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THE CELL DIMENSIONS AND SYMMETRY OF LAYER-LATTICE SILICATES

II. REGRESSION RELATIONS

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ABSTRACT

New formulae connecting the sheet dimensions (*b* axes) of layer-silicates with their chemical composition are proposed; the theoretical basis for these was described earlier (Part I). The new formulae are obtained by the multiple regression analysis of unit cell *x*-ray data and ionic proportions as given by the structural formulae. Kaolinite and serpentine minerals, chlorites, micas and montmorillonites are treated as separate groups. Tetrahedral aluminum does not increase *b* for kaolin and serpentine minerals, chlorites and micas, and only slightly increases *b* for the montmorillonites. The interlayer cation has a major effect on the cell dimensions of micas. The present *b*-axis formulae appears to be sufficiently precise to allow a number of conclusions to be drawn about individual mineral structures, and also to suggest errors in some older data in the literature.

INTRODUCTION

It has long been apparent that a close relationship exists between cell dimensions and composition for the layer-lattice silicates. In particular the sheet dimensions, b (or $a=b/\sqrt{3}$), apparently depend in a simple way on composition, so that many "*b*-axis" formulae have appeared in the literature. These have been shown in Part I (Radoslovich and Norrish, 1962) to be based on partially incorrect hypotheses. New formulae consistent with the new hypotheses were established satisfactorily by trial-and-error methods. However, it was also highly desirable to establish the significance or non-significance of certain coefficients in the formulae. For this reason the best available data have been analysed statistically (by multiple regression analysis), and new formulae for predicting "*b*" from composition were derived on this basis. Since it is now obvious that micas must be treated independently, because of the interlayer cation, it was decided to keep separate all four groups, *viz.* kaolin and serpentine minerals, micas, chlorites and montmorillonites.

Although the theoretical predictions in Part I indicated that tetrahedral Al should not appear in the formulae it was considered essential to insert the Al_{tetr} figures to check that the contribution made by Al in the tetrahedral sites is effectively zero. For each group of minerals the variation of b with composition was computed as a multiple regression equation,

$$b = b_0 + \sum a_i x_i,$$

where a_i are the required regression coefficients for cations 1, 2, . . . i . . . and x_i are the ionic proportions of the various substituting cations in the appropriate structural formulae. In order to keep all of the coefficients a_i positive the equations were set up so that b_0 should correspond to the end member mineral with the smallest dimensions, in each case the member with only Al octahedrally and only Si tetrahedrally coordinated. (The latter condition is, of course, unnecessary if Al_{tetr} makes no contribution, as is now known to be true for very many minerals.)

It is not easy to find data in the literature for layer-lattice silicates for which the particular sample is undoubtedly pure, the chemical analysis is sufficiently accurate, the basis for calculating the structural formula is known and acceptable, and the *x*-ray data are of assessable and high accuracy. Within limits the data available have been selected rather critically; data which are suspected to be inadequate have merely been checked against the new regression equations, and not used in computing them originally.

It is, of course, impossible on the simple premises proposed here to distinguish between polymorphs of the same composition, although it is known for example that kaolinite, dickite and nacrite differ slightly in b. Likewise the development of a single regression relation to cover many minerals of a given structural type does not necessarily imply the existence of a complete isomorphous series between member minerals. For example one regression relation applies to both muscovite and phlogopite despite a probable structural discontinuity between them; and similarly one relation applies (with one restriction only) to kaolins and their trioctahedral analogues (variously called serpentines, septochlorites etc.)[1] though a structural discontinuity has been claimed here by Nelson and Roy (1954).

During the course of this study it became necessary or desirable to place certain limits on the samples included in the various regression analyses. In particular, for those compositions for which $b_{oct} > b_{tetr}$, if both layers were unconstrained, the octahedral layer may or may not contract before the tetrahedral layer expands. For this reason the data used in the final regression analyses did not include those minerals for which $b_{obs} \geq b_{tetr}$; these minerals were merely compared with the results obtained. This is discussed later in relation to the saponites and serpentines.

KAOLINS[1]

The final regression relations for these minerals were first computed to give the increase in b when substitutions occur in $Al_2Si_2O_5(OH)_4$ of Al^{3+} tetrahedrally, and of Mg^{2+}, Fe^{2+} and Fe^{3+} octahedrally. This calculation

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[1] There is no generally accepted nomenclature yet which describes concisely the kaolin minerals and their trioctahedral analogues; for the sake of brevity only, the words "kaolin, kaolins" will be used in this paper to refer to all these minerals collectively.

TABLE I. REGRESSION COEFFICIENTS FOR KAOLINS, CHLORITES, MICAS AND MONTMORILLONITES

Group	No. of Specimens	R^2	b_0	Variate	Regression Coefficient	Standard Deviation	Significance Level %
Kaolins $Al_2Si_2O_5(OH)_4$	12	0.994	8.9226	Mg	0.1248	±0.0053	0.1
				Fe^{2+}	0.2290	±0.0078	0.1
				Fe^{3+}	0.0794	±0.0099	0.1
Chlorites $Al_4Si_4O_{10}(OH)_8$	21	0.765	9.23	Fe^{2+}	0.03	±0.0035	0.1
Micas $Na\ Al_2(Si_3Al)O_{10}(OH)_2$	45	0.941	8.9245	K	0.0992	±0.0344	1
				Ca	−0.0685	±0.0335	5
				Mg	0.0621	±0.0062	0.1
				Fe^{2+}	0.1160	±0.0094	0.1
				Fe^{3+}	0.0976	±0.0127	0.1
				Ti	0.1655	±0.0563	1
Montmorillonites $Al_2Si_4O_{10}(OH)_2$	30	0.987	8.9442	Mg	0.0957	±0.0062	0.1
				Fe^{3+}	0.0957	±0.0048	0.1
				Al_{tetr}	0.0367	±0.0118	1.0

gave a non-significant regression coefficient for $Al_{tetr.}$, so that the assumption that Al_{tetr} does not affect "*b*" for these minerals is fully justified. The regression analysis was therefore recalculated omitting this variate (Table 1). The very high value of the square of the multiple regression coefficient, $R^2(=0.994)$, confirms that the variations in "*b*" are almost completely explained by the regression of "*b*" on the ionic substitutions.[1]

It is assumed that the regression coefficients are linearly proportional to the difference between the ionic radii r_i and the hole filled r_h by the substituting cations, *i.e.* $(r_i - r_h) = k \cdot a_i$ where for Mg, for example, $(0.65 - r_h) = k \cdot 0.125$. A least squares determination of k also yields values for r_h (Table 2), which are highly self consistent, and close to the ionic radius of Al. On the strong probability that Mn and Ti will behave similarly regression coefficients may be predicted from their ionic radii as follows:

Mn	$0.80 - 0.52 = 0.995a$	whence	$a = 0.28$
Ti	$0.69 - 0.52 = 0.995a$	whence	$a = 0.17$

A regression analysis which also included the two antigorites and grovesite in Table 4 gave a coefficient for Mn of 0.269 with $R^2 = 0.996$. The mica analysis gives a Ti coefficient of 0.165 with $k \doteqdot 1.18 = 1$. These predicted coefficients are therefore reasonable.

The recommended regression equation to be used for predicting *b* axes for kaolin minerals is given in Table 3, and in Table 4 the observed values of *b* are compared with values calculated by this equation. Minerals in-

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[1] See any textbook on mathematical statistics, *e.g.* "Regression Analysis," by E. J. Williams, John Wiley & Sons, N. Y., 1959, p. 25.

TABLE 2. RELATIONS BETWEEN REGRESSION COEFFICIENTS AND IONIC RADII

$(r_i - r_h) = k \cdot a_i$

Group	Variate	Radius, r_i	Coefficient, a_i	"Hole, r_h"	k
Kaolins	Mg	0.65	0.125	0.521	0.995
	Fe^{2+}	0.75	0.229	0.522	
	Fe^{3+}	0.60	0.079	0.526	
	Al	0.50	—	0.50	
Micas	K	1.33	0.099	1.130	2.03
	Ca	0.99	−0.069	1.130	
	Mg	0.65	0.062	0.535	1.86
	Fe^{2+}	0.75	0.116	0.535	
	Fe^{3+}	0.60	0.098	0.484	1.18
	Ti	0.68	0.166	0.484	
	Al	0.50	—	0.50	
Montmorillonites	Mg	0.65	0.096	0.554	Put k=1
	Fe^{3+}	0.60	0.096	0.504	Put k=1
	Al	0.50	—	0.50	
	Si	0.41		0.41	
	$Al_{tetr.}$	0.50	0.074[1]	0.43	Put k=1

[1] For a valid comparison with the other a_i this coefficient has been doubled because there are two tetrahedral layers per cell.

cluded in the first part of Table 4 were those used to compute the regression coefficients; the remaining b_{obs} were simply compared with the regression relation. Table 4 also gives the calculated and available observed values of the tetrahedral twist, α (see Part I), except where b_{obs} exceeds b_{tetr}, when the twist is assumed to be zero. The agreement for the two kaolinites is excellent.

Certain minerals in Table 4 merit further discussion. For dickite Newnham (1960) gives the Si-O bonds as 1.62 Å, rather than 1.60 Å,

TABLE 3. RECOMMENDED PREDICTION RELATIONS FOR CALCULATING *b*

Kaolins	$b = (8.923 + 0.125\ Mg + 0.229\ Fe^{2+} + 0.079\ Fe^{3+} + 0.28\ Mn^{2+} + 0.17\ Ti) \pm 0.014$ Å
Chlorites	$b = (9.23 + 0.03\ Fe^{2+}) \pm 0.03$ Å
Micas	$b = (8.925 + 0.099\ K - 0.069\ Ca + 0.062\ Mg + 0.116\ Fe^{2+} + 0.098\ Fe^{3+} + 0.166\ Ti) \pm 0.03$ Å
Montmorillonites	$b = (8.944 + 0.096\ Mg + 0.096\ Fe^{3+} + 0.037\ Al_{tetr.}) \pm 0.012$ Å

TABLE 4. CELL DIMENSIONS AND TETRAHEDRAL ROTATIONS FOR KAOLINS

Mineral	Reference	Composition										b_{ob} Å	b_{calc} Å	b_{tetr} Å	α_{obs} °	α_{calc} °
		Al^{VI}	Mg	Fe^{2+}	Fe^{3+}		Al^{IV}	Si	Fe^{3+}	OH	O					
Kaolinite	Author	2.0						2.0		4.0	5.0	8.924	8.924	9.05		9°34′
Dickite	Author	2.0						2.0		4.0	5.0	8.929	8.924	9.05		9°42′
Halloysite	Author	2.0						2.0		4.0	5.0	8.904	9.924	9.05		10°18′
Dickite	Newnham (1961)	2.0						2.0		4.0	5.0	8.940	8.924	9.05	7½°	8°36′
Nacrite	Brammall *et al.* (1937)	2.0						2.0		4.0	5.0	8.95	8.924	9.05		8°36′
Serpentine	Gillery (1959)	0.75	2.25				0.75	1.25		4.0	5.0	9.193	9.204	9.432		12°54′
Serpentine	Gillery (1959)	0.375	2.62				0.375	1.625		4.0	5.0	9.245	9.250	9.242		0°
Amesite	Steinfink & Brunton (1956)	1.0	2.0				1.0	1.0		4.0	5.0	9.20	9.174	9.56	11°30′	15°48′
Amesite	Brindley *et al.* (1951)	1.06	1.50	0.41			0.99	1.01		4.0	5.0	9.19	9.205	9.56		16°0′
Chamosite	Brindley (1951)	0.76	0.16	1.73	0.02	0.15[2]	0.76	1.24		4.0	5.0	9.333	9.366	9.437		8°12′
Chamosite	Brindley *et al.* (1953)	0.81	0.22	0.02	1.83		0.68	1.32		1.02	7.3	9.10	9.100	9.397		14°28′
Chamosite	Brindley *et al.* (1953)	0.83	0.23	1.82	0.01		0.68	1.32		3.96	5.0	9.379	9.369	9.397		4°24′
Antigorite	Brindley *et al.* (1954)		2.869	0.006	0.060	0.002[3]	0.005	1.954	0.041	4.102	4.898	9.219[1]	9.288	9.052		—
Grovesite	Bannister *et al.* (1955)	0.67	0.07		0.18	2.21[3]	0.68	1.32		3.57	5.42	9.54	9.565	9.391		—
Antigorite	Zussman *et al.* (1957)	0.31	2.73	0.03	0.03		0.102	1.898		3.58	5.42	9.26	9.273	9.11		—
Hydroamesite	Erdelyi *et al.* (1959)	0.203	2.329		0.20		0.448	1.552		3.881	5.12	9.20	9.230	9.164		—
Greenalite	Gruner (1936)			2.2	0.5			2.0		4.0	5.0	9.56	9.467	9.05		—
Cronstedite	Hendricks (1939)			2.3	0.5			1.0	1.0	4.5	5.0	9.49[1]	9.490	10		18°
Cronstedite	Gossner (1935)			2.28	0.60	0.09[4]	0.07	1.07	0.86	4.41	5.59	9.50[1]	9.450	10		18°
Chrysotile	Zussman *et al.* (1957)	0.222	2.704		0.042		0.189	1.811		3.98	4.02	9.21	9.265	9.15		—
Lizardite	Zussman *et al.* (1957)	0.12	2.75		0.02			2.04		3.92	4.08	9.2	9.268	9.05		—
Colerainite	A.S.T.M. index	0.26	2.51		0.04	0.04[4]	0.30	1.70		4.26	4.74	9.20	9.240	9.20		—
Kaolinite	Zviagin (1960)	2.0						2.0		4.0	5.0	8.89	8.924	9.05	10.9°	10.8°
Kaolinite	Drits and Kashaev (1960)	2.0						2.0		4.0	5.0	8.93	8.924	9.05	9°	9°18′
Pyrophyllite	19 cm camera	2.0						4.0		2.0	10.0	8.924	8.924	9.05		9°35′
Talc	19 cm camera		3.0					4.0		2.0	10.0	9.158	9.293	9.05		—
Minnesotaite	Gruner (1944)		0.66	1.96			0.05	3.57	0.10	2.0	10.0	9.40?	9.45	<9.05		?

[1] Assuming Fe^{3+} tetrahedrally does not contribute to b_{calc}, by analogy with Al tetrahedrally. [2]Ti. [3]Mn. [4]Ca.

which should increase α_{obs} relative to α_{calc}; but the average O-Si-O angle, τ is 111.9° approx., which rather more than compensates for the larger bond length. Detailed data for τ are not quoted for amesite, for which there is a larger discrepancy between α_{obs} and α_{calc}.

The values of α for the two serpentines are interesting when compared with their symmetries. One serpentine, with $\alpha=0$, is a one-layer orthoserpentine, the other, with $\alpha=12°54'$, is a six-layer orthoserpentine. It is tempting to suppose that it is the regular surface network of the former which allows this serpentine to form an orthohexagonal cell repeating through only one layer, rather than three or six.

Grovesite and antigorite (Zussman *et al.* 1957) are examples of kaolins in which the tetrahedral layer appears to have stretched to the limit without effectively contracting the octahedral layer; this is shown by the close agreement between b_{calc} and b_{obs}. The angle τ is 106°50′ for grovesite and 106°32′ for the antigorite, *i.e.* at the apparent lower limit of $106\frac{1}{2}$–107° for this angle. The other "antigorite" (Brindley *et al.*, 1954) is clearly one in which the tetrahedral layer has set the limit to expansion; $b_{obs}=9.219$ Å is noticeably less than $b_{calc}=9.288$ Å, even after making $\tau=106°47'$ to allow the tetrahedral layer to stretch to 9.219 Å. In fact this specimen was later called an orthoserpentine. There is, indeed, some evidence suggesting that antigorites have b determined by the octahedral layer, and chrysotiles have b determined by the tetrahedral layer;[1] the chrysotile and lizardite specimens are consistent with this.

The rotation $\alpha=18°$ for cronstedite can only be roughly calculated since the increase in tetrahedral dimensions due to Fe^{3+}- for -Si substitution is not known precisely. The rotation will certainly exceed that for most other kaolins.

The data on greenalite are unsatisfactory. Gruner (1936) gives $b=2\times 9.3$ Å, though Brindley and MacEwan (1953) used another spacing of Gruner's data giving $b=9.56$. Neither of these can be accepted in relation to the quoted structural formula since for the tetrahedral layer to stretch even to 9.32 Å τ drops to $104\frac{1}{2}°$. However if the tetrahedral composition were ($Si_{1.75}\,Fe_{0.25}^{3+}$) and $\tau \doteqdot 107°$ then b_{tetr} will be about 9.3 Å. Gruner pointed out the considerable difficulty in obtaining a satisfactory analysis of greenalite, and data on this mineral obviously need revision.

Pyrophyllite, talc and minnesotaite may be expected to conform to the kaolin b-axis formula, since these layers carry no charge. The calculated and observed values of b for pyrophyllite agree precisely. For talc, however, b corresponds to two Si-O layers with Si-O bonds of 1.60 Å and $\tau=107°27'$, the minimum expected value for τ when *two* tetrahedral layers

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[1] It is hoped to discuss these results, in relation to kaolin morphology, in a later paper.

are fully stretched by *one* octahedral layer, which is itself contracted from 9.29 Å to 9.16 Å. The minnesotaite data are probably wrong, since the observed tetrahedral layer could hardly stretch to 9.40 Å. Gruner (1944) recorded lines at 1.567 Å (intensity 1.0) and 1.514 Å (intensity 0.5), and by these hypotheses the latter is the 060 line, *i.e.* $b=9.08$ Å. That is, the octahedral layer is greatly contracted, from 9.45 to 9.08 Å. This is not impossible (sauconite contracts a comparable amount octahedrally), and the layers of minnesotaite are 9.55 Å thick, compared with 9.26 Å for talc which is similarly compressed and thickened. This mineral also requires re-investigation.

CHLORITE GROUP

Six variates were used initially to compute the regression of b when substitutions occur in $Al_4Si_4O_{10}(OH)_8$, *viz.* Al^{3+} and Cr^{3+} tetrahedrally, and Mg^{2+}, Fe^{2+}, Fe^{3+} and Cr^{3+} octahedrally. Of these only the coefficient for Fe^{2+} was significant, and the overall fit was considerably less satisfactory than for the kaolins. Several two-variate relations were then computed, but the best relation obtainable from the present data is

$$b = 9.23 + 0.03\mathrm{Fe}^{2+} \pm 0.0285 \qquad (1)$$

This should be compared with the regression relation proposed by Hey (1954), *viz.*

$$b = 9.202 + 0.028\mathrm{Fe(total)} + 0.047\mathrm{Mn}^{2+}$$

The available published data on manganiferous chlorites are not sufficiently extensive or reliable to include Mn^{2+} as a variate in (1) above, but when such a term can be computed the coefficient should exceed that for Fe^{2+}, because of the larger ionic radius. The present analysis disagrees with Hey's result in that Fe^{3+} at no stage showed a significant regression coefficient. A comparison of ripidolite and thuringite data (Table 5 Nos. 1 and 3) confirms that Fe^{2+} and Fe^{3+} have quite different effects on b, and suggests that Fe^{2+} (not total Fe) should be used, as in (1).

The relative independence of the b-dimension of chlorites with respect to the smaller cations is rather less surprising when considered in relation to their structures and composition range. Normal chlorites (*e.g.* as defined by Hey, 1954) contain moderate proportions of Mg^{2+} (radius 0.65 Å) and/or Fe^{3+} (0.60 Å) and/or Cr^{3+} (0.64 Å). The analyses by Steinfink (1958) of the prochlorite and corundophillite structures suggest that the various octahedral cations may well be ordered between the two octahedral layers of normal chlorites generally. Hence it is quite possible that even in chlorites with moderate Al content one octahedral layer may contain very little Al. If so then the presence of Al (0.50 Å) in the other layer would not necessarily lead to a smaller overall b axis. That is, the presence of *two* octahedral layers and some Mg or Fe^{3+} in chlorites effectively buffers the *b* axis against variations, except those due to substitutions by much larger cations such as Fe^{2+} (0.75 Å) and Mn^{2+} (0.80 Å); Brindley and Gillery (1956) have put forward similar arguments.

Calculated and observed *b* values are compared in Table 5, which also gives the calculated tetrahedral rotations, α. The observed average rotation is given for prochlorite and corundophillite, from a plot of Steinfink's parameters. Though the agreement between α_{obs} and α_{calc} is only moderate the calculated prochlorite angle exceeds the corundophillite angle as observed. Steinfink reported the O-Si-O angle for prochlorite to be 110.8°, however, and this increases α_{calc} to $9\frac{1}{2}°$, close to $\alpha_{obs} = 10°$; the same angle is not given for corundophillite.

The unusual "chlorite" mineral, cookeite (Norrish, 1952), cannot be considered according to the regression relation above for normal chlorites, since it does not contain Fe^{3+} or Mg. It is therefore the more interesting that for cookeite $b = 8.918$ (Table 5) which is very close to *b* for kaolins and micas (Table 1). This is certainly to be expected since Li behaves much as Al in the variation of *b* with composition.

Several papers have recently reported dioctahedral chlorites, though with insufficient data for inclusion in this regression analysis. Bailey and Tyler (1960) have noted a dioctahedral chlorite for which no analysis is yet available, but which contains some magnesium. The *b* axis, 9.03 Å, is consistent with the present hypotheses. This suggests that if enough data on dioctahedral chlorites eventually become available, then the variation in *b* for all chlorites may be described by a regression relation closely similar to that for the kaolins. As a crude test of this the kaolin relation was applied to the chlorites in Table 5, assuming that the octahedral cations are equally divided between the two octahedral layers. The values of *b* calculated in this way (Table 5) are sufficiently close to b_{obs} to give considerable weight to the suggestion above.

MICAS

The following conditions were imposed on the final regression analysis, as a result of extensive preliminary studies.

1. The analysis was computed to give the increase in *b* when K and Ca, and Mg, Fe^{2+}, Fe^{3+} and Ti are substituted in the paragonite composition, $NaAl_2(Si_3Al)O_{10}(OH)_2$. Micas must contain an interlayer cation, and coefficients for *both* Na and K cannot be satisfactorily determined because these cations are very highly correlated. The early studies had confirmed that tetrahedral Al does not have a significant coefficient, and this variate was omitted.

2. The data were chosen to be sufficiently representative and numerous to give satisfactory average values of the coefficients for prediction pur-

TABLE 5. CELL DIMENSIONS AND TETRAHEDRAL ROTATIONS FOR CHLORITES

Mineral	Reference	Composition									b_{obs} Å	b_{calc} Å	$b_{\text{"kaolin"}}$ Å	α_{obs} °	α_{calc} °
		Mg	Fe^{2+}	Fe^{3+}	Al^{VI}		Al^{IV}	Si	OH	O					
Ripidolite	Gillery (A.S.T.M. index)	2.8	1.7		1.3		1.2	2.8	8.0	10.0	9.283	9.28	9.29		7°6′
Bavalite	Gillery (A.S.T.M. index)	0.4	4.2		1.5		1.4	2.6	8.0	10.2	9.365	9.36	9.43		5°24′
Thuringite	Gillery (A.S.T.M. index)	2.2	0.7	1.4	1.2		1.5	2.5	7.7	10.2	9.192	9.25	9.19		13°
Grochanite	Gillery (A.S.T.M. index)	4.2	0.22		1.22		1.4	2.6	8.0	10.0	9.227	9.23	9.21		11°12′
Diabantite	Gillery (A.S.T.M. index)	2.9	2.2	0.2	0.7		1.1	2.9	7.7	10.7	9.305	9.30	9.36		4°12′
Kammererite	Gillery (A.S.T.M. index)	5.1	0.2		0.2	0.6[3]	0.9	3.1	6.6	10.8	9.242	9.24	9.26		5°6′
Sheridanite	Gillery (A.S.T.M. index)	4.3	0.1		1.6		1.5	2.5	7.9	10.1	9.226	9.23	9.20		12°
Chrome Chlorites	Lapham (1958)	Eight similar analyses and x-ray data									9.222	9.23–9.25			
Mg-Chamosite	Bannister & Whittard (1945)	1.84	2.82		1.21		1.12	2.87	7.7	10.3	9.33	9.32	9.36		0°
Pennantite	Structure Reports, 10, 157.	0.25		0.37	1.18	3.82[1]	1.38	2.62	7.3	10.1	9.40	9.36[1]	9.47		0°
Thuringite	Structure Reports, 10, 157.	0.70	3.70	0.75	0.85		1.60	2.40	8.0	10.0	9.30	9.34	9.42		10°27′
Thuringite	Structure Reports, 10, 157.		3.85	0.75	1.40		1.30	2.70	8.6	10.3	9.31	9.35	9.39		7°
Bavalite	Structure Reports, 10, 157.	0.35	4.75	0.05	0.80		1.75	2.25	7.0	10.0	9.35	9.37	9.49		10°
Diabantite	Bannister & Whittard (1945)	2.53	2.16	0.18	0.76	0.12[5]	0.58	3.42	8.0	10.0	9.29	9.29	9.34		
		$b_{tetr.}=9.20$; tetr. layer stretched, O-Si-O$<$109°28′													
Daphnite	Bannister & Whittard (1945)	0.92	3.37	0.18	1.35	0.04[4]	1.29	2.71	8.0	10.0	9.38	9.33	9.38		0°
Chamosite	Bannister & Whittard (1945)	0.75	3.23	0.56	1.12		1.01	2.99	8.0	10.0	9.36	9.33	9.36		—
		$b_{tetr.}=9.31$; O-Si-O$<$109°28′													
Thuringite	Bannister & Whittard (1945)	0.72	3.68	0.76	0.83		1.58	2.42	8.0	10.0	9.32	9.34	9.42		9°45′
Corundophillite	Steinfink (1958)	4.9	0.07	0.17	0.75	0.18[3]	1.4	2.6	8.0	10.0	9.27	9.23	9.24	7.5°	9°30′
Prochlorite	Steinfink (1958a)	2.6	0.2	1.5	1.2		1.8	2.2	8.0	10.0	9.30	9.24	9.17	10°	11°48′
Chamosite	von Wolff (1942)	0.75	3.35	0.6	1.3		0.9	3.1	8.8	10.0	9.36	9.33	9.38		—
		$b_{tetr.}=9.28$; O-Si-O $<$109°28′													
Leuchtenbergite	McMurchy (1934)	5.2			0.82		1.1	2.9	8.0	10.0	9.19	9.23	9.24		9°55′
Sheridanite	McMurchy (1934)	4.6	0.02	0.10	1.30		1.4	2.6	8.0	10.0	9.21	9.23	9.21		11°42′
Chlorite	McMurchy (1934)	3.9	0.70		1.40		1.4	2.6	8.0	10.0	9.21	9.25	9.24		11°42′
Prochlorite	McMurchy (1934)	2.7	2.3		1.01		1.58	2.42	8.0	10.0	9.27	9.30	9.36		11°24′
Cookeite	Norrish (1952)	3.79				1.36[6]	0.85	3.15	8.16	9.84	8.918		8.924		14°10′
Chrome Chlorite	Brown and Bailey (1960)	5.05	0.11	0.04	0.17	0.71[3]	0.97	3.03	7.9	10.0	9.250	9.23[2]	9.29[2]	6°	5°58′

[1] Assuming a coefficient for Mn $=0.033$. [2] Assuming same coefficient for Cr as for Mg. [3] Cr. [4] Mn. [5] Ca. [6] Li.

TABLE 6. CELL DIMENSIONS FOR MICAS

Mineral	No.[1]	b_{obs}	b_{cal}	b_{kaolin}	Mineral	No.[1]	b_{obs}	b_{calc}	b_{kaolin}
Biotite	1	9.265	9.261	9.39	Biotite	24	9.265	9.271	9.40
Biotite	2	9.247	9.238	9.19	Phlogopite	25	9.241	9.185	9.34
Biotite	3	9.268	9.249	9.37	Phlogopite	26	9.22	9.195	9.31
Biotite	4	9.251	9.220	9.33	Phlogopite	27	9.204	9.210	9.30
Biotite	5	9.261	9.257	9.36	Fluorophlogopite	28	9.195	9.210	9.30
Biotite	6	9.251	9.266	9.41	Fluorophlogopite	29	9.188	9.208	9.30
Biotite	7	9.257	9.260	9.37	Muscovite	30	8.995	9.034	8.94
Biotite	8	9.225	9.248	9.27	Iron Muscovite	31	9.06	9.077	9.01
Biotite	9	9.254	9.249	9.35	Paragonite	32	8.90	8.925	8.92
Biotite	10	9.265	9.226	9.16	Lepidolite	33	9.006	9.008	8.94
Biotite	11	9.262	9.274	9.39	Lepidolite	34	8.97	9.024	8.94
Biotite	12	9.206	9.252	9.20	Zinnwaldite	39	9.12	9.094	9.07
Biotite	13	9.308	9.298	9.42	Zinnwaldite	40	9.06	9.063	9.02
Biotite	14	9.246	9.253	9.36	Lithium biotite	41	9.21	9.155	9.21
Biotite	15	9.255	9.231	9.20	Lithium biotite	42	9.09	9.088	9.09
Biotite	16	9.253	9.258	9.38	Gümbelite	43	9.04	9.017	8.97
Biotite	17	9.215	9.234	9.20	Lepidomelane	44	9.29	9.288	9.41
Biotite	18	9.328	9.284	9.43	Margarite	45	8.92	8.925	8.92
Biotite	19	9.266	9.258	9.35	Xanthophyllite	47	9.00	8.984	9.20
Biotite	20	9.300	9.330	9.49	Xanthophyllite	48	9.01	9.004	9.20
Biotite	21	9.323	9.303	9.45	Xanthophyllite	49	9.00	9.005	9.22
Biotite	22	9.260	9.262	9.37	Xanthophyllite	50	9.02	9.003	9.21
Biotite	23	9.271	9.234	9.37					
Celadonite	35	9.02	9.185	9.12	Celadonite	38	9.08	9.192	9.21
Celadonite	36	9.05	9.188	9.15	Ephesite	46	8.896	8.926	8.93
Celadonite	37	9.06	9.106	9.08	Bityite	51	8.713	8.856	8.92
					Bityite	52	8.67	8.859	8.93

[1] These numbers correspond with those in Table 4 of Part I, in which the structural formulae are listed.

poses. This is important because the linear model cannot be completely obeyed by all cations for all micas, and in particular the interlayer cations will sometimes increase b (*e.g.* muscovite *cf.* paragonite) and sometimes decrease b (*e.g.* xanthophyllite). The regression coefficients therefore will depend somewhat on the data analysed; the exclusion of all dioctahedral micas, for example, would probably considerably decrease the coefficient for K^+. Likewise the coefficients for the octahedral cations are not independent of the effects of the interlayer cations, and their values will not be as precise for the micas as for the kaolins.

3. The micas ephesite, bityite and celadonite were not included in the analysis, and data on these minerals (Table 6) were simply checked against the prediction relation. The new value of b for ephesite (Part I) was not available in time to include in the analysis. No precise account can be taken for Be tetrahedrally, so that bityite was omitted. Celadonites are also excluded, because the octahedral layer of this mineral is charge deficient, and it is therefore probably disproportionately thick. The preliminary regression analyses showed a marked improvement in R^2 when nos. 35–38 were omitted. No. 37 (Table 6), which has an appre-

ciable amount of Al octahedrally and probably should not be named a celadonite, may be expected to conform more readily to the model. For this mineral b_{obs} and b_{calc} differ by less than two standard errors, but for nos. 35, 36 and 38 this difference is between 4 and 6 standard errors. Lepidolites (which also are charge deficient octahedrally) conform to the regression relation simply because $b_{calc}=b_0$, *i.e.* the Li^+ does not effectively increase the volume of their octahedral layers.

The regression analysis of 45 micas (Table 6) yielded coefficients showing several interesting features (Table 1). The surprisingly high value of R^2 shows that condition 2 (above) was observed. The value of b_0 is effectively identical with that for the kaolins, which suggests that Na^+ neither increases nor decreases the dimensions set by the dioctahedral Al layer. (This is consistent with the discussion of paragonite, Part I.) The Ca^{2+} coefficient is negative, even though Ca^{2+} (0.99 Å) exceeds Na^+ (0.90 Å) in size, but this coefficient depends considerably on the xanthophyllite data, whose composition ensures that Ca^{2+} markedly contracts b.

The sizes of the holes filled, r_h, and the constants of proportionality, k, were determined from three pairs of simultaneous equations (Table 2). The coefficients for both the interlayer cations and the divalent and trivalent octahedral cations were analysed separately, since there is considerable evidence of ordering of these in the mica structures. The high values of k for the interlayer cations ($=2.03$) and divalent ions ($=1.86$) confirms that the model is not invariant for either of these groups whereas the smaller value (*viz.* 1.18) for the trivalent ions shows that these obey the model more closely. Physically the latter appear to substitute directly into Al sites, and in fact the "hole" size ($r_h=0.48$ Å) approximates the Al radius (0.50 Å). The interlayer cation sometimes increases and sometimes decreases b (2., above), and hence k is high. It appears probable that small amounts (<1.0) of divalent cations occupy mainly the unique octahedral sites, whereas larger amounts (<2.0) tend to occupy the two symmetry-related sites. (In muscovite the former is vacant and considerably larger than the Al-occupied sites.) Ordering of this kind, which under some circumstances could lead to an inconsistent model for the divalent cations (*i.e.* higher k) will be discussed in a later paper.

The effect of the interlayer cation on b may be estimated in general terms by comparing b_{obs} with b_{kaolin} (Table 6), *i.e.* with b computed for the micas using the *kaolin* relation. Since b_{kaolin} generally exceeds b_{obs} for phlogopites and biotites the K^+ apparently contracts b_{oct} in these minerals. But the high iron biotites, before and after heating to convert Fe^{2+} to Fe^{3+}, now form an interesting group. For nos. 2, 10 and 15 $b_{kaolin} < b_{obs}$, and of these the b axes of 10 and 15 represent a slight *increase*, and of 2 only a very small decrease relative to b for the unheated specimens

(9, 14 and 1, respectively). For nos. 12 and 17 $b_{\text{kaolin}} \fallingdotseq b_{\text{obs}}$, and b_{obs} is noticeably less than b_{obs} for nos. 11 and 16 respectively (the unheated specimens). This is to be expected with normal biotites since Fe^{3+} (0.60 Å) is smaller than Fe^{2+} (0.75 Å). These data suggest that in normal biotites interlayer K decreases *b* slightly, or has no effect, but for the very unusual "biotites," nos. 10 and 15, K is increasing *b;* this again indicates the varying role of the interlayer cations.

MONTMORILLONITES

The interpretation of chemical analyses of montmorillonites is much more difficult than of kaolins and micas, as Kelley (1945) has especially pointed out. The acid dissolution studies of Osthaus (1956) and others clearly show the problem of obtaining really pure specimens. The readiness with which Fe^{2+} is oxidised to Fe^{3+} in the minerals also suggests that structural formulae must be viewed cautiously. Errors in these formulae may therefore occur due to impurities, or else to more systematic errors inherent in the chemical techniques.

The final regression analysis for montmorillonites was computed to give the increase in *b* when substitutions occur in $Al_2Si_4O_{10}(OH)_2$ essentially, of Al^{3+} tetrahedrally and Mg and Fe^{3+} octahedrally. The omission of Fe^{2+} points to the restricted range of montmorillonite compositions which can be included in the regression analysis, a serious disadvantage statistically. Ferrous iron occurs in insignificant proportions in montmorillonite formulae, of course; but montmorillonites high in Mg, Fe^{3+}, Mn, Zn and other larger cations equally must be excluded. For these montmorillonites the overall composition ensures that $b_{\text{tetr}} \leq b_{\text{obs}} < b_{\text{oct}}$ which is not permitted (*v.* introduction). It is, however, reasonable to suppose that vermiculites will behave in a closely similar way to montmorillonites, and several have been included to widen the range of compositions analysed for multiple regression.

The results of the regression analysis of the minerals in Table 7a (excepting volchonskoite) are given in Table 1, the relations between ionic radii and regression coefficients in Table 2, and the recommended prediction relation in Table 3. The very high value of $R^2 = 0.987$, confirms that variations in "*b*' for these data are almost completely explained by the regression of "*b*" on the ionic substitutions. The base constant, 8.944 Å is very close to 8.923 Å for kaolins and 8.925 Å for micas. Although most minerals in Table 7a are dioctahedral, both cardenite and the vermiculites are more nearly trioctahedral; it is an artifact that the relation cannot cover more trioctahedral minerals.

It is immediately obvious that the coefficient for tetrahedral Al is significant, contrary to prediction. This may be regarded in two ways,

TABLE 7. A. CELL DIMENSIONS AND TETRAHEDRAL ROTATIONS FOR MONTMORILLONITES

Mineral	Reference	Composition (cations only)									b_{obs} Å	b_{calc} Å	b_{tetr} Å	b "kaolin" Å	α_{calc} °
		Al^{VI}	Fe^{2+}	Fe^{3+}	Mg	Zn		Si	Al^{IV}	Fe^{3+}					
Montmorillonites:															
Santa Rita, N.M.	Osthaus (1956)	1.460		0.059	0.487			4.00			8.993	8.996	9.051	8.989	6°30′
Belle Fourche, S.D.	Osthaus (1956)	1.550		0.213	0.232			3.804	0.196		8.993	8.994	9.101	8.969	8°49′
Merritt, B.C.	Osthaus (1956)	1.513		0.271	0.231			3.776	0.224		9.000	9.000	9.108	8.973	8°50′
Clay Spur, Wyo.	Osthaus (1956)	1.583		0.180	0.254			3.866	0.117	0.017	9.001	8.991	9.087	8.969	7°53′
Polkville, Miss.	Osthaus (1956)	1.465		0.030	0.489			4.000			9.002	8.997	9.051	8.989	5°55′
Amory, Miss.	Osthaus (1956)	1.458		0.181	0.310			3.912	0.088		9.004	8.994	9.074	8.976	7°6′
Plymouth, Utah	Osthaus (1956)	1.418		0.187	0.406			3.877	0.077	0.046	9.011	9.006	9.083	8.989	7°12′
Otay, Calif.	Osthaus (1956)	1.281		0.062	0.705			4.000			9.014	9.018	9.051	9.016	5°8′
Little Rock, Ark.	Earley *et al.* (1953)	1.507		0.307	0.201			3.799	0.201		8.996	9.000	9.102	8.985	8°46′
Chambers, Ariz.	Earley *et al.* (1953)	1.374		0.192	0.465			3.846	0.154		9.004	9.013	9.090	8.996	7°53′
Upton, Wyo.	Foster (1953)	1.55		0.20	0.25			3.90	0.10		8.997^1	8.991	9.076	8.970	7°36′
Belle Fourche, S.D.	Foster (1953)	1.57	0.02	0.18	0.23			3.91	0.09		8.988^1	8.989	9.074	8.971	7°54′
Lemon, Miss.	Foster (1951)	1.45	0.01	0.16	0.44			3.89	0.11		9.019^1	9.008	9.079	8.993	6°37′
Rideout, Utah	Foster (1953)	1.55		0.06	0.39			3.97	0.03		8.994^1	8.988	9.059	8.976	6°53′
San Antonio, Texas	Foster (1953)	1.57		0.12	0.30			3.99	0.01		8.997^1	8.985	9.054	8.968	6°25′
Honeycomb, Utah	Sand and Regis (1960)	1.45			0.58		0.16^2	4.00			8.979^1	8.999	9.051	8.996	7°13′
Unter-Rupsroth	Nagelschmidt (1938)	1.77		0.03	0.20			3.74	0.26		9.00	8.976	9.117	8.950	9°12′
Black Jack, Idaho	Nagelschmidt (1938)	1.96		0.04				3.46	0.54		8.94	8.950	9.188	8.926	13°10′
Black Jack, Idaho	Weir (1960)	1.98		0.02	0.01			3.48	0.52		8.978^1	8.966	9.183	8.926	12°0′
Nontronites:															
Manito, Wash	Kerr *et al.* (1950)	0.03		2.02	0.005			3.50	0.50		9.155^1	9.145	9.178	9.083	4°0′
Garfield, Wash.	Kerr *et al.* (1950)	0.05		1.93	0.12			3.50	0.50		9.175^1	9.159	9.178	9.090	0°
Nontron	Nagelschmidt (1938)	0.08		1.84	0.08			3.72	0.28		9.12	9.139	9.122	9.078	0°
Behenjy	Nagelschmidt (1938)	0.08	0.04	1.79	0.08			3.57	0.43		9.13	9.141	9.160	9.084	4°30′
Batavite	Weiss *et al.* (1955)	0.33			2.64			2.99	1.01		9.22	9.235	9.308	9.253	8°18′
Cardenite	MacEwan (1954)	0.45	0.15	0.69	1.50		0.12^3	3.09	0.91		9.20	9.207	9.283	9.200	7°40′
Galapektite	Faust (1957)	1.56		0.11	0.39			3.88	0.12		8.988	8.996	9.080	8.980	8°10′
Vermiculite	Mathieson and Walker (1954)	0.16		0.48	2.36			2.73	1.27		9.262^1	9.264	9.373	9.256	8°42′
Vermiculite	Walker (1961)	0.22	0.08	0.46	1.92		0.11^4	2.72	1.28		9.222^1	9.239	9.376	9.236	10°24′
Vermiculite	Walker (1961)	0.170	0.023	0.232	2.239			2.837	1.163		9.244^1	9.226	9.348	9.226	8°35′
Vermiculite	Walker (1961)		0.037	0.365	2.238		0.056^4	2.853	1.024	0.123	9.253^1	9.247	9.312	9.250	6°27′
Volchonskoite	Weiss *et al.* (1954)	0.40		0.58	0.82		0.35^5	3.82	0.18		8.94	9.119	9.097	9.099	

TABLE 7. B. CELL DIMENSIONS FOR SAPONITES, SAUCONITES, HECTORITES ETC.

Mineral	Reference	Composition (cations only)									b_{obs} Å	b_{calc} Å	b_{tetr} Å	b "kaolin" Å	O-Si-O angle
		Al^{VI}	Fe^{2+}	Fe^{3+}	Mg	Zn		Si	Al^{IV}	Fe^{3+}					
Saponite	Faust (1957)		0.26	0.45	2.29			3.19	0.75	0.06	9.258	9.268	9.259	9.304	109°28′
Saponite	Cahoon (1954)	0.04		0.01	2.85			3.70	0.30		9.165^1	9.230	9.127	9.280	108°12′
Saponite	Weiss *et al.* (1955)	0.03		0.02	2.95			3.38	0.62		9.218^1	9.253	2.209	9.293	109°28′
Saponite	Schmidt and Heystek (1953)			0.01	2.99			3.63	0.37		9.198^1	9.246	9.145	2.298	108°31′
Saponite	Mackenzie (1957)	0.15		0.04	2.92		0.005^6	3.495	0.505		9.178^1	9.251	9.179	9.293	109°28′
Saponite	Midgley and Gross (1956)	0.05	0.05		2.91			3.38	0.52	0.10	9.197^1	9.255	9.20	9.298	109°28′
Griffithite	Faust (1957)	0.04	0.52	0.44	1.88			3.19	0.81		9.246	9.264	9.256	9.312	109°28′
Sauconite	Ross (1946)	0.79		0.02	0.14	1.85		3.30	0.70		9.228^1		9.229	9.366	109°30′
Sauconite	Ross (1946)	0.78		0.23	0.15	1.54		3.39	0.61		9.220^1		9.206	9.313	109°14′
Sauconite	Ross (1946)	0.12		0.13	0.11	2.64		3.27	0.73		9.251^1		9.237	9.552	109°14′
Sauconite	Ross (1946)	0.04		0.02	0.10	2.89	0.01^6	3.35	0.65		9.247^1		9.216	9.599	108°56′
Sauconite	Ross (1946)	0.17		0.58	0.12	1.95		3.39	0.61		9.259^1		9.206	9.430	108°30′
Sauconite	Ross (1946)	0.22		0.17	0.18	2.40		3.47	0.53		9.252^1		9.186	9.509	108°16′
Hectorite	Kerr *et al.* (1950)	0.008			2.71		0.34^2	4.00			9.119^1	9.204	9.051	9.262	108°12′
Stevensite	Faust (1957)			0.02	2.88		0.02^6	4.00			9.156	9.221	9.051	9.290	107°30′
Talc	Stemple & Brindley (1960)				3.0			4.0			9.158	9.230	9.051	9.298	107°30′
Talc	Author				3.0			4.0			9.171^1	9.230	9.051	9.298	107°12′
Hectorite	Nagelschmidt (1938)				2.73		0.33^2	3.89	0.05		9.18	9.208	9.064	9.264	107°17′

[1] Original data, obtained using CoKα radiation, calibrated 19 cm diam. camera. [2]Li. [3]Ca. [4]Ti. [5]Cr. [6]Mn.

viz. (1) as real for these data, but that the data are systematically erroneous, or (2) as real for montmorillonites. As stated above, the first possibility cannot be entirely dismissed for montmorillonites; and in fact the *b*-axis formula for ***kaolins*** works very well for most minerals in Table 7a. It requires only small changes in certain structural formulae to make the Al_{tetr} coefficient non-significant.

The tetrahedral Al may really increase *b* for montmorillonites, however. The value of the coefficient then is very reasonable, and such an increase is not entirely incompatible with the non-significant coefficient found for Al_{tetr} for kaolins and micas. Suppose that in all the layer silicates the tetrahedral layers exert a *very* small expansive force (when $\alpha > 0$). In kaolins there is only one tetrahedral layer per octahedral layer, and in micas the interlayer cation dominates the tetrahedral twist. But in montmorillonites the small forces due to *two* tetrahedral layers per octahedral layer may just have a noticeable effect. In this case the coefficient will be small for tetrahedral Al; and in fact the observed coefficient is rather smaller than that suggested by the difference in ionic radii of Si and Al (Table 2).

The coefficients for Mg and Fe^{3+} are identical, and assuming a proportionality constant $k = 1$ for these two octahedral cations then the "hole" for Mg, 0.554, is larger than that for Fe^{3+}, 0.504, which is very close to the Al radius, 0.50. This again suggests, as for the micas, the possibility of ordering in the way in which divalent Mg and Fe^{3+} enter the octahedral sites.

If the coefficient for Al_{tetr} is real, then the base constant for montmorillonites will be slightly greater than for kaolins and micas (as observed), since montmorillonites always contain some Mg, Fe and/or Al_{tetr}.

It is worth noting that nontronites have rather smaller tetrahedral twists than montmorillonites. For vermiculite $\alpha_{obs} = 5\frac{1}{2}°$ (Mathieson and Walker, 1954) compared with $\alpha_{calc} = 8°42'$. Their paper quotes $b = 9.18$ Å, and $\sqrt{3}a = 9.23$ Å; from a 19 cm powder photograph $b = 9.262$ Å, giving $\alpha = 8°42'$. The Si-O bonds to the basal oxygens are shorter than predicted from Smith's (1954) curve, accounting for the smaller actual α.

The omission of volchonskoite raised R^2 for the regression analysis from 0.8 approx. to 0.987, confirming the doubts felt about the data for this mineral, which is very rarely pure. The value of b_{obs} seems far too low.

Table 7b gives *b*-axis data on montmorillonites for which $b_{tetr} \leq b_{obs}$. It is assumed that b_{kaolin} is close to the dimension which the octahedral layers of these minerals would have if free.

Considering the saponite data, first, these clearly suggest that the $b_{obs.}$ values are determined by the dimensions of the tetrahedral layers, to which the octahedral layers contract; $b_{obs} = b_{tetr} < b_{oct}$ for four out of the six saponites. This contrasts with the serpentines; the saponites are 2:1 minerals, compared with the 1:1 serpentines.

The tetrahedral layers of sauconites are somewhat stretched, which decreases the O-Si-O angle to about $108\frac{1}{2}°$. The octahedral layers are considerably contracted (by 0.20 to 0.25 Å) to meet the tetrahedral dimensions. Contractions in this layer will occur primarily by changes in the oxygen-cation-oxygen bond angles, and such changes will occur more easily as the radius ratio, cation/oxygen, increases. This ratio for Zn is 0.53 (*cf.* 0.46 for Mg and 0.36 for Al), so that octahedral layers of sauconites can contract further if necessary than those of, say, hectorites.

Hectorite, stevensite and talc are 2:1 minerals in which a fully siliceous tetrahedral layer is stretched to its limit by a fully magnesic octahedral layer. The O-Si-O angle is reduced to $107\frac{1}{2}°$ or slightly less. The chrysotiles, which are the 1:1 analogue, do not show a comparable octahedral contraction. The presence of only one tetrahedral layer allows the strain between octahedral and tetrahedral sheets to be relieved by curling and by adopting non-stoichiometric compositions.

Discussion

The *b*-axis formulae proposed in this paper as a result of the multiple regression analyses of kaolin, chlorite, mica and montmorillonite data separately appear to be more soundly based theoretically (see Part I) and to yield better predictions in practice than previous formulae.

There are few minerals which do not conform to the model implicit in these formulae, *viz.* (1) chrysotiles for which b_{oct} so exceeds b_{tetr} that the latter takes control; (2) celadonite, with excess octahedral layer charge; (3) dioctahedral chlorites, for which there are insufficient data to adjust the regression relations suitably; and (4) trioctahedral montmorillonites and talc, for which the tetrahedral layers again take control.

The availability of considerably more and better data in the future may alter the basis for calculating these relationships in only one major way. If many data become available on dioctahedral chlorites, then their inclusion may change the present equation to one closely similar to the kaolin relation. However, the coefficient for tetrahedral Al for montmorillonites may no longer be significant when more good data can be analysed. If so, then the prediction relations for kaolins, chlorites and montmorillonites may be sufficiently close to each other so that one relationship will serve to predict *b* axes for all these minerals. The micas, however, not only require additional terms for the interlayer cations but these cations may be indirectly affecting the coefficients for octahedral cations, so preventing the proposal of one total prediction relationship for all layer silicates.

A prediction relation for minerals for which the tetrahedral layers are hexagonal ($\alpha=0$) can scarcely be proposed because of the variety of mechanisms involved in adjusting the layer dimensions to each other.

It is instructive to reconsider the pairs of minerals from which the coefficients have been derived for previous *b*-axis formulae.

a) Pyrophyllite-muscovite. MacEwan (1951) and Brown (1951) both considered this pair in order to arrive at a contribution for tetrahedral Al. As discussed in Part I it is equally valid to consider pyrophyllite-paragonite, which gives a zero coefficient; therefore it is not valid to deduce a coefficient for tetrahedral Al in this way.

b) Pyrophyllite-talc. MacEwan (1951) and Brown (1951) deduced a coefficient for Mg from this pair of minerals, and coefficients for other ions were then taken as proportional to the ionic radii. This is very likely to be invalid since the *b* axis of talc is determined solely by the maximum limit to which a purely Si-O tetrahedral layer can be stretched (by a decrease in the O-Si-O angles).

c) Gibbsite-brucite-$Fe(OH)_2$. Brindley and MacEwan (1953) based their coefficients on the *b* dimensions of the hydroxides. Bernal and Megaw (1935), who studied the metallic hydroxides in detail, pointed out that cations with the polarizing power of Al and higher induce hydroxyl bonding on the surface of their hydroxides, with a clear shortening effect on the *b* axis. It is therefore invalid to deduce coefficients for *b*-axis formulae by considering the pair gibbsite-brucite.

d) Si-O bond lengths. Brindley and MacEwan (1953) based their tetrahedral term on the known Si-O and Al-O bond lengths, but this has now been shown to be irrevelant to the *b* dimension.

Previous *b*-axis formulae (e.g. Brown, 1951) have omitted a term for Li because better agreement with b_{obs} is obtained by treating Li, radius 0.60 Å, as if it were Al, radius 0.50 Å. The implied reason has been that since Li is more readily polarized it may be squeezed more easily into a small site. This cannot, however, be readily settled since Li does not occur in moderate ionic proportions except in hectorite, cookeite, lepidolite and zinnwaldite. No information is obtainable from hectorite in which $b_{obs}=9.16$ Å is determined by the tetrahedral layer which is stretched to the limit. Nor can deductions be made from cookeite, which is probably comparable structurally to kaolinite and dickite. In the latter the vacant site is much bigger than the Al sites, and is sufficiently large to accommodate the Li ion, so that deductions about the Li coefficient cannot be soundly based on cookeite alone.

Similar arguments do not seem to apply to lepidolites high in Li, yet the *b* dimensions of lepidolites vary surprisingly little from 9.00 Å. This suggests that Li does not increase *b*, but it would be interesting to know the Li-O bond lengths in a lepidolite. The two zinnwaldites in Table 6 also give good agreement between b_{obs} and b_{calc} when Li is equated to Al. White *et al.* (1960) have claimed to have inserted Li into the muscovite structure experimentally and state that this does not increase *b*. The vacant site is, of course, quite large enough to accept Li (0.60 Å) readily (Radoslovich, 1960).

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