

THE CELL DIMENSIONS AND SYMMETRY OF LAYER-LATTICE SILICATES. VI. SERPENTINE AND KAOLIN MORPHOLOGY

E. W. RADOSLOVICH, *Division of Soils, Commonwealth Scientific and Industrial Research Organisation, Adelaide, Australia.*

ABSTRACT

As a consequence of the hypotheses developed in earlier papers in this series the stresses between tetrahedral and octahedral layers in serpentines can be more precisely expressed in terms of bond lengths and bond angles. It is shown that the sheet dimensions of serpentines are compatible with a tetrahedral layer stretched, by changes in bond angles, to the maximum possible structurally. It is suggested that octahedral layers in chrysotiles must contract under constraints rather more than these layers in antigorites, and that the two groups may be separated on this basis. If the same hypotheses are right then endellite sheets do not curl because of forces due to misfit between the tetrahedral and octahedral layers, since these are negligible. Attention is drawn to earlier work on the surface hydroxyl bonds in basic hydroxide layer structures, and to the peculiarly sensitive position of the Al ion in the kaolin minerals.

The morphology of the serpentine minerals and kaolin minerals has been studied in many laboratories by techniques which include electron microscopy, electron diffraction, *x*-ray powder diffraction, single crystal structure analysis, chemical analysis, hydrothermal synthesis and infrared spectroscopy. The literature is extensive (*e.g.* the references herewith) but the explanations for the observed phenomena are still more often tentative rather than rigorous. In particular the dimensional misfit of various sheet structures is only discussed qualitatively in most published work.

It is widely agreed that both serpentines and kaolins adopt various morphological forms because of a misfit between the tetrahedral layer and the octahedral layer which together make up these 1:1 layer-lattice silicates. As a broad generalisation this "explains" the observed plates, plates with rolled edges, tubes and fibrils, and also the structural types such as rectified and alternating wave structures, orthohexagonal cells, etc. Bates (1959) has discussed this misfit in detail, suggesting the adoption of a 'morphological index, "M"', but this seems to the writer to be defined in a rather arbitrary manner. Moreover "M" is not explicitly related to the physical quantities which really determine the degree of misfit, *viz.* the average bond lengths and bond angles in the two layers thought to be under stress.

Different kinds of stress in layer structures are very probably relieved by several distinct structural adjustments. Hypotheses about the nature of these adjustments have been proposed recently by Radoslovich and Norrish (1962; hereafter Part I), by Veitch and Radoslovich (1963; *i.e.*

Part III) and by Radoslovich (1963a; *i.e.* Part IV). Confirmatory evidence has been obtained by the multiple regression analysis of sheet dimensions and composition *i.e.* *b*-axis data and structural formulae (Radoslovich 1962; hereafter Part II). These hypotheses are further supported by the fact that they may be satisfactorily correlated with the observed composition limits for the micas and possibly other minerals (Radoslovich 1963b; hereafter Part V).

If these ideas are essentially correct, and the present values of ionic radii, bond lengths and bond angles are reliable, then for the serpentines the limits of strain may be stated more clearly in structural terms and these limits should correspond to observed changes in morphology. On the other hand if the same ideas are right then the currently accepted explanation for curled and tubular morphology amongst the kaolins is only superficially correct and should at least be reviewed carefully. This short paper does not aim to explain all facets of serpentine and kaolin morphology, but merely to draw attention to several factors with which any rigorous theory eventually must be consistent.

SERPENTINE MINERALS

Several writers have compared the morphology and crystal symmetry of synthetic serpentines of varying composition with that observed for natural serpentine minerals. Some caution is necessary, however, because the hypotheses in Part I imply that there are considerable differences in the surface symmetry (and also in the kind of layer misfit) between certain synthetic and natural serpentines.

Mg-Ge synthetic serpentine. Roy and Roy (1954) synthesised a serpentine wherein Ge fully replaces Si in the tetrahedral layer and for which Zussman and Brindley (1957) have given detailed *x*-ray data, including cell dimensions. Because of the larger ionic radius of Ge (0.53 Å) compared with either Si (0.41 Å) or Al (0.50 Å) the tetrahedral layer will be quite large. Although the exact Ge-O bondlength for such a layer is not known a value of 1.84 Å seems reasonable,¹ so that $b_{\text{tet}}(\text{Part I}) \cong 10.4 \text{ \AA}$. The octahedral dimensions, if unconstrained, may be calculated by the kaolin regression relation (Part II) as $b_{\text{oct}} = 9.3 \text{ \AA}$. Then $\cos \alpha = 0.894$ and $\alpha \cong 26\frac{1}{2}^\circ$. Although tetrahedral rotations as high as this are possible, the theoretical maximum is 30° and it is not surprising to find the octahedral layer stretching a little to 9.415 Å (Zussman and Brindley, 1957). For $b_{\text{obs}} = 9.415 \text{ \AA}$ and $b_{\text{tet}} = 10.4 \text{ \AA}$, $\alpha = 25^\circ$.

This synthetic serpentine is therefore markedly ditrigonal in surface

¹ See *International Tabellen zur Bestimmung von Kristallstrukturen*, Vol. II, p. 610. G. Bell, London, 1935 (Pauling's values of radii).

symmetry, more than almost all other lattice silicates (Parts I, II, V). It should tend to crystallise in an orthogonal unit cell which is $3n$ layers thick in the c direction (Radoslovich, 1959). Gillery (1959) has pointed out that this Mg-Ge serpentine is a six-layer orthohexagonal structure which approximates to a two-layer cell; this is apparently the basic unit which then may be built up in a similar way to the 3T micas (Smith and Yoder, 1956).

It is quite evident that in surface properties, including the stacking of layers, this serpentine is notably different from natural serpentines in which the tetrahedral layer is invariably untwisted ($\alpha=0^\circ$) and often severely stretched. Zussman and Brindley (1957) confirmed that the Unst orthoserpentine has a six-layer cell by comparing its powder pattern with that of $\text{Mg}_6\text{Ge}_4\text{O}_{10}(\text{OH})_8$. Though their independent evidence establishes a six-layer orthohexagonal cell and though the patterns are quite similar it is hardly valid to compare these minerals without qualification; the mechanism of forming six-layer polymorphs may be considerably different in the two minerals.

This synthetic serpentine is platy because the tetrahedral layer *contracts by rotations* to the octahedral layer with practically no resistance to deformation.

Mg-Al synthetic serpentines. Gillery (1959) has synthesised a range of such minerals with the general formula $(\text{Si}_{4-x}\text{Al}_x)(\text{Mg}_{6-x}\text{Al}_x)\text{O}_{10}(\text{OH})_8$, and for x from 0 to 2.50. He observed that when $x=0.75$ a platy one-layer orthoserpentine is formed, and when $x=1.50$ a platy six-layer orthoserpentine is formed. The first decreases and the second increases as x goes from 0.75 to 1.50. In Part II it was shown that $\alpha=0^\circ$ and $12\frac{1}{2}^\circ$ respectively, and this suggested that the Mg-Al serpentine higher in Al would most readily form an orthogonal cell through $3n$ layers. Gillery (1959) mentions that it approximates to a 3-layer cell. The increase in proportion of 6-layer structure with increasing Al—which Gillery could not explain at that time—therefore seems to be a direct result of the increasing tetrahedral rotation, α , as Al increases.

The morphology of these Mg-Al serpentines was shown by Gillery to be platy, except for a fibrous morphology when $x < 0.25$, e.g. $x=0$. The above calculations show that there is no unrelieved stress between tetrahedral and octahedral layers for $x \geq 0.75$ at least, and hence these structures are platy.

Composition limits between platy and fibrous structures. In all natural serpentines the sheet dimensions of the octahedral layer would exceed those of the tetrahedral layer, if both were unconstrained. These structures re-

main platey, however, until those compositions are reached where the octahedral layer is excessively larger than the tetrahedral.

It seems reasonable to assume that dimensional adjustments are made largely by changes in bond angles rather than bond lengths. For example, the O-Si-O angles in an ideal tetrahedral layer are $109^{\circ}28'$. If such a layer is stretched the main effect probably will be to expand the basal triads of oxygens by decreasing the angles $\tau = \text{O}_{\text{apex}}\text{-Si-O}_{\text{basal}}$ (Parts I, II, IV, V). Even though the individual angles τ are not known for a given structure the *average* value for τ should reach some fairly definite minimum for those tetrahedral layers which have been stretched as far as possible for a layer silicate.

It has been assumed (Parts I, II, V) that *average* values of τ do not fall below $106\frac{1}{2}^{\circ}$ to 107° , and empirically all the calculated values of τ appear to equal or exceed this lower limit. This may also be supported theoretically as follows. The radius ratio of Si:O is too high (0.293) for the four oxygens to be in contact with each other (which implies a radius ratio = 0.225). Presumably the angles τ may be decreased easily until the basal oxygens O_B "touch" the apex oxygen O_A , when the resistance to further change in τ should increase very rapidly (Part IV). The average interatomic distances $\text{O}_A\text{-O}_B$ are given in Table 1 for a range of angles τ , assuming Si-O bonds of 1.615 Å (Smith and Bailey, 1962). These dis-

TABLE 1. INTERATOMIC DISTANCES $\text{O}_A\text{-O}_B$ FOR VARIOUS O-Si-O ANGLES

τ in degrees	105	105.5	106	106.5	107	107.5	108
$\text{O}_A\text{-O}_B$ in Å	2.563	2.571	2.580	2.587	2.596	2.605	2.613

tances are to be compared with the effective oxygen radius *towards another oxygen*, for the particular type of co-ordination involved. In the present case this is neither the ionic radius nor the van der Waal radius. Moreover tables of ionic radii are given for ions in six-fold co-ordination and the exact correction to be applied to O_A and O_B is not clearly evident. In such a distorted tetrahedra the oxygens will certainly approach closer than an oxygen diameter, 2.80 Å. But they will *not* approach as closely as twice the effective radius of the oxygens towards the silicons, *viz.* $2 \times 1.40 \times 0.88 = 2.46$ Å (where 0.88 is the co-ordination correction for 4.2 co-ordination, Internationale Tabellen, *loc. cit.*). This short distance would require quite unusual compressive forces if it is to be the *average* tetrahedral edge throughout the sheets. Some value around 2.58–2.60 Å is therefore quite reasonable, though a precise figure cannot of course be calculated. This estimate is supported, for example, by the 48 inde-

pendent O—O distances around Si tetrahedra in anorthite (Megaw, *et al.* 1962). The *shortest* (even under stress) are 2.486, 2.518, 2.519, 2.520, 2.525, 2.535, 2.537 and 2.540 Å—and the other 40 are longer. A minimum average angle of $\tau \geq 106.5^\circ$ approximately therefore seems quite acceptable. This limit may eventually need slight adjustment when more precise data on bond lengths and angles under strain have appeared in the literature. The limit will vary somewhat with the substitution of Al for Si tetrahedrally, but this substitution is quite restricted for natural serpentines.

As a useful check on these ideas interatomic distances were calculated for the clino-chrysotile structure which has been determined with moderate accuracy by Whittaker (1956). Using his preferred x parameter of 0.145 for O_x the “ O_A-O_B ” distances are approximately 2.62, 2.63, and 2.63 Å, for Si—O bonds of about 1.57, 1.63 and 1.63 Å. This confirms, within the limits of accuracy involved, that the basal oxygens are “touching” the apex oxygens of a fully stretched tetrahedral layer.

The detailed regression analysis of sheet dimensions and composition (Part II) strongly suggested that for the 1:1 minerals the tetrahedral layer will stretch until $\tau \approx 107^\circ$, *before* the octahedral layer shows any significant contraction. Beyond this degree of misfit the stretched tetrahedral layer (with $\tau \approx 107^\circ$) fixes the overall sheet dimensions and the octahedral layer must contract somewhat; *i.e.* very roughly, if $b'_{\text{tet}} = b_{\text{tet}} \times (\sin \tau / \sin 109^\circ 28')$ then

$$\begin{aligned} b'_{\text{tet}} = b_{\text{oct}} = b_{\text{kaolin}} = b_{\text{obs}} & \quad \text{for } \tau > 107^\circ \\ b_{\text{obs}} = b'_{\text{tet}} < b_{\text{oct}} (= b_{\text{kaolin}}) & \quad \text{for } \tau = 107^\circ \end{aligned}$$

where b_{tet} and b_{oct} are the *unconstrained* dimensions, and b_{kaolin} is the b axis as calculated by the kaolin regression relation.

The limit between platy and tubular serpentines may now be defined in terms of the above hypothesis and observations.

Serpentines whose composition leads to values of τ clearly greater than 107° should show very little stress due to misfit between the layers and therefore be platy. Serpentines whose composition leads to values of τ clearly less than $106\frac{1}{2}^\circ$ —as calculated (Part I) from $(9.60 + 0.27x) \sin \tau = b_{\text{oct}}$ (*i.e.* b_{kaolin})—must have very considerable stresses due to misfit between layers and therefore show strong tendencies to be fibrous or tubular, with an accompanying contraction octahedrally. Serpentines with τ around $106\frac{1}{2}^\circ$ —whether calculated from b_{obs} or b_{oct} —must be under various degrees of stress. These specimens should show quite variable morphology between plates and tubes, and possibly even show variations between different areas of the one specimen, due to subtle changes in chemistry.

These limits should apply quite generally, irrespective of the particular substitutions or deficiencies in the tetrahedral and octahedral layers. For example, in his study of the Mg-Al synthetic serpentines $(\text{Si}_{4-x} \text{Al}_x) (\text{Mg}_{6-x} \text{Al}_x) \text{O}_{10} (\text{OH})_8$ Gillery (1959) concluded that these minerals are fibrous for $x < 0.25$, and cited evidence by Nagy and Faust (1956) to support a limit at $x \geq 0.2$. Olsen (1961) has argued that "the break point between fibrous and platy polytypes might more properly lie around $x = 0.1 \text{ R}_2\text{O}_3$." For these limits the corresponding angles τ are

$x = 0.1$	0.2	0.25
$\tau = 105^\circ$	106°	$106\frac{1}{4}^\circ$

so that the higher value of x is more acceptable.

Chrysotile, lizardites, antigorites. Zussman *et al.* (1957) have summarized electron microscope data on the morphology of serpentines, concluding that chrysotiles are either tubes or laths, antigorites are plates or broad laths (with various super-lattice parameters), and lizardites are plates. As Bates (1959) has pointed out in discussing his morphological index "M" all the serpentines are so closely similar that a clear-cut division at some value of "M" would not be expected, though some trend should be observed which distinguishes platy from tubular morphology. Furthermore the strength of the hydrogen bonds between the layers will certainly influence the particular morphology by which misfit stresses are relieved in a given specimen. Nevertheless the preceding discussion suggests that chrysotiles should tend to have lower values of τ than antigorites when τ is calculated from $(9.60 + 0.27x) \sin \tau = b_{\text{oct}}$. In view of the known stresses in antigorites—resulting in a non-stoichiometric wave structure (Zussman, 1954)—the expected values of τ should be somewhat less than the lower limit of $106\frac{1}{2}^\circ$, which corresponds to relatively little octahedral compression.

It is difficult to test this in detail because there are not many good analyses of chrysotiles and antigorites in the literature, and even some of these have been made on specimens inadequately characterised by x -ray analysis (Whittaker and Zussman, 1956). Moreover there is, at present, no agreed method for calculating structural formulae from serpentine assays. For this reason the values of τ in Table 2 have mostly been calculated from the structural formulae given by Bates (1959), since these are all computed by the same method and should at least provide a suitable basis for comparison. In several cases which were checked the alternative formulae of other workers lead to very similar τ to those in Table 2. (Some of Bates' platy serpentine specimens which have been criticized by others are omitted.)

It seems fair to conclude from Table 2 that τ for chrysotiles does in

fact tend to be lower than for the platy minerals, especially when the average analyses are compared, *i.e.* for C-5 (25 chrysotiles) $\tau = 105^\circ$ but for P-5 (14 antigorites) $\tau = 106^\circ$.

It is notable that natural chrysotiles have practically no substitution tetrahedrally, so that their *b*-axes should all be close to $b = 9.60 \times \sin 106\frac{1}{2} = 9.20$ Å. Whittaker and Zussman (1956) have given accurate *d* values for four chrysotiles and nine lizardites (which are found with chrysotiles, but not with antigorites) and these lie between $b = 9.186$ and 9.222 Å. Antigorites, which may have some tetrahedral Al, have average *b*-axes of 9.241 Å. These results confirm the present arguments.

The notion of a "strain-free" layer in tubular chrysotile structures (*e.g.* Whittaker, 1957) is misleading since it is probably only a layer of *minimal* strain which is involved. For smaller radii of curvature the octahedral strains (in bond angles) should increase sharply, and for larger radii of curvature the tetrahedral strains (*i.e.* smaller τ) should do likewise; but no layer will be "strain-free."

TABLE 2. AVERAGE $O_{\text{apex}}-\text{Si}-O_{\text{basal}}$ ANGLES, τ , CALCULATED FOR SOME SERPENTINES

Specimen	Locality	(from τ/b_{kaolin})	(from τ/b_{obs})
C-1 ¹	Quebec	104°42'	
C-2 ¹	Delaware Co., Pa.	104°43'	
C-3 ¹	Aboutville, N. Y.	104°46'	
C-4 ¹	Montville, N. J.	105°5'	
C-5 ¹	Aver. of 29 chrys.	105°	
C-6 ¹	Gila Co., Ariz.	105°	
C-7 ¹	Transvaal	105°15'	
C-8 ¹	Woodsreef, N.S.W.	105°14'	
P-5 ¹	Aver. of 14 antig.	106°2'	
P-6 ¹	Val Antigorio	106°16'	107°12'
P-8 ¹	Mikonni, N. Z.	105°2'	106°10'
P-9 ¹	Caracas	105°7'	106°22'
P-12 ¹	"Deweylite"	105°21'	
P-13 ¹	"Williamsite"	105°17'	
P-14 ¹	"Baltimoreite"	105°55'	
P-15 ¹	"Yu Yen Stone"	104°50'	
Lizardite ²	Kennack Cove	105°16'	106°36'
6-layer orthohexagonal	Unst ²	105°15'	106°44'
6-layer orthohexagonal	Quebec ³	107°9'	107°50'

¹ *v.* Bates (1959).

² *v.* Zussman, Brindley and Comer (1957).

³ *v.* Olsen (1961).

Col. 3 gives τ assuming no octahedral layer contraction, whereas col. 4 gives τ allowing for any such contraction.

Kaolin minerals. Since Bates, *et al.* (1950) first reported tubular morphology amongst endellites it has become increasingly evident that the kaolin minerals are not clearly divided into two distinct morphological groups. In fact Bates and Comer (1957) have proposed a continuous transition between good plates and good tubes. As Bates (1959) has pointed out, however, there is an extremely close similarity in Si:Al ratio for kaolinites and endellites, and these two minerals may in fact only differ significantly in H₂O content.

Bates, *et al.* (1950), and also Bates (1959), have explicitly discussed the curvature of endellite in terms of a supposed misfit between a larger tetrahedral layer and a smaller octahedral layer. They also have roughly calculated an expected radius of curvature from an assumed difference in dimensions between the tetrahedral and octahedral surfaces. This concept has been widely accepted since then, but cannot (in the author's opinion) be reconciled in detail with our current understanding of the layer silicate structures.

The hypothesis has now been put forward (Parts I, II, and IV) that if the tetrahedral layer of a layer silicate would, on its own, exceed the dimensions of the neighbouring octahedral layer then the former may contract, very readily and quite markedly, simply by tetrahedral rotations leading to ditrigonal rather than hexagonal surface symmetry for many such minerals. It is not claimed that these T-O-T angles (T = tetrahedral cations) can be varied without any resistance to deformation at all; but it is strongly suggested that any such force is of an appreciably lower order of magnitude than other stresses in these structures. That is, *by comparison* the resistance to deformation of T-O-T angles is much smaller than papers on kaolin morphology generally imply. The considerable amount of detailed evidence for this is discussed in Part IV.

This has two obvious implications with respect to kaolin morphology, *viz.:*

(a) The curvature of endellite cannot be explained satisfactorily solely in terms of a misfit in dimensions between the tetrahedral and octahedral layers, or their surfaces, as Bates (1959) discusses. If a tetrahedral layer can so readily reduce its sheet dimensions by becoming more ditrigonal then there either will be no mismatch with adjacent octahedral dimensions, or at least the stresses due to any mismatch will be of very secondary importance, and inadequate to explain the tubular morphology of endellites.

(b) The morphology of different kaolin minerals is unlikely to be *directly* related to subtle differences in Si/Al ratio, as Bates (1959) has sought to establish. An increase in Al substitution tetrahedrally will result primarily in slightly greater rotations in the already ditrigonal tetrahedral network—but again this should not lead to a more tubular morphology. [A change in Si/Al ratio may, however, affect the OH content and/or interlayer bonding (as Bates (1959) has already noted) and therefore be rather indirectly related to morphological changes.]

Nevertheless endellites do form tubes, and this does imply unequal stresses at two different levels in the 7 Å kaolin layers. These forces, moreover, are highly variable and are not *too* closely related to the overall crystallinity (Bates and Comer, 1957). It appears to the writer that a reasonable guess about the nature of these forces may now be made, consistent with the discussion of interatomic forces in dickite (Part IV). No attempt has been made to obtain experimental evidence to support these ideas, which are advanced in a tentative way only.

It appears likely that the unbalanced stresses are

(i) the expansion due to $\text{Al}^{\text{VI}}\text{-Al}^{\text{VI}}$ repulsion across shared edges and (ii) a contraction within the layer of surface hydroxyls, probably by OH-OH bonds in the hydroxyl triads around vacant octahedral sites.¹

In their classical work on the hydroxyl (*i.e.* OH-OH) bond Bernal and Megaw (1935) studied the basic and amphoteric hydroxides in detail, drawing particular attention to gibbsite, $\text{Al}(\text{OH})_3$, as compared with the hydroxides of mono- and di-valent cations. By plotting the calculated electrostatic energy of the cation-hydroxyl bond against the hydroxyl-hydroxyl distance Bernal and Megaw showed conclusively that, for cations arranged in order of increasing polarizing power, Al is the first cation to induce OH-OH bonds between neighbouring hydroxyls.² An electrostatic bond strength of at least $\frac{1}{2}$ is needed to induce the necessary tetrahedral symmetry of charge distribution in the OH's.

Although the six Al-OH bonds in an octahedral group have an ideal strength of $\frac{1}{2}$ it cannot be assumed that particular bonds in a given structure also have this strength. This is emphasised by the contrasts between the diaspore and dickite structures in this respect (Part IV). Indeed it seems very likely that the polarizing power of Al in these minerals is at a critically sensitive level, so that quite subtle structural changes may produce considerable variations in OH polarisation and therefore in any surface OH-OH bonding. In dickite, for example, the Al-OH surface bonds apparently have strength around 0.6 (Part IV). Nevertheless the total configuration of bonds in dickite ensures that virtually all surface OH's form long O-H—O bonds to the adjacent tetrahedral surface. In the polymorph kaolinite, however, the O-H bonds are considered to be differently directed in relation to the superimposed oxygen network (Part IV); and the assumed arrangement is less likely to ensure that all OH's form long O-H—O bonds. In endellite the presence of interlayer water should still further disrupt such direct bonds to the next layer. Under these conditions the Al-OH bond strengths may be expected to lie between 0.5 and 0.6, and in the absence of immediate O-H—O bonds a

¹ Both types of stress are discussed fully in Part IV.

² See, *e.g.* Wells, A. F. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, 3rd. ed., p. 546 f.

looser network of OH-OH and OH-H₂O bonds would be formed. (The surface OH's should tend towards a tetrahedral charge distribution.)

That is, in endellite there is clearly the possibility of some OH-OH distances being shortened around unoccupied sites, as in gibbsite (Bernal and Megaw, 1935). But, contrary to gibbsite, this can happen only on one side of the octahedral layer. The net result should not, therefore, be a shortening of the *b*-axis as in gibbsite, but an unbalanced pair of forces ((i) and (ii) above) leading to a tubular morphology. The relationships between any such forces, crystal structure, and mineralogical history for a given kaolin will certainly be very complex. The wide variations in morphology with respect to crystallinity are not in the least surprising. The pattern of OH-OH forces may well be systematically related to the octahedral network in *some* specimens, so that one direction, *e.g.* the *b*-axis, is a preferred tubular axis.

It is interesting to compare the *b*-axes of dickite (8.95 Å), well-crystallised kaolinite (8.95 Å), halloysite (8.92 Å) and endellite (8.90 Å). The decrease is consistent with an additional contraction in endellite, *e.g.* by OH-OH bonds, rather than an additional expansion, as the misfit of tetrahedral layers implies; but this observation cannot be given too much importance, of course.

It is not possible at present to obtain direct experimental evidence for these hypotheses, primarily because the poor crystallinity and small crystal size of kaolins (especially endellites) severely curtails the accurate measurement of interatomic distances. Whereas Bernal and Megaw (1935) confirmed the presence of OH-OH bonds on the surface of gibbsite by careful structure analysis similar data cannot yet be obtained for endellite in which such surface bonds have now been proposed. However, despite this lack of *direct* proof the *indirect* evidence to support the suggested out-of-balance forces is quite strong (*e.g.*, see Part IV). It should likewise be noted that there is, of course, no direct evidence either for the currently accepted explanation of tubular morphology, in terms of layer misfit. It is, moreover, fair to comment that the implications of the work of Bernal and Megaw (1935) on the hydroxyl bond in basic hydroxides appears to have been largely overlooked in papers on kaolin morphology. The sensitive position of the Al ion in their scale of polarizing power has not been generally realized, in the same context. This, together with the demonstration (Parts I-V) of the apparent ease with which tetrahedral layers contract, indicates the need for new approaches to problems of kaolin morphology.

ACKNOWLEDGMENT

Drs. J. V. Smith and S. W. Bailey kindly made their paper available in advance of publication.

REFERENCES

- BATES, T. F. (1959) Morphology and crystal chemistry of 1:1 layer lattice silicates. *Am. Mineral.* **44**, 78.
- AND J. J. COMER (1957) Further observations on the morphology of chrysotile and halloysite. *Proc. 6th. Natl. Clay Conf.*, p. 237, Pergamon Press, N. Y.
- F. A. HILDEBRAND, AND A. SWINEFORD (1950) Morphology and structure of endelite and halloysite. *Am. Mineral.* **35**, 463.
- BERNAL, J. D. AND H. D. MEGAW (1935) The function of hydrogen in intermolecular forces. *Proc. Roy. Soc. London*, **A151**, 384.
- BUSING, W. R. AND H. A. LEVY (1958) A single crystal neutron diffraction study of diasporite, $\text{AlO}(\text{OH})$. *Acta Cryst.* **11**, 798.
- DRITS, V. A. AND A. A. KASHAEV (1960) An x-ray study of a single crystal of kaolinite. *Kristallografiya* **5**, 207 (in transl.).
- GILLERY, F. H. (1959) The x-ray study of synthetic Mg-Al serpentines and chlorites: *Am. Mineral.* **44**, 143.
- MEGAW, H. D. (1934) The crystal structure of hydrargillite, $\text{Al}(\text{OH})_3$: *Zeit. Krist.* **87**, 185.
- NAGY, B. AND G. T. FAUST (1956) Serpentines: Natural mixtures of chrysotile and antigorite: *Am. Mineral.* **41**, 817.
- NEWNHAM, R. E. (1961) A refinement of the dickite structure and some remarks on polymorphism in kaolin minerals. *Mineral. Mag.* **32**, 683.
- OLSEN, E. J. (1961) Six-layer ortho-hexagonal serpentine from the Labrador Trough. *Am. Mineral.* **46**, 434.
- RADOSLOVICH, E. W. (1959) Structural control of polymorphism in micas. *Nature*, **183**, 253.
- (1962) The cell dimensions and symmetry of layer-lattice silicates, II. Regression relations. *Am. Mineral.* **47**, 617.
- (1963a) The cell dimensions and symmetry of layer-lattice silicates, IV. Interatomic forces. *Am. Mineral.* **48**, 76.
- (1963b) The cell dimensions and symmetry of layer-lattice silicates, V. Composition limits. *Am. Mineral.* **48**, 348.
- AND K. NORRISH (1962) The cell dimensions and symmetry of layer-lattice silicates, I. Some structural considerations. *Am. Mineral.* **47**, 599.
- ROY, D. M. AND R. ROY (1954) An experimental study of the formation and properties of synthetic serpentines and related layer silicate minerals. *Am. Mineral.* **39**, 957.
- SMITH, J. V. AND S. W. BAILEY (1962) Second review of Al-O and Si-O tetrahedral distances. *Acta Cryst.*, in press.
- AND H. S. YODER (1956) Experimental and theoretical studies of mica polymorphs. *Mineral. Mag.* **31**, 209.
- VEITCH, L. G. AND E. W. RADOSLOVICH (1962) The cell dimensions and symmetry of layer lattice silicates, III. Octahedral ordering. *Am. Mineral.* **48**, 62.
- WHITTAKER, E. J. W. (1956) The structure of chrysotile, II. Clino-chrysotile. *Acta Cryst.* **9**, 855.
- (1957) The structure of chrysotile, V. Diffuse reflexions and fibre texture. *Acta Cryst.* **10**, 149.
- AND J. ZUSSMAN (1956) The characterization of serpentine minerals by x-ray diffraction. *Mineral. Mag.* **31**, 107.
- ZUSSMAN, J. (1954) Investigation of the crystal structure of antigorite. *Mineral. Mag.* **30**, 498.
- AND G. W. BRINDLEY (1957) Serpentines with 6-layer orthohexagonal cells. *Am. Mineral.* **42**, 666.
- G. W. BRINDLEY AND J. COMER (1957) Electron diffraction studies of serpentine minerals. *Am. Mineral.* **42**, 133.