

THE CELL DIMENSIONS AND SYMMETRY OF LAYER-LATTICE SILICATES IV. INTERATOMIC FORCES

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ABSTRACT

The relative importance of different kinds of interatomic forces in controlling the layer silicate structures has been roughly assessed, from a review of bond lengths and angles in published structures. This has led to some simple rules, consistent with current ideas in structural inorganic chemistry, from which detailed explanations may be deduced of many observed variations in bond lengths and angles from the expected values.

The main postulates are that bond angles are more readily changed under stress than bond lengths, that bond lengths vary inversely as electrostatic bond strengths, and that forces due to cation-cation repulsion across shared octahedral edges are of comparable importance to the stronger bonds in these structures.

It is deduced in general that forces within the octahedral layers control major features of the layer silicate structures, that these forces tend to produce ordering of the octahedral cations, and that individual octahedra cannot be geometrically regular. Tetrahedral layers may be distorted to limits set by O—O approach distances rather than by O—Si—O bond angles in the tetrahedral groups. The importance of bonds between interlayer cations and surface oxygens is greater than is usually recognized.

The specific postulates are applied firstly to some simple structures containing octahedral groups, thereby explaining several apparent anomalies in earlier data. The published dickite and the $2M_1$ muscovite structures are then critically reviewed, and satisfactory reasons proposed for many observed variations in bond lengths and angles, in terms of local forces on particular atoms. Some less accurately determined layer silicate structures are briefly reviewed in a similar way.

The successful application of these rules to known structures gives the author confidence that the atomic parameters for other layer silicate structures can now be predicted much more closely than previous "ideal structures" for these minerals allowed. The detailed understanding of local stresses in accurately known structures is beginning to suggest means of structural control over properties such as polymorphism. The probability of extensive ordering of octahedral cations should be noted in considering the limits of composition, and other physical properties of these minerals.

INTRODUCTION

The surface oxygen networks of layer silicates often have approximately ditrigonal rather than hexagonal symmetry, a characteristic which Radoslovich and Norrish (1962)¹ have recognized in proposing that the sheet dimensions of micas are controlled largely by the octahedral layers and the interlayer cations. Radoslovich (1962a)² has confirmed this suggestion by showing the negligible effect of Al—for—Si substitution tetrahedrally in new "*b*-axis formulae" computed by

¹ Hereafter Part I.

² Hereafter Part II.

multiple regression analysis. Veitch and Radoslovich (1962)¹ subsequently proposed an explicit geometrical model of the octahedral layers in these minerals, during an investigation into the possible degree of ordering of the octahedral cations. These studies together have led to the following more detailed examination of the forces within the sheets of the layer silicates, the broad conclusions of which have already been reported (Radoslovich, 1962b). The present study has sought an understanding about which forces dominate in the layer silicate structures, and which forces generally have a secondary effect only. Such an analysis cannot begin until highly accurate parameters have been published for several comparable structures, a situation only just reached for this mineral group; future accurate structural analyses should enable the refinement of the present ideas. Though very few layer silicate structures currently have been published the general concepts developed should of course be consistent with, or applicable to, other allied structures such as the feldspars to which passing reference is made. The mental approach is similar to that successfully adopted for anorthite and other feldspars in which Megaw *et al.* (1962) have considered the structures effectively as a network of forces comparable to the "Theory of Frames" used in designing bridge trusses.

TERMS OF REFERENCE, LIMITATIONS, RESTRICTIONS

Standard deviations in bond lengths. Standard deviations in bond lengths, σ , have been adequately calculated for the structures of vermiculite, dickite and muscovite, but scarcely for any other relevant structures. It is, moreover, clearly necessary to make inferences from reported bond length differences which the known (or unknown) σ do not strictly allow—a severe limitation. Such inferences can be supported in part, however, by observing that a number of previous anomalies disappear and that the concepts developed are at least in the right direction for the reported differences. It is essential that, where the minerals studied allow, future structure analyses be of a high, known and stated accuracy (Mathieson *et al.* 1959).

Ionic and covalent bonds. The length of a given cation—anion bond depends on whether it is fully ionic, fully covalent or has some of both characteristics. In discussing individual structures (below) it is assumed that reported differences in the electrostatic strength of individual bonds can be correlated reasonably with observed variations in bond lengths. Although this ignores the possibility of some change in the "ionic versus

¹ Hereafter Part III.

covalent" character of a given bond this is tolerable provided that small variations in strictly comparable bonds alone are involved.

For example, in a tetrahedral group an Al—O bond appears to be largely ionic—observed Al—O distances are consistent with the ionic radii of Al and oxygen, corrected for a ligancy of 4 and Born number = 7 (Pauling, 1960). But the tetrahedral Si—O bond may well be up to 50% covalent in character, as Pauling (1960) and others have calculated. Alternatively it may be largely ionic in character, as Verhoogen (1958) has maintained, and the effective co-ordination correction is then somewhat different from that for Al^{IV}—O bonds, "due to the higher polarizing power of the Si⁴⁺ towards the oxygens."

If, however, two structures are compared which have similar Al— for— Si substitutions then it is reasonable to compare the cation—oxygen bond lengths in relation to the charge available at the oxygens to form such a bond.

Indeed, to a first approximation the layer lattice structures may be compared with each other as if they are purely ionic structures, on the assumption that for the differences discussed below there is little change in the character of the bonds involved, and that these are largely ionic anyway. This is, of course, the customary way of treating complex silicate minerals.

Electrostatic bond strengths and shortening of bonds. Although there are experimental errors in all reported bond lengths there are undoubtedly variations in comparable ionic bond lengths due to differences in electrostatic bond strengths in different structural environments. Observed bond lengths are here assumed to be approximately inversely proportional to actual electrostatic bond strengths (e.g. Burnham and Buerger, 1961; Buerger, 1961; Jones and Taylor, 1961).

Petch *et al.* (1956) and others have explicitly pointed out, however, that although a weak bond is generally assumed to be long (and a strong bond short) this is not universally true. Particular steric effects may result in short interatomic distances where the bond strength is low or negligible; several examples of such fortuitously short bonds are mentioned below. Possible mechanisms of bond shortening with increased electrostatic bond strength are not relevant here.

Local charge balance and stability. The stability of the feldspars has been examined recently in terms of the local balance of charge structurally, by Ferguson *et al.* (1959), and others. There is, as yet, no agreement on a general theory, because of difficulties arising from the partially covalent character of some bonds, because of uncertainties about the range of electrostatic forces, and for other reasons.

Although departures from local charge balance will be briefly discussed it is not possible or desirable at present to consider the relative stabilities of the layer silicates in these or similar terms.

Pauling's rules. It is assumed that for these structures Pauling's Rules are widely applicable and indeed they appear to be obeyed in detail in most cases. In particular the Electrostatic Valence Rule (or an equivalent rule for partly covalent bonds, Pauling, 1960, p. 547) is satisfied, and deviations exceeding $\pm 1/6$ seem rare for layer silicates, as for other minerals. In so far as steric effects will allow, the shared edges between polyhedra are shortened, as they should be in ionic structures.

Tetrahedral Si—O and Al—O bond lengths. The expected lengths for Si—O and Al—O bonds in tetrahedral groups have been discussed by Smith (1954) and Smith and Bailey (1962). These values are important for layer lattice silicate structures, not only in estimating the amount of Si—Al ordering during the initial structure determination, but in assessing the magnitude of other effects (below) when the parameters are known.

Smith and Bailey (1962) suggest values of 1.61₄ Å for Si—O and 1.75 Å for Al—O for the framework structures, plus 0.01 to 0.02 Å for layer silicates. Values of 1.62 Å for Si—O bonds with an electrostatic bond strength of one, and 1.77 Å for Al—O bonds with an electrostatic bond strength of 0.75 may therefore be anticipated for the layer silicates.¹ Though these figures may be slightly adjusted later, this paper is largely limited to a comparison of tetrahedral bond lengths within the group of layer lattice silicates only and these comparisons should remain valid.

GENERAL THEORY OF LAYER LATTICE SILICATE STRUCTURES

"Balance of forces" rather than "packing structures." Pauling (1960), Bragg (1937) and many others have commented that the scale of various silicate structures is mainly determined by the packing together of the large anions, notably oxygen, whereas electrical neutrality is maintained by cations of suitable size and charge in the interstices. Alternatively, the silicates can be classified according to the types of linkage adopted by the tetrahedral groups.

Although these are still very useful generalisations their too ready application forms barriers to a detailed understanding of any particular mineral group. Thus the layer silicates are not simply close packed layers of anions, with cations of the right size stuffed in the interstices, rather passively maintaining neutrality. Each mineral, indeed, represents a

¹ The Al—O bond length is less precisely defined and values as high as 1.80 Å have been reported for recent structures.

“stable” equilibrium, at the lowest possible internal energy, of bonds under “tension” or “compression,” of atoms pushed into close proximity against their mutual repulsion, and (infrequently) of directed bonds under “torsion.” Interstices are of the “right size” for certain cations only in the sense that with those cations present the increased strains in the other bonds, distances and angles do not lead to obvious instability.

Structural elements in layer silicates. The assumptions on which the later discussion of particular structures is to be based cannot be rigorously proven, but they appear to be valid generally for complex ionic (*e.g.* mineral) structures. They are:

- (1) Bond lengths in general vary inversely with electrostatic bond strengths.
- (2) Bonds are effectively non-directional, with occasional O—H bonds as exceptions.
- (3) Bonds increase in compliance (see Megaw, Kempster and Radoslovich, 1962) from Si—O, through Al^{IV}—O, octahedral cation—O, to interlayer cation—O bonds.
- (4) Bond angles are more compliant than bond lengths, the T—O—T angles more than O—T—O (T=tetrahedral cation), as shown by Megaw, Kempster and Radoslovich (1962).
- (5) Mutual repulsion between anions increases very rapidly as interatomic distances fall below the sum of their ionic radii. In particular, the minimum observed O—O distances—*e.g.* 2.25 Å in andalusite (Burnham and Buerger, 1961) or 2.29 Å in Rb₂Ti₆O₁₃ (Andersson and Wadsley, 1962)—are “probably close to the lower limit attainable without the formation of detectable homopolar bonds.”
- (6) The mutual repulsion of multivalent cations only partly shielded electrostatically from each other may be of comparable strength to the strongest bonds. More specifically, trivalent cations sharing octahedral edges exert a mutual repulsion which is one of the dominant forces in layer silicates.
- (7) Adjacent anions whose valencies are not fully satisfied by immediate bonds will mutually repel each other, due to their charge.
- (8) The charges on silicate layers and interlayer cations cannot be too far separated, due to increased Coulomb energy.

*Octahedral layers.*¹ The cell dimensions of such a layer correspond to an equilibrium between three different kinds of forces, *viz.* (i) cation—cation repulsion across shared octahedral edges, (ii) anion—anion repulsion along shared edges and (iii) cation—anion bonds within octahedra (Fig. 1). On all the available evidence these forces result in severe deformation of all octahedral layers, except for minerals in which they are opposed by additional and strong external forces. That is, the balance of forces *within* the octahedral layer usually dominates in layer silicates.

Of these forces the cation—cation repulsion is the most influential in causing individual departures from ideal structures, for several reasons. The octahedral cations are only partly shielded from each other elec-

¹ These arguments apply equally to separate octahedral layers, as in the metal hydroxides, or to octahedral layers combined with tetrahedral layers, as in the clay minerals.

trostatically, they vary considerably in environment, valency and size, and the undirected nature of the cation—anion bonds allows wide variations in the shapes of individual octahedral layers.

If an octahedron in such a layer be viewed as an upper and lower triad of oxygens around the cation then the shortening of O—O edges shared with neighbouring octahedra results in the counter-rotation of these

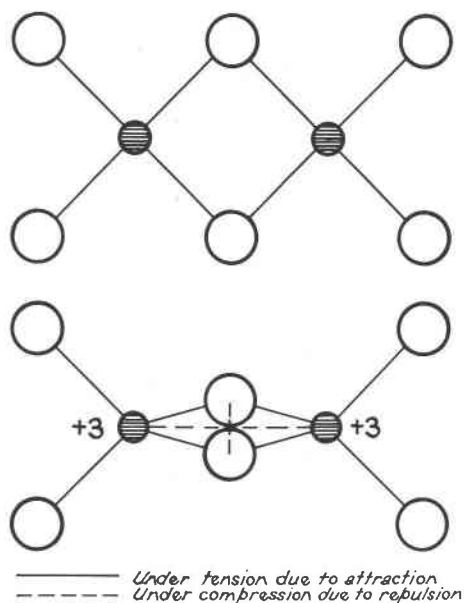


FIG. 1. Deformation of unconstrained octahedral layers to some equilibrium between (i) cation-anion bonds, (ii) cation-cation repulsion, and (iii) anion-anion mutual compression, across shared edges (diagrammatic).

triads (Part III). The operation of a “cation avoidance rule”—due to their mutual repulsion—has several implications, *viz*:

- (i) Dioctahedral structures will show strong tendencies toward regular hexagonal arrangements of cations around vacant sites (Part III).
- (ii) Sheet dimensions become as large as the cation—anion bonds and O—O approach will allow; major expansions to occur along edges of triads enclosing vacant sites. For example, equilibrium in pure Al^{3+} dioctahedral minerals corresponds to $b = 8.92\text{--}8.94 \text{ \AA}$; and strong forces external to the octahedral layer are needed to cause any marked variation from this.
- (iii) In trioctahedral minerals containing $\approx 2.0 \text{ R}^{2+}$ and some R^{3+} the R^{2+} cations tend to be disposed hexagonally around the R^{3+} , to separate adjacent R^{3+} as much as possible.
- (iv) Shared octahedral edges in layers with very different cations should be shortened to about the same minimum distance, below which the anions become more incompressible.

sible very rapidly. Again, this minimum distance is not always attained, due to forces external to some layers.

Tetrahedral layers. Unperturbed tetrahedra in the layer silicates seem to have T—O lengths close to values to be predicted from their average cation occupancy, T; individual bonds, however, can be slightly stretched under severe external stress. The T—O bonds also appear to vary systematically with the net charge available at the anion, after allowing for the bond strengths from that anion to other cations. If, for example, a given oxygen has less than one of its charges satisfied by other cations then that Si—O bond will be correspondingly stronger and hence shorter than the expected 1.62 Å approx.

Although the Si—O bonds are partly covalent the O—T—O angles appear to depart readily from the ideal $109^{\circ}28'$ to limits which are set by the minimum O—O approach along tetrahedral edges rather than by any directed nature of the T—O bonds. A review of these distances and angles in recent accurate analyses of feldspar structures confirms this (*e.g.* Megaw, Kempster and Radoslovich, 1962). In six feldspar structures the individual angles vary at least from 99° to 119° , whereas the O—O edges are always > 2.48 Å and mostly > 2.55 Å—indicating that tetrahedra can be deformed fairly easily until edge lengths approach 2.55 Å. Donnay *et al.* (1959), Jones and Taylor (1961) and others have previously noted that tetrahedra need not be perfectly regular.

In layer silicates tetrahedra share corners only. This, combined with the low radius ratio Si/O, ensures fairly good electrostatic shielding of Si's from each other—at least when compared with octahedral cations. The T—O—T angles are therefore among the most compliant elements of the layer structures as of the feldspars (Megaw *et al.* 1962). More generally they may increase from the average 138° to at least 160° (Liebau, 1961).

Interlayer cations; net surface charges. Important details of the layer structures are actively controlled by the bonds between interlayer cations and surface oxygens; the common concept that “cations of the right size occupy holes to maintain over-all neutrality” underestimates their influence. Indeed, even the T—O bonds appear to be influenced by any discrepancy between the bond strengths to, and valency of, the interlayer cations. Likewise unexpected variations in T—O bonds seem to be correlated with the net surface charge on the layers of minerals with high exchange capacities.

It is noteworthy that a given interlayer cation (*e.g.* K^{+}) can produce opposing structural effects in two micas having appreciably different octahedral layers.

SOME OCTAHEDRAL LAYERS CONTROLLED BY EXTERNAL FORCES

Corundum,¹ Al_2O_3 . This consists of successive dioctahedral layers, with the anions shared between two layers. The Al^{3+} cations are arranged so that each unoccupied site is surrounded by occupied sites. Accurate unit cell data on corundum (A.S.T.M. X-ray Data Card 10-173) refers this structure to a trigonal cell with $a=4.758 \text{ \AA}$, equivalent to a "b-axis" of 8.241 \AA if corundum is being compared with layer silicate dimensions.

Corundum obeys Pauling's Rules—single shared O—O edges are shortened to 2.61 \AA , and shared O—O edges of shared octahedral faces to 2.49 \AA . Despite this evidence of strong cation—cation repulsion the octahedral layers are both thin (2.16 \AA ; *vide* Part III) and have sheet dimensions very small in comparison with comparable dioctahedral layers, *i.e.*, 8.24 \AA as against 8.94 \AA , for example. The reason for this is that no expansion can occur around the unoccupied sites. Both triads of oxygens which together form the corners of a given unoccupied octahedra are also triads of the neighbouring occupied octahedra. Their expansion is thereby severely restricted, except for the small difference between 2.49 and 2.61 noted above. That is, the cation—cation repulsion in any one layer is restrained from increasing the sheet dimensions by the fact that the interatomic O—O distances which should become much longer are themselves, in corundum, already shortened shared edges. This same kind of structural restraint is evident in diaspore and chloritoid.

Diaspore,² AlO.OH This can be viewed as a stack of infinite ribbons two octahedra wide and one octahedra high, alternating with channels of these dimensions. The mineral has most recently been studied by Busing and Levy (1961) using neutron diffraction to locate the protons accurately. Their discussion does not resolve an anomaly noted earlier by Bernal and Megaw (1935).³ This concerns the relation between the O—OH distances across the channels, Ewing's suggested long hydrogen bond here, and the fact that infra-red analysis suggests the existence of independent OH's, not hydrogen bonds.

When the principles stated earlier are applied to the diaspore data it is clear that the $\text{O}_I\text{—O}_{II}$ distances are short almost entirely for *steric* reasons—the balance of forces within and between occupied octahedra ensure that $\text{O}_I\text{—O}_{II}$ is "shortened" to 2.65_0 \AA . Very little hydrogen or hydroxyl bonding is required or allowable, to make the observed data

¹ See, *e.g.*, Bragg, 1937, p. 93.

² See, *e.g.*, Wells, 1962, p. 556.

³ Note that O_I in B. and L. = O_{II} in B. and M.; and *vice versa*.

self-consistent, *viz.*

- (i) the O_{II} 's give I.—R. spectra of free hydroxyls.
- (ii) the protons belong to O_{II} ; observed $O_{II}-H=0.990 \text{ \AA}$, and $O_I-H=1.694 \text{ \AA}$.
- (iii) the O_I 's are bound to 3 Al's, with bond strengths therefore of $\frac{2}{3}$; and the O_{II} 's to 3 Al's, strengths $\frac{1}{3}$.

These bond lengths, Al—O and Al—OH, in diaspore may then be compared with predicted bond lengths for (a) no O—OH bond, as above *or* (b) a "hydroxyl" O—OH bond (Bernal and Megaw, 1935). Bond-lengths to be expected for various bond strengths may be estimated from the normal octahedral and tetrahedral Al—O bonds. Five co-ordinated Al in andalusite (Burnham and Buerger, 1961) provides a check with values 1.82, 1.82, 1.82, 1.86, 1.88 \AA . The observed values (Table 1) are more

TABLE 1. EXPECTED AND OBSERVED Al—O BONDS IN DIASPORE

Al—O bond lengths in relation to bond strengths ¹			Diaspore		
			O _I -O _{II} bond proposed		Observed (Busing and Levy, 1958)
Type	Strength	Length	None	Hydroxyl	
—	0.33	1.99 \AA	Al-O _{II} ¹	Al-O _I and O _{II}	1.977 \AA
Octah.	0.50	1.91			
5-coord	0.60	1.86			
—	0.66	1.83	Al-O _I		1.854 \AA
Tetrah.	0.75	1.78			

¹ These average values are proposed from an empirical consideration of a number of other structures.

² That is, with no hydrogen bonding the expected Al-O_{II} bond length will be 1.99 \AA .

closely comparable with values predicted on the assumption of *no* O_I-O_{II} bond. The angle of 12.1° which O_{II}-H makes with O_{II}-O_I (Busing and Levy, 1958) is no longer unexpected.

If the octahedral ribbons in diaspore are compared with octahedral layers in clay minerals then the ribbons have a thickness $\approx 2.2 \text{ \AA}$ (*i.e.* $a/2$) and sheet dimensions of "*b*" $\approx 8.53 \text{ \AA}$ (*i.e.* $3c$). This confirms that the unoccupied octahedra cannot expand because they share all faces with occupied octahedra—analogueous to corundum.

Chloritoid, $[(Fe^{2+}, Mg)_2Al](OH)_4Al_3[O_2(SiO_4)_2]$ Harrison and Brindley (1957) have discussed in detail the relations between the chloritoid, mica and corundum structures. In chloritoid rather incomplete tetrahedral layers alternate with two different octahedral layers, one of

which is closely similar to, and has very nearly the same dimensions as an octahedral layers in corundum.

This octahedral layer should have expanded markedly in the triads of anions about the unoccupied sites (see above), if unconstrained externally. In chloritoid, however, these triads are also the base triads of the separate tetrahedral groups, above and below (Fig. 2, Harrison and Brindley, 1957). Their maximum size is therefore fixed, and this in

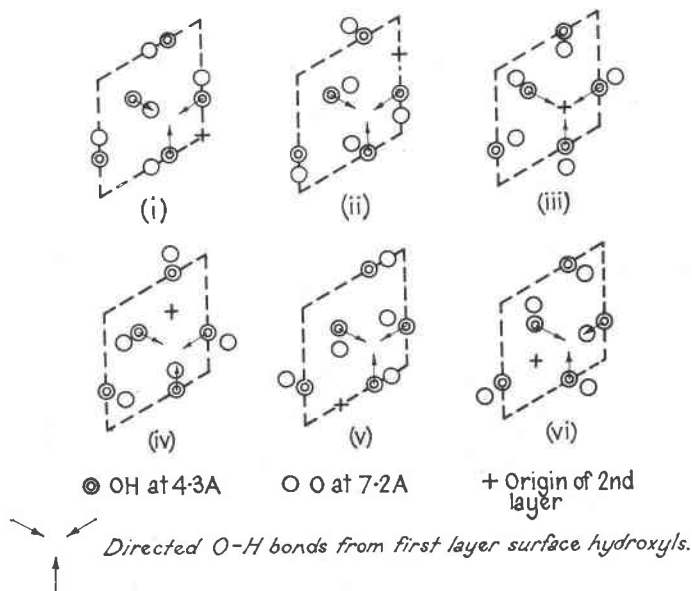


FIG. 2. Six ways of placing the oxygen layer over the hydroxyl layer (Fig. 6, N.), but with the preferred directions of the O—H bonds also shown.

fact allows practically no octahedral expansion. The octahedral sheet dimensions in chloritoid and corundum are closely comparable, controlled, respectively, by neighbouring tetrahedral faces and octahedral faces shared with the vacant octahedra.

The other octahedral layer in chloritoid is of course constrained to these short dimensions, despite being trioctahedral and containing larger cations.

Harrison and Brindley (1957) have argued that the sheet dimensions of chloritoid (*viz.* $a = 9.52 \text{ \AA}$) exceed those of micas with similar Fe^{2+} content because, they imply, the discontinuous tetrahedral layers allows more ready expansion. Unfortunately they did not compare the same orientation of the octahedral cations in chloritoid (and corundum) as in micas giving $b \approx 9.3 \text{ \AA}$. The appropriate chloritoid dimension is 8.24 \AA ,

not 9.52 Å; and this is very much *smaller* than the *b*-axes of biotites, due to the overriding restraints exerted by the discontinuous tetrahedral layers!

Gibbsite,¹ $Al(OH)_3$. Bernal and Megaw (1935) clearly demonstrated the existence of hydroxyl bonds, both between sheets and also *along the surfaces* of sheets around unoccupied sites. They specifically stated that these OH—OH bonds decreased the sheet dimensions to 8.624 Å (*i.e.* “*a*”). These bonds are not very strong, and only modify the octahedral strains as a secondary effect. Thus the average O—O distances in triads enclosing an unoccupied site, 3.20 Å, are much larger than surface O—O distances around occupied sites, 2.79 Å (Megaw, 1934). (The difference is still larger in dickite and muscovite which lack the OH—OH bonds.)

Diocahedral kaolins and micas. In these minerals dioctahedral Al—layers appear to have dimensions virtually unaffected by constraints from the structure as a whole, *viz.* $b = 8.92\text{--}8.94$ Å. Dickite, a kaolin polymorph, is discussed below. The interlayer Na in paragonite probably does not perturb the *b*-axis set by its octahedral layer (Parts I, II). Interlayer K in muscovite (5.2) is the exception, in actively increasing the overall dimensions to 8.995 Å.

Brucite, $Mg(OH)_2$ and *phlogopite*, $K Mg_3 (Si_3 Al) O_{10}(OH)_2$. Although Mg (0.65 Å) is larger in radius than Al (0.51 Å) brucite and gibbsite layers have a comparable thickness, around 2.1 Å, set for both by the limit of O—O approach along shared octahedral edges (see above). The longer Mg—O bonds allow Mg—Mg repulsion to extend the *b*-axis to 9.44 Å, greater than for almost all other trioctahedral layer lattice silicates. That is, most such layers—except brucite—have some constraint applied by the rest of the structure. For example the K—O bonds in phlogopite probably limit the overall expansion to the observed 9.2 Å; both the tetrahedral and octahedral layers could have gone to ≈ 9.44 Å.

ACCURATELY DETERMINED LAYER STRUCTURES¹

Dickite, $Al_2Si_2O_5(OH)_4$. *Newnham, 1961*.² Newnham's highly accurate data fully confirm the concepts stated earlier, just as these enable his careful discussion of the dickite structure to be extended or amended at some points.

The very short shared octahedral edges (2.37 Å), which Newnham

¹ In standard texts, *e.g.* Wells, 1962.

² In this section references are, for brevity, given to tables and figures in the original papers, *e.g.* “Table 1, N.”

noted, result from the uninhibited Al—Al repulsion which produces, in dickite, a maximum expansion for such a layer. Average O—O distances in one anion layer are much larger around unoccupied sites (3.43 Å) than occupied sites (2.78 Å). The corresponding counter-rotation of the octahedral triads (Part III) is -3° and $+8^\circ$, as Brindley and Nakahira (1958) observed.

The average Al—"O" bonds also fall into two groups, *viz.* Al—(surface) OH = 1.85₇ Å and Al—(interior), O, OH = 1.94₈ Å; the Al—"O"—Al angles are consistent with this difference. Both distances should be compared with an expected 1.91 Å, and with an observed mean in muscovite of 1.93₆ Å (omitting Al—O_B = 2.04₈ Å). Newnham commented on the closer approach of the Al's to the surface hydroxyls, but he has apparently misunderstood the diaspore structure in quoting diaspore and dickite as "very similar" in this respect. The relevant bonds are in direct contrast (Table 2). In dickite the surface hydroxyls form long hydrogen bonds to tetrahedral oxygens on the adjacent surfaces (Newnham,

TABLE 2. AVERAGE Al—"O" BONDS IN DIASPORE AND DICKITE, IN Å

Diaspore ¹		Dickite ²	
Al ₁ -O _{II} (<i>i.e.</i> OH)	1.98 ₀ Å	Al ₁ -OH (surface)	1.85 Å
Al ₂ -O _{II} (<i>i.e.</i> OH)	1.97 ₅	Al ₂ -OH (surface)	1.86
Al ₁ -O _I	1.85 ₈	Al ₁ -(20, OH)	1.96
Al ₂ -O _I	1.85 ₁	Al ₂ -(20, OH)	1.94

¹ Busing and Levy, 1958

² Newnham, 1961.

1961). This bond formation is assisted by the high polarization induced in each OH by the two Al³⁺ to which it is bonded internally. Thus the protons of the OH's are strongly directed away from the Al's, so that in each OH

- (i) the O—H bond shows a marked tendency to be coplanar with the two Al—OH bonds (see below), and
- (ii) there is considerable asymmetry of charge, with increased negative charge towards the Al's.

As a result of (ii) the electrostatic strength of the Al—OH bonds significantly exceeds the expected $\frac{1}{2}$, and these bonds are shortened from 1.91 Å to 1.86 Å; from Table 1 the strengths are about 0.6–0.65.

The excess strength of the Al—OH bonds is confirmed by their marked contraction despite the strong Al—Al and O—O repulsions with which they are in equilibrium. In diaspore, however, each Al—OH bond has an expected strength of $\frac{1}{3}$ (see above) and should, according to Bernal and

Megaw (1935), cause relatively little OH polarization; their length of 1.98 Å agrees with this.

If the valency of the Al^{3+} is to be closely satisfied in dickite the remaining bonds must have strengths $< \frac{1}{2}$, which the average Al—O, OH distances of 1.95 Å, rather than 1.91 Å, confirm. In diaspore, however, the expected Al—O bond strength is $\frac{2}{3}$; (*i.e.* $> \frac{1}{2}$) and three such bonds to each oxygen will inhibit any further bonding to the opposing OH's. For further comparison the surface OH—OH bonding in gibbsite (Megaw, 1934) ensures a strength near $\frac{1}{2}$ in all Al—OH bonds, and the average bondlength of 1.89 Å is close to an expected 1.91 Å.

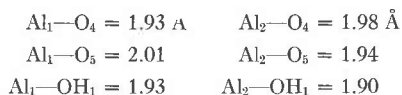
The Al distribution determines the pattern of counter rotations in the octahedral layer (Part III). The directions of the required tetrahedral rotations (Parts I and II) are therefore set by the octahedral layers so that basal oxygens are matched to surface hydroxyls (N., 1961) to shorten the O—H—O bonds to 2.94, 2.97 and 3.14 Å. These rotations are less than ideal (Part II) because the tetrahedra are "contracted in the oxygen basal plane and elongated along c .*" This basal compression, which Newnham attributed to general misfit, may be explained in detail by observing that

- (i) the Si—O and O—H—O bonds are not very compliant,
- (ii) the O—H bonds are strongly directed, at an angle inclined to c^* (see above), and
- (iii) the O—Si—O angles are quite compliant.

It follows from (i) and (ii) that although the basal oxygens of one layer are bound at about 3 Å from the opposing OH's they will not be vertically above them (see Fig. 3, N.). The directed O—H—O bonds are acting to reduce the size of the tetrahedral base triads, which is achieved—in agreement with (i) and (iii)—by τ increasing from $109^{\circ}28'$ to an average 111.8° (Table 2, N.). The final tetrahedral configuration is a balance between the Si—O bond lengths, the inclined and directed O—H—O bonds, and the O—O compression in the basal triads, shown by $\text{O}_1\text{—O}_3 = 2.58 \text{ \AA}$ and $\text{O}_2\text{—O}_3 > \text{O}_1\text{—O}_2 = 2.59 \text{ \AA}$.

This is linked with the buckles in dickite surfaces whereby OH_3 protrudes from the layers and O_3 is depressed into them. Newnham's explanation in terms of tetrahedral tilting (by the apex oxygens, O_4 and O_5) is inadequate in view of the high compliance of tetrahedral angles. Rather, the directed bonds from OH_2 and OH_4 largely fix the positions of O_1 and O_2 , whereas O_3 —which is above an unoccupied octahedral site—is pushed into its own layer by the compression along $\text{O}_1\text{—O}_3$ and $\text{O}_2\text{—O}_3$. This depression of O_3 stretches $\text{OH}_3\text{—O}_3$, but only to 3.12 Å, because OH_3 can be (and is) elevated above OH_2 and OH_4 . The shortness of the shared edge $\text{OH}_3\text{—OH}_1$ is easily maintained since OH_1 (unlike the corresponding O_4 and O_5) is not firmly held by the rest of the structure.

The elevation of OH_3 fully explains other variations observed by Newnham, *viz.*



The bonds to OH_1 should have strength $\frac{1}{2}$ because the OH_1 charge is satisfied, and their lengths are close to the predicted 1.91 Å. Each Al now has four bonds to OH's with a total strength of about $(3 \times 0.6 + 0.5) = 2.3$ approx., leaving only 0.7 as the combined strengths for the two Al—O bonds in each case. The observed lengths are consistent with strengths $< \frac{1}{2}$, with one bond of each pair noticeably longer than the other. From Fig. 3, N., it is obvious that the long bonds, $\text{Al}_1\text{—O}_5$ and $\text{Al}_2\text{—O}_4$ are the bonds directly opposite the bonds $\text{Al}_1\text{—OH}_3$ and $\text{Al}_2\text{—OH}_3$ in their respective octahedra, whereas $\text{Al}_1\text{—O}_4$ and $\text{Al}_2\text{—O}_5$ are at about 90° to the Al—OH₃ bonds. On the understanding (above) that the overall structure holds the O_4 , O_5 fairly firmly then clearly the elevation of the OH_3 (and the strong Al—OH₃ bonds) mainly stretches $\text{Al}_1\text{—O}_5$ and $\text{Al}_2\text{—O}_4$, as observed. Moreover the OH_3 are attracted to O_3 's in such a way (Fig. 3, N.) that $\text{Al}_1\text{—O}_5$ should exceed $\text{Al}_2\text{—O}_4$, and Al_1 should be lifted relative to Al_2 ; both these consequences are observed.

In both tetrahedra the external distribution of bond strengths should lead to $\text{Si—O}_{\text{basal}}$ bonds of strengths < 1.0 (due to interlayer O—H—O) and $\text{Si—O}_{\text{apex}}$ bonds > 1.0 (due to asymmetric Al—O, OH groups). The mean 1.619 Å agrees with Smith and Bailey's (1962) predictions for an Si—O group with external bonds exactly balancing to strength 4, as expected. It is, however, likewise to be expected that *within* each group the $\text{Si}_1\text{—O}_4$ and $\text{Si}_2\text{—O}_5$ bonds would be rather shorter than the other three, and the lack of any such trend in the observed bonds is a little surprising.

There appears to be no alternative explanation for the tetrahedral distortion, for the lack of direct superposition of O on OH, and for the small tetrahedral twists, other than the directed nature of the O—H—O bonds. This surface property obviously bears on the polymorphism of the kaolins and its recognition allows Newnham's detailed discussion to be both simplified and extended. The six ways of placing the oxygen surface over the hydroxyl surface (Fig. 6, N.) are no longer equivalent, if O—H bonds are directed (Fig. 2). Although all six ways lead to some torsion of these bonds the strains involved in (ii) and (v) are less than in (i), (iv) and (vi), whilst (iii) is quite unlikely to occur at all.

Amongst the single layer structures in Table 7, N., the most probable are therefore nos. 7 and 25—the same conclusion, but a more explicit argument than that from the Coulomb energy. The two layer structures

in Table 8, N., must now (a) minimise the Coulomb energy, (b) satisfy the pucker conditions *and* (c) minimise the angular strain in the O—H bonds. The sequence 11, 27, 11, 27 . . . (superpositions ii, v) is more likely to occur as a stable mineral than 20, 36, 20, 36 . . . (superpositions iv, vi). That is, the abundance of dickite (11, 27, 11, 27 . . .) relative to nacrite (20, 36, 20, 36 . . .) is at least consistent with, if not explained by, control exerted by the directed O—H bonds.

These directed bonds are discussed further in relation to kaolinite (below) and kaolin morphology (Radoslovich, 1963b).

Muscovite, $K Al_2(Si_3Al)O_{10}(OH)_2$ ¹ Radoslovich, 1960. The previous discussion (R., 1960) can now be carried further.² Extension of the octahedral layer occurs mainly around the vacant site (3.3.2). For coplanar O's around these sites O—O = 3.34₁ Å aver. and (Vacant Site)—O = 2.20₄ Å aver. whereas for the two occupied sites O—O = 2.82₄ Å aver. and Al—O = 1.95₄ Å aver. Shared octahedral edges are shortened, but not equally so (Table 5, R.). One edge, O_A—O_A = 2.39₆ Å, close to the 2.37 Å in dickite. Another, OH—OH = 2.51₁ Å, possibly a little longer due to OH—OH repulsion following their polarization (below). The third edge O_B—O_B = 2.76₈ Å is apparently not shortened at all, but this is quite misleading. In fact all bonds to O_B are severely stretched (see below) and O_B—O_B edges *are* shortened, but only as far as the strong Si₂—O_B bonds will allow. The Si₂ are firmly held by the three bonds to O_C, O_D and O_E, aver. 1.60₀ Å, whereas Si₂—O_B = 1.64₈ Å. The differences between edges of 2.39₆, 2.51₁ and 2.76₈ Å are quite real, and the octahedral anions are not strictly coplanar (Part III). The Si₂—O_B bonds hold the O_B's above the plane of the O_A's and OH's, and also help to stretch one Al—O_B bond to 2.04₈ Å. The average Al—O = 1.93₆ for the remaining five bonds still exceeds the calculated 1.91 Å.³ In muscovite the K⁺ stretches the sheet dimensions (Part I) beyond the 8.92–8.94 Å set by the octahedral layer. Since two shared edges are held larger than the three edges in dickite (with $b = 8.94$ Å) the Al—O bonds must extend, as observed.

¹ These arguments become clearer from a true model (e.g. Radoslovich and Jones, 1961).

² Note that Radoslovich studied the $2M_1$ structure. In fact the detailed differences between the probable or known structures of the various polymorphs now have become more obvious and some structural factors controlling mica polymorphism will be described in a subsequent paper.

³ In occupied octahedra in muscovite, therefore, several strong forces are in equilibrium, and it is not surprising to find that about 80% of these octahedra must be occupied by Al³⁺ in particular, in order to maintain a stable muscovite-type structure (Radoslovich, 1963a).

The two tetrahedral sites ("Si₂" and "Si₁") which alternate throughout the layer appear to contain, respectively, no Al^{IV} and—on the average—Si_{1/2} Al_{1/2}. This is shown by the mean bond lengths, Si₂—O = 1.61₂ Å and Si₁—O = 1.69₅ Å. This ordering of cations means that neither the octahedral nor the surface anions can form fully coplanar networks, nor can both tetrahedra remain perfectly regular in shape—with the smaller (Si₂) tetrahedra showing the greater strains. The whole structure, however, adjusts to the mismatch of tetrahedral sizes—by "waves" in the planes of anions, by the tilting of both tetrahedra, and by the elongation of Si₂ groups along *c** with a very slight flattening of Si₁ groups. This elongation is shown by the basal edges around Si₂, compressed to 2.58₂, 2.58₈ and 2.59₁ Å, together with the Si—O_{apex} bond, stretched to 1.64₈ Å; by contrast the six O—O edges around Si₂ are normal contact distances, mean 2.76₉ Å. The angles at Si₂ confirm this, with O_{basal}—Si₂—O_{basal} = 107°22' (mean) but O_{basal}—Si₂—O_{apex} = 111°5' (mean).

The disproportionate deformation of Si₂ rather than Si₁ groups is due to the overall control exercised jointly by the octahedral layers and interlayer K⁺. Within the tetrahedral layer alone it would seem easier to flatten Si₁ groups a little more and thereby strain Si₂ groups less severely. This would immediately increase *b*_{tetr}, which the octahedral and interlayer forces totally prevent.

The forces in 2M₁ muscovite are best discussed by comparing the observed atomic positions with the "ideal" positions of Jackson and West (1933). The configuration of the octahedral layers means that all O_B—O_B shared octahedral edges are (in a projection along the *c*-axis) parallel to the *a*-axis, and all O_A—O_A and OH—OH edges are at ±120° to this. Moreover the lack of bonds from O_A, O_B and OH towards the vacant octahedral sites allows the anions to be pulled away from their "ideal" positions as the shared edges are shortened. Of the two kinds of apex oxygens each O_A, attached to the larger tetrahedra, can and does move much more freely than each O_B. The shift of O_A is directly away from O_D. The Si₁ groups adjust themselves a little by tilting (see below) and Si₁—O_A = 1.71 is slightly longer than Si₁—O_{C,D,E}; but the primary deformation is an increase in angle O_A—Si₁—O_D from 109½° to 115½° (*i.e.* O_A—O_D up to 2.87 Å), in agreement with the earlier postulates.

Each K⁺ is surrounded by six O's at 2.81₂ Å (aver.) and six at 3.39₀ Å (aver.) and 2 OH's at 3.98₄ Å, so that effectively there are direct K—O bonds only to the six nearest oxygens which are approximately octahedrally arranged around it. These oxygens can only form bonds of strength ⅙, since they already have bonds to Si₁ and Si₂ of strength ⅘ and 1. The sum of the K and O radii is 2.73, given for six-coordination which implies a strength of ⅙. The expected bondlengths for six bonds of

strength $\frac{1}{8}$ should be close to $2.73 \times 1.04 = 2.84 \text{ \AA}$, where 1.04 is a correction factor for eight-coordination. The mean of 2.81 \AA reflects the general compression of these weak bonds (Part I, and this paper) by the rest of the structure.

Each K^+ is hardly shielded at all electrostatically from O_A 's, O_B 's and OH 's, above and below. The O_A 's carry an unsatisfied charge of about $-\frac{1}{8}$, and the K^+ of $+2/8$. To a first approximation each K^+ is attracted towards, and its charge largely satisfied by, one O_A from each layer. For K 's at the $c/4$ level these attractions give a resultant force which moves each K directly along $+b$; at the $3c/4$ level each K is moved along $-b$. The separate $K-O_A$ attractions through the $2M_1$ cell are in fact disposed just as shown in Fig. 7b, R., and these attractions clearly are the unknown forces postulated by Radoslovich (1960) as a possible "mechanism" for forming the $2M_1$ polymorph, and explaining the observed β .

This net attraction, *e.g.* towards $-b$, makes the $K-O_{C,D,E}$ bonds unsymmetrical. The total arrangement is such that the K is pulled towards an O_D , above and below, and away from an O_E , above and below. Thus $K-O_D = 2.77_5 \text{ \AA}$ is really an ideal (weak) bond of $2.83-2.84 \text{ \AA}$ under compression, and this assists the depression of O_D . By contrast $K-O_E = 2.86_2 \text{ \AA}$ is a similar bond under tension; O_E is restrained by $Si_2-O_E = 1.62_3 \text{ \AA}$ ($Si_2-O_D = 1.59_6$ and $Si_2-O_C = 1.58_1$) and ultimately by the bonds from Si_2 through O_B to the Al network. The tension in $K-O_E$ and $Si-O_E$ explains why the Si_2 move a little in the same direction as an associated K .

The attraction and movement of K^+ by O_A compresses the bonds $Si_2-O_C = 1.59_6 \text{ \AA}$ and $Si_2-O_D = 1.58_1 \text{ \AA}$ for which Smith and Bailey (1962) would predict 1.62 \AA . At the same time Si_2-O_B is being severely stretched. This appears to redistribute the bond strengths in the Si_2 tetrahedra a little, so that O_B is left with a slight negative charge to be satisfied by the K^+ . This would account for a movement of O_B towards K (even though this *lengthens* the shared octahedral edge O_B-O_B), and would correctly explain why one $Al-O_B$ bond (2.04_8 \AA) is longer than the other (1.93_2 \AA). This movement of O_B raises $O_B-Si_2-O_C$ from $109\frac{1}{2}^\circ$ to $114\frac{1}{2}^\circ$.

The $O-H$ bonds in muscovite, as in dickite, should be directed at an expected inclination of about $65-70^\circ$ to the sheets. Infrared studies (*e.g.* Serratos, and Bradley 1958) point to an angle of $\approx 20^\circ$ which is a likely compromise between the directed nature of the $O-H$ bonds and the repulsion of the proton by the K^+ directly above. The shortening of the $OH-OH$ edge further separates the proton from the K^+ .

In $2M_1$ muscovite the interlayer K^+ is held in place by six bonds under compression, on the average. In detail, the K^+ occupies an

equilibrium position determined by a complex balanced system of interlocking strong bonds reaching right through the adjacent layers to K's at the next level, above and below. This system of bonds is a direct consequence of $2M_1$ muscovite being a dioctahedral mineral with 2 Al_3^+ octahedrally, and with an ordered arrangement of 2 Si and 2 $Si_{1/2} Al_{1/2}$ tetrahedrally. It is hardly surprising that this polymorph is one of the most stable micas under natural weathering. This view of the role of K^+ in muscovite is far removed from the early concepts of an ion of the right charge flopping into a hole of comfortable size!

These two accurate structures illustrate in detail the factors previously discussed as general postulates.

LAYER SILICATE STRUCTURES LESS PRECISELY DESCRIBED

For several published structures the tables of bond lengths and angles are incomplete, or the accuracy is low, and only a brief comment is warranted in support of these ideas.

Vermiculite, $(Mg_{2.36}Fe^{3+}_{0.48}Al_{0.16})(Al_{1.28}Si_{2.72})O_{10}(OH)_2 \cdot 4.32 H_2O$. Since Mathieson and Walker (1954) and Mathieson (1958) were primarily interested in the interlayer water they did not look for octahedral ordering or compute all individual bond lengths within the layers. The structure shows several anomalies. The T—O bonds are $1.63 \pm 0.02 \text{ \AA}$, whereas Smith and Bailey (1962) would have predicted 1.67 \AA ; such a discrepancy may possibly mean that the actual crystal has a composition differing from the bulk analysis. The octahedral layers are thin (*i.e.* stretched) but the shared edges are not short, 2.76 \AA . The angles $O_{\text{apex}}\text{—}T\text{—}O_{\text{basal}} = 108^\circ 42'$ (mean) and the *b*-axis is longer than $b = 9.18 \text{ \AA}$ for phlogopite $K Mg_3 Si_3 Al O_{10} (OH)_2$. Note the error in *b* for vermiculite, which is more nearly 9.26 \AA , Part II.

These apparent contradictions are removed by applying the concepts in the earlier section and by noting that (a) the net tetrahedral charge is divided between octahedral and intercalated ions, and (b) "direct electrostatic interaction between cations and surface oxygens is unimportant" (Mathieson and Walker, 1954, p. 254). It is then reasonable that:

- (i) T— O_{basal} bonds have excess strength and are noticeably shortened because their surface charge is not satisfied by *direct* bonds, as in micas. But O_{apex} should contribute excess charge to the octahedral bonds, if anything, and T— $O_{\text{apex}} = 1.67 \pm 0.01$ is nearer prediction.
- (ii) All surface oxygens mutually repel each other because of their net negative charge. This explains why $O_{\text{apex}}\text{—}T\text{—}O_{\text{basal}} = 108^\circ 42'$ ($< 109\frac{1}{2}^\circ$). Moreover this repulsion will tend to untwist the surface ditrigonal network, so that the substitution of $Al^{IV}\text{—}$ for—Si increases *b* in vermiculites—but *not* because of the larger radius of Al^{IV} ! The

shortening of T—O and decrease of τ to $108^\circ 42'$ gives an $\alpha_{\text{calc}} = 4^\circ 42'$, *c.f.* $\alpha_{\text{obs.}} = 5\frac{1}{2}^\circ$ and $\alpha_{\text{calc.}} = 8^\circ 42'$ (Part II). The lack of K—O bonds allows (ii) to increase b for vermiculite to values $> b$ for phlogopite, even though the octahedral cations would suggest the reverse.

- (ii) The apex oxygens carry a net negative charge which should shorten the bonds to the octahedral cations and prevent the shortening of shared edges; the latter is observed. The bonds have a length of 2.07 Å against an expected 2.05 Å, so that any shortening is balanced by an overall stretching from the tetrahedral layers.

Celadonite, $K_{0.8}(Mg_{0.7}Fe_{1.4}^{3+})(Al_{0.4}Si_{3.6})O_{10}(OH)_2$ (*Zviagin, 1957*). The key to this unusual structure is found in the fact that about half the $K_{0.8}^+$ charge is satisfied tetrahedrally and half octahedrally. The observed K—O bondlengths (Fig. 7, Z.) show that these bonds are (at 2.78 Å, mean) under compression due to the strong negative charge on the octahedral layer. The tetrahedra confirm this by being flattened (to $\tau = 107^\circ 0'$) to a limit set by the limited expansion possible in the octahedral layer. Thus the T—O_{basal} bonds are strongly compressed and—as for Si₂ groups in muscovite—this appears to redistribute the tetrahedral charge to contract T—O_{basal} to 1.60–1.61 Å and lengthen T—O_{apex} to 1.71 Å, both from an expected 1.63–1.64 Å.

The apex oxygens carry the large net octahedral charge, plus a further charge due to this redistribution, all satisfied by the distant interlayer K⁺. They therefore mutually repel each other strongly, so that shared edges are lengthened to about 3 Å and the octahedral layer is very thick, 2.48 Å (against 2.12 Å). (The distribution of charges on apex oxygens also ensures that celadonite is a 1M polymorph with $\beta_{\text{obs}} = \beta_{\text{ideal}}$). In agreement with previous sections the octahedral cations fill two out of three sites and leave only 0.1 Mg in the third site.

The final structure is an equilibrium between the strong O—O repulsion octahedrally, the stretched (Mg, Fe)—O bonds octahedrally (mean of 2.11 Å, against an expected 2.05 Å), the compressed and flattened tetrahedra, and the strong K—O_{apex} attraction. The result is a structure with three regular octahedra, one empty, with an abnormally thick octahedral layer, and with an otherwise unexpected interlayer separation and ditrigonal surface (Part I).

Xanthophyllite, $Ca(Mg_2Al)(SiAl_3)O_{10}(OH)_2$. Each Ca is six-coordinated with surface oxygens (Takéuchi and Sadanaga, 1959) and its charge is fully satisfied by them. The observed Ca—O bonds = 2.38 Å, very close to an expected 2.39 Å. This means that the real bond strength of T—O_{basal} is 0.843 instead of 0.813 and it is understood that these bonds are tending to be a little shorter than ideal in the refinement now in progress.

Lepidolites. No structural information is available but the fact that the

charge resides octahedrally should give comparable structural effects to celadonites. The short *b*-axis and apparently large interlayer separation have already been noted (Part I).

Kaolinite (*Zviagin, 1960; Drits and Kashaev, 1960*). These analyses are admittedly imprecise, especially when compared with the more crystalline polymorph, dickite. The results show comparable features to dickite, e.g. (a) shorten shared octahedral edges and counter-rotations of octahedral triads (*viz.* $+3^\circ$, -5° ; $+6.5^\circ$, -4°), (b) O—H—O bonds of about 3 Å, (c) shortened Al—OH_{surface} bonds, and (d) one OH raised out of surface. Some contrasts may be highly significant, when related to the directed interlayer bonds discussed for dickite. Thus the *c*-axis is bigger and the *b*-axis is smaller than in dickite, and the surface oxygen is *elevated* from the layer, not depressed into it. The accuracy of the kaolinite analyses do not justify further discussion of these interesting observations here.

Amesite ($Mg_2Al(Si\ Al)O_5(OH)_4$) (*Steinfink and Brunton, 1956*). This kaolin-type mineral has excess charge on the octahedral cations, which results in longer T—O_{apex} bonds ($=1.71 \pm 0.03$ Å) and shorter T—O_{basal} bonds ($=1.67 \pm 0.02$ Å). These latter account for an observed $\alpha = 11\frac{1}{2}^\circ$ but a calculated $\alpha = 16^\circ$ (Part II).

Trioctahedral micas. No structures have been published, but the *b*-axis of phlogopite ($=9.22$ Å) versus brucite ($=9.44$ Å) shows how the K—O bonds act to inhibit the octahedral expansion. Bassett (1960) has proposed a repulsion of K⁺ by the vertically directed OH proton in phlogopite. The smaller *b* = 9.188 and smaller thickness of fluorophlogopite (with *d* (003) = 3.329 against 3.387 in phlogopite) are consistent with this. In phlogopite such a repulsion would increase *c*, and also shorten OH—OH shared edges, *i.e.* increase *b*.

Chlorites. Although these concepts should apply in full to chlorite structures it seems wise to await a really accurate analysis, in view of the complications caused by the additional octahedral layers.

Montmorillonite group. No structural data are available but some observations connected with Part II are pertinent. Thus the octahedral layers of saponites and hectorites can certainly conform to the smaller dimensions set by their tetrahedral layers, especially since only Mg²⁺—Mg²⁺ repulsion is involved.

Beidellites and nontronites are unique amongst this group in that their

cation exchange capacity originates from tetrahedral substitutions almost entirely. That is, the surface oxygens themselves carry most of the net negative charge for these layers. In both cases there should be a comparable surface O—O repulsion to that postulated for vermiculite; and it is very interesting that these montmorillonites appear to have anomalous and high values for b (Table 7A, Part II). It is also notable that there appears to be a complete series between nontronites and beidellites (MacEwan, 1961) whereas nontronites and montmorillonites have separate composition fields (*e.g.* Radoslovich, 1963a).

OTHER STRUCTURES

The general concepts of this paper should apply to other minerals than layer lattice silicates, and they were therefore tested against a few comparable structures, as recorded very briefly below.

Lithiophorite (Al, Li) $MnO_2 (OH)_2$ (Wadsley, 1952). Although O—H—O bonds undoubtedly exist between the two octahedral layers they are not, as Wadsley suggested, the classical hydroxyl bonds of Bernal and Megaw (1935) between two OH's. In the Al, Li layer the $(Al_{0.68} Li_{0.32})$ —OH bond strength is ideally 0.393, and predicted bondlength therefore 1.966, compared with observed bonds of 1.93 and 1.95 Å. In the Mn layer the ideal $(Mn_{0.17}^{2+} Mn_{0.82}^{4+})$ —O bond strength is 0.603, giving a predicted 1.96 Å against an observed 1.93 and 1.97 Å. Moreover the hydroxyls can be fairly readily polarized, and hence 1.93 and 1.95 are both < 1.966 Å. It is simply this polarization of the hydroxyls (*c.f.* dickite) which sets up O—H—O bonds of 2.76 Å between the layers. The bond strengths are too low ($0.39 < \frac{1}{2}$) to tetrahedrally polarize the OH's, and the matching surface is an oxygen, not an hydroxyl surface, as in gibbsite.

Sanbornite, $Ba Si_2O_5$ (Douglass, 1958). The four different Si—O bond-lengths are directly related to the Ba—O bonds and the Si—Si repulsion across shared tetrahedral edges. Each O_I , O_{II} and O_{III} has one Ba—O bond of strength about $\frac{2}{3}$ and therefore two Si—O bonds of strength $\frac{8}{9}$. Each O_{III} has three Ba—O bonds of strength $\frac{2}{3}$ each and hence one Si— O_{III} bond of strength $\frac{1}{3}$. Hence Si— O_{III} = 1.60, *i.e.* less than an expected 1.62–1.63 Å, and Si— O_{II} = 1.64 and 1.65, greater than 1.62–1.63. The combined Si—Si repulsion and Si— O_{III} attraction act together to stretch still further the weakened Si— O_I bonds and these are even greater than Si— O_{II} , *viz.* 1.68 Å.

Cumingtonite ($Mg_{4.05} Fe_{2.50} Mn_{0.17} Ca_{0.35}$)($Si_{7.9} Al_{0.1}$) $O_{22} (OH)_2$. It is unnecessary to invoke a rather unlikely covalent Fe^{2+} —O bonding as

proposed by Ghose (1961) to explain the short bond of 2.04 Å between M_4-O_4 (Fig. 1, G.) The bond strengths from O_4 are about 1.0 to Si_2 , $\frac{1}{6}$ to M_2 , and hence $\frac{5}{6}$ to M_4 which is $Fe_{0.75}^{2+} Mg_{0.25}$. The expected length for an $(Fe_{0.75}^{2+} Mg_{0.25})-O$ bond of strength $\frac{5}{6}$ is around 2.02 Å, close to the observed 2.04 Å. This distribution of bond strengths is the reason for the high proportion of Fe^{2+} in this site. If M_4 were occupied by Mg entirely for example, then these strong bonds would bring oxygens in neighbouring chains much closer together than 2.97 Å, and this is not tolerable.

These three examples help to confirm the general application of the present concepts, and suggest that a more critical look at bond strengths and lengths in accurate structure analyses of complex ionic minerals often would be profitable.

In this connection the structure of tilleyite (Smith, 1953) appears markedly to disobey Pauling's Valency Rule if due allowance is made for the totally covalent nature of the bonds in the carbonate radical (e.g. Wells, 1962). Perhaps, this is to be expected for ionic structures containing such radicals, however.

DISCUSSION OF CONSEQUENCES OF THEORY

It must be re-emphasised that, although the present concepts appear to be applicable with marked success to published data, it is most desirable that they be tested against further precisely determined structures as soon as possible. Any implications in other studies on clay minerals should be viewed with considerable reservations at present. Nevertheless some of these will be of wide interest.

It follows from the "cation avoidance rule" (above) that octahedral cations will tend to be largely ordered, in the way that Veitch and Radoslovich have sought to establish (Part III). Likewise the geometrical model adopted in that analysis is fully consistent with present theories about the actual structures—at least in as much as it is a geometrical model. The varying role of the interlayer cations, and the various restraints on the b -axis expansion (Parts I, II, III) also are fully consistent with present hypotheses. In particular the positive regression coefficient for Al^{IV} for montmorillonites is now thought to be understood, and is not due simply to the larger radius of Al^{IV} than Si. From Table 7A, Part II it is seen by comparing b_{obs} and b_{kaolin} that the coefficient for Al^{IV} has gained most weight from the beidellite, nontronite and vermiculite samples. In each of these minerals the tetrahedral location of the charge results in an expansion of the sheets, and is of course proportional to the Al— for —Si substitution. On this basis the coefficient for Al^{IV} is real but is of quite different origin from the other coefficients.

Problems of mica stability under weathering are so complex that they

must await some trioctahedral mica structures, but at least the position of K^+ in muscovite (the most resistant mica) is now seen to be unique in several significant ways.

The discussion of $2M_1$ muscovite has clearly linked that polymorph and its "distorted" structure with asymmetric forces between the K^+ and the apex oxygens, and also with the distribution of octahedral cations. The writer has already guessed at similar forces distributed rather differently which appear to control the formation of other mica polymorphs generally, and this subject is at present under more intensive study.

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