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POLYMORPHISM OF THE KAOLIN MINERALS

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ABSTRACT

The polymorphism of the kaolin minerals is analyzed in terms of two factors: 1) direction and amount of interlayer shift, and 2) location of the vacant octahedral site in successive layers. Kaolinite and dickite have the same interlayer shift of $-\frac{1}{3}a_1$ when referred to a standard layer orientation. The two structures differ only in regard to the distribution of the vacant cation site in successive octahedral sheets and the consequences of this distribution in terms of symmetry, layer distortion, and Z-axis periodicity. In well-crystallized kaolinite the vacant site is the same in each layer. The structure is triclinic and may be right-hānded or left-handed, because either of two octahedral positions, related by a mirror plane in an undistorted monoclinic structure, may be vacant. In dickite the vacant site alternates between these two positions in successive layers, creating a two-layer monoclinic superstructure that is a regular alternation of right- and left-handed kaolinite layers. Comparison of the two structures is facilitated by changing the standard orientation of the dickite unit cell to correspond to that of kaolinite. The interlayer shift in nacrite is $\frac{1}{3}b_1$ relative to the same axes as for kaolinite and dickite. The layer sequence is that of a 6R polytype, but the pattern of vacant sites reduces the symmetry to *Cc* and allows selection of a smaller two-layer unit cell. A modified system of polytype notation is suggested for describing the kaolins and other minerals in which the actual Z-axis periodicity or crystal system differs from that of the ideal trioctahedreal polytype as a result of cation or vacancy ordering.

INTRODUCTION

The descriptions in the literature of the individual kaolin structures do not attempt to analyze the relationship of the sequence of interlayer shifts in one mineral to those in the other two. An understanding of the relative layer sequences is necessary, however, if one is to appreciate fully the structural reasons for the polymorphism of the kaolins.

The polymorphism is most easily analyzed in terms of two factors: 1) the direction and amount of the interlayer shift, and 2) the location of the vacant octahedral site in successive layers. The similarities and differences in the structures of the three minerals caused by these two factors can be summarized by reference to their *x*-ray powder patterns. Kaolinite and dickite have identical interlayer shifts and give powder patterns that are similar with respect to most of the stronger reflections. The differing location of the vacant octahedral site in the two structures governs the symmetry and the Z-axis periodicity of each mineral and accounts for the observed differences in the powder reflections of medium to weak intensity. Nacrite has a sequence of interlayer shifts that is entirely different from that in kaolinite and dickite, and its powder pattern is also markedly different.

Hendricks (1938) first showed the importance of interlayer hydrogen

bonds in governing the permissible positions of successive kaolin layers. Figure 1 illustrates an ideal trioctahedral 7 Å layer in which octahedral hydroxyl ions at the top of the layer are paired with tetrahedral oxygens at the base of the overlying layer. This OH–O pairing results in the formation of long hydrogen bonds, approximately 3.0 Å between the anion centers, that hold the neutral layers together. Hydrogen bond arrangements similar to that shown in Fig. 1, although differing in detail, can be formed by several different positions of the layers relative to one an-

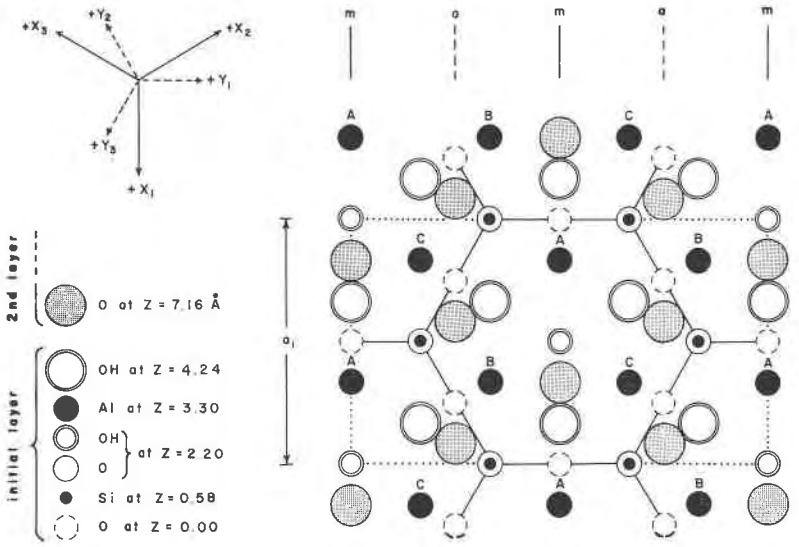

FIG. 1. Normal projection onto (001) of an undistorted 7 Å layer of space group *Cm*. The three possible octahedral sites, only two of which are occupied in kaolins, are labeled A, B and C. The second layer has been shifted by $-\frac{1}{3}a_1$, as in kaolinite and dickite, to provide long hydrogen bonds between the paired OH and O atoms at the layer interface.

other. These will be described here in terms of shifts and rotations of the upper layer relative to a fixed initial layer.

If the initial layer is oriented as in the first layer of Fig. 1, making no assumption as to the distribution of the two aluminum cations and one vacancy over the three available octahedral sites, interlayer hydrogen bonds will result from the following three layer sequences.

1) No shift of the succeeding layer. The hexagonal, or ditrigonal, Si_6O_{24} rings in adjacent layers may be either exactly superimposed or rotated by $\pm n(60°)$ relative to one another.

2) Shift of the second layer by $-\frac{1}{3}a$ along one of the three pseudohexagonal X-axes of the initial layer, with or without a rotation of the second layer by $\pm n(60°)$. A shift along

the positive X direction does not lead to pairing of OH—O anions for the orientation defined in Fig. 1.

3) Shift of the second layer by $\pm\frac{1}{3}b$ along one of the three pseudohexagonal Y-axes of the initial layer, with or without a rotation of the second layer by $\pm n(60°)$.

If the three sorts of stacking sequences above are not intermixed, it can be shown for trioctahedral 7 Å layer silicates that there are twelve possible polytypes having regular Z-axis periodicities between one and six layers, plus four enantiomorphs (Bailey, in preparation). For dioctahedral 7 Å layers there are many more regular polytype possibilities (Zvyagin, 1962), but Newnham (1961) has concluded that certain layer sequences are favored as a result of the effects of cation-cation superimposition and of the distortion of the layer due to the position of the vacant site. The most stable dioctahedral structures turn out to be those of kaolinite, dickite and nacrite. Radoslovich (1963) has reached a similar conclusion based on consideration of the directed nature of the interlayer hydrogen bond for dioctahedral compositions.

Kaolinite and Dickite

The structure of kaolinite was established originally by powder methods (Brindley and Robinson, 1946; Brindley and Nakahira, 1958) and later refined by single crystal x-ray and electron diffraction techniques (Drits and Kashaev, 1960; Zvyagin, 1960). The structure of dickite, for which larger and more perfect crystals can be obtained, has been determined in considerable detail by Newnham and Brindley (1956) and by Newnham (1961).

Analysis of the structures shows that kaolinite and dickite have identical layer sequences in which each layer is shifted by $-\frac{1}{3}a_1$, as defined in Fig. 1, relative to the layer below. The two structures differ only in regard to the distribution of the vacant cation site in successive octahedral sheets and the consequences of this distribution in terms of symmetry, layer distortion and Z-axis periodicity. This means that if the two minerals were trioctahedral, rather than dioctahedral, they would be identical. They would have a one-layer monoclinic (1M) structure with $\beta = 104°$ and space group Cm, as in the monoclinic form of 7 Å chamosite described by Brindley (1951).

The kaolinite unit cell is similar in shape to that of its trioctahedral analogue, 1M chamosite, but is distorted slightly to triclinic geometry. The three possible octahedral sites, only two of which are filled in the kaolin minerals, are labeled in Fig. 1 as A, lying on the mirror plane of the ideal Cm structure, and B and C, lying on opposite sides of the mirror plane. Brindley and Robinson (1946) chose C as the vacant site in kaolinite, whereas Zvyagin (1960) and Drits and Kashaev (1960) chose site

B. The two structures so defined are mirror images of one another and are not distinguishable by the methods used. Choice of either B or C as the vacant site imposes triclinic symmetry on the structure due to loss of the symmetry planes. The distortion of the unit cell to triclinic geometry is a separate anorthic effect, although also dependent upon the location of the vacant site at B or C.

Figure 2 illustrates the pattern of vacant octahedral sites in successive layers in kaolinite and dickite. In well-crystallized kaolinite each layer is identical and has octahedral site C (or B) vacant. In dickite the vacant

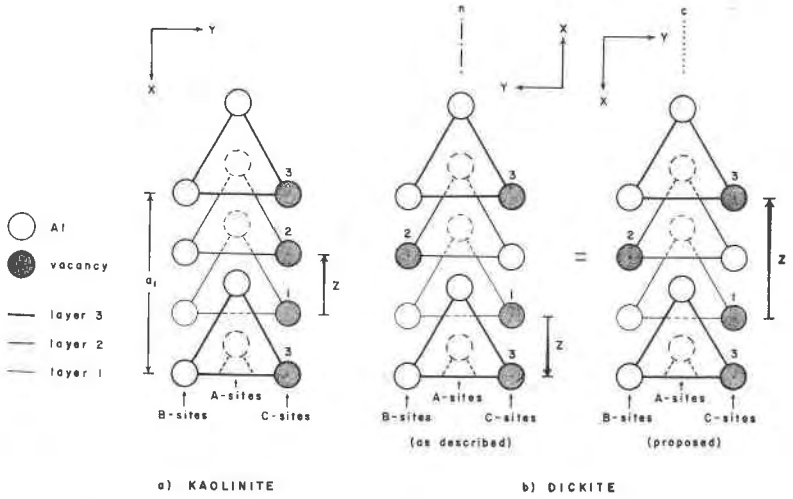

FIG. 2. Normal projection onto (001) of the octahedral portions of three layers (labeled 1, 2, 3) of the kaolinite and dickite structures, showing distribution of cations and vacancies over the A, B and C octahedral sites. In both structures each layer is shifted by $-\frac{1}{3}a_1$ relative to the layer below. The projected Z-axis vector is shown as a solid line arrow. For dickite the cation distribution may be interpreted as related by an *n*-glide plane or by a *c*-glide plane, depending on definition of the Z-axis vector. Two sets of octahedral positions, separated by a_1, are shown in layer 3 to illustrate the two choices for the Z-axis vector in dickite.

site alternates between C and B in successive layers to create a two-layer structure. The alternation of vacant sites in dickite tends to balance the stress distribution in the two layers so that the cell shape remains monoclinic. The pattern of vacant sites also creates *c* and *n* glide planes parallel to (010) and changes the space group to *Cc*. Thus, dickite can be considered as a regular alternation of right- and left-handed kaolinite layers, in one sense, or as a superstructure of the ideal 1M polytype due to a particular ordering pattern of octahedral cations and vacancies.

In poorly-crystallized kaolins it is quite conceivable that the vacancy does not always occur in the same octahedral site in each layer, as in kaolinite, or alternate regularly between two sites in successive layers, as in dickite. Newnham (1961) has suggested that the diffraction effects shown by certain fire clays could be interpreted as a random interleaving of right- and left-handed kaolinite crystals, *i.e.* random choice of C or B as the vacant site in different layers.

The description presented in this paper emphasizing the similarity in the layer sequence and the difference in the vacant site distribution in

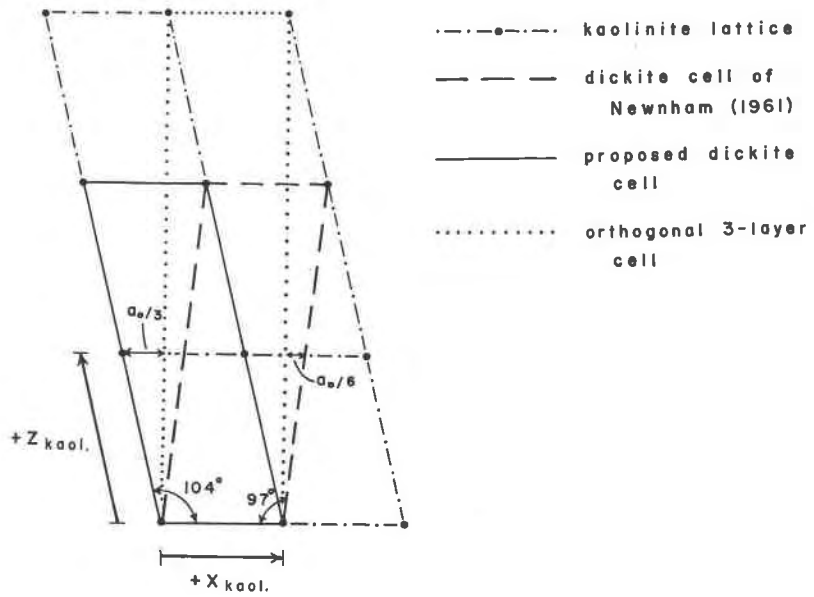

FIG. 3. Two alternative 2-layer cells for dickite shown in relation to a group of six kaolinite unit cells in the (010) plane. The values of the β angles are only approximate. An orthogonal 3-layer cell, as described for "monoclinic kaolinite," is also shown.

the kaolinite and dickite structures has not appeared elsewhere in the literature, to the writer's knowledge, and does not seem to be generally recognized. One reason may be that the dickite unit cell selected by Newnham and Brindley (1956) and by Newnham (1961) is not easily comparable with that of kaolinite. Figures 2 and 3 show that the Z-axis of dickite is inclined in the opposite direction to that of kaolinite, *i.e.* along $+X_1$ as defined in Fig. 1, and opposite to the direction of interlayer shift. This gives a β angle of approximately 97°, corresponding to a unit cell

slope of $+\frac{1}{6}\ a_1$ per layer in terms of the axes of Fig. 1, but measured in a direction opposite to that of the actual structural shift, which is $-\frac{1}{3}a_1$ per layer.

It is proposed here that the standard orientation of the dickite unit cell be changed to correspond to that of kaolinite. This proposal has the advantages that it will facilitate comparison of the two structures and that, by having Z inclined in the direction of interlayer shift, it provides a more realistic relationship between the unit cell and the layer sequence. The β angle is then a direct function of the amount of interlayer shift. The writer believes that these advantages outweigh the disadvantages of using a larger β value and of deviating from the morphological cell chosen by Miers (*in* Dick, 1888). Figure 3 compares the kaolinite unit cell with the present and the proposed unit cells for dickite.

The new unit cell would change β from 96° 44′ (Newnham, 1961) to 103° 35′ and c from 14.424 Å to 14.736 Å. Figure 2*b* illustrates the geometric fact that redefinition of the Z-axis direction and repeat distance changes the n-glide plane in the present axial orientation to a c-glide plane in the proposed orientation. Similarly, the c-glide plane changes to an n-glide plane. Convention requires that the origin in the new cell be shifted by $\frac{1}{4}b_1$ to keep it on a c-glide plane, and it is convenient to move the origin in the direction that will place it approximately at the center of a ditrigonal ring, as in Fig. 1 and in the Brindley and Robinson structure of kaolinite.

The matrix for the direct transformation from the old unit cell to the proposed cell for axes and Miller indices is given below (International Tables, Vol. I, p. 15–17).

$$
\begin{array}{l}
x_1\ h_2\ a_2 \\
y_1\ k_2\ b_2 \\
z_1\ l_2\ c_2
\end{array}
\qquad
\left[\begin{array}{ccc}
\bar{1} & 0 & 0 \\
0 & \bar{1} & 0 \\
1 & 0 & 1
\end{array}\right]
\qquad
\begin{array}{l}
x_2\ y_2\ z_2 \\
h_1\ k_1\ l_1 \\
a_1\ b_1\ c_1
\end{array}
\qquad I
$$

The matrix of the inverse transformation II is the same as I so that the new atomic coordinates can be obtained by reading matrix I top to bottom as indicated, taking care to subtract $\frac{1}{4}$ from the y coordinate to take into account the origin shift. The new coordinates are listed in Table 1. A powder pattern indexed on the new cell is given in Table 2.

TABLE 1. DICKITE ATOMIC COORDINATES RELATIVE TO NEW CELL[1]

Atom	x_2	y_2	z_2
Si_1	.0288	.3499	.0405
Si_2	.5400	.1768	.0402
Al_1	.3166	.4966	.2320
Al_2	.8116	.3330	.2306
O_1	.0385	.5127	−.0061
O_2	.7355	.2776	−.0058
O_3	.2412	.2395	.0058
O_4	.0720	.3624	.1523
O_5	.6416	.1687	.1526
$(OH)_1$	.5756	.4742	.1574
$(OH)_2$	.0509	.4767	.2948
$(OH)_3$	.5509	.3551	.2981
$(OH)_4$	.9635	.1668	.2963

[1] Data from Newnham (1961) transformed to $x_2 = -x_1 + z_1$; $y_2 = -y_1 - 1/4$; $z_2 = z_1$. New cell has $a = 5.150$ Å, $b = 8.940$ Å, $c = 14.736$ Å, and $\beta = 103°35'$.

MONOCLINIC KAOLINITE

A one-layer structure analogous to kaolinite but with octahedral site A vacant would belong to the monoclinic space group *Cm*, as noted by Gruner (1932), and it is tempting to speculate that this may be the structure of the "monoclinic kaolinite" from Yugoslavia described by Krstanovic and Radoševic (1961). Although originally described relative to a large orthogonal cell with $c = 21.5$ Å and $\beta \cong 90°$, this is probably not the smallest cell possible. The only two permissable monoclinic space groups for 7 Å layer silicates are *Cm* and *Cc*, and the smallest unit cells for these two space groups contain one and two layers respectively. It should be possible, therefore, to select a smaller monoclinic-shaped cell with $c \cong 7.37$ Å and $\beta \cong 104°$ for the Yugoslavia material, as in Fig. 3, if the proposed structure is correct. Approximate structure amplitudes, d-values, and powder intensities to be expected for this structure are given in Table 3. A layer distorted to a degree intermediate between that reported for dickite (7.3° tetrahedral rotations) by Newnham (1961) and that found for kaolinite (11.1° rotations) by Drits and Kashaev (1960) has been used as a model for the intensity calculations. Unfortunately, no published data are available for comparison purposes. An alternative would be an average structure in which the vacant site is distributed at random over the three possible octahedral positions.

NACRITE

The structure of nacrite that is presently accepted was determined by Hendricks (1938). It is described as a six-layer structure with β close to

TABLE 2. DICKITE POWDER PATTERN INDEXED ON NEW CELL

d_{obs}	I_{obs}	hkl	d_{calc}	I_{calc}
7.152	100	002	7.162	100
4.442	30	020	4.470	4
		$11\bar{1}$	4.439	34 } 38
4.362	30	110	4.368	38
4.264	20	021	4.267	28
4.119	65	$11\bar{2}$	4.124	60
3.954	10	111	3.958	13
3.790	55	022	3.792	45
3.578	90	$11\bar{3}$	3.612	9
		004	3.581	77 } 86
3.428	20	112	3.430	19
3.261	8	023	3.263	5
3.095	10	$11\bar{4}$	3.098	6
2.936	8	113	2.937	6
2.794	10	024	2.795	8
2.657	2	$11\bar{5}$	2.658	1
2.558	35	130	2.561	16
		$20\bar{2}$	2.557	11 } 27
		114	2.527	8
2.505	50	$13\bar{2}$	2.509	28 } 50
		200	2.503	14
2.412	2	025	2.412	2
2.386	15	006	2.387	9
2.324	95	132	2.324	60
		$20\bar{4}$	2.324	26 } 86
2.211	15	$13\bar{4}$	2.212	7
		202	2.207	5 } 12
2.183	2	220	2.184	2
2.132	2	042	2.134	1
2.104	5	026	2.106	3
2.062	2	$22\bar{4}$	2.062	1
2.026	3	043	2.024	1
1.974	40	$20\bar{6}$	1.975	11
		134	1.974	20 } 31
1.937	5	$22\bar{5}$	1.939	2
		116	1.935	1 } 3
1.896	10	044	1.896	6
1.860	15	$13\bar{6}$	1.861	7
		204	1.857	4 } 14
1.852		223	1.848	3
1.805	8	$22\bar{6}$	1.806	5
1.790	10	008	1.790	6
		$11\bar{8}$	1.790	1 } 7
1.764	3	045	1.762	2
1.717	3	224	1.715	2
1.685	10	$24\bar{1}$	1.687	2
		$31\bar{2}$	1.686	1
		150	1.683	1 } 7
		$24\bar{2}$	1.683	3
1.668	10	$15\bar{2}$	1.669	2
		240	1.667	5 } 7
1.650	50	151	1.657	4
		$20\bar{8}$	1.651	12 } 40
1.643	5	136	1.650	24
		$31\bar{4}$	1.642	5
		310	1.640	3 } 8
1.626	3	241	1.627	2
1.611	10	152	1.611	2
		$24\bar{4}$	1.611	3 } 5
1.589	10	$31\bar{5}$	1.591	3
		225	1.587	2 } 5
1.573	3	$15\bar{4}$	1.572	2
1.557	20	$13\bar{8}$	1.558	11
		206	1.555	4 } 15
1.552	3	153	1.550	1
		$22\bar{8}$	1.549	2 } 3
1.526	3	312	1.524	2
1.507	3	047	1.509	2
1.489	40	060	1.490	10
		$33\bar{2}$	1.488	21 } 31
1.469	5	226	1.468	5
		062	1.459	3
1.457	15	$33\bar{4}$	1.457	2 } 10
		330	1.456	5
1.432	10	$22\bar{9}$	1.434	3
		0, 0, 10	1.432	2 } 5
1.428	3	$15\bar{6}$	1.430	1
		244	1.428	1 } 2
		155	1.404	1
1.398	B 10	048	1.397	4
		2, 0, $\bar{10}$	1.392	1 } 9
1.392		138	1.391	3
		064	1.376	3
1.375	15	314	1.376	1
		$33\bar{6}$	1.375	4 } 10
		332	1.373	2
1.362	3	227	1.361	1
1.329	3	2, 2, $\bar{10}$	1.329	2
1.318	35	1, 3, $\bar{10}$	1.319	17
		208	1.317	9 } 26
1.296	2	049	1.296	1
1.288	10	$26\bar{1}$	1.289	1
		$26\bar{2}$	1.287	6 } 10
		$40\bar{2}$	1.285	3
1.279	4	260	1.280	2
		$40\bar{4}$	1.279	2 } 4
		066	1.264	1
1.263	6	$33\bar{8}$	1.263	1 } 4
		334	1.262	2
1.253	15	$26\bar{4}$	1.254	6
		400	1.252	5 } 11
		$17\bar{1}$	1.239	2
		170	1.238	1
1.236	15	262	1.235	3 } 10
		$35\bar{3}$	1.234	2
		$40\bar{6}$	1.234	2
1.223	5	316	1.226	1
		$42\bar{1}$	1.224	2
		$35\bar{4}$	1.221	2 } 6
		350	1.220	1
1.206	5	172	1.208	1
		0, 4, 10	1.206	1
		$15\bar{9}$	1.205	1 } 5
		420	1.205	1
		$35\bar{5}$	1.199	1
1.191	10	0, 0, 12	1.194	2
		2, 0, $\bar{12}$	1.192	1
		1, 3, 10	1.191	3 } 9
		$26\bar{6}$	1.189	2
		$42\bar{6}$	1.189	1
1.182	2	2, 4, $\bar{10}$	1.182	1
		421	1.179	1 } 2

Specimen from Geneva mine, Michigan. I_{obs} measured visually from 114.6 mm film, CuKα radiation. $I_{cal}=mLpF^2$ computed from parameters of Table 1 and adjusted to relative scale.

TABLE 3. THEORETICAL X-RAY PATTERN OF "MONOCLINIC KAOLINITE"

hkl	F_{calc}	d_{calc}	I_{calc}[1]		hkl	F_{calc}	d_{calc}	I_{calc}	
001	46	7.151	100		$24\bar{2}$	32	1.609	4	6
020	57	4.455	59		151	22	1.605	2	
110	49	4.352	84		$15\bar{2}$	39	1.569	6	
$11\bar{1}$	19	4.124	11		241	29	1.564	3	
021	27	2.781	19		$13\bar{4}$	50	1.558	10	31
002	82	3.576	78		$22\bar{4}$	34	1.551	5	
111	41	3.412	36		203	61	1.546	7	
$11\bar{2}$	44	3.103	33		114	1	1.543	—	
022	29	2.789	12		$31\bar{3}$	34	1.528	4	
$20\bar{1}$	47	2.555	13	28	311	35	1.517	4	
130	36	2.552	15		060	83	1.485	12	34
112	18	2.515	4		$33\bar{1}$	78	1.484	22	
$13\bar{1}$	56	2.503	39		$24\bar{3}$	2	1.479	—	
200	53	2.494	15		152	11	1.474	—	
003	41	2.384	9		223	29	1.461	3	
$20\bar{2}$	91	2.326	39		$33\bar{2}$	36	1.456	4	
131	67	2.314	43		061	27	1.454	2	13
$11\bar{3}$	20	2.306	4		$11\bar{5}$	22	1.453	2	
040	5	2.228	—		330	23	1.451	2	
$22\bar{1}$	8	2.216	1		005	34	1.430	2	
$13\bar{2}$	29	2.210	7		$15\bar{3}$	21	1.428	1	4
201	43	2.195	8		242	18	1.422	1	
220	10	2.176	1		$20\bar{5}$	35	1.395	2	
$04\bar{1}$	33	2.127	8		044	14	1.394	1	3
023	21	2.102	3		134	27	1.386	2	
$22\bar{2}$	22	2.062	4		$31\bar{4}$	18	1.381	1	
$20\bar{3}$	54	1.979	10		$33\bar{3}$	16	1.375	1	
221	31	1.969	6	30	062	40	1.371	5	17
132	59	1.965	24		312	11	1.368	—	
113	28	1.926	5		331	49	1.367	7	
042	17	1.891	2		025	23	1.362	1	
$13\bar{3}$	44	1.861	11		$22\bar{5}$	39	1.331	4	
202	28	1.846	2		$24\bar{4}$	30	1.328	2	26
$22\bar{3}$	25	1.808	3		153	18	1.322	1	
$11\bar{4}$	19	1.792	2	8	$13\bar{5}$	83	1.319	19	
004	47	1.788	6		204	78	1.311	8	
222	30	1.706	4		$26\bar{1}$	37	1.284	3	
$31\bar{1}$	44	1.682	9		$40\bar{1}$	54	1.282	4	
$24\bar{1}$	5	1.679	—	19	115	19	1.281	1	17
150	47	1.678	10		$40\bar{2}$	38	1.277	2	
$15\bar{1}$	24	1.664	3		260	38	1.276	4	
240	27	1.661	3	17	$15\bar{4}$	32	1.276	3	
024	11	1.659	1		243	16	1.270	1	
$20\bar{4}$	66	1.655	10		$33\bar{4}$	25	1.265	2	
133	73	1.643	24		063	23	1.260	1	
$31\bar{2}$	16	1.641	1	25	224	37	1.257	3	18
310	11	1.634	1		332	16	1.255	1	
043	45	1.628	9	10	$26\bar{2}$	63	1.252	9	
					400	31	1.247	1	

[1] Powder pattern intensity $I = mLpF^2$, adjusted to relative scale, where m is multiplicity and Lp is the Lorentz-polarization factor.

90°. The space group is *Cc*, although there are only a few deviations from a pseudo-space group of *R3c*. Relative to the orientation of Fig. 1, each layer is shifted by $\frac{1}{3}\ b_1$ and alternate layers are also rotated by 180°. This is an entirely different layer sequence from that in kaolinite and dickite. Another significant difference is the interchange of the conventional X- and Y-axes of layer silicates. The glide planes of space group *Cc* in this case are found to be normal to the 5.1 Å axis, which is normally X but now must be labeled Y. Hendricks accounted for the similarity to the pseudo-space group *R3c* by fixing the coordinates of all atoms except the octahedral Al according to *R3c* requirements. The Al atoms were positioned according to requirements of space group *Cc*. This amounts to a partial filling of the general position of space group *R3c*, as *Cc* is a subgroup of *R3c*.

Several years ago the writer made a single crystal study of nacrite in connection with the discovery of the mineral in iron ore at the Tracy mine in upper Michigan (Bailey and Tyler, 1960). It was determined that the space group is *Cc* and that the conventional X- and Y-axes are interchanged, in agreement with Hendricks' findings. However, the smallest unit cell is of monoclinic shape and contains only two kaolin layers. Two alternative two-layer unit cells exist, exactly as in the case of dickite, with β values of approximately 100° and 114°. The Z-axis is inclined in the direction of structural interlayer shift in the unit cell with $\beta \cong 114°$ and is inclined in the opposite direction in the cell with $\beta \cong 100°$. The former unit cell is preferred, therefore, and has been used for indexing the powder pattern listed in Table 4. This pattern supersedes that given by Bailey and Tyler (1960), in which small amounts of dickite impurity were later detected.

Discovery of the two-layer nature of nacrite does not mean that Hendricks' six-layer structure is incorrect, only that it can be described on the basis of a smaller unit cell, a fact also recognized by Newnham (1961). The calculated powder intensities given in Table 4, computed on the basis of layers distorted in the same manner as in dickite but stacked in the sequence postulated by Hendricks, agree closely with the observed intensities. This means that the layer sequence is that of a true six-layer structure, which would have rhombohedral symmetry *R3c* if trioctahedral (6R). The pattern of vacant octahedral sites causes the loss of the three-fold axes, reducing the symmetry to *Cc*, and allows selection of an alternate Z-axis that has true two-layer periodicity. Another interesting feature of the structure is that β deviates from the relation $\cos^{-1}[-2a/3c]$ by $1\frac{1}{2}°$, so that the interlayer shift is slightly, but significantly, greater than $\frac{1}{3}a$ per layer (where $a \cong 8.9$ Å). Dickite, on the other hand, has an interlayer shift almost exactly $\frac{1}{3}a$ per layer (where $a \cong 5.1$ Å).

TABLE 4. NACRITE POWDER PATTERN INDEXED ON 2-LAYER CELL

d_{obs}	I_{obs}	hkl	d_{calc}	I_{calc}	d_{obs}	I_{obs}	hkl	d_{calc}	I_{calc}
7.178	100	002	7.186	100	1.755	2	026	1.753	4
4.441	30	$11\bar{1}$	4.438	34	1.736	5	$40\bar{8}$	1.739	4 } 8
4.361	80	$20\bar{2}$	4.383	46 } 79			314	1.734	4
		110	4.352	33	1.710	2	224	1.706	2
4.130	70	$11\bar{2}$	4.137	64 } 70			$22\bar{7}$	1.685	2
		200	4.079	6			$42\bar{3}$	1.684	1
3.943	20	111	3.938	10	1.682		$13\bar{1}$	1.683	1
3.629 }	5	$11\bar{3}$	3.633	8			$51\bar{4}$	1.681	1
3.588 }	80	004	3.593	76			$51\bar{3}$	1.680	1
3.476	20	$20\bar{4}$	3.477	20			130	1.679	3 } 23
3.413	20	112	3.413	19		B 15	$42\bar{2}$	1.676	4
3.117	7	$11\bar{4}$	3.119	6			$42\bar{4}$	1.668	5
3.061	20	202	3.059	18			$13\bar{2}$	1.665	1
2.929	10	113	2.924	5			$51\bar{5}$	1.660	2
2.675	2	$11\bar{5}$	2.677	2	1.655		$51\bar{2}$	1.657	3
		020	2.573	3			131	1.652	1
2.571	10	$31\bar{2}$	2.571	6 } 11	1.627		$13\bar{3}$	1.627	3
		$20\bar{6}$	2.564	2		10	$31\bar{0}$	1.622	5 } 14
		$31\bar{3}$	2.541	3	1.619		$51\bar{6}$	1.618	5
2.533 }		021	2.533	8 } 22			$51\bar{1}$	1.614	1
B	20	$31\bar{1}$	2.522	4			027	1.605	5 } 8
2.518 }		114	2.518	7	1.605	5	132	1.605	3
2.432		022	2.438	34 } 72	1.589	5	315	1.587	6
	60	$31\bar{4}$	2.422	38			225	1.580	2
		310	2.404	38 } 46	1.574	5	$42\bar{6}$	1.579	2 } 7
2.404	40	006	2.395	8			$13\bar{4}$	1.572	3
2.321	15	$11\bar{6}$	2.319	5			$22\bar{8}$	1.559	2
2.287 }		$31\bar{5}$	2.287	4 } 8	1.558	5	510	1.555	1 } 4
B	5	204	2.280	1			118	1.548	1
2.273 }		023	2.267	3	1.531	5	421	1.536	1 } 5
2.247	5	311	2.245	6			404	1.529	4
2.213	2	$22\bar{2}$	2.219	1 } 2	1.514	2	$42\bar{7}$	1.513	1
		$40\bar{2}$	2.209	1			$51\bar{8}$	1.492	1
2.179	2	220	2.176	2			4, 0, $\bar{10}$	1.490	1
2.111	5	$31\bar{6}$	2.114	6	1.486	40	3, 1, $\bar{10}$	1.488	10 } 42
2.092	5	024	2.092	7			$33\bar{2}$	1.485	20
2.071	7	312	2.069	8 } 9			$60\bar{4}$	1.484	10
		$22\bar{4}$	2.068	1			028	1.473	8 } 11
2.039	2	400	2.039	2 } 3	1.473	5	422	1.465	3
		$11\bar{7}$	2.033	1			226	1.462	4
1.996	2	$40\bar{6}$	1.999	2			$60\bar{6}$	1.461	1
1.970	5	222	1.969	4 } 7	1.460	20	316	1.458	9 } 20
		$20\bar{8}$	1.960	3			$33\bar{4}$	1.458	2
		$22\bar{5}$	1.948	3			330	1.451	4
1.937	15	$31\bar{7}$	1.938	14 } 18			$60\bar{2}$	1.446	2
		116	1.931	1			$22\bar{9}$	1.444	3 } 8
1.917	15	025	1.917	15	1.441 B	2	$42\bar{8}$	1.441	1
1.898	15	313	1.896	11			0, 0, 10	1.437	2
1.842	2	223	1.838	3			$51\bar{9}$	1.419	1 } 3
1.818	5	$22\bar{6}$	1.816	5	1.415	4	512	1.412	2
1.797	5	008	1.797	6			$60\bar{8}$	1.385	2 } 5
		402	1.783	1	1.381	5	$33\bar{6}$	1.379	3
1.774	5	206	1.777	1 } 9					
		$31\bar{8}$	1.773	7					

Specimen from Tracy mine, Michigan. I_{obs} measured visually from 114.6 mm film, CuKα radiation. I_{calc}=mLpF^2 computed for dickite-tpye layer in unit cell with a=8.909Å, b=5.146Å, c=15.697Å, and β=113°42′.

TABLE 4—(*continued*)

d_{obs}	I_{obs}	hkl	d_{calc}	I_{calc}	d_{obs}	I_{obs}	hkl	d_{calc}	I_{calc}
1.369	5	3, 1, $\bar{1}\bar{1}$	1.370	5	7	1.244	3	602	1.247	1	
		332	1.366	2				318	1.243	4	7
		600	1.360	1				043	1.242	2	
1.357	5	029	1.357	3	7			71$\bar{5}$	1.235	1	
		13$\bar{7}$	1.356	1		1.235		53$\bar{4}$	1.235	2	
		227	1.355	2				24$\bar{1}$	1.235	1	
1.342 B	3	317	1.343	3	5		B 5	71$\bar{6}$	1.231	2	12
		2, 2, $\bar{1}0$	1.339	2				71$\bar{4}$	1.231	2	
1.317 B	3	136	1.324	1	3			240	1.227	2	
		406	1.314	2		1.231		53$\bar{5}$	1.226	1	
		040	1.287	1				24$\bar{3}$	1.225	1	
		62$\bar{4}$	1.286	2				53$\bar{6}$	1.209	1	
1.287		62$\bar{5}$	1.283	1		1.208	5	24$\bar{4}$	1.207	2	4
B	5	4, 0, $\bar{1}2$	1.282	2	10			53$\bar{1}$	1.207	1	
		13$\bar{8}$	1.281	1		1.197	3	0, 0, 12	1.198	2	3
1.282		041	1.281	1				71$\bar{8}$	1.195	1	
		62$\bar{3}$	1.278	1				242	1.186	1	
		6, 0, $\bar{1}0$	1.277	1		1.184	5	62$\bar{9}$	1.184	1	4
1.270		62$\bar{6}$	1.271	6				530	1.182	1	
		33$\bar{8}$	1.270	1				3, 1, $\bar{1}3$	1.176	1	
B	20	3, 1, $\bar{1}2$	1.267	4	24			426	1.170	1	
		042	1.266	6				71$\bar{9}$	1.167	1	
		62$\bar{2}$	1.261	6		1.166	3	0, 2, 11	1.165	1	6
1.263		228	1.259	1				621	1.164	1	
	3	0, 2, 10	1.255	4	6			2, 2, $\bar{1}2$	1.160	1	
1.254		334	1.255	2				6, 0, $\bar{1}2$	1.159	1	

At the present time a three-dimensional refinement of the nacrite structure is being carried out in collaboration with I. M. Threadgold. Further comment on nacrite is reserved until completion of this refinement.

POLYTYPE SYMBOLS

Smith and Yoder (1956) have used structural symbols, such as 1M, $2M_1$, and 3T, to designate the Z-axis periodicities and the crystal systems of mica polytypes having different stacking sequences of 10 Å layers. Their polytypes were derived for trioctahedral compositions, but have proved valid for the dioctahedral micas as well. No example is yet known of a mica for which the layer periodicity or the space group is changed from that of the ideal polytype as a result either of location of the vacant octahedral site, if dioctahedral, or of cation ordering. In the kaolin minerals, however, the location of the vacant octahedral site has caused a reduction of the ideal symmetry in all three minerals and a change in the layer periodicity in two of the three.

The writer believes that a modification of the standard polytype notation is desirable for describing structures in which the actual Z-axis periodicity or crystal system differs from that of the ideal trioctahedral polytype as a result of cation or vacancy ordering. A considerable gain

in clarity and in structural detail can be obtained in such cases by a notation that relates the actual structure to that of the ideal polytype. The symbol of the ideal polytype has special structural significance because it refers to the specific sequence of interlayer shifts used in the derivation of the polytype, thus defining the positions of all atoms in the structure to a first approximation. Cation or vacancy ordering taking place within the structural framework provided by a given layer sequence is a secondary structural effect, although it may have a very drastic effect on the resulting size, shape and symmetry of the unit cell.

A suggested procedure is to list two symbols, first the symbol appropriate to the actual structure and then, in brackets, the symbol of the ideal trioctahedral polytype with a subscript attached, such as $[1M_0]$ or $[2M_{1-ord}]$, to indicate that it is ordered. Only one symbol is necessary if the ordered structure retains the periodicity and symmetry of the ideal polytype. The notation for the three kaolin minerals under this procedure would be:

kaolinite	1Tc $[1M_0]$
dickite	2M $[1M_0]$
nacrite	2M $[6R_0]$

Zvyagin (1962) has made a systematic study showing that it is possible to derive a total of 52 regular dioctahedral 7 Å polytypes with Z-axis periodicities between one and six layers. Zvyagin's system of notation is inconvenient because it gives the same symbol to all unit cells of the same size, shape and symmetry without regard to their different structures.The system of notation suggested in this paper takes the differing structures into account by incorporating the symbol of the ideal polytype, as illustrated below for Zvyagin's eight two-layer monoclinic polytypes of space group *Cc*.

Zvyagin		
Number	*Symbol*	*Suggested Symbol*
I,3	$2M_1$	$2M_1$
I,4	$2M_1$	2M $[1M_0]$
IV,3	$2M_1'$	2M $[2T_0]$
IX,1	$2M_1'$	2M $[1T_0]$
V,4	$2M_2$	$2M_2$
II,2	$2M_2$	2M $[6R_0]$
III,1	$2M_2'$	2M $[2H_{1-ord}]$
V,1	$2M_2'$	2M $[20_0]$

The suggested notation restricts the use of number subscripts to symbols of the ideal polytypes. This keeps subscripts at a minimum and, in particular, reserves the symbols $2M_1$ and $2M_2$ for the theoretical $2M_1$ and $2M_2$ 7 Å polytypes, whose interlayer shifts are analogous to the

shifts within the octahedral sheet in the mica polytypes of the same designation.

It is essential in the suggested notation that the symbols of the ideal 7 Å polytypes, some of which are used above, be defined relative to a sequence of interlayer shifts. A systematic derivation and the proposed nomenclature will be given in a separate paper (Bailey, in preparation).

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