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THE CELL DIMENSIONS AND SYMMETRY OF LAYER-LATTICE SILICATES. III. OCTAHEDRAL ORDERING

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ABSTRACT

The 3n octahedral sites in the unit cells of the layer silicates are accepted as being topologically distinct from each other, and the octahedral cations are known to be largely ordered for several published structures. The present study sought to determine quantitatively any differences between divalent and trivalent octahedral sites, by a suitable form of regression analysis of dimensional and composition data; and with this there is the implication of widespread ordering. Certain difficulties inherent in this statistical analysis of clay mineral data have thereby become obvious. Moreover the initial results made it essential to reconsider the model by which regression coefficients commonly have been related to ionic radii in unit cell formulae.

It has been necessary to abandon the simplest geometrical model (which assumes that the octahedra remain essentially regular) for one in which the expansion due to the subsitution of larger ions is several-fold greater in the direction normal to the layers than it is in the a–b plane. The new regression analyses confirm the results of the previous study and lead to simpler prediction relations for unit cell dimensions.

The new geometrical model is readily justified physically by considering several structures already accurately determined.

INTRODUCTION

Layer silicates are classified as trioctahedral or dioctahedral according to whether nearly all, or only two-thirds of the possible sites for cations in the octahedral layer are occupied. The unit cell of such a mineral may contain 6n (n = integer) sites per unit cell, but the overall symmetry generally reduces the number of octahedral sites in the asymmetric unit to three. Of these, two sites are generally symmetry-related or at least topologically equivalent, and the third site is distinct. For example, in $2M_1$ muscovite (Radoslovich, 1960) the two octahedral aluminum cations (hereafter Al^{VI}) are in symmetry-related sites, whereas the larger and vacant third site is a center of symmetry for the structure as a whole.

As the layer structures have become increasingly well understood the evidence has grown that ordering of the octahedral cations according to valency and radius may be widespread, and fairly complete in many minerals. Evidence for such ordering is in general only circumstantial, but the structural analysis of several layer silicates has already shown that ordering exists, at least in those minerals—for example celadonite (Zviagin, 1957), prochlorite (Steinfink, 1958), xanthophyllite (Takéuchi and Sadanaga, 1959), muscovite (Radoslovich, 1960), kaolinite (Drits and Kashaev, 1960) and dickite (Newnham, 1961).

The general hypothesis, however, seemed worthwhile testing statistically over a wide range of minerals if possible, without determining each structure in detail. As the simplest initial hypothesis it is supposed that there are two kinds of octahedral sites, A and B, such that A is smaller than B, and that there are either two A sites and one B site, or vice versa, for each three octahedral sites. It is further supposed that the trivalent (and quadrivalent) cations tend to occupy A sites and the divalent (and monovalent) cations tend to be in the B sites. This is obviously an approximation to the actual structural characteristics of these minerals. For example, the two small (A) sites in dioctahedral minerals may differ from the single small site in the trioctahedral minerals. Furthermore, some trioctahedral minerals *cannot* obey this model strictly, *e.g.* phlogopites. If such minerals nevertheless are assumed to have (2B+1A) sites then the excess of *divalent* cations (over 2.00) must occupy a "wrong" A site. For the purposes of this statistical analysis the excess of divalent cations is "transferred" to the trivalent group, smallest cations first.

Our previous study of the variation of sheet dimensions with composition (Radoslovich, 1962; hereafter Part II) suggested the possibility of establishing (by suitable statistical methods) whether there are two different kinds of octahedral sites into which cations substitute. Of the four major mineral groups the micas are the most amenable to analysis of this kind. The chlorites cannot be studied this way because there are two octahedral layers in the stacking unit, and ordering may also occur *between* these. The montmorillonites are difficult to study, not only because of uncertainties in the structural formulae (Part II), but also because of unsuspected complexities in these structures (Cowley and Goswani, 1961). Furthermore, most of the trioctahedral montmorillonites must be excluded because they follow a different model (Part II). This severely restricts the range of values for the *b*-axis and ionic proportions, increasing the difficulties statistically. The available data in the literature for the kaolin minerals are likewise restricted. In addition some of the more reliable data (Part II) have been obtained from synthetic or heated specimens, and there is some doubt whether these can have reached an equilibrium state of ordering in laboratory times. The importance of some of these restrictions only became apparent as the analysis proceeded.

A further major difficulty—with implications beyond the present study—has become increasingly obvious. For any expression connecting sheet dimensions and ionic proportions (*e.g.* Part II) each coefficient should be related to the appropriate ionic radius by a factor depending explicitly on the geometry of the structures. Brindley and MacEwan (1953), and Brown (1951), implied this in stating that "very similar results (to the empirical coefficients) are obtained if the argument is based on ionic radii." The form of regression analysis used (see below) may not only test for two significantly different "hole sizes" but yield estimates of the geometrical factor. The values obtained for this factor should agree, within their fiducial limits, with the theoretical value for the model used.

In the simplest model for the octahedral layers of these minerals the octahedra are assumed on the average to remain geometrically regular in shape. The anions may only be in mutual contact when the cation is sufficiently small; when larger cations are substituted the anions move apart, but the bond angles for a regular octahedron are preserved. Under these conditions the increase in *b* for an increase in cation radius from r_i to r_j is

$$\delta b = \sqrt{2}\,(r_j - r_i)x_j \qquad 1.1$$

where x_j = ionic proportions, of j^{th} atoms, in three sites—*i.e.* as expressed in most structural formulae (*e.g.* Part II). The relation between the regression coefficients, b_j and the ionic radii, r_j is, therefore,

$$b_j = \sqrt{2}\,(r_j - r_i) \qquad 1.2$$

and the predicted geometrical factor is $g = \sqrt{2}$, where (for convenience in writing) g is the inverse of the constant k as discussed in Part II, and the a_i in that paper have been re-named b_j.

Even in the preliminary calculations the statistical value of this factor was considerably less than $\sqrt{2}$. As the analysis was refined it became clear that the value statistically is close to half this figure. This required the formulation of the more general *geometrical* model—*i.e.* with less severe restraints—which is developed below. The new choice of restraints is then justified by some simple physical arguments from known structures and the statistical analysis follows.

The development of a satisfactory geometrical model, and the physical justification of this in general terms, has led to a detailed re-examination of the interatomic forces in layer silicates. These are to be discussed in Part IV, in which it is shown that the earlier hypotheses (Parts I and II) and the present model of the octahedral layers follow as reasonable consequences of the total balance of interatomic forces in these minerals.

NEW GEOMETRICAL MODEL FOR THE OCTAHEDRAL LAYERS

Restraints

The preservation of completely regular octahedra has been abandoned in favor of the following set of restraints:

(1) centers of octahedral cations lie in a plane,
(2) there are two A sites for each B site,[1]
(3) centers of anions lie in two planes parallel to the cation plane, and distant t/2 above and below it,
(4) anions are constrained to remain on the surfaces of spheres about the cations as centers,
(5) the radius of such a sphere is the accepted cation-anion bondlength, *i.e.*, either l_A or l_B,
(6) the network of cation sites is hexagonal.

As a corollary of these restraints it follows that only two kinds of cations (*i.e.* for A and for B sites) may be accepted by an ideal structure. In actual structures both A and B sites accept cations of several different radii; the most probable compromise is in condition (3).

When substitutions of various cations occur in A and B sites the bondlengths change by amounts of dl_A and dl_B respectively, and the thickness t by dt. It is then assumed that:

(7) $dt = \lambda db$ where λ is some proportionality "constant."

This is simply for descriptive convenience, and λ is only a "constant" in the sense of having some average value over many minerals. Assumption (7) implies that these layers may become thicker at some rate disproportionate to their increase in sheet dimensions.

Calculation of the b-axis of unit cell (b_U)

From (6) the *b*-axis is three times any cation-cation distance. From (2), (3) and (6) the cation-anion bondlengths must have a common value, l_A, for both A sites. If such an octahedral layer is projected on to a plane through the cations (Fig. 1) then the common value for l_A means that the anions around B have, in projection, hexagonal symmetry and hence BCD is an equilateral triangle (Fig. 1). [The upper equilateral triad of anions around an A site is, however, rotated relative to the corresponding lower equilateral triad.] From (5) the spheres around A and B sites have radii l_A and l_B; let the same spheres cut the anion planes in circles of radii ρ_A and ρ_B respectively. Then it follows that

$$\rho_A = \left(l_A^2 - \frac{t^2}{4}\right)^{1/2} = AC: \qquad \rho_B = \left(l_B^2 - \frac{t^2}{4}\right)^{1/2} = BC$$

$$AB = \left(\rho_A^2 - \frac{\rho_B^2}{4}\right)^{1/2} + \left(\rho_B^2 - \frac{\rho_B^2}{4}\right)^{1/2}$$

whence the *b*-axis dimension becomes

$$b_U = \frac{3}{2}\left[4l_A^2 - l_B^2 - \frac{3t^2}{4}\right]^{1/2} + \frac{3\sqrt{3}}{2}\left[l_B^2 - \frac{t^2}{4}\right]^{1/2}. \qquad 2.1$$

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[1] All subsequent formulae hold good by interchanging A and B for the cases where the ratio is 2B sites for each A site.

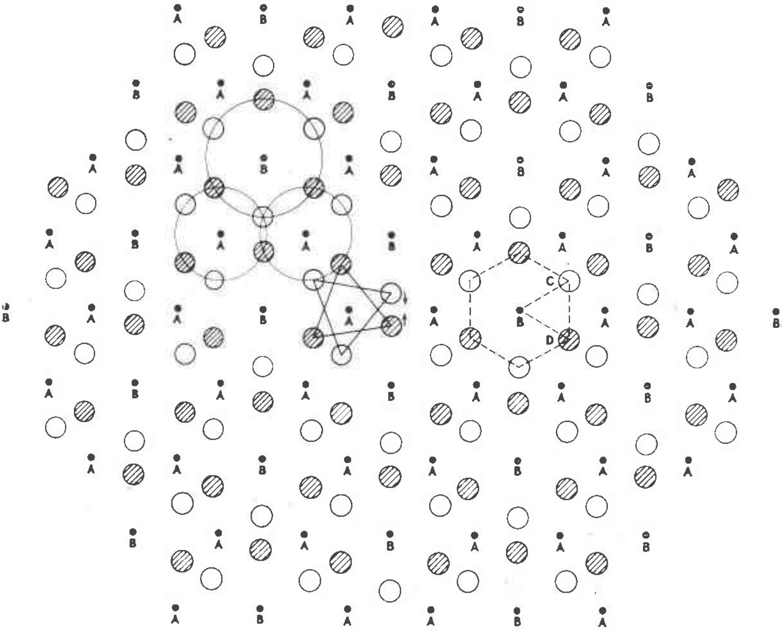

FIG. 1. Schematic drawing of a geometrically ideal octahedral layer, showing two small A sites for each large B site. Note triads of oxygens above (unshaded) and below (shaded) cations. These triads are counter-rotated about any A site, but have hexagonal symmetry, in projection, about any B site. Cations A and B are also on a hexagonal grid in this model.

Average values for muscovite (Radoslovich, 1960) are $l_A = 1.95_4$, $l_B = 2.20$, $t = 2.12$ from which $b_{calc} = 8.99_6$ compared with $b_{obs.} = 8.99_5$ Å. The agreement is fortuitously close, since not all the conditions (1) to (7) are fulfilled precisely; nevertheless equation 2.1 seems to be a very good approximation for real octahedral layers.

Variations in b_U as l_A, l_B and t vary

Totally differentiating equation 2.1 with respect to l_A, l_B and t gives

$$\begin{aligned} db_U = {} & 6l_A \left(4l_A^2 - l_B^2 - \frac{3t^2}{4}\right)^{-1/2} dl_A \\ & + \frac{3\sqrt{3}}{2} l_B \left[\left(l_B^2 - \frac{t^2}{4}\right)^{-1/2} - \frac{1}{\sqrt{3}}\left(4l_A^2 - l_B^2 - \frac{3t^2}{4}\right)^{-1/2}\right] dl_B \\ & - \frac{3\sqrt{3}}{8} t \left[\sqrt{3}\left(4l_A^2 - l_B^2 - \frac{3t^2}{4}\right)^{-1/2} + \left(l_B^2 - \frac{t^2}{4}\right)^{-1/2}\right] dt. \end{aligned} \qquad 2.2$$

The earlier model, in which the octahedra remain regular, has the special conditions that

$$dt = \frac{\sqrt{2}\, db}{3\sqrt{3}};\ l_A = l_B = l;\ \text{and}\ t = 2l/\sqrt{3}.$$

Substitution in equation 2.2 gives

$$db_U = \sqrt{2}\,(2dl_A + dl_B)$$

or, assuming that the anion radius is constant,

$$db_U = \sqrt{2}\,(dr_A + dr_B)$$

for the three octahedra in an asymmetric unit. Taking the average, as required by the definition of the x_j, gives

$$db = \sqrt{2} \sum dr_j x_j \qquad 2.3$$

which is, in fact, equation 1.1.

Dioctahedral micas

Substituting muscovite data in equation 2.2,

$$db_U = 4.422dl_A + 1.718dl_B - 1.616dt$$

and if condition (7) is obeyed then

$$db_U = (0.4523 + 0.7309\lambda)^{-1}2dl_A + (0.5821 + 0.9406\lambda)^{-1}dl_B \qquad 2.4$$

Trioctahedral micas

No accurate determinations of t are yet published, but trioctahedral micas may reasonably be assumed to have regular octahedra initially, if cell dimensions are considered in relation to ionic radii. That is,

$$db_U = \frac{3}{\sqrt{2}}(2dl_B + dl_A) - \frac{3\sqrt{3}}{2\sqrt{2}}dt$$

or

$$db_U = (0.4714 + 0.8661\lambda)^{-1}(2dl_B + dl_A) \qquad 2.5$$

Relation between geometrical constant g and λ

Consider the dependence of the separate geometrical constants on λ for the two extreme cases immediately above. From the calculated factors in Table 1 it is clear that, provided λ remains the same for the total suite of micas, the geometrical factor g does not vary seriously between A and B sites or between di- and trioctahedral minerals. This produces a considerable simplification in the model for statistical analysis.

PHYSICAL PLAUSIBILITY OF NEW GEOMETRICAL MODEL

It is sufficient, for a valid discussion of the present statistical analysis, to show that the geometrical model now adopted is readily acceptable physically. In the following paper the interatomic forces are considered in more detail; and again the conclusions support this model. Of the seven restraints listed previously, several may be regarded as axiomatic, viz. (1), (3), (4), (5), and these are seen to be quite closely obeyed by structures already accurately determined. The second restraint, (2), is in fact

TABLE 1. SEPARATE GEOMETRICAL FACTORS[1] AT A AND B SITES IN MICAS, CALCULATED FOR A RANGE OF VALUES OF λ

λ	Dioctahedral		Trioctahedral	
	A sites	B sites	A sites	B sites
0.2	1.671[1]	1.298[1]	1.551[1]	1.551[1]
0.4	1.343	1.043	1.223	1.223
0.6	1.123	0.872	1.009	1.009
0.8	0.964	0.749	0.859	0.859
1.0	0.845	0.657	0.748	0.748
1.2	0.752	0.585	0.662	0.662
1.4	0.678	0.527	0.594	0.594

[1] The factors in columns 2–5 correspond to the coefficients of $2d1_A$, $d1_B$, $2d1_B$ and $d1_A$ in equations 2.4 and 2.5.

the postulated characteristic which the statistical analysis was designed to test.

Implicit in restraints (1) to (6), taken together, is the requirement that if there *are* two kinds of sites (as in (2)) then they are in an ordered arrangement. It is emphasized again that this analysis tests for different hole sizes only; but in so far as this geometrical model appears to conform to real structures (*e.g.* in leading to geometrical factors consistent with experimental data) it lends support to the hypothesis of ordering. The restraint (6) is, in any case, fairly closely followed by known structures. It is a highly probable consequence of the controlling forces in the layer silicates. Again, the counter-rotation of triads around A sites—deduced as a consequence of (2), (3) and (6)—is observed experimentally; for example, in kaolinite (Drits and Kashaev, 1960) the upper and lower triads around Al sites rotate $+6\frac{1}{2}°$ and $-4°$ respectively.

The final restraint (7) needs rather more discussion. The concept of octahedral layers varying in thickness according to externally applied constraints is not entirely new (*e.g.* Bradley, 1957). The writers, however, are not aware of any attempt to calculate an average rate by which the thickness varies with sheet dimensions, over a wide range of minerals, using valid statistical methods.

A simple comparison of observed sheet dimensions with those calculated on the assumption of three equal and regular octahedral sites (Table 2) shows the necessity for some moderately large factor, λ. Taking the micas particularly, case 3 shows that many Fe^{2+} biotites may have approximately *regular* octahedral layers. For these $b_{obs.} \approx 9.3$ Å, and the radius of Fe^{2+} (0.75 Å) is not too different from 0.79 Å. There are no data yet available for t, but their octahedral layers must be considerably thicker than that of muscovite (2.12 Å), since the *total* layer thickness is

TABLE 2. OCTAHEDRAL DIMENSIONS[1] FOR VARIOUS IONIC RADII, r_i

	Case 1	Case 2	Case 3
r_i in Å	0.58	0.70	0.79
t in Å	2.29	2.42	2.53
b in Å	8.4	8.91	9.3

[1] Assuming regular, and equal, octahedra; and that the anion radius is constant at 1.40 Å (Ahrens, 1952).

very similar (d(001) = 10.0 Å for each) yet muscovite alone should have (Part I) a large interlayer separation (≈ 0.6 Å). An observed $t \approx 2.53$ Å would, therefore, be expected.

The dioctahedral micas have sheet dimensions comparable with case 2, yet the radius of the cations is nearer 0.50 than 0.70, and the thickness will typically be about 2.1 Å (muscovite 2.12 Å) rather than 2.42 Å. For the micas, then, we may predict that b increases from 8.9 to 9.3 as t goes from 2.1 to 2.5, *i.e.* if $dt = \lambda db$ then $\lambda \approx 1.0$. Since $b \approx 4.5t$ this means that the percentage increase in thickness is, on the average, more than four times the percentage increase in sheet dimensions. This is confirmed by the analysis which follows.

Less definite information is available for the kaolins and montmorillonites, but for both groups it is known that 8.9 and 9.3 are the lower and upper limits to b, and that for the former dimension r_i is much less than 0.7 and for the latter r_i is near 0.79. Moreover dickite has a thickness $t = 2.06$ Å, *i.e.* much less than 2.42 Å. Gibbsite, $Al(OH)_3$ (Megaw, 1934) is much thinner (2.12 Å) than an array of regular octahedra with the same $b(= 8.64$ Å).

Case 1 shows that oxygens of radius 1.40 Å can be close packed (*i.e.*, 0–0 distances = 2.80 Å) to form regularly-shaped octahedral layers with interstices easily large enough (0.58 Å) to accommodate Al ions (0.50 Å). In three aluminum-bearing minerals *average* 0–0 distances in the planes of the sheets are 2.93 Å (gibbsite), 2.997 Å (dickite) and 2.99_4 Å (muscovite).

It is concluded that for the micas, kaolins and montmorillonites at least, the dioctahedral layers are noticeably stretched and thin, but that the corresponding trioctahedral layers are more nearly regular. That is, restraint (7) appears acceptable physically.

STATISTICAL ANALYSIS FOR TWO DISTINCT KINDS OF OCTAHEDRAL SITES

The regression coefficients of Part II are expressed as

$$b_j = g_i(r_j - r_i) \qquad 4.1$$

where

r_i = characteristic radius of the ith site
g_i = geometrical factor for the ith site ($=1/k$ in Part II)
r_j = radius of the cation substituting in that site
b_j = corresponding regression coefficient ($=a_i$ in Part II).

The subscript i, which typically refers to octahedral sites, may if necessary refer to interlayer and tetrahedral sites. The average sheet dimensions which are given by

$$b = b_0 + \sum_{j=1}^{p} b_j x_j \qquad 4.2$$

for an average proportion x_j substituting in ith sites, then becomes

$$b = b_0 + \sum_{i} \left[g_i \sum_{j=1}^{p_i} r_j x_j - g_i r_i \sum_{j=1}^{p_i} x_j \right] \qquad 4.3$$

where p_i = number of different cations substituting in the ith site.

Denote $\sum_{j=1}^{pi} r_j x_j$ by u_{1i} and $\sum_{j=1}^{p_i} x_j$ by u_{2i}.

Then the regression coefficient of u_{1i} estimates the geometrical factor g_i at the ith site, and the regression coefficient of u_{2i} estimates $(-g_i r_i)$ from which the characteristic radius r_i is obtained.
Let

$i=1$ for interlayer sites
$i=2$ for larger octahedral sites (B), occupied by R^{2+}.
$i=3$ for smaller octahedral sites (A), occupied by R^{3+},
$i=4$ for tetrahedral sites.

The first geometrical model and physical considerations (Part II) led us to expect that $g_1=1.5$, $g_2=g_3=\sqrt{2}$, $g_4=0$ except for the montmorillonites possibly, $r_1=0.95$ Å, $r_2>r_3$, $r_2=0.65$ Å, $r_3=0.50$ Å, and $r_4=0.41 \times 0.88=0.36$ Å. The actual results contradicted some of these expectations so strongly that the model based on effectively regular octahedra has been discarded.

In the following analyses an excess over 2.00 of x_j at B sites has been arbitrarily transferred to A sites. This may introduce errors into the u variates which would cause the regression coefficients to bias towards zero. If, however, g_2 is made equal to g_3 the appropriate variate to be used for estimating a common g_0 is $(u_{12}+u_{13})$, which is independent of such transfers.

Mica minerals

A set of 39 micas was used initially, which involved 12 different cations. Since a preliminary analysis had indicated that g_2 was not significantly different from g_3 the restriction was imposed of a common $g = g_0$ at both kinds of octahedral sites. The appropriate variates are given in Table 3, in which u_4 owes its form to the fact that in the structural formulae $(x_{\mathrm{Al}^{\mathrm{IV}}} + x_{\mathrm{Si}}) = 4$ always, so that there is effectively only one variate and this depends on the difference $r_{\mathrm{Al}} - r_{\mathrm{Si}} = 0.09$ Å. The expected non-significance of u_4 (Parts I and II) was confirmed and this variate then omitted in obtaining the final regression relation (Table 4).

TABLE 3. FORMS OF VARIATES USED FOR DIFFERENT CALCULATIONS

1. *Set of 39 micas*

$u_{11} = 1.33x_{\mathrm{K}} + 0.95x_{\mathrm{Na}} + 0.99x_{\mathrm{Ca}}$
$u_1 = (u_{12} + u_{13}) = 0.75x_{\mathrm{Fe}^{2+}} + 0.65x_{\mathrm{Mg}} + 0.60x_{\mathrm{Li}} + 0.80x_{\mathrm{Mn}} + 0.68x_{\mathrm{Ti}} + 0.50x_{\mathrm{Al}} + 0.65x_{\hat{\mathrm{M}}\mathrm{g}}$
$u_4 = 0.09x_{\mathrm{Al}^{\mathrm{IV}}}$
$u_{21} = x_{\mathrm{K}} + x_{\mathrm{Na}} + x_{\mathrm{Ca}}$
$u_{22} = x_{\mathrm{Fe}^{2+}} + x_{\mathrm{Mg}} + x_{\mathrm{Li}} + x_{\mathrm{Mn}}$
$u_{23} = x_{\mathrm{Fe}^{3+}} + x_{\mathrm{Ti}} + x_{\mathrm{Al}} + x_{\hat{\mathrm{M}}\mathrm{g}}$

2. *Set of 15 kaolin and serpentine minerals*

$u_{12} = 0.08x_{\mathrm{Mn}} + 0.65x_{\mathrm{Mg}} + 0.75x_{\mathrm{Fe}^{2+}} + 0.60x_{\mathrm{F}\hat{\mathrm{e}}^{3+}}$
$u_{13} = 0.50x_{\mathrm{Al}} + 0.60x_{\mathrm{F}\hat{\mathrm{e}}^{3+}} + 0.65x_{\hat{\mathrm{M}}\mathrm{g}} + 0.75x_{\mathrm{F}\hat{\mathrm{e}}^{3+}}$
$u_1 = u_{12} + u_{13}$
$u_{22} = x_{\mathrm{Mn}} + x_{\mathrm{Mg}} + x_{\mathrm{Fe}^{2+}} + x_{\mathrm{Fe}^{3+}}$
$u_{23} = x_{\mathrm{Al}} + x_{\mathrm{Fe}^{3+}} + x_{\mathrm{M}\hat{\mathrm{g}}} + x_{\mathrm{F}\hat{\mathrm{e}}^{2+}}$

3. *Set of 28 montmorillonite minerals*

$u_1 = 0.75x_{\mathrm{Fe}^{2+}} + 0.65x_{\mathrm{Mg}} + 0.60x_{\mathrm{Li}} + 0.60x_{\mathrm{Fe}^{3+}} + 0.68x_{\mathrm{Ti}} + 0.50x_{\mathrm{Al}} + 0.65x_{\mathrm{M}\hat{\mathrm{g}}}$
$u_4 = 0.09x_{\mathrm{Al}^{\mathrm{IV}}}$
$u_{22} = x_{\mathrm{Fe}^{2+}} + x_{\mathrm{Mg}} + x_{\mathrm{Li}}$
$u_{23} = x_{\mathrm{Fe}^{3+}} + x_{\mathrm{Ti}} + x_{\mathrm{Al}} + x_{\mathrm{M}\hat{\mathrm{g}}}$

The accent $\hat{\mathrm{T}}$ refers to proportions of various cations which have been transferred as discussed in the Introduction.

The least squares estimates of r_2 and r_3 are 0.62 Å and 0.54 Å respectively. Although these values are encouragingly close to the predicted "hole sizes," and also the value for $g_0 = 0.811$ corresponds to $\lambda \approx 1.0$ and seems reasonable, they are nevertheless suspect because the other values, *viz.* $g_1 = 0.285$, $r_1 = 1.48$ Å contrast strongly with expected values, indicating the possibility that the interlayer cations in such a set of micas behave heterogeneously (Parts I and II). Hence a subset of 23 trioctahedral micas was studied. For these the interlayer cation should have little effect, or at least behave homogeneously. The results (Table 4) show that the interlayer cations do not affect the *b*-axis; this confirms the earlier hypotheses (Parts I and II) and proves the heterogeneity of the first set of 39 micas. However, a new difficulty arises because the

Table 4. Regression Relations and Corresponding Analyses of Variance

1. *Set of 39 micas*

$$b=9.114+\overset{***}{0.2849}(\pm0.03789)u_{11}+\overset{***}{0.8106}(\pm0.0493)u_{1}-\overset{***}{0.4207}(\pm0.06405)u_{21}$$

$$\overset{***}{-0.5003}(\pm0.04315)u_{22}\overset{***}{-0.4402}(\pm0.04385)u_{23}$$

Variation	D.F.	S.S.	M.S.	V.R.	R²
due to regression	5	0.594167	0.118833	231.64	0.9723
due to residuals	33	0.016945	0.000513		
Total	38	0.611112			

2. *Subset of 23 trioctahedral micas*

$$b=8.927\overset{N.S.}{-0.2017}(\pm0.1596)u_{11}+\overset{***}{0.7034}(\pm0.08393)u_{1}+\overset{N.S.}{0.1128}(\pm0.2163)u_{21}$$

$$\overset{N.S.}{-0.2603}(\pm0.3739)u_{22}\overset{***}{-0.4221}(\pm0.05583)u_{23}$$

2.1 *Prediction relation, from subset of 23 trioctahedral micas*

$$b=8.244+\overset{***}{0.7071}(\pm0.08728)u_{1}\overset{***}{-0.4116}(\pm0.05716)u_{23}$$

Variation	D.F.	S.S.	M.S.	V.R.	R²
due to regression	2	0.0212019	0.0106009	32.88	0.7668
due to residuals	20	0.0064487	0.0003224		
Total	22	0.0276506			

3. *Set of 15 kaolin and serpentine minerals*

$$b=9.012+\overset{***}{0.9197}(\pm0.05335)u_{1}\overset{***}{-0.4892}(\pm0.04176)u_{22}\overset{***}{-0.5042}(\pm0.03875)u_{23}$$

Variation	D.F.	S.S.	M.S.	V.R.	R²
due to regression	3	0.839569	0.279856	874.55	0.9958
due to residuals	11	0.003521	0.000320		
Total	14	0.843090			

4. *Set of 28 montmorillonite and vermiculite minerals*

$$b=9.114+\overset{***}{0.8375}(\pm0.07761)u_{1}+\overset{***}{0.6664}(\pm0.1548)u_{4}\overset{***}{-0.5170}(\pm0.06439)u_{22}$$

$$\overset{***}{-0.5068}(\pm0.06213)u_{23}$$

Variation	D.F.	S.S.	M.S.	V.R.	R²
due to regression	4	0.336929	0.084232	427.57	0.9867
due to residuals	23	0.004528	0.000197		
Total	27	0.341457			

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[1] In table 4 the number of asterisks refers to the statistical significance (3, 2 and 1 refer to 0.1%, 1% and 5% levels respectively, N.S. = not significant at 5%). The numbers in brackets are the standard errors of the regression coefficients. D.F. = degrees of freedom, S.S. = sums of squares, M.S. = mean square, V.R. = Variance ratio F, R^2 = square of multiple correlation coefficient (Part II).

variate u_{22} has a very nearly constant value of 2.0 in such a set, so that it is not possible to estimate r_2 (*i.e.* r_B). The estimation of r_2 requires a suitable set of dioctahedral micas which unfortunately is not available.

The best relation to use for predicting *b*-axes for trioctahedral micas is also given in Table 4. This result, with an s^2 (=mean square due to residuals) of 0.00032, is appreciably better than for the analysis of 45 micas in Part II, in which $s^2=0.00091$. The improvement reflects the choice of a more homogeneous set of micas. The value for $k_0=0.707$ is highly significantly different from the earlier prediction that $g_0=\sqrt{2}$. The least squares estimate of $r_3=0.58$ Å is somewhat higher than expected. The low $b=8.244$ is due to the fact that the variation in u_{22} does produce a real physical effect, but its value is virtually fixed at 2.0 by the choice of data. [For example, putting the value of -0.5003 for the regression coefficient of u_{22} (*i.e.*, from set of 39 micas) changes *b* to 9.244.]

It has not been possible to select a homogeneous set of micas which will give satisfactory estimates of both r_2 and r_3 or even of r_2 above. Hence it cannot be shown statistically whether r_2 is significantly different from r_3.

Kaolin and serpentine minerals

The variates (Table 3) and regression relations (Table 4) refer to a set of 15 minerals selected from Part II. Since g_2 and g_3 were shown not to differ significantly a common g_0 was estimated by combining u_{12} and u_{13}; at $g_0=0.92$ it is highly significantly different from $\sqrt{2}$. The least squares estimates of r_2 and r_3 are 0.53 Å and 0.54 Å, so that ordering is not proven. The possibility of heterogeneous behavior cannot be excluded, but no satisfactory subset could be chosen.

A subset of 11 minerals in Part II (Mg, Fe^{2+} and Fe^{3+} substituting for Al) gave a value for s^2 of 0.000271, slightly better than 0.000320 obtained here.

Montmorillonite minerals

The choice of minerals is severely restricted (see Introduction) leading to a very high correlation between u_{12} and u_{13}; the reasonable restriction, as in 3.3 and 3.4, that $g_2=g_3=g_0$ (*i.e.* $u_1=u_{12}+u_{13}$, Table 3) overcame this difficulty. The results (Table 4) confirm the significant contribution of Al^{IV}, shown in Part II. Again $g_0(=0.84)$ is much less than $\sqrt{2}$, and the least squares estimates of r_2 and r_3, *viz.* 0.62 Å and 0.61 Å, are inconclusive. The value of $s^2=0.000197$ is slightly higher than 0.000153 obtained in Part II.

DISCUSSION

The results over the three sets of minerals indicate that for studies of this kind the problem of obtaining statistically adequate sets of data which behave in a homogeneous manner within a set has considerable difficulties. In addition the montmorillonite data suffered from very high correlation between determining variates which gives results unduly sensitive to small sampling differences; and the mica subset did not have an adequate range of variation in the determining variates.

Only in the kaolin data was it possible to show that g_2 was not significantly different from g_3, and there still remains some doubt about the physical homogeneity of a set containing heated and synthetic minerals.

Statistically the *strong* results of the analysis are to show that:

(1) g_0 is about 0.8 for the three sets, highly different from $\sqrt{2}$,

(2) the regression coefficients of the octahedral cations can be usefully and simply approximated to

$$b_j = 0.8(r_j - C)$$

where $C = 0.55$ to 0.60.

Although the values of g_0 do not differ *significantly* from each other for the micas, kaolins and montmorillonites,[1] their differences are self-consistent with the regression coefficients in Part II. The b-axes of the Al-dioctahedral minerals (*e.g.*, paragonite, kaolinite and Al montmorillonite) are all close to 8.92. The largest individual regression coefficients b_j should, therefore, be found for the mineral group in which the sheet thickness increases least rapidly, *i.e.* λ is smallest, or g is greatest. The regression coefficients for Mg, Fe^{2+} and Fe^{3+} (taken from Part II) are given in Table 5. The coefficients for Mg and Fe^{2+} are consistent with the relative size of g for these three groups. The coefficient for Fe^{3+} for the kaolins is anomalously low. This coefficient depends entirely on the data (Part II) for a heated Fe^{2+}-chamosite, and may well

TABLE 5. REGRESSION COEFFICIENTS IN RELATION TO GEOMETRICAL CONSTANTS

	g	Mg[1]	Fe^{2+}	Fe^{3+}
Kaolins	0.92	0.125	0.229	0.079
Montmorillonites	0.84	0.096	—	0.096
Micas	0.811	0.062	0.116	0.096

[1] These values for the regression coefficients are taken from Table 1, Part II.

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[1] To test the homogeneity of the estimates of g_0 between the three groups we used the procedure given by Williams (1959, pp. 131–2) which resulted in a value for F on 2 and 54 degrees of freedom being equal to 2.62. This contradicts homogeneity at a level between 5% and 10%, *i.e.* the level is not quite significant. The greatest contribution towards heterogeneity comes from the mica estimate.

be suspect. A value of about 0.1 seems more consistent. It is interesting that the "hole size" for Fe^{3+} (Table 2, Part II) is then 0.50, as for Al, again hinting at ordering of the octahedral cations in this group.

If the differences in g (*i.e.* λ) are indeed real then the external constraints resisting marked expansion in the *a-b* planes are strongest in micas and weakest in the kaolins. This is discussed further in the following paper on the interatomic forces.

The postulate (2) that there are two hole sizes, A and B, is not proven statistically primarily because of insurmountable limitations in the published—and probably in the potentially available—data. However, the present explicit geometrical model seems to be essentially correct. In so far as this is true octahedral ordering follows as a consequence.

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