). The Al cations are slightly closer to the upper plane of hydroxyls than to the lower apical oxygen plus
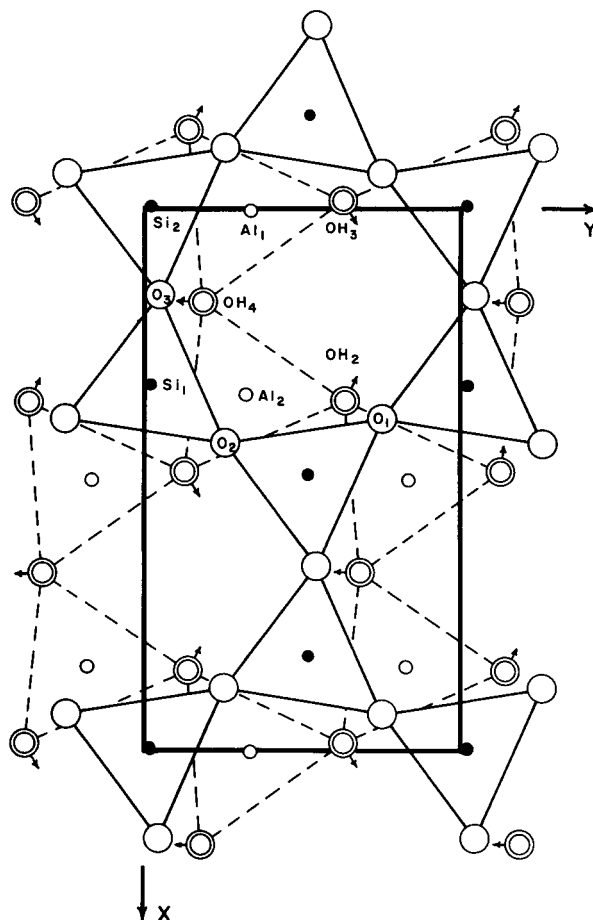
Fig. 6. Positioning of the basal tetrahedra of second layer (full line) on octahedra at top of first layer (dashed line). Basal oxygens have rotated by 7·3° to shorten the nearest O—OH interlayer contact. Ideal directions of long hydrogen bonds from OH (coplanar with two Al—OH bonds) shown by small arrows.

hydroxyl plane, suggesting an asymmetric charge distribution on the hydroxyls with the positive charge towards the interlayer.

Stability of kaolin minerals

Newnham (1961) justified nature's preference for the layer stacking sequences found in kaolinite, dickite, and nacrite on the basis of two assumptions regarding stable configurations.

(1) The highly charged Si^{4+} and Al^{3+} cations tend to avoid one another as much as possible.

(2) Oxygens and hydroxyls approach one another as close as possible to promote strong interlayer bonding.

Radoslovich (1963) has suggested an additional criterion of stability, namely that the favored layer sequences are those that minimize the angular strains in the directed interlayer hydrogen bonds. Kaolinite and dickite, which have the same layer sequence, impose less angular strain on the interlayer bonds than is the case for nacrite, accounting for the lesser abundance of nacrite. Figure 6 shows that in nacrite only one basal oxygen (O_3) is located so that it can pair up ideally with a directed hydrogen bond. O_1 and O_2 are located so that the actual bonds must be at right angles to the ideal directed bonds. This must impose considerable strain on the interlayer region and must affect the nacrite stability adversely.

The nacrite layer (7·186 Å) is slightly thicker than the dickite (7·162 Å) and kaolinite (7·124 Å) layers. Within the limits of accuracy of the kaolinite and nacrite structures, this difference appears due to a slightly greater interlayer separation in nacrite (2·92 Å) than in dickite (2·89 Å) and kaolinite (2·84 Å). This suggests that the packing of layers is less favorable in nacrite because of the strain in the directed interlayer bonds. It is tempting to speculate that this is also the reason for the fact that the interlayer shift is not exactly $a/3$ in nacrite, so that the observed β angle (113°42′) deviates by $1\frac{1}{2}°$ from the ideal value (112°14′). The thicker layer is compensated by a shorter lateral repeat distance in nacrite (8·909 Å) than the corresponding repeats in kaolinite (8·932 Å) and dickite (8·940 Å).

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Résumé — La structure du cristal de nacrite de la région de Pike's Peak, au Colorado, à été raffinée en carrés minima et en cartes de différence de densite d'électrons en utilisant dix niveaux de données. Le raffinement complet à été gêné par des domaines épais comportant des déplacements de couches intermédiaires $a/3$ dans la "mauvaise direction". La structure idéale est basée sur une séquence d'empilement $6R$ de couches de kaolin, dans lesquelles chaque couche successive est déplacée relativement à la couche inférieure par $-1/3$ de la répétition latérale 8·9 Å. Dans le nacrite, cette direction est X, contrairement à la convention habituelle des couches des silicates, à cause de la position des plans symetrie (010) normaux par rapport à la repetition de direction 5·1 Å les couches alternatives sont également basculees a 180°. Le modèle de l'emplacement octaédrique vacant reduit la symétrie à Cc et permet la description de la structure comme étant une formation à 2 couches avec un axe Z incline.

Les adjacentes tétraédriques sont détournées de 7·3° en directions opposées si bien que les oxygènes de base se rapprochent des cations Al de la même feuille et des surfaces hydroxiles de la couche inférieure. Les ondulations enchevêtrées des surfaces d'oxigène et d'hyroxiles des couches adjacentes concourent alternativement et parallèlement aux zones (110) et (1$\overline{1}$0) des couches successives. Les anions triades supérieurs et inférieurs de chaque octaédre A1 sont bascules de 5·4° et de 7·0° dans les directions opposées résultant d'un raccourcissement partagé de la bordure. La nacrite possède une séparation de couche supérieure et des dimensions latérales inférieures à la dickite et à la kaolinite, et l'angle β observé dévie de $1\frac{1}{2}°$ par rapport à la valeur idéale. Ces caractéristiques, ainsi que sa stabilité générale moindre, paraissent être dues a la position moins favorable des oxygènes de base à l'interieur de la nacrite, comparativement aux chaines d'hydrogene situées entre chaque couche aux liens d'entre-couches d'hydrogène.

Kurzreferat — Die Kristallstruktur von Nakrit aus dem Pike's Peak Gebiet in Colorado wurde unter Verwendung von zehn Datenniveaus durch Anwendung der kleinsten Quadrate und Darstellungen der Unterschiede in der Elektronendichte geklärt. Eine vollkommene Klärung wurde durch Verdickungen infolge von $a/3$ Zwischenschichtverschiebungen in der "falschen Richtung" verhindert. Die Idealstruktur stützt sich auf eine $6R$ gestapelte Folge von Kaolinschichten, wobei jede der aufeinander

folgenden Schichten um −1/3 der 8,9 Å seitlichen Wiederholung in Bezug auf die darunter liegende Schicht verschoben ist. Diese Richtung ist X im Nakrit, im Gegensatz zu den sonst bei geschichteten Silikaten üblichen Verhältnissen, und zwar wegen der Lage der (010) Symmetrieeben normal zu der 5,1 Å Wiederholungsrichtung. Abwechselnde Lagen sind gleichfalls um 180° verdreht. Das Muster leerstehender oktaedrischer Stellen vermindert die Symmetrie auf Cc und erlaubt es, die Struktur als eine zweischichtige Form mit geneigter Z-Achse anzusprechen.

Benachbarte Tetraeder sind in entgegengesetzter Richtung um 7,3° verdreht, so dass die Basis-Sauerstoffe näher an die Al Kationen in der gleichen Schicht, sowie an die Oberflächenhydroxyle in der darunter liegenden Schicht, herankommen. Ineinandergreifende Rippen in den Sauerstoff- und Hydroxyloberflächen benachbarter Schichten verlaufen abwechselnd parallel zu den [110] und [1$\bar{1}$0] Zonen in aufeinander folgenden Schichten. Die oberen und unteren Aniontriaden in jedem Al-Oktaeder werden durch gemeinsame Kantenverkürzung um 5,4° und 7,0 in entgegengesetzten Richtungen verdreht. Nakrit hat grössere Zwischenschichttrennung und kleinere seitliche Masse als Dickit und Kaolinit, und der beobachtete β Winkel weicht um 1½° vom Idealwert ab. Diese Merkmale, sowie die geringere Gesamtbeständigkeit des Nakrits, hängen vermutlich mit der weniger günstigen Lage der Basis-Sauerstoffe in Bezug auf die gerichteten Zwischenschicht-Wasserstoffbindungen im Nakrit zusammen.

Резюме—Кристаллическая структура накрита из района Пайкс Пик (шт. Колорадо) была уточнена с помощью метода наименьших квадратов и разностных синтезов электронной плотности (использованы данные для десяти уровней) Полному уточнению структуры препятствовала большая толщина доменов с межслоевыми смещениями $a/3$ в "неправильном направлении". Идеальная модель структуры основана на последовательности упакованных по закону 6R каолиновых слоев, в которой каждый последующий слой смещен по отношению к расположенному ниже на — 1/3 от трансляции 8,9 А в плоскости слоя. Это направление в накрите является осью Хвопреки обычному выбору осей слоистых силикатов, так как плоскость симметрии (010) перпендикулярна к периоду повторяемости 5,1 А. Чередующиеся слои повернуты на 180° один по отношению к другому. Распределение вакантных октадрических позиций уменьшает симметрию до Сс и позволяет описать структуру как двуслойную с наклонной осью Z.

Смежные тетраэдры повернуты на 7,3° в противоположных направлениях так, что базальные атомы кислорода оказываются более близкими как к катионам Al в том же слое, так и к поверхнос гидроксилов нижнего слоя.

Примыкающие друг к другу выступы и впадины соприкасающихся кислородных и гидроксильных слоев располагаются параллельно [110] и [1$\bar{1}$0]. Верхние и нижние анионные треугольные основания в каждом Al-октаэдре повернуты на 5,4° и 7,0° в противоположных направлениях (результат укорочения общего ребра). Накрит имеет больший межслоевой и меньшие латеральные размеры, чем диккит и каолинит; измеренный угол β накрита отклоняется на 1 ½° от идеального значения. Эти особенности, а также меньшая устойчивость накрита, по-видимому, объясняются менее благоприятным положением в его структуре базальных атомов кислорода для образования ориентированных межслоевых водородных связей.