THE AMERICAN MINERALOGIST, VOL. 48, MARCH–APRIL, 1963

THE CELL DIMENSIONS AND SYMMETRY OF LAYER-LATTICE SILICATES. V. COMPOSITION LIMITS

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

ABSTRACT

The reported limits of stability (from synthesis studies) and also the observed ranges of compositions for natural specimens may be used as independent checks on the validity of current theoretical models of these structures. These models (Parts I–IV) allow broad limits to be set to the strains from preferred lengths and shapes which different structural components (bonds, polyhedral groups) can reasonably tolerate in adjusting to some local dimensional misfit. The formation of micas in which such strains should far exceed these limits should not be possible, even in the laboratory. Micas in which the strains would need to be unusually large may be expected to adjust their compositions rapidly, as soon as their environment allowed any change. They may therefore be synthesized but should—for at least this reason—be rare as natural specimens. It is not yet possible, of course, to predict precise composition limits for micas on structural grounds.

An examination of the detailed published composition limits for micas shows that the present structural models are not at all incompatible with these, nor is there any discrepancy with the rather less well defined limits of other layer silicates.

INTRODUCTION

A preliminary attempt has been made to relate recent theoretical models of structures of the layer silicates[1] to their reported limits of chemical composition. Although at this stage several severe restrictions must be observed it is still useful to review the structural concepts in relation to observed limits of composition for at least two reasons. Firstly, if the structural concepts are essentially correct then no minerals (natural or synthetic) should be found for which the internal stresses would appear to be totally incompatible with even a metastable existence at room temperature. The observance of such a "forbidden" structure would require re-appraisal of the structure models. Secondly, it now seems possible to suggest at what compositions the internal stresses and strains (due to increasing misfit within these structures) should start to become large. It seems reasonable to assume that minerals existing metastably but with very large internal stresses would undergo some change as soon as any factor in the local environment becomes at all conducive to change. That is, the probability of such minerals being found naturally should be small for this reason alone, in addition to any other controlling factors. Natural composition limits (*e.g.* those of Foster 1956, 1960 a, b, c) are not likely to include minerals for which large internal stresses would be predicted structurally. Again this is mainly a test of the compatibility of

---

[1] Discussed in Parts I–IV, *i.e.* Radoslovich and Norrish (1962), Radoslovich (1962a), Veitch and Radoslovich (1962), and Radoslovich (1962b).

present structural concepts with observed composition limits. There may, however, be some instance where there is no other acceptable explanation for an observed restriction of composition, and the suggested structural restraint then merits further study.

Since the studies defining composition limits have been of at least two distinct kinds it is necessary to set certain restrictions on the present discussion.

Foster (1956; 1960 a, b, c) has very carefully assessed the probable composition limits for naturally occurring micas from a critical review of published chemical analyses, essentially of specimens found by geologists exploring the earth's surface. Nothing is thereby implied about the possibilities for forming micas of more extreme composition either in the laboratory or in some quite unusual geological environment. The observed limits of natural micas include those imposed by the requirements that a given mica must exist at least metastably under near surface conditions (*e.g.* of temperature, pressure and chemical environment) for a sufficient period after formation, so that there can be a small but real probability of a specimen being found somewhere.

Yoder (1959) and others have, as an entirely different approach, studied experimentally the stability fields for the layer silicates for varying temperatures, pressures, known melt compositions and other parameters. Such laboratory studies not only define the appropriate stability fields, but also confirm that many layer silicates formed stably at elevated temperatures and pressures can be quenched and retained for indefinite periods metastably at atmospheric conditions. However, the stability fields of natural micas are probably more restricted, because more elements are available under geologic conditions (allowing alternative minerals to crystallize) and because the natural abundance of the elements may not be favorable for the formation of certain micas. Furthermore their formation temperatures and pressures may differ considerably from those at which the experimental studies have been made, *e. g.* by having a smaller range.

Any discussion of observed composition limits in relation to structural ideas must therefore take note of the nature of those reported limits. Moreover, there may well be no direct relation between structure and composition limits in many cases. For example a mica of a certain unusual composition may never be found naturally simply because nature never provides the right physical and chemical conditions of formation. Again, such a mica may not persist metastably at normal temperatures even though natural conditions have existed suitable for its formation; or if it persisted through quenching then it may break down extremely rapidly for physico-chemical rather than specifically structural reasons.

It is equally difficult to use the available structural data to predict an acceptable stability field for some unusual theoretical mica. Even if the available structure analyses permit sensible estimates of the internal stresses such a mineral would have at room temperature they do not allow satisfactory extrapolation of these estimates to the conditions of rock formation. There are virtually no direct studies of the variation of given bondlengths with temperature, except unpublished data by Young (1962) which show—within the moderate errors involved—no significant change in the Si-O bonds in quartz up to 600° C.

From the empirical study (Part IV) of various interatomic forces in the layer silicates it seems that micas should be rare whose compositions would contravene one or more of the following restraints.

(1) In the interlayer region structural adjustments should be possible which allow each cation to approach approximately to within contact distance (sum of ionic radii for the requisite coordination) with at least six surface oxygens (Part I). Also, two interlayer cations which would strongly influence the layers of a structure in opposing directions are unlikely to be found together in one mineral; the local strains would be too severe.

(2) For the tetrahedral layers there are limits to the stretching (in their own plane) which may be imposed by the rest of the structure. Any such stretching should not require the basal oxygens to approach intolerably close (aver. O-O not less than 2.55 Å) to the apex oxygens along tetrahedral edges.[1]

(3) For the octahedral layers there are limits both of dimensions and (probably) of arrangement. Such layers tend to be as large in the *a-b* plane as the shortening of shared octahedral edges to about 2.35 Å (with some slight lengthening of bonds) will allow (Part IV), but can be no larger. Conversely a contraction can be imposed on the *a-b* dimensions of octahedral layers, by lengthening shared edges, giving a closer approach of octahedral cations. Clearly the mutual repulsion of the cations will rise rapidly as they come closer together, especially since the intervening (and partially shielding) anions must move apart along shared edges at the same time. Thus any contraction which a given octahedral layer must undergo to fit into some hypothetical structure will be effectively limited by this increasing cation-cation repulsion.

The apparently general tendency towards the ordering of octahedral cations of different valency and size (Parts III and IV) implies further possible structural restraints on composition limits.

---

[1] This is discussed further in Part VI (Radoslovich, 1962c).

Foster's studies (1956, 1960a, b, c), which also summarize much other work, have shown that the layer compositions of micas are best discussed under the following headings:

Dioctahedral micas: muscovites, celadonites.
Trioctahedral micas: phlogopites, biotites, siderophyllites
Lithium micas: lithium muscovites, lepidolites, siderophyllites

SOME OBSERVED COMPOSITION LIMITS

Muscovite-paragonite. Eugster and Yoder (1955) studied the stability limits of solid solution between muscovite and paragonite. Their preliminary phase diagram for the subsolidus region of this join shows very limited solid solution at normal temperatures (about 3% paragonite in muscovite and vice versa) with a steady rise in solid solution with temperature. These results appear to be explained by the very different situation of K in muscovite and Na in paragonite (Parts I and IV). In $2M_1$ muscovite the K actively increases the sheet dimensions which the octahedral layers would otherwise adopt, and also props successive layers far apart. The average twist tetrahedrally is 13.7° and half the tetrahedra are forced to be elongated along c^*. In paragonite Na should affect neither the b nor c dimensions, but possibly causes a flattening of tetrahedra along c^*, along with rotations of about $19\frac{1}{2}°$. Opposing tetrahedral surfaces (of oxygen) also should be in contact.

If isolated Na ions are made to replace K in muscovite then the larger b-axis (8.995 Å) will require further tetrahedral flattening and rotation around these Na ions beyond that predicted for paragonite ($b=8.90$ Å). The difference in layer separation ($\eta=3.37$ Å observed for muscovite and $\eta=2.6$ Å predicted for paragonite, Part I) is especially important here. That is, the local strains and stresses around "impurity" Na ions would appear to be extremely severe; and excess of Na during muscovite formation should certainly lead to a mixture containing some paragonite. Likewise the amount of, say, Na tolerated by muscovite would be expected to rise with temperature as the increased thermal motions allow the muscovite structure to accommodate local strains more readily.

Sodium micas. Sodium analogues of the trioctahedral micas are not compatible with the proposed restraints. The most favorable hypothetical case in Na-phlogopite. If we allow the octahedral layer (which is 9.4 Å in brucite, Part IV) to be as short as 9.1 Å it is still impossible to establish six Na-O distances under 2.5 Å. To do so would require grossly flattened tetrahedra (τ about 99°, well below the limit of 106°, Part II) and a high rotation, α, of 22°.

Similar calculations show that in any hypothetical Na-lepidolite the weak Na-O bonds must grossly distort the tetrahedra (*i.e.* aver. $\tau<106°$)

and also contract the octahedral layers to some value below b = 8.8 Å. Even if such a structure could be synthesized it should be very rare naturally.

On the other hand the additional Al^{IV} in ephesite, $Na_{1.11}Ca_{0.10}$ $(Al_{1.90} \cdot Fe_{0.026}{}^{3+}Li_{0.40}Mg_{0.40}Mg_{0.04}Mg_{0.04}Fe_{0.02}{}'')(Si_{1.95}Al_{2.05})O_{0.63}(OH)_{2.34}F_{0.04}$ taken with the short b axis set by the dioctahedral layer ensures a high rotation ($\alpha = 21°36'$, Part I) which permits the appropriate Na-O contacts. This rare brittle mica, together with paragonite, seem to represent the only reasonable Na-mica compositions from a structural viewpoint.

Turning to the potassium trioctahedral micas, Foster (1960b) has critically examined the published analyses of more than 200 natural specimens, drawing detailed conclusions about their observed composition limits. Her results are summarized in Fig. 1, the two main areas of which are discussed below.

Triocathedral micas very high in Fe^{2+}. The absence of such micas naturally is at least compatible with the marked contraction required in their octahedral layers. For example annite, K $Fe_3{}^{2+}$ $(Si_3Al)O_{10}(OH)_2$ has not been observed naturally (Foster, 1960b) but has been studied extensively as a synthetic product (Eugster and Wones, 1962). It can, of course, only be assumed that annites synthesized in the presence of iron oxide at con-

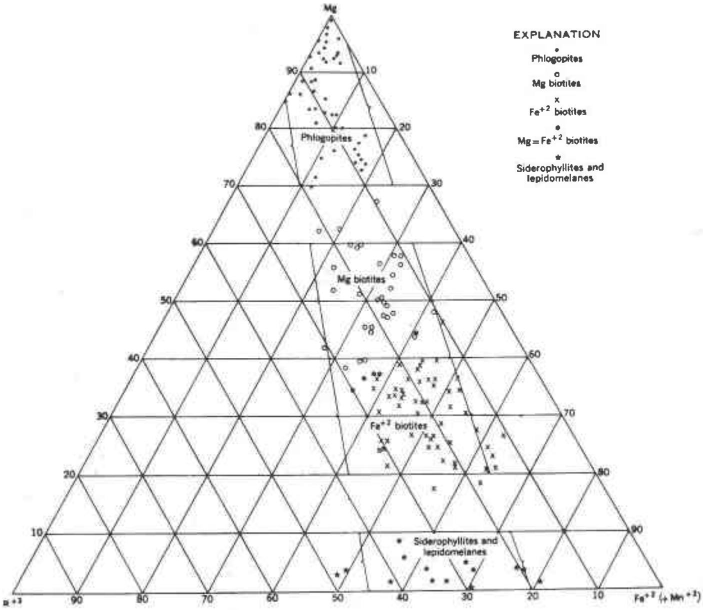

FIG. 1. Relation between Mg, Fe^{2+} (Mn^{2+}) and R^{3+} (Al, Fe^{3+} and Ti) in trioctahedral micas, from Foster (1960b).

ditions of high hydrogen fugacity represent a close approach to the ideal formula. Assuming also that the kaolin regression relation gives a usable estimate of the "unconstrained" octahedral dimensions (Parts II to IV) then b_{oct} is around 9.6 Å. The required contraction to b_{obs} (=9.348 Å) is then quite large. Moreover, with $b_{tetr}=9.31$ Å the tetrahedral layer must expand and rotate to establish K-O contact distances (≈ 2.8 Å); the estimated average O-Si-O angle $\tau=107°10'$ and rotation $\alpha=8°6'$ (Part I).

The analogue, ferri-annite, K $Fe_3^{2+}(Si_3Fe^{3+})O_{10}(OH)_2$ has also been synthesized, and cell dimensions determined by Donnay and Kingman (1958). This, too, should have flattened and slightly rotated tetrahedra, with τ about $107\frac{1}{2}°$ and $\alpha=8°$, if K-O bonds around 2.8 Å are to be established.[1] In both these synthetic high Fe^{2+} micas the tetrahedra and octahedra must be severely distorted from their *preferred* shapes in layer structures, in order to fit together with each other and with the desired interlayer distances. Under most natural conditions a little Al, Fe^{3+} or Mg will be available, and it seems very likely that smaller cations such as these will enter the octahedral sites also, rather than Fe^{2+} cations alone, giving the naturally occurring siderophyllites, lepidomelanes and high iron biotites. Very little unit cell data are available on such minerals, but the regression relations (Parts I, II) may be used to estimate roughly the tetrahedral and octahedral distortions required to assemble such micas allowing six K-O bonds around 2.8 Å. Three specimens for which Foster (1960a) gives explicit structural formulae are particularly high in Fe^{2+}, and for these

	b_{oct}	b_{calc}	b_{tetr}	$b_{oct}-b_{calc}$	τ	α
siderophyllite, no. 132	9.44	9.29	9.31	0.15 Å	$108\frac{1}{2}°$	7°
lepidomelane, no. 126	9.48	9.33	9.32	0.15	$107\frac{1}{2}$	$7\frac{1}{2}$
biotite, no. 36	9.46	9.30	9.37	0.16	$109\frac{1}{2}$	7

where $(b_{oct}-b_{calc})$ is an estimated octahedral contraction, τ measures the tetrahedral flattening (aver. O-Si-O_{apix} angle), and α is the angle of tetrahedral rotation.

For each of these natural high Fe^{2+} micas the (estimated) octahedral contraction from the expected (usual) dimensions should not lead to unduly long shared edges octahedrally. Likewise the predicted tetrahedral adjustments are readily made, especially for the biotites which tend to have > 1.00 Al^{IV} (nearer 1.25 Al^{IV}, Foster, 1960b)—for these a simple tetrahedral rotation is sufficient.

These data obviously allow no rigorous conclusions, but suggest that

---

[1] The structure analysis in progress (Morimoto and Donnay, 1962) shows a small but definite tetrahedral rotation.

the structural strains will exceed tolerable limits for natural biotites at about those composition limits drawn in the high Fe^{2+} region by Foster (1960b).

Trioctahedral micas high in R^{3+}. Most biotites appear to be 1M polymorphs and presumably belong to space group C2/m (Smith and Yoder, 1956), in which one octahedral site is at a center of symmetry, and the remaining two are symmetry-related. It is believed that under these symmetry conditions for trioctahedral micas the R^{3+} (and R^{4+}) cations tend to substitute into the phlogopite structure mainly in the unique site. This hypothesis of considerable ordering was studied statistically in Part III, and has an acceptable physical basis in terms of interatomic forces (Part IV). If the substitution were $1R^{3+}$ for $1R^{2+}$ and entirely as above then the limit would be clearly 1.00 R^{3+} in the trioctahedral mica structures. In fact, as Foster points out, the charge relations mean that as little as 0.67 R^{3+} substitutes for $1R^{2+}$, and also some R^{3+} will, on the average, be found in the symmetry-related sites. Most biotites high in R^{3+} are therefore likely to be somewhat deficient in all three octahedral sites. Nevertheless Foster (1960 b) has shown conclusively that in the trioctahedral micas the essential upper limit to the number of R^{3+} and R^{4+} cations octahedrally is 1.00 $(R^{3+}+R^{4+})$ per three sites. A strong correlation with cation ordering structurally may reasonably be deduced.

There is, as yet, no direct structural evidence for ordering amongst the octahedral positions of biotites. Takéuchi and Sadanga (1959) have published a preliminary analysis of the xanthophyllite structure (space group *C2/m*) in which they place the $Al_{0.72}$ octahedrally at $x, y, z=0, \frac{1}{2}, \frac{1}{2}$ and the $Mg_{2.18}$ mainly at $x, y, z=\frac{1}{2}, 0.328, \frac{1}{2}$ and $\frac{1}{2}, 0.672, \frac{1}{2}$.

Foster also showed that the total occupancy octahedrally falls from three to about 2.6[1] as $(R^{3+}+R^{4+})$ rises from zero to one. The lower limit of $(1.6R^{2+}+1.0R^{3+})$ implies, however, that the corresponding trioctahedral mica structures require approximately 0.75 to 0.8 R^{2+} in each of the two symmetry related sites. This lower limit of, say, 0.75 R^{2+} in each related site cannot be predicted structurally, but in view of the necessary balance of forces octahedrally (Part IV) it is at least to be expected that a majority of sites should be occupied in specimens persisting naturally—as Foster has observed.

Muscovite—trioctahedral micas. It is well known that there is very little solid solution of muscovite towards the trioctahedral micas (*e.g.* Foster, 1960 b; Yoder, 1959); muscovite departs only slightly from dioctahedral status, by the addition or substitution of R^{2+} and R^{3+} octahedrally. In

---

[1] The criticism by Eugster and Wones (1962) implying that the octahedral occupancy is usually nearer 3.0 strengthens the present discussion.

discussing the possible solid solution of muscovite and phlogopite, biotite and siderophyllite the latter minerals impose the conditions that Al^{IV} lies between 1.00–1.50 cations and K between 0.90–1.00 cations per formula unit (Foster, 1960 b). A dioctahedral mica with $Al^{IV} < 1.00$ lies in the muscovite—celadonite join, discussed later. By considering two extreme cases it then becomes clear that the maximum octahedral occupancy in the muscovite structure (excepting Li-muscovite) is effectively <2.2 per three sites.

(1) Suppose that the structure retains 2.00 Al octahedrally but accepts R^{2+} or R^{3+} into the vacant and larger octahedral site. Then to maintain charge balance Al^{IV} increases at the rate of 2n Al^{IV} substituted for 2n Si, for each n R^{+2} added octahedrally; and this is more favorable than the addition of R^{3+}. For example the hypothetical muscovite

$$(Al_2Mg_{0.15})(Si_{2.70}Al_{1.30})O_{10}(OH)_2K_{1.00}$$

is a typical biotite tetrahedrally and in K content; but the additional 0.3 Al^{IV} would unduly strain the muscovite structure as follows. The 0.15 Mg would easily fit into vacant sites without effectively increasing $b=9.0$ Å. Then $b_{tetr}=9.38$ Å, $\alpha=16°24'$ and $\eta=3.60$ Å (Part I); i.e. the increased tetrahedral dimensions should require successive layers to be far out of contact even beyond the observed muscovite separation, $\eta=3.37$ Å. The stresses in the interlayer region obviously are becoming critical very rapidly compared with the small increase in octahedral occupancy from 2.00 Al to 2.15 $(Al+R^{2+})$.

(2) The interlayer stresses are not increased if the tetrahedral composition is held constant at Si_3Al and R^{2+} (or less favourably R^{3+}) substitutes for Al chemically. There appears, however, to be a lower limit to the amount of Al^{3+}—or possibly $(Al^{3+}+R^{3+})$—required to maintain a stable muscovite structure. In a survey by the writer of 40 good muscovite analyses in the literature the total number of octahedral cations ranged from 1.9 to 2.2 and the *minimum* number of Al was 1.7 per three sites. Studies on Li-muscovites (below) also suggest a minimum of 1.7 Al octahedrally, for a stable muscovite structure.

It should be noted that in the $2M_1$ muscovite structure (Radoslovich, 1960) the occupied sites are symmetry related and the unoccupied site is crystallographically distinct, $\bar{1}$; and the average Al-O bond is 1.95 Å but the average "radius" of the vacant site is 2.2 Å. These facts support the proposed ordering of octahedral cations (Part III) by which the larger divalent ions (and Li) "substitute" for Al mainly into this distinct site rather than directly into the Al sites. The lower limit of 1.7 Al is equivalent to 85% of the occupied sites retaining Al in a stable muscovite structure, which at least is not surprising when the appropriate forces are considered in detail (Part IV). Below this level of R^{3+} occupancy (or with excessive replacement of Al directly by the larger Fe^{3+}) the muscovite structure is either unstable or open to rapid attack. This is interesting in relation to the similar level of occupancy by R^{2+} ions (about 75%) in the *same* sites, proposed above for trioctahedral micas.

If an effective limit of 1.6 cations octahedrally is accepted for Al (or possibly $Al+Fe^{3+}$) then this implies a maximum of 0.60 R^{2+} to maintain charge balance, and a total of 2.20 cations octahedrally.

These two extremes both lead to the conclusion that muscovites should not exceed approximately 2.20 cations octahedrally; and of course most muscovites will generally be nearer 2.00. The conclusion is still valid for the majority of specimens which simultaneously show some excess Al^{IV} and some deficiency of Al^{VI}. Muscovites therefore can show very little solid solution with the trioctahedral micas.

Muscovite-celadonite. Foster (1956) has studied the structural formulas and charge relations for the complete composition range of natural dioctahedral micas from muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$ to celadonite, $K(Mg, Fe)Si_4O_{10}(OH)_2$. Throughout this range the layer charge and potassium content remain effectively *constant;* the major change is in the shift of the charge from the tetrahedral to the octahedral layers. This suite of micas also remains strictly dioctahedral.

Yoder and Eugster (1955) have discussed four possible substitution schemes in muscovite, *viz.*

(a) $Si \rightarrow KAl$
(b) $(H_3O)^+ \rightarrow K$
(c) $MgSi \rightarrow 2Al$
(d) $2Mg \rightarrow KAl$

and have plotted (Fig. 2) the observed composition ranges of natural minerals. They point out that (a) is unlikely because "on Morey's evidence a given leaching of K_2O implies a six-fold loss of SiO_2;" and (d) which leads towards the trioctahedral micas is only possible to a limited extent.

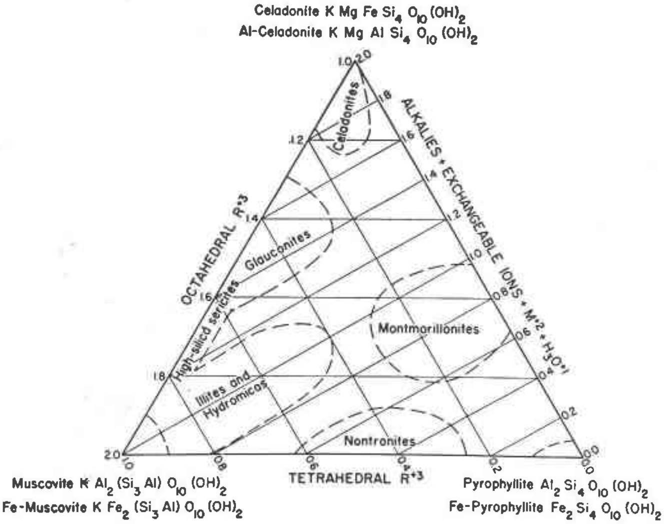

FIG. 2. Plot of tetrahedral R^{3+} and octahedral R^{3+} in atom proportions of dioctahedral micas and related minerals; from Yoder and Eugster (1955).

Yoder and Eugster suggested that some synthetic muscovites lie close to the muscovite-oxonium muscovite join, rather than the muscovite-montmorillonite join (substitution (b)). Substitution (c) leads to high-silica sericites, an observed solid solution effect.

Both of the hypothetical substitution schemes, $Si \rightarrow KAl^{IV}$ and $2Mg \rightarrow KAl^{IV}$, seem unlikely to occur to any extent when the bonding of K in muscovite is considered in detail (Part IV). Both substitutions result in fewer and weaker *direct* bonds between the remaining K and their six *nearest* anions. At the same time the surface anions around unoccupied K sites no longer have their valence charge fully satisfied by immediate bonds, and this should result in some anion-anion repulsion between layers at those sites. That is, although these substitutions preserve overall neutrality they appear to weaken the effective K-O bonds and to induce localised repulsions between layers at unoccupied cation sites. The net effect would seem to be that K-rich regions will hold any incoming K and K-poor regions are more readily able to lose their remaining K. (Such effects are masked in vermiculites because the intercalated ions are surrounded by hydration shells and do not form direct bonds in six-coordination.) The substitutions $Si \rightarrow KAl$ and $2Mg \rightarrow KAl$, which both lead to low-K muscovites, should be of very limited occurrence in unique structures for this reason alone; but the substitution $H_3O^+ \rightarrow K$ should be rather more possible because in this case K^+ is simply replaced by $(H_3O)^+$, with the *same* charge and similar size.

The substitution $MgSi \rightarrow 2Al$ is not of course limited in this way, and high-silica sericites (*i.e.* phengites) are well known. There is a limit to this substitution, however, which will be set by the lower limit of Al^{VI} required for the stable muscovite structure (see above), *viz.*

$$R^{3+}_{1.6}Mg_{0.4}(Si_{3.4}Al_{0.6})O_{10}(OH)_2K_{1.0}.$$

This is in fact a composition on the muscovite-celadonite join at the extreme limit of the high-silica sericites towards glauconites (Fig. 2). In the series of structural formulae quoted by Foster (1956) the Al-dominant micas with the least Al^{IV} are successively:

Phengite $X_{0.96}(Al_{1.50}\overset{+3}{Fe}_{0.15}\overset{+2}{Fe}_{0.07}Mg_{0.28})(Si_{3.40}Al_{0.60})O_{10}(OH)_2$
$K_{0.83}$
Metasericite $X_{0.92}(Al_{1.45}\overset{+2}{Fe}_{0.33}Mg_{0.25})(Si_{3.57}Al_{0.43})O_{10}(OH)_2$
$K_{0.82}$
Alurgite $X_{1.01}(Al_{1.28}\overset{+3}{Fe}_{0.06}Mn_{0.04}\overset{+2}{Fe}_{0.01}Mg_{0.61})(Si_{3.59}Al_{0.41})O_{10}(OH)_2$
$K_{0.96}$

Whereas phengites are known which have a unique structure it is possible that metasericite may refer only to mixed structures or mixtures, as

Yoder (1959) and Burst (1958) have suggested that the "glauconites" will also prove to be. Heinrich and Levinson (1955) have shown that alurgite may have the 2M or 3T structure, but the only analysis of unquestioned alurgite is very old (Penfield, 1893) and was a made on both uniaxial and biaxial material.

The celadonite structure (Zviagin, 1957) is different in important respects (Part IV) from the muscovite structure, although it is a 1M mica (Foster, 1956) with spacegroup $C2/m$. Zviagin examined a "celadonite" of composition

$$(Fe_{1.4}Mg_{0.7})(Si_{3.6}Al_{0.4})O_{10}(OH)_2K_{0.8}$$

in which the 1.4 Fe is all Fe^{3+} (by implication, to keep the charges balanced). Although the three octahedral sites are of equal size the two related sites contain ($1.4\ Fe^{3+}+0.6\ Mg$) and the unique site only 0.1 Mg. If the size of the "hole" available to the octahedral cations was the main factor in controlling their occupancy then for this celadonite an equal distribution of two cations between the three sites of equal size would be expected; this further supports the discussion in Part IV. The cation distribution for Foster's end member celadonite

$$K_{0.98}(Al_{0.07}\overset{3+}{Fe}_{0.93}\overset{2+}{Fe}_{0.24}Mg_{0.77})Si_{4.00}O_{10}(OH)_2$$

is not known but seems just as likely to include a practically vacant third octahedral site, with the implication that celadonite is stable with only 0.5 Fe^{3+} in the (related) sites.

Foster (1956) has observed that celadonites contain Fe^{3+} rather than Al^{3+}, and indeed the theoretical end member (see Yoder, 1959) $K\ (AlMg)\ Si_4\ O_{10}\ (OH)_2$ has not yet been found or synthesized. The unsatisfied charge octahedrally leads to long shared edges in celadonite (Part IV), presumably due to increased anion-anion repulsion. If Al is substituted for Fe^{3+} then the average cation-oxygen bonds are correspondingly shortened, and the octahedral cations brought closer together—in fact unduly close. (A rough estimate suggests that an (Al, Mg) to (Al, Mg) distance of <2.65 Å is required, across a shared edge exceeding 3 Å, giving a large cation-cation repulsion.) The apparent discontinuity in the muscovite—celadonite series of minerals may therefore be due to this shift of charge from tetrahedral to octahedral anions which leads to a need for octahedral bonds to be as long as possible at the celadonite end.

Foster (1956) has discussed the composition range of hydrous micas and "illites," pointing out that "the fact that a rational formula can be derived from an analysis does not guarantee that there is only one mineral present." Yoder and Eugster (1955) and Yoder (1959) also have emphasized that most "illites" are mixtures or mixed-layer structures, which "can be regarded only as composed of two or more phases." It is now shown that dioctahedral micas near to the muscovite composition cannot be expected to have single *unique* structures if they are K-deficient, except for the replacement, $(H_3O)^+ \rightarrow K^+$. The region "illites and hydromicas" on Fig. 2 must therefore represent mixed structures or mixtures, since a pure $(H_3O)\ Al_2\ (Si_3Al)\ O_{10}(OH)_2$ mica would be plotted coincident with muscovite in this diagram. A "structural compositional diagram" matching Fig. 2 may be drawn tentatively as in Fig. 3, in which the names refer to "structure type" specifically.

This further implies that mixed layer structures with dioctahedral mica layers as components must have the interlayer sites between successive mica layers largely occupied by K. Equally there should be little K between the remaining layers, except as loosely held exchangeable K. Hence it seems desirable to reserve the name "hydromica" for single phase minerals with the three-dimensional muscovite type of structure, in which an approximately 1:1 replacement of K^+ by $(H_3O)^+$ can be shown to have occurred.

Muscovite-lepidolite. Micas with compositions between muscovite and polylithionite have been extensively studied, *e.g.* Stevens (1938), by Levinson (1953) who particularly studied lepidolite polymorphism, and by Foster (1960 c) who has also discussed the relations between structural type and composition.

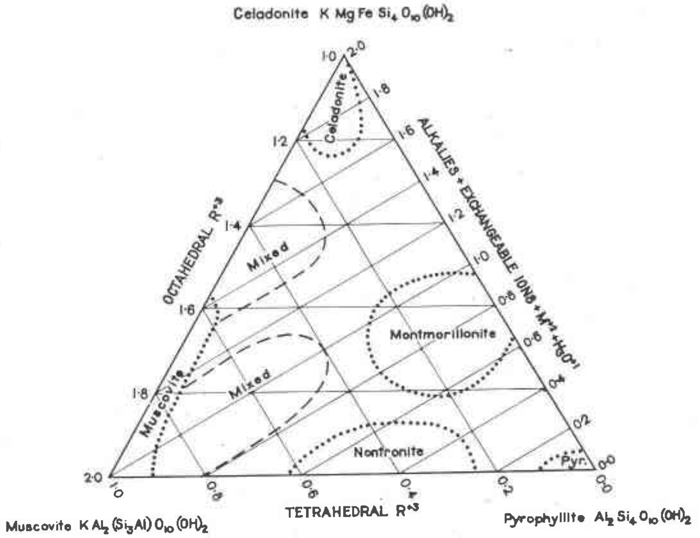

FIG. 3. Same plot as Fig. 2, showing suggested limits for various "structure types."

Foster (1960 c) has considered in detail chemically the ways in which Li can substitute for Al in muscovite, and has set composition limits by examining the structural formulae of 80 naturally-occurring aluminum lithium micas. It has been realized for some time that the trioctahedral lepidolite structures are quite distinct from the dioctahedral muscovite structures. Foster has therefore restated earlier work about their structural composition limits, reaching the conclusion that "both the compositional and structural continuity of the aluminum-lithium series is broken at the point in which change of structure takes place, and the isomorphous series that starts with muscovite extends only to an octahedral occupancy of about 2.45 sites and a Li occupancy just short of 1.00 octahedral site." Levinson (1953) suggested that the maximum Li occupancy compatible with the true muscovite structure is about 3.3% Li_2O, corresponding to about 0.85 Li per three sites. Further Li up to 4.3 %Li_2O (*i.e.* 1.1 Li per three sites) results in the so-called "lithian muscovite" structure.

Lithium can substitute for Al^{VI} in muscovite in all proportions from the simple addition of Li in the vacant site down to a ratio of 1 Li for 1 Al (Foster, 1960 c). Figure 4 shows that natural micas may only slightly exceed the replacement ratio of 3 Li:1 Al^{VI} for specimens low in Li, and otherwise not at all. This is due to the position of K in the muscovite (and presumably in the lepidolite) structure (Part IV). For higher ratios —*e.g.* simple addition of Li in the vacant site—the necessity for charge balance requires that Al^{IV} increases and Si^{IV} decreases. This means greater twists, α, and therefore even greater layer separation, η, than in muscovite; such structures should be readily changed, if they are formed at all.

On the other hand the substitution of Li in natural muscovites would hardly induce a disproportionate decrease in Al^{IV} rather than in Al^{IV} since this would shift the layer charge to the octahedral layer for a mica with essentially the *muscovite* structure. The theoretical mica $K(Al_{1.5}\ Li_{0.5})(Si_4)\ O_{10}\ (OH)_2$, which is the end member for the 1:1 replacement, represents such an unlikely structure leading to high anion-anion repulsion and close cation-cation approach octahedrally. Figure 4 in fact implies that Al^{IV} and Al^{VI} decrease equally (2:1 replacement ratio) or else Al^{IV} decreases by a smaller number of ions than Al^{VI}, *e.g.* a Li:Al^{VI} replacement ratio of 2.5:1. This keeps the layer charge largely tetrahedral which is very reasonable structurally for the muscovite arrangement of octahedral cations.

It was suggested above that the muscovite structure required about 0.8 Al in two sites. It is probable that such a muscovite could accept, on the average, a further 0.8–0.9 Li in the larger vacant site; and this leads

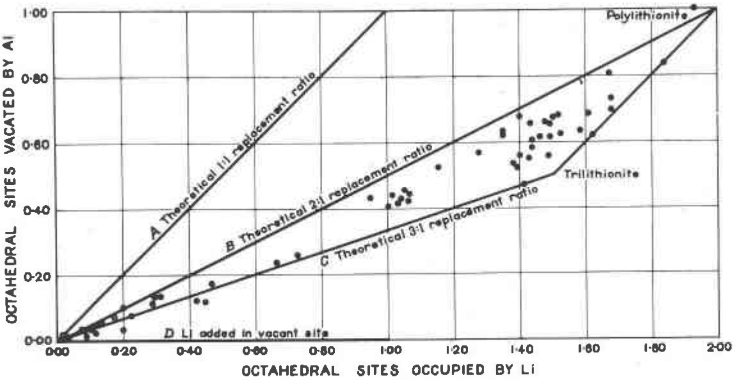

FIG. 4. Relation between octahedral sites occupied by Li and vacated by Al in aluminum lithium micas; after Foster (1960c).

to an acceptable decrease in Al^{IV} of 0.35, slightly smaller than the decrease in Al^{VI} of 0.40, *viz.*

$$(Al_{1.60}Li_{0.85})(Si_{3.35}Al_{0.65})O_{10}(OH)_2K_{1.00}$$

The lower limit to Al^{VI} appears to set a lower limit to Al^{IV}, *i.e.* an upper limit to Li, which is consistent, moreover with the structural requirements. This mica should represent about the maximum octahedral occupancy for *muscovites;* and the sum of the octahedral cations, 2.45, is the same as Foster's observed limit.

Lepidolites near polylithionite, $K(Al\ Li_2)\ Si_4\ O_{10}\ (OH)_2$, in composition will probably have highly ordered octahedral layers, with the Al in the unique site and the 2 Li in the symmetry related sites. Foster (1960 c) noted however that lepidolite structures may contain as much as 1.4 Al^{VI} (implied *e.g.* in Fig. 4) with an ideal composition,

$$(Al_{1.40}Li_{1.40})(Si_{3.60}Al_{0.40})O_{10}(OH)_2K_{1.00}$$

Although partial octahedral ordering of the above type *may* still remain the Al^{VI} obviously must occupy some of the symmetry-related sites. At present it can only be noted that such structures occur naturally, and that lepidolite structures show little-understood peculiarities in this as in some other aspects (Part I).

Trioctahedral micas-lepidolites. Foster (1960 c) has examined about 45 ferrous lithium micas ranging in composition between siderophyllites and lepidolites (Fig. 5). She also records data on taeniolite, ideally $(Mg_2\ Li)\ Si_4\ O_{10}\ (OH)_2\ K$, and on three Li-biotites; these data have been inserted as nos. 1–4 on Fig. 6. Foster comments:

"The prototype, siderophyllite, is structurally trioctahedral, and, as replacement tends to

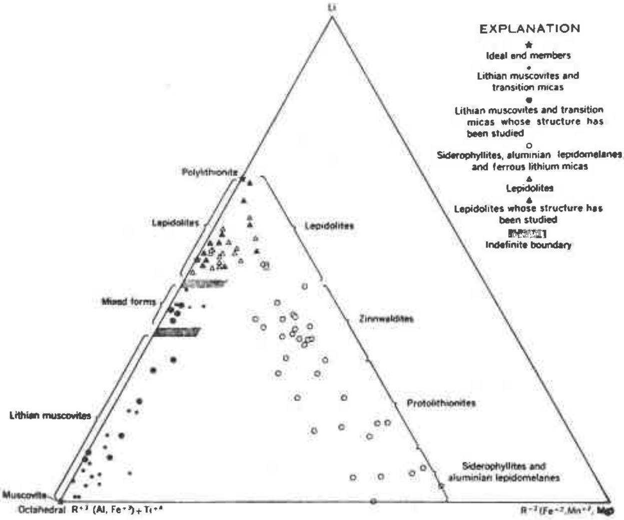

FIG. 5. Relation between Li, R^{2+} (Fe^{2+}, Mn^{2+}, Mg) and octahedral R^{3+} (Al, Fe^{3+})+Ti^{4+} in lithium micas; from Foster (1960c).

increase octahedral occupancy, the ferrous lithium micas are also trioctahedral and no structural adjustments are necessary. The ferrous lithium mica series is, therefore, not broken as is the aluminium lithium mica series."

On this basis a "structural composition diagram" is now proposed (Fig. 6) in which the trioctahedral and dioctahedral areas each correspond to *continuous* structural series. These composition limits are reasonable in terms of the structures involved, as follows. Taeniolite represents the maximum Li substitution possible in phlogopite to maintain charge balance. Approximate sheet dimensions and other data for this and its iron analogue may be calculated (Part II) to be:

Composition	b_{calc}	b_{tetr}	τ	new b_{tetr}	α
$(Mg_2Li)Si_4O_{10}(OH)_2K$	9.14	9.05	107°	9.18	5°24′
$(Fe_2^{2+}Li)Si_4O_{10}(OH)_2K$	9.26	9.05	105.7°	9.32	6°42′

That is, in taeniolite (which is rare) the stretching required in the tetrahedral layers to meet the expected sheet dimensions is just within the acceptable limits ($\tau = 106\frac{1}{2}°$). In the ferrous analogue the misfit is excessive, and if such a mica were formed the octahedral layer would have to be quite unusually short and thick for a ferrous mica. Structurally this seems unlikely to be formed, and even less likely to persist naturally. Taeniolite is reported to have the 1M structure (Foster, 1960 c) with which on ordered octahedral arrangement would be consistent. Similar arguments show that the present structural concepts are compatible with the other limits sketched for biotites (Fig. 6). Normal micas cannot of course have compositions in the blank upper right portion of this diagram where there would be an inherent lack of charge balance. The discontinuity between muscovite and siderophyllite was discussed earlier.

The join siderophyllite-lepidolite (Fig. 5) appears to be continuous from chemical data (Foster, 1960 c) which may be expected from structural considerations also. Foster gives as average formulae:

siderophyllite $(\overset{3+}{R}_{1.05}\overset{2+}{Fe}_{1.50})(Si_{2.85}Al_{1.15})O_{10}(OH)_2K_{1.00}$
zinnwaldite $(\overset{3+}{R}_{1.05}\overset{2+}{Fe}_{0.75}Li_{1.00})(Si_{3.35}Al_{0.65})O_{10}(OH, F)_2K_{1.00}$
lepidolite $(\overset{3+}{R}_{1.05}\overset{2+}{Fe}_{0.37}Li_{1.50})(Si_{3.61}Al_{0.39})O_{10}(F, OH)_2K_{1.00}$
(ferroan)

The octahedral layer is probably largely ordered throughout this range, with the $R_{1.05}{}^{3+}$ mainly in the unique site. The two related sites are then largely occupied by Fe^{2+} in siderophyllites and by Li in polylithionite; *i.e.* structurally the Li ions replace Fe^{2+} ions directly. (An interesting consequence is that the role of K changes continously from contracting siderophyllite layers to expanding lepidolite layers and propping them apart.) Though there is as yet no *direct* structural evidence the likelihood of octahedral ordering (Parts III, IV), and Foster's chemical data both strongly support this hypothesis. In the ferrous lithium micas "the octa-

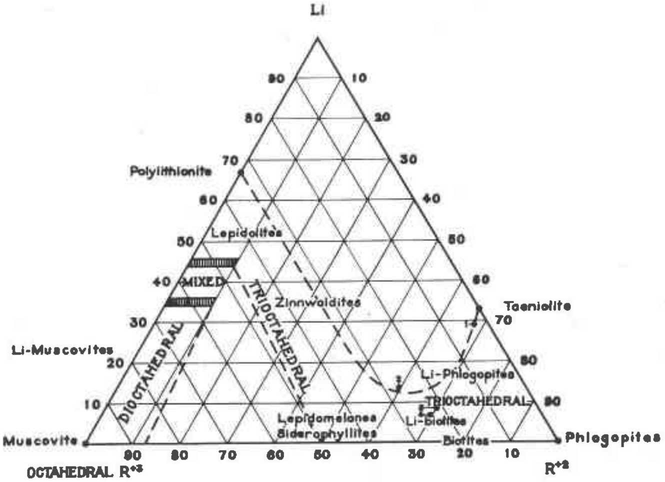

FIG. 6. Same plot as Fig. 5, showing suggested limits fo. various dioctahedral and trioctahedral structural series.

hedral R^{3+} content is remarkably constant over a range in Li_2O content of from 1.5% to 4.8% "suggesting that these cations are not involved in the addition of Li." But a study of the Li-Fe^{2+} relation shows an approximately linear decrease in Fe^{2+} with increase in Li "which is suggestive of replacement." The replacement ratio is about 1.3:1 rather than 1:1 because of other adjustments made in the number of vacant sites and in layer charge distribution. Chemically the range of R^{3+} for minerals between siderophyllites and lepidolites is $(1.15 \pm 0.10)R^{3+}$ approx., suggesting that most of the R^{3+} ions are in a particular octahedral site throughout this series.

Other clay mineral groups. At present the other clay mineral groups are generally less well defined chemically and structurally than the micas, and considerable restraint is needed in extending the present discussion of composition and structure to them. However, the study of interatomic forces (Part IV) and of the probable ordering of octahedral cations (Part III) applies to the layer silicate structures generally. It may therefore at least be noted here that these structural concepts are compatible with several broad conclusions about composition ranges in these other minerals. In particular a discontinuity between dioctahedral and trioctahedral minerals may be expected in other groups (as in micas) if octahedral ordering of cations is fairly widespread. The discontinuities will be more obvious if there are lower limits to the number of symmetry-related sites which must be occupied by certain cations (as discussed above for the micas).

MacEwan (1961) has noted that amongst the naturally occurring minerals in the montmorillonite group "there are two distinct series (dioctahedral and trioctahedral) with very limited solid solution." In dioctahedral montmorillonites there are between 2.0 and 2.2 cations per three sites. In the trioctahedral analogues Mg ranges from 1.8 to 3.0; or in the sauconites Zn ranges from 1.5 to 2.5 (Ross, 1946) with a total cation occupancy of 2.7 to 3.0. The present ideas about octahedral ordering are entirely consistent with these figures.[1]

---

[1] Roy and Roy (1955) have studied the system MgO-Al_2O_3-SiO_2-H_2O extensively. They state that due to considerable experimental difficulties "the present study appears to be fairly conclusive only insofar as it shows the existence of relatively pure "single" phase montmorillonites extending about 10 molar per cent into the diagram from each of the ternary systems" (*i.e.* from talc and pyrophyllite). It is also to be noted that their "ideally" stable montmorillonite has an octahedral composition of approximately $(Mg_{0.75}Al_{1.5})$, which is within the proposed structural limitations. If the present concept of octahedral ordering is widely applicable, then their assumption of a continuous series of montmorillonites (made "to greatly simplify the representation of the phase relations") is not in fact valid.

Nelson and Roy (1958) have argued strongly that there is a clear structural discontinuity between dioctahedral kaolins and their trioctahedral analogues, adding that "the crystal chemistry of kaolins admits no isomorphous substitutions in the ideal formula." The structure analysis of dickite (Newnham, 1961) and kaolinite (Zviagin, 1960) show no sign of Al in the third site, from which we may conclude that in these minerals the appropriate octahedral sites must be occupied and the arrangement a fully ordered one. In view of the tight network of octahedral forces, at least in dickite (Part IV), perhaps it is not too surprising that defects in the form of substituted ions of larger radius, or simply of occasionally unoccupied sites are not readily tolerated.

With the chlorites the additional octahedral layer per unit cell allows many more variations in cation ordering, and it is hardly possible to consider the observed composition ranges (Foster, 1962) until several structure analyses have been published. However the high degree of octahedral ordering in prochlorite (Steinfink, 1958) may be noted with interest. In the refinement of Mg-vermiculite Mathieson (1958) made no attempt to distinguish between the occupancy of the three crystallographically distinct sites. The Cr-chlorite structure recently determined by Brown and Bailey (1963) is fully ordered octahedrally in the sense predicted in Part III. All three sites in the talc layer are occupied by Mg; and in the brucite layer the unique site, $\bar{1}$, contains ($Cr_{0.7}Al_{0.2}\,Mg_{0.1}$) and the related sites are occupied by Mg.

Discussion

The internal strains which the layer silicates can tolerate—in the form of stretched bonds and highly distorted polyhedra—are limited, and some broad physical limits can be suggested from the previous empirical study of their interatomic forces (Part IV). On this basis we may conclude that certain hypothetical micas are structurally prohibited (*e.g.* Na-biotites) or highly unlikely to be synthesized (*e.g.* Na and K equally in muscovite). In other cases it seems that should the particular structure be formed naturally then it would at least have large internal stresses at surface conditions (*e.g.* annite). It may be inferred that these minerals would be rather readily altered if a new environment favors any change, and natural specimens should be rare for this reason alone.

A review of observed composition limits for natural micas shows that the present structural ideas are at least compatible with these limits. It is not, of course, to be implied that the structural factors necessarily have controlled any of the observed limits because of the known importance of other factors during formation.

The need for detailed studies of bond lengths in known structures at elevated temperatures is again obvious.

ACKNOWLEDGMENTS

Thanks are due to both Dr. Margaret D. Foster and Dr. Hatten S. Yoder, Jr., for their helpful comments on the original manuscript.

REFERENCES

BROWN, B. E. AND S. W. BAILEY (1963) Chlorite polytypism: II. Crystal structure of a one-layer Cr-chlorite. *Am. Mineral.*, **48,** 42.

BURST, J. F. (1958) Mineral heterogeneity in "glauconite" pellets. *Am. Mineral.* **43,** 481.

DONNAY, G. AND P. KINGMAN (1958) *Carnegie Inst. of Wash. Year Book No.* **57,** 252.

EUGSTER, H. P. AND D. R. WONES (1962) *Jour. Petrology,* **3,** 82.

——— AND H. S. YODER (1955) *Carnegie Inst. of Wash. Year Book No.* **54,** 123.

FOSTER, M. D. (1956) Correlation of dioctahedral potassium micas on the basis of their charge relations. *U. S. Geol. Survey Bull.* **1036-D,** 57.

——— (1960a) Layer charge relations in the dioctahedral and trioctahedral micas. *Am. Mineral,* **45,** 383.

——— (1960b) Interpretation of the composition of trioctahedral micas. *U. S. Geol. Survey Prof. Paper,* **354-B,** 11.

——— (1960c) Interpretation of the composition of lithium micas. *U. S. Geol. Survey Prof. Paper,* **354-B,** 115.

——— (1962) Interpretation of the composition and a classification of the chlorites. *U. S. Geol. Survey Prof. Paper,* **414-A,** 1.

HEINRICH, E. WM. AND A. A. LEVINSON (1955) Polymorphism among the high-silica sericites. *Am. Mineral.* **40,** 983.

LEVINSON, A. A. (1953) Relationship between polymorphism and composition in the muscovite-lepidolite series. *Am. Mineral.* **38,** 88.

MCEWAN, D. M. C. (1961) Montmorillonite minerals, in "*X-ray Identification and Crystal Structures of Clay Minerals,*" Mineral Soc., London.

MATHIESON, A. MC. L. (1958) Mg-Vermiculite: a refinement and re-examination of the 14.36 Å phase. *Am. Mineral.* **43,** 216.

MORIMOTO, N. AND J. D. H. DONNAY (1962) Private communication.

NELSON, B. W. AND R. ROY (1958) Synthesis of the chlorites and their structural and chemical constitution. *Am. Mineral.* **43,** 707.

NEWNHAM, R. E. (1961) A refinement of the dickite structure. *Mineral. Mag.* **32,** 683.

PENFIELD, S. L. (1893) On some minerals from the manganese mines of St. Marcel in Piedmont, Italy. *Am. Jour. Sci.* **46,** 288.

RADOSLOVICH, E. W. (1960) The structure of muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$. *Acta Cryst.* **13,** 919.

——— (1962a) The cell dimensions and symmetry of layer lattice silicates; II, Regression relations. *Am. Mineral.* **47,** 617.

——— (1962b) The cell dimensions and symmetry of layer lattice silicates; IV, Interatomic forces. *Am. Mineral.* **48,** 76.

——— (1962c) The cell dimensions and symmetry of layer lattice silicates; VI, Serpentine and kaolin morphology. *Am. Mineral.* **48,** 368.

——— AND K. NORRISH (1962) The cell dimensions and symmetry of layer lattice silicates; I, Some structural considerations. *Am. Mineral.* **47,** 599.

ROSS, C. S. (1946) Sauconite—a clay mineral of the montmorillonite group. *Am. Mineral.* **31,** 411.

SMITH, J. V. AND H. S. YODER (1956) Experimental and theoretical studies of the mica polymorphs. *Mineral. Mag.* **31,** 209.

STEINFINK, H. (1958) The crystal structure of prochlorite. *Acta Cryst.* **11,** 191.

STEVENS, R. E. (1938), New anlayses of lepidolites and their interpretation. *Am. Mineral.* **23,** 607.

TAKÉUCHI, Y. AND R. SADANAGA (1959) The crystal structure of xanthophyllite. *Acta Cryst.* 12, 945.

VEITCH, L. G. AND E. W. RADOSLOVICH (1962) The cell dimensions and symmetry of layer lattice silicates; III, Octahedral ordering. *Am. Mineral.* **48,** 62.

YODER, H. S. (1959) Experimental studies on micas; a synthesis. *Clays and Clay Minerals, Sixth Conf. Proc.*, 42. Pergamon Press, N. Y.

——— AND H. P. EUGSTER (1955) Synthetic and natural muscovites. *Geochim. Cosmochim. Acta*, **8,** 155.

YOUNG, R. A. (1962) Private communication.

ZVIAGIN, B. B. (1957) Determination of the structure of celadonite by electron diffraction. *Kristallografiya*, **2,** 388 (in transl.).

——— (1960) Determination of the structure of kaolinite by electron diffraction. *Kristallografiya*, **5,** 32 (in transl.).

Manuscript received, July 27, 1962; accepted for publication, January 2, 1963.