# Interpretation of the Composition of Trioctahedral Micas

**GEOLOGICAL SURVEY PROFESSIONAL PAPER 354-B** 



# Interpretation of the Composition of Trioctahedral Micas

By MARGARET D. FOSTER

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

GEOLOGICAL SURVEY PROFESSIONAL PAPER 354-B

A study of the compositional and layer charge relations of phlogopites, biotites, siderophyllites and lepidomelanes



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### SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

# **INTERPRETATION OF THE COMPOSITION OF TRIOCTAHEDRAL MICAS**

By MARGARET D. FOSTER

#### ABSTRACT

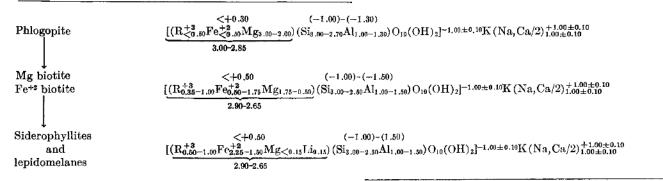
Structural formulas calculated for more than 200 published analyses of phlogopites, biotites, siderophyllites, and lepidomelanes indicate that the additional positive charges carried by trivalent cations proxying for bivalent Mg in the octahedral group of trioctahedral micas are accommodated in two different ways, (1) by a positive charge on the octahedral layer, which is neutralized by an equivalent increase in the negative tetrahedral charge (increased replacement of Si by Al), and all the octahedral sites are occupied, or (2) are neutralized by negative charges associated with unoccupied octahedral sites.

In almost all the structural formulas the octahedral group had a positive charge and octahedral occupancy was less than 3.00, indicating some degree of accommodation by both methods. The degree to which accommodation is made by (1) or (2) varies greatly. In general, however, there is a greater accommodation by (2) than by (1) the greater the octahedral trivalent cation content. As a result, there is also a general decrease in octahedral occupancy with increase in octahedral trivalent cation content. In most biotites, siderophyllites, and lepidomelanes octahedral occupancy is significantly less than 3.00 sites-hence they are not truly trioctahedral, nor are they octaphyllites. The few formulas in which trivalent cations occupy more than one octahedral site suggests that this is the essential limit of replacement of  $\mathbf{R}^{+2}$  by  $\mathbf{R}^{+3}$  in these micas. It is also strong evidence against the existence of a complete series between phlogopite and muscovite.

Coincident with replacement of Mg by  $\mathbb{R}^{+3}$ , there is also replacement of Mg by  $\mathbb{F}e^{+2}$ , ion for ion. With few exceptions

the calculated formulas show both types of octahedral replacement. But the two types, although coincident, are independent; there is no relation between the amount of  $\mathbb{R}^{+3}$  present and the amount of  $\mathbb{F}e^{\pm 2}$  present. Neither type of replacement forms a separate series, as a series of  $\mathbb{F}e^{\pm 2}$  only replacing Mg, of which Winchell's annite is the theoretical end member. No representative of this end member was found among the more than 200 analyses collected. On the evidence of the analyses and their calculated formulas, an octrahedral occupancy of more than 2.20 positions by  $\mathbb{F}e^{\pm 2}$  is not to be expected.

The only trioctahedral micas in which more than 90 percent of the octahedral positions are occupied by one species of cation are some phlogopites. From pure phlogopite as the prototype, the composition of all other trioctahedral micas may be derived by replacement of Mg by, most commonly, Fe<sup>+2</sup> and R<sup>+3</sup> (Al and Fe<sup>+3</sup>). In phlogopites the proxying of such cations for Mg is minor, and Mg occupies more than 70 percent of the occupied positions. Progressively greater proxying of these other cations for Mg leads successively to Mg biotites, in which Mg is still the dominant octahedral cation but in which Fe<sup>+2</sup> is present in significant amounts, Fe<sup>+2</sup> biotites, in which Fe<sup>+2</sup> is the dominant octahedral cation, with Mg present in subordinate but significant amounts, and siderophyllites and lepidomelanes, in which Mg is essentially absent, with Fe<sup>+2</sup> the greatly dominant bivalent octahedral cation and with significant amounts of aluminum and (or) ferric iron. These relations are expressed in the following formulas, which show the range in composition of the different groups:



Thus the trioctahedral micas can be considered members of a complete system, at one end of which is phlogopite, with essentially complete octahedral occupancy by Mg, and at the other end of which is siderophyllite and lepidomelane, with essentially zero octahedral occupancy by Mg.

There is not a clear distinction in the composition of biotites from different kinds of rocks. Biotites from different igneous rocks, granites, diorites, granodiorites, nepheline syenites may be very similar in composition; on the other hand, biotites from the same kind of rock may differ greatly in composition. Micas at the extreme ends of the trioctahedral replacement system, phlogopites and siderophyllites-lepidomelanes, which have extremely high or extremely low Mg content, occur in more extreme types of rocks, peridotites and other ultramafic rocks, metamorphosed limestone, and contact zones of metamorphism on the one hand, and pegmatites and greisen on the other.

# INTRODUCTION

This study of the compositional and layer charge relations of the trioctahedral micas is an extension of a similar study (Foster, 1956) of the composition and layer charge relations of the dioctahedral potassium micas. In that study it was shown that these micas may be classified and correlated on the basis of the relation between the charges on their tetrahedral and octahedral layers. It is the purpose of this paper to present a similar interpretation of the composition and layer charge relations of the trioctahedral micas.

# LAYER CHARGE RELATIONS OF THE TRIOCTAHEDRAL MICAS, THEORETICAL

Ideally, the layer charge relations of the trioctahedral micas are the same as those of muscovite, as expressed in their theoretical or ideal formulas,

$$\begin{array}{r} 0.00 & -1.00 \\ [(Mg, Fe^{+2})_{3.00}(Si_{3.00}Al_{1.00})O_{10}(OH)_2]^{-1.00}K_{1.00}^{+1.00}, \\ 0.00 & -1.00 \\ [Al_{2.00}(Si_{3.00}Al_{1.00})O_{10}(OH)_2]^{-1.00}K_{1.00}^{+1.00}. \end{array}$$

In both of these formulas the octahedral group is neutral; all the inherent unit layer charge is on the tetrahedral group, owing to occupation of one-fourth of the tetrahedral cationic sites by Al.

Few natural micas, however, have the exact composition specified by these theoretical or ideal formulas. In the dioctahedral micas bivalent cations occupy some of the octahedral positions ideally presumed to be occupied by Al, and in the trioctahedral micas some of the octahedral positions, ideally presumed to be occupied by bivalent ions like Mg or Fe<sup>+2</sup>, are occupied by trivalent ions like Al or Fe<sup>+3</sup>. Proxying of a bivalent for a trivalent octahedral cation, ion for ion, in the dioctahedral micas induces a negative charge on the octahedral layer equivalent to the number of bivalent octahedral cations. Constancy of charge and K content is preserved by an equivalent decrease in the negative tetrahedral charge, that is, equivalent decrease in tetrahedral Al content and increase in Si content. These changes can be expressed by the equation,  $+n\mathbf{R}^{+2}+n\mathbf{Si}=-2n\mathbf{R}^{+3}$ . Replacement of one-half of the trivalent octahedral cations by bivalent cations produces the tetrasilicic end member of the trisilicictetrasilicic series,

$$\begin{array}{ccc} -1.00 & 0.00 \\ [(\mathrm{R}^{+3}_{1.00} \mathrm{R}^{+2}_{1.00}) \mathrm{Si}_{4.00} \mathrm{O}_{10} (\mathrm{OH})_2]^{-1.00} \mathrm{K}^{+1.00}_{1.00} \end{array}$$

in which all the inherent unit layer charge is on the octahedral layer.

By analogy, proxying of a trivalent cation for a bivalent ion, ion for ion, in the octahedral group of a trioctahedral mica should induce a positive charge on the octahedral layer, which, for constancy of inherent layer charge and K content, would require an equivalent increase in the negative tetrahedral charge and, consequently, equivalently increased proxying of Al for Si. This charge relation is assumed in Winchell and Winchell's (1951, p. 373) formulas (recast in the notation used in this paper) for eastonite,

$$^{+0.5}_{\rm [(Al_{0.5}Mg_{2.5})(Si_{2.5}Al_{1.5})O_{10}(OH)_2]^{-1.00}}\rm K_{1.00}^{+1.00}$$

and siderophyllite,

$$^{+0.5}_{[(Al_{0.5}Fe^{+2}_{2.6})(Si_{2.5}Al_{1.5})O_{10}(OH)_2]^{-1.00}} K^{+1.00}_{1.00}$$

In these formulas it is also assumed that all 3 octahedral positions are occupied, as they would be if the proxying of trivalent for bivalent cations were 1 to 1.

Holzner (1936, p. 435) noticed, however, that in formulas calculated from biotite analyses, the number of occupied octahedral positions is between 2.89 and 2.49; in none of his formulas were 3.00 positions occupied. To explain this low octahedral occupancy he postulated that biotite is intermediate between phlogopite and muscovite in composition and that the crystal structure is built up of the 2 mica types, most biotites approximating the composition of 2 of phlogopite to 1 of muscovite, which yields a formula for biotite of:

$$\underbrace{[\underbrace{\mathrm{Al}_{0,67}\,\mathrm{Mg}_{2.06}}^{0.00}}_{\mathbf{2.67}}(\mathrm{Si}_{3.00}\mathrm{Al}_{1.00})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.00}}_{\mathbf{2.67}}\mathrm{K}_{1.00}^{+1.00}$$

In this formula the tetrahedral group has the same composition and charge as it has in the ideal formulas for phlogopite and muscovite, and the octahedral layer is neutral, as in the theoretical or ideal formulas. The 0.67 additional positive charges carried by the 0.67 trivalent ions are neutralized by the 0.67 negative charges associated with the 0.33 unoccupied octahedral positions.

Thus in Winchell's formulas for eastonite and siderophyllite and in the formula suggested by Holzner for biotite, trivalent octahedral ions are accommodated in two quite different ways. In one the proxying of trivalent for bivalent octahedral ions is 1:1; all the octahedral cationic positions are occupied; and the additional positive charges carried by the trivalent octahedral ions form a positive charge on the octahedral layer and are neutralized by an equivalent increase in the negative tetrahedral charge owing to greater proxying of Al for Si. These relations are expressed in the equation

$$(+2n\mathbf{R}^{+3}) = (-n\mathbf{R}^{+2}) + (-n\mathbf{Si}^{+4})$$
 (A)

In the other way of accommodating trivalent octahedral cations, 2 trivalent cations proxy for 3 bivalent cations. There is, consequently, no increase in the number of positive charges present, nor is there any change in the layer charge relations, between the octahedral and tetrahedral groups, but there is a decrease in the number of octahedral positions occupied equivalent to one-half of the number of trivalent octahedral cations. These relations are expressed in the equation

$$(+2nR^{+3}) = (-3nR^{+2}) + (-n \text{ Oct. Pos.})$$
 (B)

In the first type of accommodation for trivalent octahedral ions, the formula is characterized by full octahedral occupancy, a positive octahedral charge, and a negative tetrahedral charge greater than 1.00 by the number of trivalent octahedral cations; in the second type of accommodation the formula is characterized by deficient octahedral occupancy, a neutral octahedral layer, and a negative tetrahedral charge very close to 1.00.

#### ACCOMMODATION OF TRIVALENT CATIONS IN NATURAL TRIOCTAHEDRAL MICAS

#### CALCULATION OF FORMULAS

For a study of the general characteristics of natural trioctahedral micas and, particularly, their accommodation of trivalent octahedral cations, structural formulas were calculated from more than 200 analyses of phlogopites, biotites, siderophyllites, and lepidomelanes. The formulas were calculated by the method devised by Marshall (1949, p. 58) and modified by the author (Foster, 1951, p. 728). The calculations involved are illustrated by example in table 1. The gram-equivalents of cationic constituents in the structure are obtained by dividing the percent of each constituent present by a factor obtained by dividing the molecular weight of that constituent by the number of cationic valencies in its molecular formula. Thus for  $\mathrm{Fe}_{2}\mathrm{O}_{3}$  the factor to be used is the molecular weight of Fe<sub>2</sub>O<sub>3</sub>, 159.70, divided by 6, which is 26.617; for FeO it is 71.85 divided by 2, or 35.925.

TABLE	1.—Calculation	of	structural	formula
	11Por 49 1	tah'	le 11]	

		[For 49, table 11]		
Percent	Gram- equivalents of cationic constituents	Cationic valencies per unit cell	Cations per unit cell	Charge
SiO <sub>2</sub> 36. 32÷ (60. 04÷4	£)=2. 419÷0. 1109	9=21, 912÷4=	5. 453 2. 547 hedral 8. 000 group	2. 547
$\begin{array}{c} Al_2O_{3} 14.\ 66\div(101,\ 96\div6\\ TiO_{2}\ 3.\ 42\div\ (79,\ 90\div4\\ Fe_2O_{3}\ 4.\ 80\div(159,\ 70\div6\\ FeO_{1}14.\ 74\div\ (71,\ 85\div2\\ MgO_{12},\ 38\div\ (40,\ 32\div2\\ MnO_{}\ 0.\ 34\div\ (70,\ 93\div2\\ \end{array}$	$\begin{array}{l} () = .171 \div .1109 \\ () = .180 \div .1109 \\ () = .410 \div .1109 \\ () = .614 \div .1109 \end{array}$	$\theta = 1.542 \div 4 = 0$ $\theta = 1.623 \div 3 = 0$ $\theta = 3.697 \div 2 = 0$ $\theta = 5.537 \div 2 = 0$	$\begin{array}{c c} 94 \rightarrow 0. \ 047 \\ . \ 385 \\ . \ 541 \\ 1. \ 848 \\ 2. \ 768 \\ . \ 045 \end{array} + \begin{array}{c} \text{octa-} \\ \text{hedral} \\ \text{group} \\ . \\ 045 \end{array}$	+ 0. 630
	–Si and Al) dral Al cations×3	$\begin{array}{c} 12.489\\ 3 \rightarrow .141 \end{array}$	5. 634 (octahedra occupancy)	
		+12.630 -12.000		
		+ 0.630 (octahed charg		
CaOTrace Na <sub>2</sub> O 0. $90 \div$ (61. $98 \div 2$ K <sub>2</sub> O 8. $63 \div$ (94. $20 \div 2$			0. 261 1. 650	
	$\begin{array}{c} 4. \ 879 \\ 4. \ 879 \div 44 \!=\! 0. \end{array}$	1. 911 1109	1.911 (interlayer ————————————————————————————————————	
H <sub>2</sub> O 2. 72		+		
	Struc	tural formula (half-cell)		
	+0.27	-1,27		1.0.07
[(Al <sub>0.02</sub> Ti <sub>0.10</sub>	$\mathrm{Fe_{0.27}^{+8}Fe_{0.92}^{+2}Mg_{1.38}N}$	$(\mathrm{In}_{0.02}^{+2})(\mathrm{Si}_{2.73}\mathrm{AI}_{1.27})0_{10}$	(OH) <sub>2</sub> ]-1.00(K <sub>0.82</sub> , Na <sub>0.1</sub>	3)0.95 3)0.95
	2.80			

The second step in the calculation is to convert gram-equivalents of the cationic constituents to cationic valencies in the unit cell. As the number of cationic valencies must be the same as the number of anionic valencies present, the number of cationic valencies present is usually based on the number of anionic valencies furnished by the  $H_2O+$  and F reported in the analysis. However, in many of the analyses insufficient data were given for this; in some F was not reported, in others plus and minus waters were not reported, only total water, and in still others the  $H_2O+$  and F together were much too low. The formulas were, therefore, all calculated on the basis of the cationic and anionic valence content of the idealized unit cell, 44. The sum of the gram-equivalents of the cationic constituents was, therefore, divided by 44 to obtain the factor for converting them to cationic valencies per unit cell. After dividing the gram-equivalents of each cationic constituent by this factor, the number of valencies per unit cell thus obtained of each cation is then divided by its valence to obtain the number of cations per unit cell.

The aluminum cations are divided between the tetrahedral and octahedral groups; enough Al is allocated to the tetrahedral group to bring the total, with silicon, to 8.00, and the remainder is assigned to the octahedral group. The sum of the cations in the octahedral group should, theoretically, be 6.00, but in most of the calculated formulas for trioctahedral micas it is less than 6.00.

Throughout this paper the discussion is based on the half-cell formula. To write the half-cell formula, the values for the cations and charges per unit cell are merely halved, as in the formula at the bottom of table 1. Attention is called to the order in which the groups and cations within each group in the formula are written. First the octahedral group (enclosed in parentheses) is noted, with the cations in that group written in order of decreasing valence, except for Ti. which is written after Al. Then the tetrahedral group (also enclosed in parentheses) is noted, with Si, the principle cation, written first. Above each group its charge is noted. After these two groups, which indicate the cationic composition, the anionic composition,  $O_{10}(OH)_2$ , is written; and the whole is bracketed, as indicating the composition of the composite layers. After the upper part of the closing bracket, the total negative charge on the composite layer unit is written. This is followed by a notation of interlayer cation content, with the positive charge carried by these cations being written at the top of the closing parenthesis, and the number of positions occupied by these cations at the bottom. The interlayer cations are written last. rather than first, the more conventional position, because the amount and charge of the interlayer cations is dependent on and must neutralize the charge on the composite layers.

Theoretically 32 of the 44 anionic or negative charges are allocated to the tetrahedral group and 12 to the octahedral group. Thus if the tetrahedral group is entirely made up of Si cations, which are quadrivalent, the number of positive charges present is exactly equal to the number of negative charges,  $4 \times 8 = 32$ , and the tetrahedral layer is neutral. But if the tetrahedral group contains some Al, which is trivalent, there are not enough positive charges to neutralize all the negative charges present and the tetrahedral layer has a negative charge. Thus in the example given in table 1, the tetrahedral group contains 5.453 Si cations and 2.547 Al cations, which carry 29.453 positive charges, and the tetrahedral layer has a negative charge of 2.547, exactly equal to the number of Al cations in that layer. If all the 6 octahedral positions in the unit cell of a mica are occupied by bivalent cations, as by Mg in phlogopite, the 12 positive charges they carry exactly equal the 12 negative charges allocated to that layer, and the layer is neutral; but if some of the positions are occupied by trivalent ions, the octahedral layer may have a positive charge, even though all the octahedral positions are not occupied, as in the example given in table 1. The number of positive octahedral charges present is calculated by multiplying the number of cations of each constituent by its valence and by adding these together. More simply, the same result can be obtained by taking the sum of the gram-equivalents per total of 44 of all the octahedral cations except Al cations and adding to this the number of octahedral Al cations (from the column headed cations per unit cell) multiplied by 3, as is shown in table 1. If this number, as in the example given, exceeds 12.000, the octahedral layer has a positive charge equal to the excess; if it is less than 12.000, the octahedral layer has a negative charge.

The algebraic sum of the tetrahedral and octahedral charges is the inherent charge on the unit layers and should closely agree with the charge on the interlayer cations, as it does in the example given. The negative inherent charge on the unit layers and the positive charge on the interlayer cations should be close to 2.00 (1.00 in the half-cell formula) for trioctahedral micas like the phlogopites and biotites. In evaluating the half-cell formulas used in this study, a variation of plus or minus 0.1 (0.2 in the unit cell) was permitted in these values. Formulas, in which either the negative inherent charge on the unit layers or the positive interlayer cation charge, or both, were greater or less than 1.00 by more than 0.1, were not used in the study. This was done in order to exclude from the study the formulas that may represent hydrous micas,

in which the interlayer cations are generally lower than in true micas, or, possible contamination of trisilicic trioctahedral micas with other materials.

The role of titanium in micas is ambiguous. Apparently no studies have been made to determine whether or not the titanium reported is actually in the mica structure. In some micas discrete crystals of rutile can be discerned, but what proportion of the total titanium content these represent is not known. In other micas discrete crystals of rutile are not discernible, and the color of the micas suggests that the titanium is in the layer structure. For some analyses used in this study, formulas were calculated as if all the titanium were in the layer structure and as if none of the titanium were in the layer structure. These calculations showed that for the amount of titanium usually reported, the inclusion or exclusion of titanium in calculating the formula has only a slight effect on the number of positions occupied by other octahedral cations. In accordance with general usage, therefore, titanium was included in the octahedral group in calculating the formulas herein used. The analyses (and data from which their calculated formulas may be written) that were used in the study are given in table 11; the excluded analyses (and data from which their calculated formulas may be written) are given in table 12.

#### EXCLUDED ANALYSES AND FORMULAS

Exclusion of certain analyses and formulas from the study does not necessarily indicate that they represent poor specimens or poor analyses. Many of the formulas in which the negative inherent unit layer charge and the positive interlayer cation charge is less than 0.90 represent very high magnesium trioctahedral micas, that is, phlogopites. In addition to their low inherent unit layer charge and low interlayer cation charge these formulas are, in general, characterized by a positive octahedral layer charge greater than the number of extra positive charges carried by their trivalent octahedral cations, and by a high octahedral occupancy, many of the formulas having an octahedral occupancy greater than 3.00. These characteristics indicate the allocation of too many cations to the octahedral layer, and too few to interlayer cation positions. Reallocation of some octahedral cations in these formulas to interlayer positions would produce more rational formulas.

For many years it was customary in calculating formulas from analyses of montmorillonite, which has the same structure as the micas, to allocate all the Mg to the octahedral group. The result was that in most formulas for montmorillonite the number of occupied octahedral positions was greater than 2.00, up to 2.24, and Ross and Hendricks (1945, p. 44) concluded that in montmorillonite more than 2.00 octahedral positions were characteristically occupied. However, the writer (Foster, 1951, p. 725) determined the exchangeable cations in a number of montmorillonites and found that they all contained some exchangeable Mg, and that when only nonexchangeable Mg was allocated to the octahedral layer, the number of octahedral positions occupied was  $2.00\pm0.02$  in the same specimens that apparently had as many as 2.12 octahedral positions occupied when all the Mg was allocated to the octahedral group.

These facts indicate that Mg can occupy interlayer positions and suggest that in the highly magnesium micas mentioned some of the magnesium should be considered as occupying interlayer positions. For example, if all the MgO, 24.60 percent, analysis D15, table 12, is allocated to the octahedral group in the usual way, the positive octahedral layer charge is 0.44, whereas only 0.32 additional positive charges are carried by the trivalent octahedral cations present; an excessive number of octahedral positions are occupied, 3.06; the inherent unit layer charge is only --0.82; and the interlayer cation charge in only +0.83. If, however, 0.75 percent of the MgO is allocated to the interlayer cations the positive octahedral layer charge is 0.28, 0.04 less than the number of positive charges carried by the trivalent octahedral cations present, 2.98 octahedral positions are occupied, the inherent unit layer charge is -0.98, and the interlayer cations charge is 0.99. A comparison of the two formulas,

$$\underbrace{[(Al_{0,16}Ti_{0,06}Fe_{0,04}^{+3}Fe_{0,16}^{+2}Mg_{2,51})}_{3,06}(Si_{2,74}Al_{1,28})O_{10}(OH)_2]^{-0.82}}_{(K,Na,Ba/2)_{0,81}^{+0.83}}$$

$$\underbrace{[(Al_{0,16}Ti_{0,06}Fe_{0,04}^{+3}Fe_{0,19}^{+2}Mg_{2,53})}_{2,98}(Si_{2,74}Al_{1,26})O_{10}(OH)_2]^{-0.98}}_{2,98}$$

(K,Na,Ba/2,Mg/2)<sup>+0.99</sup><sub>0.89</sub>

shows that the only change in layer occupancy is in the number of octahedral positions occupied by Mg; the number of positions occupied by all the other cations, in both the octahedral and tetrahedral layers, is the same in both formulas. Therefore, if Mg does occupy interlayer positions in micas, analyses like this group which contain considerable Mg and in which the negative inherent layer charge and the positive interlayer cation charge are low, may not be faulty, or represent poor materials, but may simply represent trioctahedral micas in which some of the Mg occupies interlayer positions.

Another group of formulas was excluded from the study because their negative inherent unit layer charge and their positive interlayer ion charge was greater than 1.10. In formulas calculated from analyses in which lithium was not determined the high unit layer and interlayer charges may be due to the failure to separate lithium from sodium. Failure to separate lithium from sodium has a double effect on the formula calculation, as it is reported as sodium and is calculated as an interlayer cation rather than as an octahedral cation. Thus, in the formula the interlayer cations and their charge are high, the octahedral cations and the positive octahedral charge are low; and, consequently, the negative inherent unit layer charge is high. This double effect is shown in the formulas below for D58, table 12,

 $\begin{array}{c} +0.31 & -1.54 \\ \underline{[(Al_{0.00}Ti_{0.04}Fe^{+3}_{1.09}Fe^{+2}_{1.13}Mg_{0.17}Mn^{+2}_{0.14})}_{2.57} (Si_{2.46}Al_{1.34}Fe^{+3}_{0.20})O_{10}(OH)_2]^{-1.33} \\ \underline{[(Al_{0.00}Ti_{0.04}Fe^{+3}_{1.09}Fe^{+2}_{1.12}Mg_{0.17}Mn^{+2}_{0.14}Li_{0.34})} \\ \end{array}$ 

$$\frac{11_{0,00} 1 1_{0,04} F e_{1,00} F e_{1,12} Mg_{0,17} Mh_{0,14} Lh_{0,34}}{2.87}$$

$$-1.55$$

$$(Si_{2,45} Al_{1,34} F e_{0,22}^{+3}) O_{10} (OH)_2]^{-0.99} (K, Na, Ca/2)_{0,97}^{+0.93}$$

In the first formula, which is calculated from the analysis as reported, the negative inherent layer charge and the positive interlayer cationic charge are very high, but the octahedral occupancy is quite low. The second formula is a recalculation from the same analysis on the assumption that the Na<sub>2</sub>O reported contained 1 percent of Li<sub>2</sub>O. The formula content of other cations present is very little changed, but the octahedral occupancy is raised from 2.57 to 2.87, and the negative unit layer charge and the positive interlayer cation charge are reduced to 0.99 and 0.98, respectively. Thirteen of the eighteen formulas that were not used because of high unit layer charge and high interlayer cation charge were of the type most likely to contain lithium, high in Fe<sup>+2</sup> and very low in Mg. Thus, although high unit layer and interlayer cation charges may be due to faulty analysis, particularly in determination of the alkalies, it is also possible that a calculated formula may show such high charges because of the analyst's failure to separate sodium and lithium. Failure to separate and determine Rb and Cs may also contribute to an apparently high alkali content.

In calculating the formulas for several analyses published as analyses of phlogopites or biotites, it was found necessary to allocate all the  $Al_2O_3$ , all the  $Fe_2O_3$ , and some of the TiO<sub>2</sub> to the tetrahedral layer to complete the filling of that layer, and in one phlogopite analysis it was necessary to assign all the  $Al_2O_3$ ,  $Fe_2O_3$ , TiO<sub>2</sub>, and FeO to the tetrahedral layer, leaving only MgO and **a** little Li<sub>2</sub>O in the octahedral layer—even so, the octahedral occupancy was high, 3.08 positions. All such analyses and formulas were excluded from the study as not representing the general chemical composition of trioctahedral micas, the subject of this study, whether or not the analyses themselves may be faulty or may represent contaminated materials.

Two other small groups of analyses with their derived formulas that were excluded from the study were not representative of the kind of micas under consideration. In one group the K content was very low, occupying fewer than 0.75 positions, with relatively high Ca and (or) Na content; in the other group the octahedral trivalent occupancy was very high, greater than 1.50, and total octahedral occupancy was very low, less than 2.50 positions. In several of the latter group the trivalent octahedral cations made up more than 65 percent of the octahedral cations. In one analysis, D61, table 12, which has 19.49 percent of Fe<sub>2</sub>O<sub>3</sub>, and 14.10 percent of FeO, Clarke (1903, p. 77) suspected alteration. A later analysis showed 24.22 percent of Fe<sub>2</sub>O<sub>3</sub> and 13.11 percent of FeO. Another analysis reports 27.19 percent of Fe<sub>2</sub>O<sub>3</sub> with only 0.64 per cent of FeO. In the formula for this analysis bivalent cations occupy less than 30 percent of the occupied octahedral positions, all the rest are occupied by trivalent cations. In analyses that yield formulas with unusually high octahedral Al content, contamination with muscovite may be suspected. For example, the material represented by one analysis was obtained from arborescent aggregates of biotites with muscovite occurring in the terminals of the aggregates.

# ACCOMMODATION OF EXTRAPOSITIVE OCTAHEDRAL CHARGES IN MICAS STUDIED

In a few of the formulas included in the study, the proxying of trivalent for bivalent octahedral cations is in accordance with equation A,  $(+2nR^{+2})=(-nR^{+2})$ + $(-nSi^{+4})$ , as in the following formula for a mica from Russia (26, table 11),

$$\underbrace{\{\underbrace{(\mathrm{AI}_{0.12}\mathrm{Ti}_{0.06}\mathrm{Fe}_{0.38}^{+2}\mathrm{Fe}_{0.46}^{+2}\mathrm{Mg}_{2.29})}_{3.01}(\mathrm{Si}_{2.67}\mathrm{AI}_{1.33})\mathrm{O}_{10}(\mathrm{OH})_{2}]^{-0.99}}_{(\mathrm{K}_{0.74},\mathrm{Na}_{0.14}\mathrm{Ca}/2_{9.66})_{0.92}^{+0.97}}$$

In this formula the proxying of trivalent for bivalent ions is 1:1, 0.26 Al, Ti, and Fe<sup>+3</sup> ions proxy for 0.25  $R^{+2}$  ions, and all the octahedral positions are occupied. The additional positive charges carried by Al, Fe<sup>+3</sup>, and Ti form a positive charge of 0.34 on the octahedral layer, which is neutralized by an equivalent increase in the negative tetrahedral charge. On the other hand, a few formulas exhibit the type of accommodation for trivalent octahedral ions expressed by equation B,  $(+2nR^{+3})=(-3nR^{+2})+(-nOct. Pos.)$ , as does this formula for a biotite from Låven Island (84 table 11),

$$[\underbrace{(Al_{0.10}Ti_{0.04}Fe_{0.38}^{+0.04}Fe_{1.36}^{+2}Mg_{0.95}Mn_{0.06}^{+2})}_{2.79}(Si_{2.92}Al_{1.07})O_{10}(OH)_{2}]^{-1.03}$$

$$(K_{0.85}Na_{0.25})_{1.08}^{+1.08}$$

In this formula the proxying of trivalent for bivalent octahedral cations is approximately 2:3; 0.42 Al, Ti, and Fe<sup>+3</sup> cations carrying 0.46 additional positive charges proxy for 0.63 R<sup>+2</sup> cations, and 0.21 unoccupied octahedral positions furnish 0.42 negative charges to neutralize 0.42 of the additional positive charges. The octahedral layer is, therefore, almost neutral, having a positive charge of only 0.04; and the tetrahedral charge is 1.07, close to the 1.00 of the theoretical formula. However, most of the formulas calculated for this study are characterized by both a positive octahedral charge and a deficiency in octahedral occupation; this indicates a dual adjustment, as in this formula for a phlogopite from Uganda, 33, table 11.

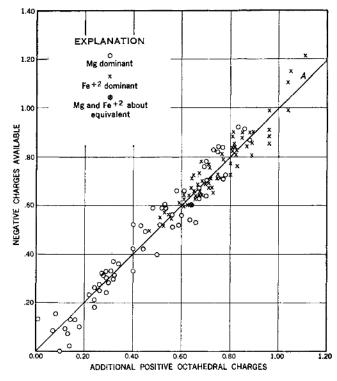
$$\underbrace{ \underbrace{ [(\mathrm{Al}_{0.60}\mathrm{Ti}_{0.15}\mathrm{Fe}_{0.22}^{+3}\mathrm{Fe}_{0.31}^{+2}\mathrm{Mg}_{2.15}\mathrm{Mn}_{0.02})}_{\mathbf{2.85}} (\mathrm{Si}_{2.71}\mathrm{Al}_{1.29})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.07}}_{\mathbf{(K}_{0.89},\mathrm{Na}_{0.03},\mathrm{Ca}/2_{0.03}\mathrm{Ba}/2_{0.04})_{0.98}^{+1.04}}$$

In this formula the trivalent and quadrivalent octahedral cations carry 0.52 positive charges in excess of the number of positive charges carried by the same number of bivalent cations. Of these additional charges, 0.30 are neutralized by 0.15 unoccupied octahedral positions and 0.22 form a positive charge on the octahedral layer, which is neutralized by an increase in the negative charge on the tetrahedral layers. The inherent layer charge is, consequently, very close to 1.00 (1.07), and is balanced by interlayer cations, K, Na, Ba, and Ca, carrying an equivalent positive charge.

As illustrated by this example, in dual accommodation for trivalent and quadrivalent octahedral cations in trioctahedral micas, the additional positive octahedral charges are neutralized by the negative tetrahedral charge in excess of 1.00, in accordance with equation A, and by the negative octahedral charges left available by unoccupied octahedral positions, in accordance with equation B. Theoretically, the sum of these negative charges should exactly equal the number of additional positive charges carried by the trivalent and quadrivalent octahedral actions. This relation in the trioctahedral micas studied is shown in figure 6, in which the number of additional positive charges carried

FIGURE 6.—Relation between additional positive octabedral charges and negative charges available to neutralize them.

by trivalent and quadrivalent octahedral cations in each formula is plotted against the number of negative charges available to neutralize them; that is, the sum of the tetrahedral charge in excess of -1.00 plus the number of unoccupied octahedral positions doubled. Points for formulas in which the number of additional positive octahedral charges is exactly equal to the sum of negative charges available fall on the line bisecting the figure. Location of a point above or below the line indicates that in the formula represented by the point the negative charges available are greater or less, respectively, than the number of additional positive octahedral charges, by the distance of the point from the line. The close clustering of the points along the line indicates that there is a fairly close agreement in the formulas between the number of additional positive octahedral charges and the number of negative charges available to neutralize them The points on or close to the line represent formulas in which the inherent unit layer negative charge and the interlayer cation positive charge is almost exactly 1.00. Those farthest from the line represent formulas in which the inherent unit layer negative charge and the interlayer cation positive charge is near 0.90 or 1.10. In the formulas in which the inherent unit layer negative charge and the interlayer cation charge is less than 1.00, the tetrahedral negative charge in excess of -1.00is less than the octahedral positive charge; in formulas



in which the inherent layer negative charge and the interlayer cation positive charge is greater than 1.00, the tetrahedral negative charge in excess of -1.00 is greater than the octahedral positive charge. As pointed out in the discussion on the calculation of formulas (p. 13), these discrepancies may be due to analytical error, particularly in the determination of Ca, Na, and K, to failure to determine Li or CO<sub>2</sub>, or to the use, in calculating the formulas, of the theoretical oxygen and hydroxide, fluorine values (O<sub>10</sub>(OH,F)<sub>2</sub>) because of lack or obvious inaccuracy of data on these constituents in the analyses.

The degree of accommodation for additional positive octahedral charges by each of the two methods in the trioctahedral micas under study is shown (fig. 7) by plotting, for each formula, the additional positive octahedral charges against the number of negative tetrahedral charges in excess of 1.00. Points for

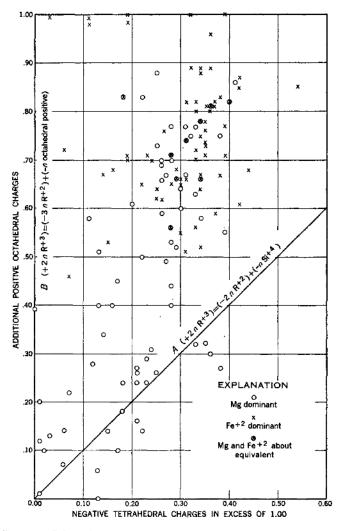


FIGURE 7.—Relation between additional positive octahedral charges and negative tetrahedral charges in excess of 1.00.

formulas that exhibit accommodation for trivalent and quadrivalent octahedral cations exclusively in accordance with equation A fall on line A, those for formulas that exhibit accommodation for trivalent and quadrivalent octahedral cations exclusively in accordance with equation B fall on the ordinate, and those for formulas exhibiting both types of accommodation for trivalent octahedral cations fall between these two lines. The location of most of the points between these two lines makes it quite apparent that in most of these trioctahedral micas both types of accommodation for trivalent and quadrivalent octahedral cations are represented. In formulas represented by points near the middle of the area between lines A and B, accommodation has been made both ways about equally; in formulas represented by points closer to line A or to the ordinate of the graph, line B, that type of accommodation represented by line A or line B was made to a greater degree than by the other type.

The average adjustment in trioctahedral micas for different amounts of additional positive octahedral charges due to trivalent cations is shown by the average formulas in table 2. To arrive at these average formulas the calculated formulas used in this study were grouped according to the number of additional positive charges carried by their trivalent (and quadrivalent) octahedral cations. If the formula contains no Ti, the number of additional octahedral positive charges is equivalent to the number of octahedral positions occupied by trivalent cations, usually Al and Fe<sup>+3</sup>. But if the formula contains Ti, the number of positions occupied by Ti must be multiplied by 2, as Ti<sup>+4</sup> carries 2 more charges than a bivalent cation, and this number is added to the number of octahedral positions occupied by trivalent cations. For example, in the formula for No.33, table 11, trivalent cations occupy 0.22 octahedral positions and Ti occupies 0.15 octahedral positions. Thus the number of additional positive octahedral charges present is  $0.22 + (0.15 \times 2) = 0.52$ . From the formulas in each of these groups, separate average formulas were derived for the magnesium and for the bivalent iron-dominant micas when both are sufficiently represented in a group. However, sufficient numbers of formulas to permit derivation of average Fe<sup>+2</sup>dominant formulas are found only in the groups in which the number of additional positive charges is greater than 0.50. In only three Fe<sup>+2</sup>-dominant formulas were the number of additional positive charges carried by trivalent and quadrivalent octahedral cations less than 0.50. On the other hand, Mg-dominant formulas are found in all the groups, and from these the general mode of adjustment of trioctahedral micas to the presence of trivalent and quadrivalent cations in the octahedral layer can be deduced.

# INTERPRETATION OF TRIOCTAHEDRAL MICAS

			in order of number of additional positive		onal goo
Group	Number of additional positive octahedral charges	Number of formulas	Mg-dominant formulas	Number of formulas	Fe+2-dominant formulas
A	0.00-0.10 0.05	6	$\underbrace{(\mathbf{Al_{0.00}Fe_{0.05}^{+3}Fe_{0.05}^{+2}Mg_{2.90}}_{3.00}}_{3.00}(\mathbf{Si_{2.05}Al_{1.05}})$	None	
В	0. 11-0. 20 0.15	8	$\underbrace{(\underline{Al_{0.10}Fe_{0.05}^{+3}Fe_{0.10}^{+2}Mg_{2.75}}_{3.00}(Si_{2.85}Al_{1.15})}^{+1.15}$	None	
c	0. 21-0. 30 0.25	14	$\underbrace{(\underline{Al_{0.15}Fe_{0.10}^{+3}Fe_{0.30}^{+2}Mg_{2.45}})}_{3.00}(\underline{Si_{2.75}Al_{1.45}})$	None	
D	0. 31-0. 40 0.35	11	$\underbrace{(\mathrm{Al}_{0.18}\mathrm{Ti}_{0.05}\mathrm{Fe}_{0.10}^{+3}\mathrm{Fe}_{0.30}^{+2}\mathrm{Mg}_{2.35})}_{2.95}(\mathrm{Si}_{2.75}\mathrm{Al}_{1.25})$	1	
E	0. 41-0. 50 0.45	11	$\underbrace{(\underbrace{\mathrm{Al}_{0.15}\mathrm{Ti}_{0.05}\mathrm{Fe}_{0.20}^{+3}\mathrm{Fe}_{0.55}^{+2}\mathrm{Mg}_{1.85}}_{2.90}}_{2.90}(\mathrm{Si}_{2.75}\mathrm{Al}_{1.26})$	2	
F	0.51-0.60 0.55	6	$\underbrace{(\mathrm{Al}_{0.20}\mathrm{Ti}_{0.10}\mathrm{Fe}_{0.15}^{+3}\mathrm{Fe}_{0.65}^{+2}\mathrm{Mg}_{1.75})}_{2.85}(\mathrm{Si}_{2.75}\mathrm{Al}_{1.26})$	6	$\underbrace{\frac{+0.25}{(\mathrm{Al}_{0.10}\mathrm{Ti}_{0.15}\mathrm{Fe}_{0.15}^{+3}\mathrm{Fe}_{1.55}^{+2}\mathrm{Mg}_{0.90})}_{2.85}(\mathrm{Si}_{2.75}\mathrm{Al}_{1.25})}_{2.85}$
G	0. 61-0. 70 0.65	9	$\underbrace{(\underbrace{Al_{0.15}Ti_{0.15}Fe_{0.20}^{+3}Fe_{0.90}^{+2}Mg_{1.40}}_{2.80})(Si_{2.75}Al_{1.25})}_{2.80}$	14	$\underbrace{\frac{(\mathrm{Al}_{0.15}\mathrm{Ti}_{0.15}\mathrm{Fe}_{0.20}^{+3}\mathrm{Fe}_{1.45}^{+2}\mathrm{Mg}_{0.85})}_{2.80}(\mathrm{Si}_{2.75}\mathrm{Al}_{1.26})}_{2.80}$
н	0. 71–0. 80 0.75	8	$\underbrace{(Al_{0.20}Ti_{0.15}Fe_{0.25}^{+3}Fe_{0.35}^{+2}Mg_{1.30})}_{2.75}(Si_{2.75}Al_{1.25})$	17	$\underbrace{\underbrace{(Al_{0,20}Ti_{0,15}Fe_{0,25}^{+3}Fe_{1,35}^{+2}Mg_{0,80})}_{2.75}(Si_{2,75}Al_{1,25})$
I	0.81-0.90 0.85	4	$\underbrace{(\mathrm{Al}_{0.25}\mathrm{Ti}_{0.20}\mathrm{Fe}_{0.20}^{+3}\mathrm{Fe}_{0.80}^{+2}\mathrm{Mg}_{1.25})}_{2.70}(\mathrm{Si}_{2.75}\mathrm{Al}_{1.25})$	12	$\underbrace{ \underbrace{ (\mathrm{Al}_{0.35}\mathrm{Ti}_{0.16}\mathrm{Fe}_{0.20}^{+3}\mathrm{Fe}_{1.25}^{+2}\mathrm{Mg}_{0.7b})}_{2,70} (\mathrm{Si}_{2.75}\mathrm{Al}_{1.25})}_{2,70}$

 TABLE 2.—Average octahedral and tetrahedral cation content of formulas for phlogopites, Mg-dominant biotites, and Fe<sup>+2</sup>-dominant biotites in order of number of additional positive octahedral charges

The average Mg-dominant formulas indicate, in general, that if the number of additional positive charges carried by trivalent and quadrivalent octahedral cations is less than 0.25, all the additional positive charges form a positive charge on the octahedral layer, the negative tetrahedral charge is greater than 1.00 by an amount equivalent to the positive octahedral charge, and all the octahedral cationic positions are occupied; that is, adjustment for the additional positive octahedral charges is predominantly in accordance with equation A. Thus the average formula for group A, in which the average number of additional octahedral positive charges is 0.05, has a positive octahedral charge of 0.05, a negative tetrahedral charge of 1.05, and all the octahedral positions are occupied. Similarly in the average formulas for groups B and C, in which the average number of additional positive octahedral charges is 0.15 and 0.25, respectively, the positive charge on the octahedral layer is equivalent to the number of additional positive charges carried by R<sup>+8</sup> octahedral cations, the negative tetrahedral charge is greater than 1.00 by an equivalent amount and all the octahedral positions are occupied. In the average formula for group D, however, in which the number of additional positive charges carried by R<sup>+8</sup> (and R<sup>+4</sup>) octahedral cations averages 0.35, only 0.25 of these extra charges form a positive charge on the octahedral layer-the remaining 0.10 charges are neutralized by the 0.10 negative charges associated with the 0.05 unoccupied octahedral positions. In succeeding group formulas the increasingly greater number of additional positive charges is reflected not in greater positive charges on the octahedral layer and greater negative tetrahedral charges but in greater nonoccupancy of octahedral positions, that is, an increasingly greater proportion of the adjustment for trivalent and quadrivalent octahedral cations is made in accordance with equation B. Thus, in the average formulas for groups E, F, G, H, and I, the average positive octahedral charge is the same, 0.25, but the average number of octahedral positions

occupied progressively decreases from 2.90, in formula E, to 2.70, in formula I.

These relations between positive octahedral charge (equation A) and octahedral occupancy (equation B) with increase in the number of additional positive octahedral charges suggest that the amount of positive charge on the octahedral layer that can be accommodated comfortably by the structure is somewhat limited, and that with a greater number of positive octahedral charges to be neutralized, neutralization by negative charges associated with unoccupied octahedral positions is generally more tolerable to the structure than neutralization by a greater negative tetrahedral charge and the necessarily greater proxying of Al for Si. Throughout the range there are, of course, some formulas that deviate greatly from the average in their mode of adjustment (fig. 7) but the average formulas illustrate the general way in which different amounts of additional positive charges carried by trivalent octahedral cations are accommodated in the trioctahedral micas.

The general decrease in octahedral occupancy with increase in the number of additional positive octahedral charges is shown graphically in figure 8. In this figure, for each formula, the number of occupied octahedral positions is plotted against the number of additional positive charges carried by trivalent (and quadrivalent) octahedral cations. If three octahedral positions were generally occupied in the trioctahedral micas and if

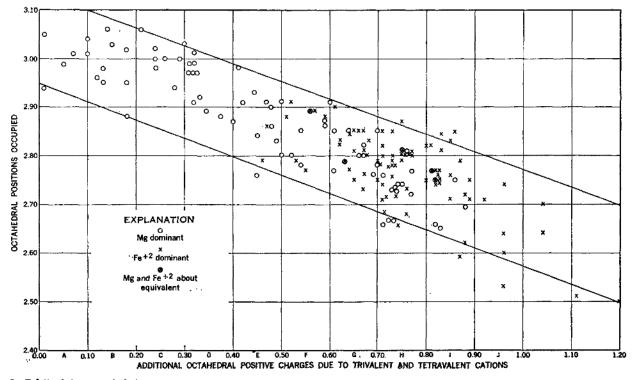


FIGURE 8.-Relation between octahedral occupancy and the number of additional octahedral positive charges due to trivalent and quadrivalent cations in trioctahedral micas.

. . .

accommodation for trivalent octahedral cations were generally made according to equation A, the points representing the extra R<sup>+3</sup> charge-octahedral occupancy relation of the formulas would fall in a narrow horizontal band across the top of the figure. The general trend of the points diagonally downward from left to right indicates a general decrease in octahedral occupancy with increase in the number of additional octahedral positive charges due to some degree of adjustment for these additional charges in accordance with equation B. The width of the band indicates the variation in the degree to which adjustment for trivalent and quadrivalent octahedral cations is made in one way or the other. Formulas having quite different amounts of additional R<sup>+3</sup> (and R<sup>+4</sup>) positive octahedral charges may have the same octahedral occupancy, and vice versa, depending on the degree to which accommodation for additional R<sup>+3</sup> (and R<sup>+4</sup>) positive octahedral charges has been made in accordance with equation A or equation B. For example, the formulas for analysis 84, table 11,

$$\underbrace{[(Al_{0.10}Ti_{0.04}Fe_{0.23}^{+3}Fe_{1.36}^{+2}Mg_{0.95}Mn_{0.00}^{+2})}_{2.79}(Si_{2.93}Al_{1.07})O_{10}(OH)_2]^{-1.02}$$

(K<sub>0.85</sub>, Na<sub>0.23</sub>)<sup>+1.08</sup>

and for 109, table 11

$$\frac{+0.45}{[(Al_{0.08}Ti_{0.22}Fe_{0.35}^{+3}Fe_{1.46}^{+2}Mg_{0.58})}(Si_{2.58}Al_{1.42})O_{10}(OH)_2]^{-0.97}}{2.79}$$

 $(K_{0.70}, Na_{0.13}, Ca/2_{0.02})^{+0.96}_{0.94}$ 

differ greatly in the number of additional R<sup>+3</sup> positive charges present, 0.46 and 0.87, respectively, and in positive octahedral charge but have the same octahedral occupancy. In the formula for 84 accommodation for  $R^{+3}$  (and  $R^{+4}$ ) cations has been made almost entirely in accordance with equation B, 0.42 R<sup>+3</sup> (and R<sup>+4</sup>) ions proxying for 0.63  $\mathbb{R}^{+2}$  ions, whereas in the formula for 109 accommodation has been made almost equally by both methods. Of the 0.87 additional positive charges carried by the  $R^{+3}$  (and  $R^{+4}$ ) octahedral cations present in the formula for 109, 0.45 form a positive charge on the octahedral layer and are neutralized by an approximately equivalent increase in the negative tetrahedral charge, and 0.42 are neutralized by the 0.42 negative charges associated with 0.21 unoccupied octahedral positions. The formulas for analyses 36.

$$\underbrace{\frac{((Al_{0.21}Ti_{0.06}Fe_{0.18}^{+3}Cr_{0.01}^{+3}Fe_{0.54}^{+3}Mg_{1.73}Mn_{0.02}^{+2}Li_{0.03})}{2.78}}_{-1.13}_{(Si_{2.57}Al_{1.12})O_{10}(OH)_2]^{-1.06}(K_{0.74}, Na_{0.12}, Ca/2_{0.12})_{0.99}^{+1.11}}$$

and 96, table 11,  
+0.34 -1.34  
$$[(Al_{0.02}Ti_{0.02}Fe_{0.25}^{+.34}Fe_{1.34}^{+.2}Mg_{0.87}Mn_{0.07}^{+2})(Si_{2.66}Al_{1.34})O_{10}(OH)_2]^{-1.00}$$

2,91

 $(K_{0.89}, Na_{0.13})^{+1.02}_{1.02}$ 

have the same number of additional  $\mathbb{R}^{+3}$  (and  $\mathbb{R}^{+4}$ ) charges, 0.51 and 0.52, respectively, but differ greatly in octahedral occupancy, in positive octahedral charge, and in negative tetrahedral charge. In the formula for 36, accommodation for  $\mathbb{R}^{+3}$  and  $\mathbb{R}^{+4}$  octahedral cations has been made predominantly in accordance with equation B, with 0.45  $\mathbb{R}^{+3}$  and ( $\mathbb{R}^{+4}$ ) cations proxying for 0.68  $\mathbb{R}^{+2}$  cations; in the formula for 96 about twothirds of the accommodation for  $\mathbb{R}^{+3}$  (and  $\mathbb{R}^{+4}$ ) octahedral cations is in accordance with equation A, and one-third in accordance with equation B.

Thus the vertical location of a point in figure 8 depends on the manner in which octahedral R<sup>+3</sup> (and R<sup>+4</sup>) cations have been accommodated in the structure. Points near the top of the diagonal band represent formulas of individuals in which the accommodation was predominantly in accordance with equation A; points near the bottom of the diagonal band represent formulas of individuals in which accommodation was predominantly in accordance with equation B. The width of the diagonal band indicates, therefore, the degree of variation in the manner in which the trioctahedral micas represented by the points have accommodated themselves to the presence of trivalent octahedral cations. However, despite such variations in manner of accommodation, it is quite obvious, from the average formulas in table 2, and from the downward trend of the band in figure 8, that there is, in the trioctahedral micas, a general decrease in octahedral occupancy with increase in octahedral trivalent cations. The trioctahedral micas are, in general, therefore, not strictly trioctahedral, nor are they strictly octaphyllites, as they contain fewer than eight cations per half cell.

Although Holzner (1936, p. 435) noted deficiency in octahedral occupancy in his biotite formulas and attempted to account for it by postulating that the biotite structure is made up of 2 layers of phlogopite to 1 of muscovite, he apparently failed to notice that in his formulas tetrahedral aluminum and consequently, tetrahedral charge, is, with but 2 exceptions (21 and 30, table 4) greater than 1.00, ranging from 1.01 to 1.40. On the other hand, the K(Na,Ca) values are, with but five exceptions, lower than the corresponding tetrahedral Al values. As the number of interlayer cations present is dependent on, and is usually equivalent to, the inherent layer charge, this discrepancy between Holzner's Al[4] (which represents the tetrahedral charge) and his K(Na,Ca) values suggests that the octahedral layer in his formulas must carry a positive charge approximately equivalent to the difference between his Al[4] and K(Na,Ca) values. As Holzner included in his tables II and III the octahedral bivalent (Y'') and trivalent (Y''') ion content, it is possible to calculate from them the octahedral charge and the inherent layer charge of his formulas. The results of these calculations are given in tables 3 and 4, together with Holzner's values for Y'', Y''', Y'''+Y''' (equivalent to octahedral occupancy), Al[4] (equivalent to tetrahedral charge), and K(Na,Ca). All but five (2, table 3, and 13, 18,

 TABLE 3.—Selected data on phlogopites from Holzner (1936, table 2) with added data for octahedral and total charge

No, of analysis	Υ"	Y‴	Y"+Y"	Octa- hedral charge	Al[4]= Tetra- hedral charge	Total charge	K(Na, Ca)
1 2	3, 031 2, 906 2, 931 2, 843 2, 815 2, 891 2, 809 2, 695 2, 809 2, 675 2, 657 2,	0.020 0.033 0.082 0.092 1.927 2066 223 266 270 287 303 337 338 338 339 4488	3.031 2.926 2.925 3.007 3.013 3.005 2.901 3.032 2.945 2.945 2.945 2.945 2.945 2.945 2.946 3.001 2.903 2.903 2.908 2.908 2.908 2.908 2.908 2.908	$\begin{array}{c} +0.062 \\ -1.28 \\ +.021 \\ +.068 \\ +.106 \\ +.148 \\ +.259 \\ +.258 \\ +.258 \\ +.236 \\ +.236 \\ +.236 \\ +.236 \\ +.239 \\ +.323 \\ +.230 \\ +.323 \\ +.404 \\ +.328 \end{array}$	$\begin{array}{c} -1, 127\\ -1, 049\\ -1, 134\\ -1, 158\\ -1, 086\\ -1, 155\\ -1, 223\\ -1, 086\\ -1, 155\\ -1, 223\\ -1, 123\\ -1, 217\\ -1, 180\\ -1, 132\\ -1, 110\\ -1, 170\\ -1, 120\\ -1, 180\\ -1, 232\\ -1, 2$	$\begin{array}{c} -1.065\\ -1.177\\ -1.117\\ -1.113\\ -1.090\\980\\9804\\9804\\9804\\940\\948\\9804\\966\\978\\980\\918\\980\\918\\940\\938\\787\\940\\988\\1.005\\884\\1.005\\$	1.077 1.180 1.081 1.077 .985 .993 .950 1.210 .794 1.066 1.066 1.066 1.066 1.066 2.993 .878 .921 .783 .942 .938 1.002 .888 1.002 .888 1.002

TABLE 4.—Selected data on biotites from Holzner (1936, table 3) with added data for octahedral and total charge

No. of analysis	Y″	¥"."	Y"+Y"	Octa- hedral charge	Al[4]= Tetra- hedral charge	K(Na, Ca)	Total charge
1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18           19           20           21           22           23           24           25           26           27           28           30           32           33           34	$\begin{array}{c} 2.402\\ 2.358\\ 2.162\\ 2.307\\ 2.015\\ 2.015\\ 2.015\\ 2.015\\ 2.010\\ 2.000\\ 2.$	$\begin{array}{c} \hline \\ 0.418\\ -499\\ -654\\ -333\\ -791\\ -614\\ -614\\ -614\\ -614\\ -681\\ -356\\ -574\\ -413\\ -681\\ -681\\ -681\\ -681\\ -681\\ -681\\ -681\\ -681\\ -681\\ -681\\ -798\\ -707\\ -461\\ -706\\ -706\\ -706\\ -706\\ -526\\ -706\\ -807\\ -745\\ -861\\ -807\\ -882\\ -881\\ -873\\ -873\\ -882\\ -873\\ -882\\ -812\\ -873\\ -882\\ -812\\ -812\\ -873\\ -882\\ -812\\ -882\\ -812\\ -882\\ -812\\ -882\\ $	2.820 2.857 2.857 2.856 2.866 2.866 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.884 2.875 2.772 2.775 2.775 2.775 2.775 2.775 2.2755 2.2755 2.2755 2.2755 2.27555 2.275555 2.275555555555	$\begin{array}{c} 0.658\\ -0.658\\ +1.2286\\ +2.286\\ +2.283\\ +1.123\\$	$\begin{array}{c} -1.186\\ -1.232\\ -1.232\\ -1.233\\ -1.330\\ -1.254\\ -1.254\\ -1.140\\ -1.254\\ -1.140\\ -1.1254\\ -1.254\\ -1.063\\ -1.063\\ -1.063\\ -1.063\\ -1.181\\ -1.2221\\ -1.221\\ -1.22$	$\begin{array}{c} 1.078\\ 1.078\\ 2.051\\ .951\\ .951\\ .997\\ .997\\ .997\\ .997\\ .997\\ .997\\ .997\\ .997\\ .997\\ .997\\ .997\\ .997\\ .903\\ 1.016\\ 1.085\\ .993\\ 1.035\\ .993\\ 1.035\\ .993\\ 1.035\\ .993\\ 1.035\\ .993\\ 1.035\\ .993\\ 1.035\\ .993\\ 1.027\\ .834\\ .974\\ .834\\ .994\\ .834\\ .994\\ .983\\ .948\\ .983\end{array}$	$\begin{array}{c} -1, 128\\ -1, 019\\ -, 986\\ -, 987\\ -, 986\\ -, 987\\ -1, 071\\ -1, 032\\ -1, 071\\ -1, 032\\ -1, 017\\ -1, 032\\ -1, 017\\ -1, 032\\ -1, 017\\ -1, 032\\ -1, 013\\ -1, 032\\ -1, 013\\ -1, 042\\ $
85	2.119	. 678	2.797	+.272	-1.027	. 952	855

21, and 23, table 4) have a positive octahedral charge, and the algebraic sum of these positive octahedral charges and the corresponding negative tetrahedral charges yields values for inherent layer charge consistent with the corresponding values for K(Na,Ca). Thus Holzner's formulas also exhibit the 2 types of adjustment for  $\mathbb{R}^{+3}$  cations that were found in the formulas used in this study, 1 of which, adjustment in accordance with equation A, is not explained by his hypothesis, which is based entirely on accommodation in accordance with equation B.

# R+2-R+3 RELATION IN TRIOCTAHEDRAL MICAS

In the accommodation of trivalent octahedral cations according to equation A,  $(+2nR^{+3})=(-nR^{+2})+$  $(-nSi^{+4})$ , the proxying of trivalent for bivalent octahedral ions is 1 to 1. In accommodation according to equation B,  $(+2nR^{+3}) = (-3nR^{+2}) + (-nOct.Pos.)$ , the proxying of trivalent for bivalent octahedral cations is 2 to 3 or 0.67 to 1. As both methods are exhibited to varying degrees in the natural trioctahedral micas studied, it follows that the proxying of trivalent for bivalent octahedral cations in these micas must vary between 1:1 and 0.67:1, depending on the relative degrees to which accommodation was made by one way or the other. This is illustrated in figure 9, in which the number of R<sup>+2</sup> cations displaced is plotted against the number of proxying octahedral R<sup>+3</sup> and R<sup>+4</sup> cations. With few exceptions all the points fall along or between line A, which represents the proxying ratio of equation A,  $R^{+3}:R^{+2}=1:1$ , and line B, which represents the proxying ratio of equation B,  $R^{+3}$ :  $R^{+2}$ = 0.67:1. Most of the points representing formulas having a trivalent octahedral cation content of less than 0.40 positions, as in most trioctahedral micas very high in Mg, that is, phlogopites, lie on or close to line A, whereas points representing formulas having a trivalent octahedral ion content of more than 0.40 positions lie closer to line B. These relations agree with the type of adjustment found for different amounts of additional trivalent octahedral positive charges in the average formulas (table 2). In trioctahedral micas in which the trivalent ion content is low, accommodation for their extra charges is predominantly in accordance with equation A, and the proxying ratio is 1 to 1. With increase in trivalent octahedral ion content an increasingly greater degree of accommodation is made according to equation B, and the proxying ratio approaches more nearly 0.67 to 1.0. As the trioctahedral micas generally exhibit both types of accommodation for octahedral trivalent cations, an equation representing the change in composition involved, as compared with the ideal, must be a combination of equations A and B. However, as the relative degree

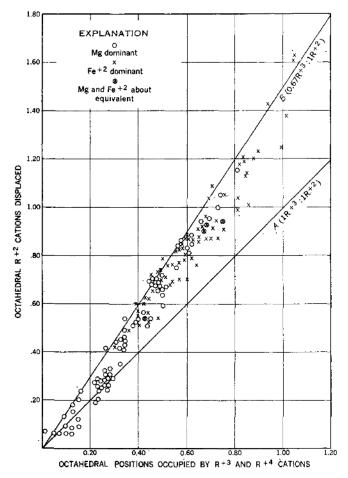


FIGURE 9.—Relation between R<sup>+2</sup> cations displaced and proxying R<sup>+3</sup> (and R<sup>+4</sup>) octahedral cations.

to which the two types are used differs with each individual, the equation would, consequently, differ with each individual. The difficulties are further complicated by Ti which carries twice as many extra charges as octahedral positions occupied.

The scarcity of formulas having an octahedral  $\mathbf{R}^{+3}$  (+ $\mathbf{R}^{+4}$ ) occupancy of more than 0.90 positions suggests that this  $R^{+3}$  (+ $R^{+4}$ ) occupancy (about onethird of the occupied octahedral positions) is about the upper limit of the  $R^{+2}$  by  $R^{+3}$  (+ $R^{+4}$ ) replacement in the trioctahedral micas. This is shown another way in figure 10, in which histograms represent the type and number of formulas in each additional positive octahedral charge group. Group H, in which the number of additional octahedral positive charges is between 0.71 and 0.80, includes the greatest number of formulas (25). From this high the number of formulas in each successive group drops to 16 in group I and to 2 in group J. This sharp drop in the number of formulas in each succeeding group from the high in group H. and the scarcity of formulas having an R<sup>+3</sup> occupancy greater than 1.00, supports the suggestion that an

 $R^{+3}$  (+ $R^{+4}$ ) octahedral occupancy of one-third of the octahedral positions is the essential limit of replacement of octahedral  $R^{+2}$  (Mg) by  $R^{+3}$  (and  $R^{+4}$ ) in the trioctahedral micas.

The small number of formulas having more than 1.00 positions occupied by R<sup>+3</sup> and R<sup>+4</sup> is also strong evidence against the existence of a complete series between phlogopite and muscovite and supports Deer (1937, p. 449) and Hutton (1947, p. 482) in their conclusions that it is not likely that the number of octahedral positions occupied varies between 2 and 3, as postulated by Pauling (1930, p. 128). Deer believed that any value between 2.5 and 3.0 is possible, but Hutton set the lower limit for octahedral occupancy at not less than 2.75. In six formulas used in the present study in which  $R^{+3}$  and  $R^{+4}$  occupied  $1.00 \pm 0.10$  octahedral positions, total octahedral occupancy was between 2.45 and 2.75 positions, and averaged 2.60. In the two formulas having the lowest octahedral occupancy, 2.45 and 2.51 positions, accommodation for trivalent octahedral cations is almost entirely in accordance with equation B.

# Mg-Fe<sup>+2</sup> RELATION IN TRIOCTAHEDRAL MICAS

In addition to replacement of Mg by  $R^{+3}$  cations in the octahedral layer of trioctahedral micas, there is also replacement of Mg by Fe<sup>+2</sup> cations. With but very few exceptions, all the formulas calculated from analyses of trioctahedral micas contain both Fe<sup>+2</sup> and R<sup>+3</sup> cations in the octahedral group. The exceptional analyses are of two kinds-almost pure phlogopites that contain only a very small amount of Fe<sup>+2</sup> cations but no octahedral R<sup>+3</sup> cations, or vice versa, and biotites in which Fe<sup>+2</sup> was not determined but was included in total Fe as  $Fe_2O_3$  in the analysis. Thus, coincident with replacement of Mg by R<sup>+3</sup> cations, there is also replacement of Mg by Fe<sup>+2</sup> cations. A very general relation between the amounts of Fe<sup>+2</sup> and octahedral  $\mathbb{R}^{+3}$  is suggested by the histograms in figure 10; (1) in formulas having very little octahedral  $\mathbb{R}^{+3}$ , Mg is greatly predominant, (2) in formulas having moderate amounts of octahedral R<sup>+3</sup>, Mg is still dominant but less so than in (1), and (3) in formulas having more than 0.60 octahedral positions occupied by  $\mathbf{R}^{+3}$ ,  $\mathbf{Fe}^{+2}$  is the dominant octahedral cation in most of the formulas. However, the histograms also show the presence of some Mg-dominant biotites in the higher  $\mathbf{R}^{+3}$  groups. This fact, and the great variability in the Fe<sup>+2</sup>-octahedral R<sup>+3</sup> ratio in the formulas indicate that no real relation exists, and that the two series, although concurrent, are independent. Also, the amount of octahedral R<sup>+3</sup> present has no relation to the amount of Fe<sup>+2</sup> present, and vice versa. On the other hand, the presence in all but a very few of the formulas of

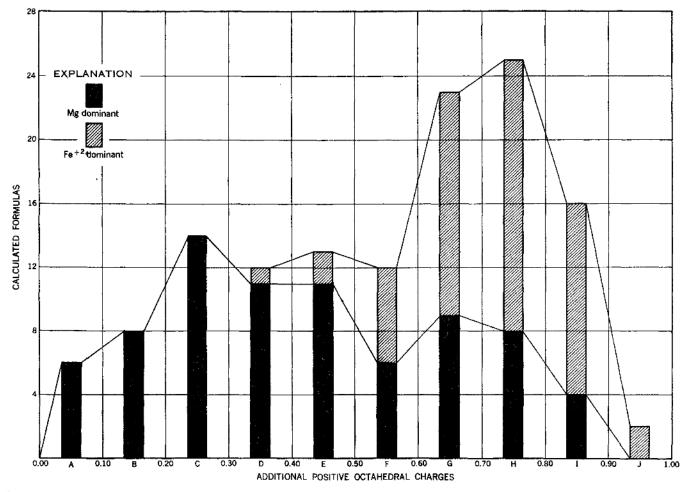


FIGURE 10.-Distribution of trioctabedral micas with respect to the number of additional positive octahedral charges carried by trivalent and quadrivalent octahedral cations.

both  $R^{+3}$  and  $Fe^{+2}$  in the octahedral group indicates that neither type of replacement forms a separate series. This statement includes Winchell's annite, the  $Fe^{+2}$ analog of phlogopite, and the theoretical end member of a Mg-Fe<sup>+2</sup> replacement series. Such a mica was not found among the more than 200 analyses collected for this study.

Substitution of  $Fe^{+2}$  for Mg poses no problem of adjustment as does the substitution of  $R^{+3}$  for Mg. Both cations are bivalent, no excess nor deficiency of charge is involved, and substitution is ion for ion with no other change in the octahedral or tetrahedral layers.

On the evidence of the analyses and their derived formulas, an octahedral occupancy of more than 2.20 positions by  $Fe^{+2}$  is not to be expected. The highest  $Fe^{+2}$  in the formulas studied was 2.17, and only 4 formulas had an  $Fe^{+2}$  octahedral occupancy of more than 2.00.

# MAGNESIUM REPLACEMENT SYSTEM

It has been shown that the only trioctahedral micas in which all, or almost all, the octahedral positions are occupied by one kind of cation are some phlogopites in which more than 90 percent of the octahedral positions are occupied by Mg. The Fe+2 analog of phlogopite, Winchell's annite, apparently does not exist in nature, or is very rare. With pure phlogopite as the prototype, all the other trioctahedral micas may be derived by the replacement of Mg by, most commonly, Fe<sup>+2</sup> and R<sup>+3</sup>. Thus, the trioctahedral micas may be considered as members of a system in which two principal types of replacement proceed concurrently but independently. The relation between Mg, (Fe<sup>+2</sup> and Mn), and (Al, Fe<sup>+3</sup>, and Ti) in this system is shown in figure 11, in which, for each formula, the percent of occupied octahedral positions occupied by Mg is plotted against the percent of occupied octahedral positions occupied by Fe<sup>+2</sup> and R<sup>+3</sup> on a triangular diagram. The points fall into 2 large groups and 1 small group. The first large group, at the top of the triangle, is made up of points representing trioctahedral micas in which Mg occupies more than 70 percent of the occupied octahedral positions; in the second large group are the points that represent trioctahedral micas in which Mg occupies

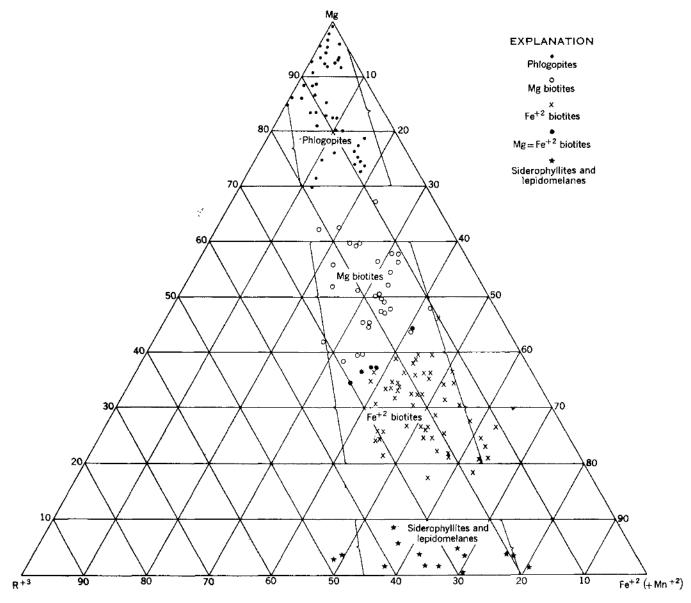


FIGURE 11.-Relation between Mg, Fe<sup>+2</sup> (Mn<sup>+2</sup>), and R<sup>+2</sup> (Al, Fe<sup>+2</sup>, and Ti) in trioctahedral micas.

between 63 and 20 percent of the occupied octahedral positions; in the small group, at the bottom of the triangle, are points representing trioctahedral micas in which Mg occupies fewer than 10 percent of the occupied octahedral positions.

Three-fourths of the analyses from which the formulas represented by points in the first group were derived were designated as analyses of phlogopite in the literature. A few were termed "biotites", with biotite being used in a general sense, simply meaning a trioctahedral mica. Consequently, the first group is considered as being made up of phlogopites and the first hiatus in the grouping of the points is considered as differentiating phlogopites from Mg biotites. The second group of points represent biotites. Points representing Mg biotites occupy the upper half of this area, and, about halfway down the area, mingle with the points representing  $Fe^{+2}$  biotites, which occupy the lower half of the biotite area.

The third group of points represent  $Fe^{+2}$  dominant formulas having a very low Mg content, less than 0.15 octahedral positions, and high amounts of Al and (or)  $Fe^{+3}$ , that is, siderophyllites and lepidomelanes.

The trioctahedral micas may, therefore, be thought of as members of a system characterized by concurrent but independent replacement of Mg by  $Fe^{+2}$  and  $R^{+3}$ ions. At the beginning of the system, Mg occupies more than 98 percent of the octahedral positions; at its end, Mg occupies fewer than 1 percent of the occupied positions. Thus phlogopite,  $Mg_{3.00}(Si_{3.00}Al)O_{10}(OH)_2 K$ , is the prototype of the trioctahedral system, from which by displacement of Mg all other trioctahedral micas may be considered to be derived.

It is obvious that the character and composition of the members of a system like this cannot be adequately expressed by the kind of formulas usually given for these minerals. Such formulas suggest minerals of definite composition, not members of a system that are variable, within limits, in composition and that merge into one another. For members of such a system the formulas should indicate permissible limits of composition. The failure to define compositional limits has led in the past to considerable confusion in differentiating the various members of the system.

# PHLOGOPITES

The name "phlogopite" refers to a trioctahedral mica in which almost all the octahedral positions are occupied by Mg. The formula usually given for phlogopite,  $Mg_3(Si_3Al)O_{10}(OH)_2K$ , specifies a complete occupancy of the octahedral group by Mg. Naturally-occurring phlogopites, however, contain other octahedral cations, most commonly Al, Fe<sup>+3</sup>, and Fe<sup>+2</sup>, and so do not conform perfectly to the ideal formula, although some, like the one below (1, table 11), approach the ideal very closely

$$[\underbrace{(\mathrm{Al}_{0.01}\mathrm{Ti}_{0.02}\mathrm{Fe}_{0.01}^{+3}\mathrm{Fe}_{0.01}^{+2}\mathrm{Mg}_{2.94}}_{2.99})(\mathrm{Si}_{2.92}\mathrm{Al}_{1.08})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.04}}_{\mathrm{K}_{0.78},\mathrm{Na}_{0.14},\mathrm{Ba}/2_{0.09})_{0.08}^{+1.04}}$$

This formula has the highest Mg occupancy of any of the formulas studied, Mg occupying 98 percent of the octahedral positions. Even in this formula, however, there are determinable amounts of Al, Ti,  $Fe^{+3}$ , and  $Fe^{+2}$ . Other formulas of phlogopites, arranged in order of decreasing Mg content, exhibit increasingly greater occupancy of octahedral positions by other cations,  $Fe^{+2}$ ,  $Fe^{+3}$ , and (or) Al. However, all the formulas represented by points in the phlogopite area, figure 11, have more than 70 percent of their occupied octahedral positions occupied by Mg.

The average octahedral composition of phlogopites, based on the 42 formulas at hand, are shown in table 5. Only 4 of these formulas had a Fe<sup>+2</sup> occupancy of more than 0.45 octahedral positions; in 2 of these Fe<sup>+2</sup> occupied 0.50 positions, in the other 2, Fe<sup>+2</sup> occupied 0.54 positions. The number of octahedral positions occupied by  $\mathbf{R}^{+3}$  ions varies up to 0.54, with Al occupying between 0.00 and 0.35 positions, Ti

TAI	BLE	5.—Range	; in octahe	dral compos	sition of	phlogopites (	in order
	of	decreasing	Mg conte	ent in terms	of octah	edral positio	ns)

Number of formulas	Mg	R <sup>+3</sup> extra charge	Al	Fe+3	Fe+2	Octa- hedral positions
15 5 15 8	3.00-2.75 2.75-2.50 2.50-2.25 2.25-2.00	$\begin{array}{c} \textbf{0.00-0.25}\\ \textbf{.2535}\\ \textbf{.2045}\\ \textbf{.2550} \end{array}$	0.00-0.15 .1020 .0025 .0035	0.00-0.10 .0520 .0030 .0525	0.00-0.15 .0020 .1550 .8050	3, 00-2, 95 3, 00-2, 95 3, 00-2, 85 3, 00-2, 85
	Formula	indicating ra	nge in compo	sition of phlo	90pites	·
	<+0.30		(-1.00)-(-1			
$(R^{+3}_{< 0.50}F$	$e^{+2}_{<0.50}Mg_{3}$	.00-2.00) (Siz	.00-2.70Al1.0	x01.30)		
	3.00-2.85					

 $O_{10}(OH)_2 K(Na, Ca/2)_{1.00\pm0.10}$ 

between 0.00 and 0.10 positions, and  $Fe^{+3}$  between 0.00 and 0.30. However, in 30 of the 43 phlogopite formulas Al occupies 0.15 or fewer octahedral positions, and in 7 of these there is not only no octahedral Al, but also insufficient Al to complete the filling of the tetrahedral group, necessitating allocation of some  $Fe^{+3}$  to this group. Although  $Fe^{+3}$  occupies up to 0.30 positions, most of the phlogopite formulas had less than half that many positions occupied by  $Fe^{+3}$ . Titanium is generally very low, occupying an average of 0.10 positions.

From the ranges for Mg,  $Fe^{+2}$ , and  $R^{+3}$  in these formulas, general limits for these constituents in phlogopites may be formulated as shown at the bottom of table 5. The low of 2.00 octahedral positions occupied by Mg is equivalent to approximately 19 percent of MgO, and the high of 0.50 positions occupied by  $Fe^{+2}$  is equivalent to approximately 8.5 percent of FeO.

A number of phlogopite analyses were discarded because the formulas derived from them were low in interlayer ion content, that is, deficient in the amount of K, or other large cations present, and (or) were excessively high in octahedral occupancy. The implication of these features is discussed earlier in this paper.

# EASTONITE

The name "eastonite" for pure dialuminum magnesium mica,  $H_4K_2Mg_5Al_4Si_5O_{24}$ , or  $(Al_{0.5}Mg_{2.5})$  $(Si_{2.5}Al_{1.5})O_{10}(OH)_2K$ , in the notation used in this study, was derived from Easton, Pa., where, quoting Winchell (1925, p. 322, footnote 30) "Eyerman found a sample which approaches this composition very closely." Eyerman (1904, p. 46) published three analyses of biotite from Easton. One of these, analysis B, has only 6.30 percent K<sub>2</sub>O, which is very low for a potassium mica. In the formulas derived from his analyses A and C, 16 and 15, table 11,

$$\underbrace{ \begin{bmatrix} +0.14 & -1.16 \\ [(Al_{0.24}Fe_{0.16}^{+3}Mg_{2.47}) \\ 2.87 \end{bmatrix}}_{2.87} (Si_{2.84}Al_{1.16}) O_{10}(OH)_2]^{-1.02} }_{(Ka.84, Nan.94, Ca/2a.65)}$$

and

$$(K_{0.84}, Na_{0.06}, Ca/2_{0.07})^{+1.04}_{0.97},$$

$$\underbrace{[\underbrace{(\mathrm{Al}_{0.15}\mathrm{Fe}_{0.29}^{+3}\mathrm{Mg}_{2.93}}_{2.93}}_{\mathrm{S1}_{2.72}\mathrm{Al}_{1.28}}(\mathrm{S1}_{2.72}\mathrm{Al}_{1.28})\mathrm{O}_{10}(\mathrm{OH})_2]^{-0.98}(\mathrm{K}_{0.90},\mathrm{Ca}/2_{0.03})_{0.93}^{+0.96},$$

Al occupies only 0.24 and 0.15 octahedral positions, respectively, not 0.50 as specified in Winchell's formula. These formulas can be said to approach the composition specified by Winchell's eastonite formula only if Al is interpreted broadly as meaning R<sup>+3</sup> ions and to include  $Fe^{+3}$ . Furthermore, it is very doubtful whether the values given for Fe<sub>2</sub>O<sub>3</sub> represent the actual Fe<sup>+3</sup> content of the samples. No FeO is reported, and it is very probable that FeO was not determined and that the value given for  $Fe_2O_3$  represents the total iron content of the sample, not Fe<sup>+3</sup> only. In most samples of similar Mg and total iron content, in which both Fe<sub>2</sub>O<sub>3</sub> and FeO were determined, FeO makes up one-half or more of the total iron content. It is very likely, therefore, that the  $Fe_2O_3$  reported in these analyses includes FeO and that the actual trivalent ion content of these biotites is considerably less than shown in the formulas.

Aside from the Al and the total trivalent ion content, there are other points of disagreement between these formulas and Winchell's eastonite formula. In the eastonite formula it is presumed that all the octahedral positions are occupied, and, because tetrahedral Al, and consequently, tetrahedral charge, is 1.5, that all the extra charges (+0.50) carried by octahedral A! induce a positive charge on the octahedral layer. In the Easton formulas only 2.87 and 2.93 octahedral positions, respectively, are occupied, and only part of the additional charges carried by trivalent ions form a positive charge on the octahedral group, the rest being neutralized by negative charges associated with unoccupied positions. Consequently, the positive octahedral charge, the negative tetrahedral charge, and octahedral occupancy of the Easton formulas are all less than in the eastonite formula. X-ray study of the Easton, Pa., samples show them to be mixtures of serpentine and phlogopite. (Hatton S. Yoder, oral communication, 1957.)

Because in trioctahedral micas the extra charges carried by trivalent octahedral cations are accommodated in two different ways, in accordance with equation A or equation B, because decrease in Mg content is accompanied by increase in  $Fe^{+2}$  and  $R^{+3}$ , and because increase in  $R^{+3}$  is made up of increase in  $Fe^{+3}$  as well as increase in octahedral Al, none of the Mg dominant formulas studied closely approach Winchell's eastonite

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formula, in which accommodation for extra trivalent charges is assumed to be made only in accordance with equation A, and in which replacement of Mg is by Al only. All the formulas with a Mg content comparable to that in the eastonite formula contain  $Fe^{+3}$  and  $Fe^{+2}$  and have some unoccupied octahedral positions.

Among the analyses of trioctahedral micas collected for this study, only one had been called that of an eastonite (Simpson, 1932, p. 63), (D27, table 12). This analysis yielded the following formula,

$$\underbrace{[\underbrace{(\mathrm{Al}_{0.20}\mathrm{Ti}_{0.02}\mathrm{Fe}_{0.24}^{+2}\mathrm{Fe}_{0.93}^{+2}\mathrm{Mg}_{1.56}\mathrm{Mn}_{0.02}^{+2})}_{2.97}(\mathrm{Si}_{2.71}\mathrm{Al}_{1.29})0_{10}(\mathrm{OH})_2]^{-0.87}}_{(\mathrm{K}_{0.82},\mathrm{Na}_{0.02})_{0.89}^{+0.89}}$$

In this formula Mg occupies only three-fifths and Al occupies only two-fifths of the number of octahedral positions designated in the eastonite formula, and the octahedral and tetrahedral charges are both considerably lower than in the eastonite formula. Only if Mg and Al in the eastonite formula are interpreted broadly as representing  $K^{+2}$  and  $R^{+3}$  ions generally, does the formula for Simpson's eastonite,

$$\underbrace{ \{ \underbrace{(A1, Ti, Fe^{+3})_{0.46}(Fe^{+2}, Mg, Mn^{+2})_{2.51}}_{2.97} (Si_{2.71}Al_{1.20}) 0_{10}(OH)_2 \}^{-0.87}}_{(K, Na)_{0.89}^{+0.89}}$$

approach Winchell's formula for eastonite. However, Winchell's formula represents the hypothetical dialuminum magnesium mica which was used by him as one of the components of biotite and as an analog of siderophyllite. A broader interpretation, as above, would tend to engender confusion with biotites proper.

In view of the confusion a broader interpretation would tend to engender, the apparent lack of natural representatives and the fact that the name had been previously given by Hamilton (1899, p.19) to a vermiculite occurring in the same locality as an alteration product of biotite, it is recommended that the name "eastonite" be discarded as referring to a natural trioctahedral mica and retained only as a hypothetical end-member.

# BIOTITES

The term "biotite," although also used as a group name for the trioctahedral micas, is here specifically applied to trioctahedral micas that contain significant amounts of both Mg and Fe<sup>+2</sup>. Biotites in which Mg is the dominant octahedral cation are termed Mg biotites; those in which Fe<sup>+2</sup> is the dominant octahedral cation are termed Fe<sup>+2</sup> biotites. Occurring midway in the Mg Fe<sup>+2</sup>-R<sup>+3</sup> system (fig. 11) between a Mg octahedral percentage of 50 and 20, the biotites occupy the greatest area and constitute the greatest number of samples. Magnesium biotites dominate the upper part of the biotite area, with points representing formulas having the highest Mg content occupying the uppermost part of the area. With decreasing Mg content and increasing  $Fe^{+2}$  content Mg is gradually superseded by  $Fe^{+2}$  as the dominant octahedral cation, and  $Fe^{+2}$  biotites dominate the lower part of the biotite area. In the transition zone, points representing Mg biotites,  $Fe^{+2}$  biotites, and biotites having about equivalent amounts of Mg and  $Fe^{+2}$  intermingle.

The highest Mg content in any of the biotite formulas studied is 1.77 octahedral positions, the lowest is 0.48 octahedral positions. The highest  $Fe^{+2}$  content in any biotite formula is 1.78 octahedral positions; the lowest is 0.47. Thus Mg and  $Fe^{+2}$  in these biotite formulas have the same range, 1.75 to 0.50 octahedral positions (in rounded figures), but they are present in a reciprocal relation. This relation is illustrated in the following formulas, 36 and 116, table 11,

$$\underbrace{ [(\underline{Al_{0.21}Ti_{0.09}Fe_{0.13}^{+3}Fe_{0.54}^{+2}Mg_{1.73}Mn_{0.02}^{+2}Li_{0.03})}_{2.78} (Si_{2.87}Al_{1.13})0_{10}(OH)_2]^{-1.08}}_{(K_{0.75},Na_{0.12},Ca/2_{0.12})_{0.99}^{+1.11}} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{1.78}^{+2}Mg_{0.59}Mn_{0.08}^{+2})}_{2.82} (Si_{2.73}Al_{1.25})0_{10}(OH)_2]^{-0.99}}_{2.82} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{1.78}^{+2}Mg_{0.59}Mn_{0.08}^{+2})}_{2.82} (Si_{2.73}Al_{1.25})0_{10}(OH)_2]^{-0.99}}_{2.82} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{1.78}^{+2}Mg_{0.59}Mn_{0.08}^{+2})}_{0.98}}_{(Si_{2.73}Al_{1.25})0_{10}(OH)_2]^{-0.99}}_{2.82} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{1.78}^{+2}Mg_{0.59}Mn_{0.08}^{+2})}_{0.98}}_{(Si_{2.73}Al_{1.25})0_{10}(OH)_2]^{-0.99}}_{2.82} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{1.78}^{+2}Mg_{0.59}Mn_{0.08}^{+2})]}_{0.98}}_{(Si_{2.73}Al_{1.25})0_{10}(OH)_2]^{-0.99}}_{0.98} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{1.78}^{+2}Mg_{0.59}Mn_{0.08}^{+2})]}_{0.98}}_{(Si_{2.73}Al_{1.25})0_{10}(OH)_2]^{-0.99}}_{0.98} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{1.78}^{+2}Mg_{0.59}Mn_{0.08}^{+2})]}_{0.98}}_{(Si_{2.73}Al_{1.25})0_{10}(OH)_2]^{-0.99}}_{0.98} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{1.78}^{+2}Mg_{0.59}Mn_{0.08}^{+2})]}_{0.98} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{0.19}^{+2}Mg_{0.59}Mn_{0.08}^{+2})]}_{0.98}}_{(Si_{2.73}Al_{1.25})} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.13}^{+3}Fe_{0.19}^{+2}Mg_{0.59}Mn_{0.08}^{+2})]}_{0.98} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.19}^{+3}He_{0.19})]}_{(Si_{2.73}Al_{1.25})}_{(Si_{2.73}Al_{1.25})} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.19}^{+3}He_{0.19})]}_{(Si_{2.73}Al_{1.25})}]}_{(Si_{2.73}Al_{1.25})} \\ \underbrace{ [(\underline{Al_{0.09}Ti_{0.20}Fe_{0.19}^{+3}He_{0.19})]}_{(Si_{2.73}Al_{1.25})}]}_{(Si_{2.73}Al_{1.25})} \\ \underbrace{ [(\underline{Al_{0.09}Fe_{0.19})]}_{(Si_{2.73}Al_{1.25})}]_{(Si_{2.73}Al_{1.25})} \\ \underbrace{ [(\underline{Al_{0.09}Fe_{0.19})]}_{(Si_{2.73}Al_{1.25})}]}_{(Si_{2.73}Al_{1.25})} \\ \underbrace{ [(\underline{Al_{0.09}Fe_{0.19})]}_{(Si_{2.73}Al_{1.25})} \\ \underbrace{ [(\underline{Al_{0.09}Fe_{0.19})]}_{(Si_{2.73}Al_{1.25})} \\ \underbrace{ [(\underline{Al_{0.09$$

which belong, respectively, very near the high Mg-low  $Fe^{+2}$  and the low Mg-high  $Fe^{+2}$  ends of the Mg-Fe<sup>+2</sup> range in biotites. In other biotite formulas, the Mg-Fe<sup>+2</sup> relation varies between these extremes. However, because  $R^{+3}$  ions are present in different amounts, the relation between Mg and  $Fe^{+2}$  is quite variable. Formulas with similar Mg contents may have quite different  $Fe^{+2}$  contents and formulas with quite different Mg contents may have the same  $Fe^{+2}$  contents. Similarly, the relation between Mg and  $R^{+3}$  content is quite variable, as is also the relation between Mg and any of the ions making up  $R^{+3}$ . The relation between Mg and  $(Fe^2+R^{+3})$  is however, quite regular.

Fe<sup>+3</sup> generally occupies fewer than 0.35 octahedral positions in the biotite formulas. Only 6 formulas had a greater Fe<sup>+3</sup> content, and of these 6 only 1 had a Fe<sup>+3</sup> content greater than 0.45. There is no significant difference in the Fe<sup>+3</sup> content of Mg dominant and Fe<sup>+2</sup> dominant biotites. Indeed, the average Fe<sup>+3</sup> content of these two types of biotites is essentially the same, 0.23 octahedral positions in Mg biotites, 0.25 octahedral positions in Fe<sup>+2</sup> biotites.

With respect to Al content the biotite formulas fall into two groups; in about one-half the formulas there is little or no octahedral Al (fewer than 0.10 octahedral positions), in the other half, Al occupies between 0.20 and 0.55 octahedral positions. In about one-third of the low Al group, Al is so deficient that there is not only no octahedral Al, but there is not even sufficient Al present to complete the filling of the tetrahedral group; this requires the allocation of some Fe<sup>+3</sup> to this group to complete it. Lack of sufficient Al to fill the tetrahedral group may be due simply to low Al content, or it may be due to low Si content, which would require proportionately more Al to complete the tetrahedral group. A comparison of the amounts of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> reported in the analyses from which the formulas were derived shows, however, that low  $Al_2O_3$  content, rather than low SiO<sub>2</sub> content, is the reason for the insufficiency of Al in formulas containing little or no octahedral Al. The  $SiO_2$  content in analyses for the 2 groups is about the same, varying between 32 and 38 percent in analyses for both groups, with an average  $SiO_2$  content of 35.5 percent for the low Al group, and an average of 34.8 percent for the higher Al group. The range in  $Al_2O_3$ content in analyses of the low Al group, 11.0 to 16.3 percent, is, however, considerably lower than the range in  $Al_2O_3$  content of the higher Al group, 15.7 and 21.3 percent, and the average Al<sub>2</sub>O<sub>3</sub> content in analyses for the low Al group is almost 4 percent lower than the average  $Al_2O_3$  content in analyses for the higher Al group, 14.6 percent as compared with 18.4 percent.

The compositional characteristics of each of the groups for different ranges of Mg content are summarized in table 6, and the average octahedral composition of each group for the same ranges of Mg content are given in table 7. For comparable Mg contents the low octahedral Al biotites are, in general, lower in  $\mathbb{R}^{+3}$  but higher in Ti and Fe<sup>+3</sup> content than the higher

TABLE 6.-Range in octahedral composition of biotites

[In order of decreasi	ng Mg content in terms of	octahedral positions occupied]
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	Mg					
	1.75-1.50	1.50-1.25	1.25~1.00	1.00-0.75	0.75-0.50	
		AI<0.15			·	
Number of formulas R <sup>+3</sup> Al Ti Fe <sup>+3</sup> Fe <sup>+3</sup> (Fe <sup>+3</sup> +R <sup>+3</sup> )	7 0, 35-0, 70 .0005 .2025 .1045 .6090 1.05-1.30	8 0.60-0.75 .0015 .1020 .2035 .8095 1.25-1.50	8 0.50-0.80 .0015 .2030 .1045 .90-1.35 1.45-1.85	11 0.45-0.80 .0015 .0530 .1035 1.25-1.55 1.75-2.05	9 0.55-0.85 .0015 .1030 .0545 1.45-1.75 2.05-2.20	
	u <u></u>	AI>0.15				
Number of formulas R <sup>+3</sup> Al Tl. Fe <sup>+3</sup> Fe <sup>+4</sup> (Fe <sup>+1</sup> 4;R <sup>+3</sup> )	6 0.45-0.70 .2055 .0015 .0025 .5095 1.00-1.35	4 0.60-0.80 .2040 .1020 .1025 .6595 1.30-1.55	6 0.60-0.90 .3050 .0015 .0040 .70-1.25 1.50-1.80	12 0.70-1.00 .2040 .1030 .0535 1.00-1.35 1.70-2.00	11 0. 65-0. 90 . 25 50 . 05 20 . 05 30 1. 15-1. 70 1. 90-2. 20	

# INTERPRETATION OF TRIOCTAHEDRAL MICAS

Mg	Al <0.15	A1 >0.15
75-1. 50	$+0.25 \\ _{0.60} \underbrace{(\mathrm{Al}_{0.00}\mathrm{Ti}_{0.20}\mathrm{Fe}_{0.15}^{+3}\mathrm{Fe}_{0.80}^{+2}\mathrm{Mg}_{1.70})}_{2.85}$	$\overset{+0.25}{\underset{0.55}{(\mathrm{Al}_{0.30}\mathrm{Ti}_{0.05}\mathrm{Fe}_{0.15}^{+3}\mathrm{Fe}_{0.70}^{+2}\mathrm{Mg}_{1.65})}}_{2.85}$
. 50–1. 25	$+0.25 \\ +0.25 \\ (Al_{0.05} Ti_{0.15} Fe_{0.30}^{+3} Fe_{0.90}^{+2} Mg_{1.40}) \\ 2.50$	$\underbrace{(Al_{0.30}^{+0.25} Fe_{0.15}^{+3} Fe_{0.15}^{+2} Mg_{1.30}^{+0.25})}_{2.75}$
. 25-1. 00	$\substack{ \substack{ +0.30 \\ 0.65 (\underline{\mathrm{Al}_{0.05}\mathrm{Ti}_{0.25}\mathrm{Fe}_{0.15}^{+3}\mathrm{Fe}_{1.25}^{+2}\mathrm{Mg}_{1.10}) \\ 2.80 } }$	$\underbrace{(\mathrm{Al}_{0.35}\mathrm{Ti}_{0.10}\mathrm{Fe}_{0.25}^{+3}\mathrm{Fe}_{0.25}^{+2}\mathrm{Mg}_{1.10})}_{2.75}$
. 00–0. 75	$\substack{+0.25\\_{0.65}}_{0.65}\underbrace{(\mathrm{Al}_{0.05}\mathrm{Ti}_{0.15}\mathrm{Fe}_{0.30}^{+3}\mathrm{Fe}_{1.40}^{+2}\mathrm{Mg}_{0.90})}_{2.80}$	${}^{+0.25}_{0.35}\underbrace{(\mathrm{Al}_{0.30}\mathrm{Ti}_{0.20}\mathrm{Fe}_{0.15}^{+3}\mathrm{Fe}_{1.20}^{+2}\mathrm{Mg}_{0.85})}_{2.70}$
0. 75-0. 50	$+0.25 \\ +0.75 \underbrace{(\mathrm{Al}_{0.05}\mathrm{Ti}_{0.20}\mathrm{Fe}_{0.30}^{+3}\mathrm{Fe}_{1.60}^{+2}\mathrm{Mg}_{0.60})}_{2.75}$	$^{+0.25}_{0.85}(\underbrace{\mathrm{Al}_{0.40}\mathrm{Ti}_{0.10}\mathrm{Fe}_{0.25}^{+3}\mathrm{Fe}_{1.35}^{+2}\mathrm{Mg}_{0.60}}_{2.70})$

TABLE 7.—Average octahedral composition of biotites in order of decreasing Mg content [The figures preceding the parentheses enclosing the octahedral-group notation refer to the extra R<sup>+3</sup> charge of the octahedral groups they precede]

octahedral Al biotites, although formulas with low octahedral Al are found throughout the entire  $R^{+3}$ range. Fe<sup>+2</sup> is consistently higher, for comparable Mg contents, in low Al biotites than in higher Al biotites. Because of this difference in Fe<sup>+2</sup> content with the same Mg content, the average formula for low Al biotites in the Mg range 1.25–1.00 has Fe<sup>+2</sup> as the dominant octahedral cation, whereas the average formula for the higher Al biotites has Mg as the dominant octahedral cation. In an average of all formulas in this Mg range Mg and Fe<sup>+2</sup> are present in approximately equivalent amounts,

$$\frac{[(A_{1_{0,20}} T_{1_{0,15}} F_{e_{1,30}}^{+3} F_{e_{1,15}}^{+2} M_{g_{1,10}})}{2.80} (S_{1_{2,70}} A_{1_{1,30}}) \mathbf{0}_{10} (OH)_2]^{-1.00}}{K(Na_2 Ca/2)_{1.00\pm.10}^{+1.00}}$$

Thus the Mg range of 1.25 to 1.00 octahedral positions is the transition zone between Mg and  $Fe^{+2}$  dominant biotites. All biotites having more than 1.25 octahedral positions occupied by Mg are Mg dominant; all biotites having fewer than 1.00 positions occupied by Mg are  $Fe^{+2}$  dominant. When the Mg content is between 1.25 and 1.00 octahedral positions, Mg is dominant in some biotites,  $Fe^{+2}$  is dominant in others, and Mg and  $Fe^{+2}$ are present in approximately equivalent amounts in still others.

On the basis of the ranges in content of Mg,  $Fe^{+2}$ , and  $R^{+3}$  shown in table 6, the ranges in content of these

constituents to be expected in biotites may be formulated as

$$\underbrace{ (\mathbf{R}_{0.35-1.00}^{+3} \mathbf{F}_{0.50-1.75}^{+2} \mathbf{M} \mathbf{g}_{1.75-0.50}^{-1.00})}_{2.90-2.65} (\mathbf{S}_{13.00-2.50}^{-1.00} \mathbf{A} \mathbf{I}_{1.00-1.50}^{-1.50}) \mathbf{O}_{10} (\mathbf{OH})_2$$

 $K(Na, Ca/2)_{1.00\pm0.10}$ .

# ANNITE

Originally the name "annite" was applied by Dana (1868, p. 308) to a high Fe<sup>+3</sup> biotite that occurs at Cape Ann, Mass., which was analyzed and described by Cooke (1867, p. 222). This material contained 12.07 percent Fe<sub>2</sub>O<sub>3</sub>. Subsequently Winchell (1925, p. 323) applied the name to a hypothetical Fe<sup>+2</sup> analog of phlogopite, Fe<sup>+2</sup><sub>3</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>2</sub>K, which was used by him as 1 of the 4 components of biotite. Thus the name which Dana gave to a high trivalent iron mica was applied by Winchell to a hypothetical bivalent iron mica which was presumed to contain no trivalent iron.

One of the most significant features brought out by this study is the complete absence of  $Fe^{+2}$  dominant micas analogous to phlogopite. Only two formulas have as many as 2.00 octahedral positions occupied by  $Fe^{+2}$ , the lower limit for Mg in phlogopite, and in these, although Mg is very low,  $R^{+3}$  ions occupy about 0.50 octahedral positions.

Considering that the name "annite" had been used previously by Dana for a high Fe<sup>+3</sup> biotite and the name and formula was used by Winchell for a hypothetical ferrous trioctahedral mica, which does not, on the evidence of the formulas gathered, occur in nature, it is recommended that annite be discarded as referring to a natural trioctahedral mica, and retained only as a hypothetical end member.

# SIDEROPHYLLITES AND LEPIDOMELANES

A group of  $Fe^{+2}$  dominant trioctahedral mica formulas in which Mg occupies less than 0.15 octahedral positions represents the end of the Mg replacement system. Points representing these formulas fall close to the base of the triangular diagram shown in figure 11, and are separated from the biotite area by narrow, very sparsely populated area. Some of these formulas are characterized by high Al content; others, by high  $Fe^{+3}$  content; and still others, by significant amounts of both Al and  $Fe^{+3}$ .

Siderophyllite, according to Winchell and Winchell (1951, p. 373) has the formula,  $H_4K_2Fe_5Al_4Si_5O_{24}$ , or, in the notation herein used, and assuming Fe to represent  $Fe^{+2}$ 

# $(Al_{0.5}Fe_{2.5}^{+2})(Si_{2.50}Al_{1.50})O_{10}(OH)_2K_{1.00}$

The full octahedral occupancy and the composition of the tetrahedral in this formula indicate that all the accommodation for extra positive charges (+0.50)carried by octahedral Al is assumed to have been made in accordance with equation A. Nockolds and Richey (1939, p. 38) suggested the formula,  $H_4K_2Fe_3Al_4Si_8O_{24}$ . or  $(Al_{1,00}Fe_{1,50}^{+2})(Si_{3,00}Al_{1,00})O_{10}(OH)_2K$ , for siderophyllite, as this formula was closer to the composition of a specimen studied by them (129; table 8). In this formula all the additional positive charges carried by octahedral aluminum (+1.00) are accommodated in accordance with equation B. The octahedral layer is neutral, and the tetrahedral layers have the same charge as in the classic formulas for phlogopite and muscovite. These two formulas, therefore, represent the two extremes in the accommodation of extra positive octahedral charges by the biotite structure. Octahedral Al in this formula occupies twice as many positions as in the Winchell formula and Fe<sup>+2</sup> occupies only three-fifths as many positions.

In the formulas shown in table 8, octahedral Al varies between 0.47 and 0.99 positions. These relations suggest an isomorphous series in which  $Fe^{+2}$  is replaced by Al. Hypothetically, the beginning of the series would be a mineral similar to Winchell's annite, which would yield on increasing replacement of  $Fe^{+2}$  by Al, minerals whose compositions, except for lack of Li, approximate those of the siderophyllites shown in table 8:

The first half of the series, up to an Al content of 0.50 octahedral positions, is not represented among the formulas studied. The second half is represented by formulas in table 8. Variations in octahedral occupancy, octahedral charges and tetrahedral charge are due to the varying degrees to which the structure has accommodated the extra positive charges carried by Al in accordance with equation A or equation B. In the formula for 132, table 8, 0.33 of the extra 0.47 charges carried by Al are balanced by the deficiency in the number of charges carried by Li, as one Li and one Al together carry the same number of charges as two bivalent cations. The 0.16 negative charges associated with 0.08 unoccupied octahedral positions are more than sufficient to neutralize the rest of the additional positive charges, and the octahedral layer has a slight negative charge. In the formula for 135, table 8, part of the additional positive octahedral charges are neutralized by negative charges associated with unoc-

Number in table 11 Formula -0.02-1.03 $[(Al_{0.47}Fe_{2.02}^{+2}Mg_{0.03}Mn_{0.07}^{+2}Li_{0.33})(Si_{2.97}Al_{1.03})O_{10}(OH)_2]^{-1.05}(K_{0.93}Na_{0.90}Rb_{0.01})_{1.03}^{+1.03}$ 132\_\_\_\_\_ 2.92+0.35 -1.35  $[\{Al_{0.73}Fe_{0.08}^{+3}Fe_{1.88}^{+2}Mg_{0.01}Mn_{0.02}^{+2}Li_{0.19}\}(Si_{2.68}Al_{1.35})O_{10}(OH)_2]^{-1.00}(K_{0.90}Na_{0.07}Ca/2_{0.01})_{0.98}^{+0.99}$ 135\_\_\_\_\_ 2.82 -0.06 -1.08 $[(Al_{0.99}Ti_{0.01}Fe_{0.05}^{+3}Fe_{1.32}^{+2}Mg_{0.05}Mn_{0.02}^{+2})(Si_{2.97}Al_{1.08})O_{10}(OH)_2]^{-1.99} (K_{0.86}Ca/2_{0.12})_{0.98}^{+1.10}$ 129\_\_\_\_\_ 2.44

TABLE 8.—Formulas of representative siderophyllites

2.50

cupied octahedral positions. In 129 all the extra positive  $\mathbf{R}^{+3}$  charges are neutralized by negative charges associated with unoccupied octahedral positions, as in Nockolds and Richey's formula for siderophyllite. Because of these various degrees to which the extra positive charges carried by R<sup>+3</sup> ions have been accommodated in accordance with equations A and B in these siderophyllite formulas, the formulas for the siderophyllite series are written to represent similar mixed accommodation of extra positive charges.

"Lepidomelane" is a term that has not been definitely defined and that has different meanings for different mineralogists. Dana (1892, p. 634) defines lepidomelane as a variety of biotite characterized by a large amount of ferric iron. Winchell and Winchell (1951, p. 376) states that "lepidomelane is any kind of biotite rich in iron." The state of valence of the iron is, apparently, unimportant, as this definition would include his annite. Kunitz (1924, p. 388) suggests that all the iron was originally in the ferrous state, and gives a formula in which all the iron is present in the ferrous state, KH<sub>2</sub>AlFe<sup>+2</sup>(SiO<sub>4</sub>). However, Hallimond (1926, p. 30) considers that there is no reason "\* \* \* to believe that the natural melts are so deficient in oxygen as this assumption would imply, and it is much more probable that the average fresh biotite is substantially in the condition in which it crystallized." The formula given by Hey (1955, p. 193),  $2[K_2]$  $(Fe^{+3}Fe^{+2}Mg)_{4-6}$ ,  $(Si, Al, Fe^{+3})_{8}O_{20}(OH)_{4}$ ], which includes both trivalent and bivalent iron, is qualified by the remark "\* \* \* with high Fe<sup>+3</sup> and low Mg (usually Fe<sup>+2</sup>>Mg)." Hey includes Fe<sup>+3</sup> in the tetrahedral group, as does also Grigoriev (1935, p. 79) in his formula for fluor (or hydroxyl) lepidomelane FK(MgFe<sup>+2</sup>)<sub>3</sub> [(Al,Fe<sup>+3</sup>)Si<sub>3</sub>]O<sub>10</sub>, although Grigoriev includes only Fe<sup>+2</sup> in the octahedral group. These examples illustrate the lack of agreement among mineralogists as to the meaning of the term "lepidomelane."

Among the Fe<sup>+2</sup> dominant formulas studied was a group characterized by very low Mg content and analogous to the siderophyllite formulas but containing Fe<sup>+3</sup> in place of Al. These formulas, of which typical examples are presented in table 9, bear the same relation to each other as do the siderophyllite formulas; that is, they represent part of an isomorphous series in which there is proxying of  $Fe^{+2}$  by  $Fe^{+3}$ , and their composition can be expressed by the same general formulas as given for the siderophyllite half series, by substituting Fe<sup>+3</sup> for Al.

$$\begin{array}{c} \overset{0.00}{[\mathrm{Fe}_{2.00}^{+3}(\mathrm{Si}_{3.00}\mathrm{Al}_{1.00})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.09}} \mathrm{K}_{1.00}^{+1.00} & \mathrm{Not \ represented.} \\ \\ \overset{0.00}{[(\mathrm{Fe}_{0.50}^{+3}\mathrm{Fe}_{2.25}^{+2})(\mathrm{Si}_{3.00}\mathrm{Al}_{1.00})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.09}} \mathrm{K}_{1.00}^{+1.00} \mathrm{Approximates} \\ \overset{0.00}{[(\mathrm{Fe}_{0.50}^{+3}\mathrm{Fe}_{2.25}^{+2})(\mathrm{Si}_{3.00}\mathrm{Al}_{1.00})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.09}} \mathrm{K}_{1.00}^{+1.00} \mathrm{Approximates} \\ \overset{0.00}{[(\mathrm{Fe}_{0.50}^{+3}\mathrm{Fe}_{0.50}^{+2})(\mathrm{Si}_{3.00}\mathrm{Al}_{1.00})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.09}} \mathrm{K}_{1.00}^{+1.00} \mathrm{Approximates} \\ \overset{0.00}{[(\mathrm{Fe}_{0.50}^{+3}\mathrm{Fe}_{0.50}^{+2})(\mathrm{Si}_{3.00}\mathrm{Al}_{1.00})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.09}} \mathrm{K}_{1.00}^{+1.00} \mathrm{Approximates} \\ \end{array}$$

As in the siderophyllite series, only the latter half of the series is represented.

It is suggested here that the term "lepidomelane" be applied to minerals similar in composition to the formulas above and to those in table 9-minerals characterized by high Fe<sup>+2</sup> and Fe<sup>+3</sup> and by very low octahedral Al and Mg content, and analogous to siderophyllite (as herein defined) but containing Fe<sup>+3</sup> in place of Al.

Another group of formulas characterized by high Fe<sup>+2</sup> and very low Mg content contain significant amounts of both octahedral Al and Fe<sup>+3</sup> (table 10), These formulas are intermediate in composition be-

	<b>TABLE 9.</b> —Formulas of representative lepidomelanes
Number (table 11)	Formula
126	$[\underbrace{(Al_{0.00}Ti_{0.18}Fe_{0.35}^{+3}Fe_{1.91}^{+2}Mg_{0.09}Mn_{0.20}^{+2})}_{2.73}(Si_{2.77}Al_{1.02}Fe_{0.21}^{+3})O_{10}(OH)_2]^{-1.06}(K_{9.83}Na_{0.16}Ca/2_{9.06})_{1.05}^{+1.11}$
125	$[\underbrace{(\mathrm{Al}_{0.01}\mathrm{Ti}_{0.24}\mathrm{Fe}_{0.47}^{+3}\mathrm{Fe}_{1.73}^{+2}\mathrm{Mg}_{0.09}\mathrm{Mn}_{0.09}^{+2})}_{2.63}(\mathrm{Si}_{2.59}\mathrm{Al}_{1.41})\mathrm{O}_{10}(\mathrm{OH})_2]^{-0.89}(\mathrm{K}_{0.72}\mathrm{Na}_{0.13})_{0.69}^{+0.89}$
124	$[\underbrace{(\mathrm{Al}_{0.05}\mathrm{Ti}_{0.02}\mathrm{Fe}_{0.51}^{+3}\mathrm{Fe}_{2.17}^{+2}\mathrm{Mg}_{0.11}\mathrm{Mn}_{0.02}^{+2})}_{2.89}(\mathrm{Si}_{2.58}\mathrm{Al}_{1.42})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.63}(\mathrm{K}_{0.91}\mathrm{Na}_{0.11})_{1.02}^{+1.02}$
123	$[\underbrace{(\mathrm{Al}_{0.16}\mathrm{Ti}_{0.05}\mathrm{Fe}_{0.79}^{+3}\mathrm{Fe}_{1.37}^{+2}\mathrm{Mg}_{0.16}\mathrm{Mn}_{0.07}^{+2}\mathrm{Li}_{0.16})}_{2.75} \overset{-1.36}{(\mathrm{Si}_{2.64}\mathrm{Al}_{1.36})\mathrm{O}_{10}(\mathrm{OH})_2]^{-0.97}(\mathrm{K}_{0.79}\mathrm{Ca}/2_{0.08})_{0.87}^{+0.96}}$

123, table 9.

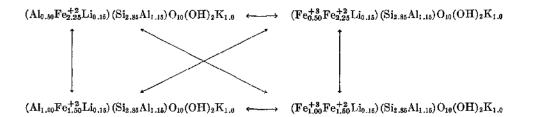
31

## SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

TABLE 10.—Formulas of micas intermediate in composition between siderophyllites and lepidomelanes

Number (tables 11 and 12) Formula +0.36-1.31  $\{(Al_{0.39}Fe_{0.47}^{+3}Fe_{1.70}^{+2}Mg_{0.04}Mn_{0.05}^{+2}Li_{0.20})(Si_{2.69}Al_{1.31})O_{10}(OH)_2]^{-6.95}(K_{0.79}Na_{0.08}Ca/2_{0.04})_{0.91}^{+0.95}(Na_{0.09}Ca/2_{0.04})_{0.91}^{+0.95$ 130\_\_\_\_\_ 2.85 +0.25-1.32 $[(Al_{0.52}Ti_{0.01}Fe_{0.62}^{+3}Fe_{1.22}^{+2}Mg_{0.09}Mn_{0.02}^{+2}Li_{0.13})(Si_{2.68}Al_{1.32})O_{10}(OH)_2]^{-1.07}(K_{0.82}Na_{0.02}Ca/2_{0.06})_{0.98}^{+1.04}$ 127\_\_\_\_\_ 2.61+0.01 -1.02 D63  $[(Al_{0.45}Fe_{0.68}^{+3}Fe_{1.09}^{+2}Mg_{0.07}Mn_{0.04}^{+3}Li_{0.18})(Si_{2.98}Al_{1.02})O_{10}(OH)_2]^{-1.01}K_{1.01}^{+1.04}$ 2.51

tween those given in tables 8 and 9. Other formulas, which could not be used because of their high alkali content (see discussion, p. 16), contain varying proportions of Al and Fe<sup>+3</sup> and suggest the existence of an isomorphous series between siderophyllite and lepidomelane as they are herein defined. The interrelations possible between siderophyllites and lepidomelanes are expressed in the following diagram.



Micas intermediate in composition between siderophyllites and lepidomelanes can be referred to as ferrian siderophyllites or aluminian lepidomelanes, depending on whether aluminum or trivalent iron is the dominant trivalent octahedral cation. By this terminology all the formulas in table 10 would be called aluminian lepidomelanes, as the number of octahedral positions occupied by trivalent iron is greater than the number of positions occupied by aluminum in all of them.

Only one formula in tables 8, 9, and 10 contains tetrahedral trivalent iron, as specified in Hey's and Grigoriev's formulas for lepidomelane. The presence or absence of tetrahedral Fe<sup>+3</sup> in a formula is indicative, not of high Fe<sup>+3</sup>, but of insufficient Si or Al to fill the tetrahedral group, as Fe<sup>+3</sup> is assigned to the tetrahedral group only when there is insufficient Si and Al to fill that group. Some of the phlogopite formulas calculated for this study contain tetrahedral Fe<sup>+3</sup> because the Al content is very low and is not sufficient to complete the filling of the tetrahedral group, although the Fe<sup>+3</sup> content is also very low. Thus tetrahedral Fe<sup>+3</sup> is not a necessary characteristic of high Fe<sup>+3</sup> biotites.

# CHEMICAL COMPOSITION AND GEOLOGIC OCCURRENCE

The trioctahedral micas form under a great variety of conditions and occur in many kinds of rocks—in igneous rocks, both intrusive and extrusive, ranging in composition from felsic to ultramafic; in metamorphic rocks, such as gneiss, schist, marble, and "serpentine" (serpentinite); in pegmatites; and in hydrothermal veins. As the chemical composition of trioctahedral micas depends not only on kinds and relative proportions of elements present at the time of their formation but also on other environmental factors, micas from different kinds of rocks would be expected to differ in composition.

Information on geologic occurrence was available for about two-thirds of the analyses used in this study. Most of the analyses for which such information was available were those of biotites, siderophyllites, and lepidomelanes. Information on the phlogopites was sparse, and that available indicated quite diverse occurrences. The kinds of rocks from which there were enough micas to furnish an adequate conception of the composition of the micas in them were divided into the following groups: Granite, monzonite and quartz monzonite granodiorite, diorite and quartz diorite; nepheline syenite, gneiss and schist, and pegmatite. Micas that formed under apparently atypical conditions such as a biotite from a large zenolith (plagioclase) in biotite granite, or a biotite from a dark veinlet in granite, are not included in this discussion.

The relation between the chemical composition of the micas and their geologic occurrence is shown in figure 12. In this figure the Mg-(Fe<sup>+2</sup>,Mn)-(Al,Fe<sup>+3</sup>,

32

INTERPRETATION OF TRIOCTAHEDRAL MICAS

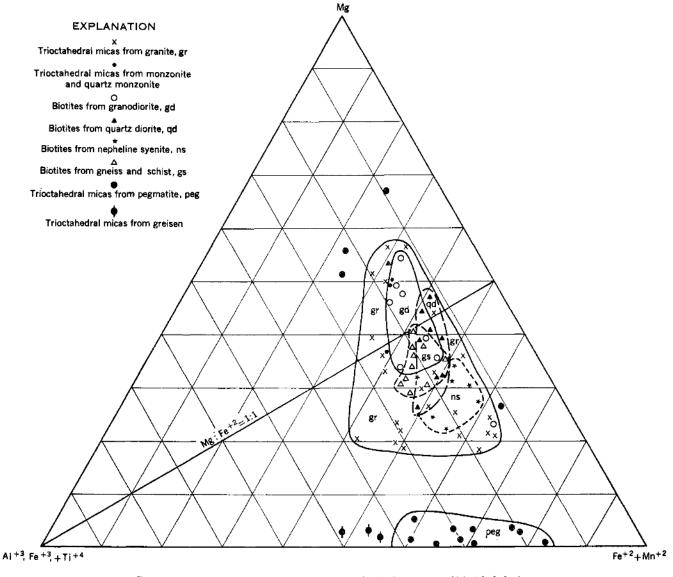


FIGURE 12.-Relation between chemical composition and geologic occurrence of trioctahedral micas.

Ti<sup>+4</sup>) relation in the octahedral group of each mica is plotted on a triangular diagram, as in figure 11, and the area occupied by points representing micas from a given kind of rock is enclosed. The occupied areas indicate that the micas from the first six groups of rocks are all biotites; those from the seventh group, with a few exceptions, are siderophyllites or lepidomelanes.

Biotites from granite.—Biotites from granite comprise the largest group (23). Points representing these biotites occupy an area (gr) in figure 12 which embraces almost the entire biotite area as shown in figure 11. Thus biotites from granite vary widely in character, from those in which Mg is greatly predominant, as in these formulas calculated from analyses 41 and 42, table 11.

$$\begin{array}{c} \begin{array}{c} +0.26 & -1.34 \\ \hline \\ [(\mathrm{Al}_{0.22}\mathrm{Ti}_{0.17}\mathrm{Fe}_{0.02}^{+3}\mathrm{Fe}_{0.51}^{+3}\mathrm{Mg}_{1.61}\mathrm{Mn}_{0.01}^{+2}) & (\mathrm{Si}_{2.66}\mathrm{Al}_{1.34})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.08} \\ \hline \\ 2.84 & (\mathrm{K}_{0.69},\mathrm{Na}_{0.14},\mathrm{Ca}/2_{0.02})_{1.06}^{+1.08} \\ \hline \\ \underline{(\mathrm{Al}_{0.03}\mathrm{Ti}_{0.20}\mathrm{Fe}_{0.10}^{+2}\mathrm{Fe}_{0.39}^{+2}\mathrm{Mg}_{1.00}\mathrm{Mn}_{0.01}^{+2})} & (\mathrm{Si}_{2.72}\mathrm{Al}_{1.28})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.07} \\ \hline \\ 2.84 & (\mathrm{K}_{0.91},\mathrm{Na}_{0.14},\mathrm{Ca}/2_{0.01})_{1.07}^{+1.08} \end{array}$$

to those in which  $Fe^{+2}$  is similarly dominant, as in these formulas calculated from analyses 116 and 120, table 11.



 $(K_{0.86}, Na_{0.06}, Ca/2_{0.05})^{+1.03}_{0.98}$ 

$$\underbrace{ \underbrace{ (\mathrm{Al}_{0.25}\mathrm{Ti}_{0.14}\mathrm{Fe}_{0.14}^{+3}\mathrm{Fe}_{1.69}^{+3}\mathrm{Mg}_{0.52}\mathrm{Mn}_{0.11}^{+2})}_{2.85} (\mathrm{Si}_{2.66}\mathrm{Al}_{1.34})\mathrm{O}_{10}(\mathrm{OH})_2]^{-0.97}}_{\mathrm{(K}_{0.74},\mathrm{Na}_{0.07},\mathrm{Ca}/2_{0.07})_{0.83}^{+0.95}}$$

In terms of percent composition, biotites from granite varied between 14.92 and 4.70 in MgO and between 12.69 and 26.80 in FeO.

In about one-half the biotites from granite, octahedral aluminum occupies fewer than 0.15 positions, as in 42 and 116, table 11 above. In some of these there is no octahedral aluminum, the aluminum present being insufficient to complete the filling of the tetrahedral group, and it was necessary to allocate some  $Fe^{+3}$  to that group. On the other hand, in other biotites from granite, octahedral aluminum is quite high, occupying 0.50 or more positions, as in this formula calculated from analysis 110, table 11,

$$\frac{^{+0.36}}{^{(Al_{0.51}Ti_{0.07}Fe_{0.23}^{+3}Fe_{1.22}^{+2}Mg_{0.65}Mn_{0.03}^{+2}Li_{0.66})}}_{2.77}(Si_{2.63}Al_{1.37})O_{10}(OH)_2]^{-1.01}}$$

In these biotites from granite,  $Al_2O_3$  varies between 13.64 and 20.55 percent.

 $Fe_2O_3$  content is also quite variable in these biotites between 0.35 and 8.0 percent. These amounts of  $Fe_2O_3$  are equivalent to 0.02 and 0.44 octahedral positions, respectively, occupied by  $Fe^{+3}$ . In the biotite in which  $Fe^{+3}$  occupies 0.44 octahedral positions, as well as in one other in which  $Fe^{+3}$  is fairly high and octahedral Al is fairly low,  $Fe^{+3}$  is the dominant trivalent octahedral cation. However, in most of the biotites from granite in which there is little or no octahedral aluminum, there is less  $Fe^{+3}$  than there is in those that have considerable octahedral aluminum. There is no apparent relation between FeO and  $Fe_2O_3$ , individuals of moderate FeO content may contain more  $Fe_2O_3$  than others with twice as much FeO and vice versa.

The  $TiO_2$  content of the granite biotites is quite uniform, varying between only 2.0 and 3.75 percent in 18 of the 22 analyses of biotites from granite.

In their accommodation of the additional charges carried by trivalent or quadrivalent octahedral cations the granite biotites apparently do not greatly tend to favor one method over the other, but exhibit a fairly equal degree of adjustment by both methods. Thus they are characterized by a moderate octahedral positive charge, +0.20 to +0.35, with an equivalent excess over 1.00 in tetrahedral negative charge, and by a moderate decrease (below 3.00) in octahedral occupancy, the number of octahedral positions occupied being generally between 2.85 and 2.70.

In summary, therefore, biotites from granite differ greatly in character and composition, varying from those in which Mg is the considerably predominant octahedral cation, through those in which Mg and  $Fe^{+2}$  are approximately equal, to those in which  $Fe^{+2}$  is considerably predominant. In any of these, octahedral Al may be very low or absent, moderate or high, and  $Fe^{+3}$  may be insignificant or an important constituent. Fuller data on the kinds of granite from which these biotites are derived might permit correlation between a particular type of granite and a particular type of biotite, but with the data at hand this is not possible.

Biotites from monzonite and quartz monzonite.—Only three of the biotites for which information as to geologic occurrence is available were from monzonite or quartz monzonite. Of these, the 2 from quartz monzonite (1 from Colorado and 1 from California) were very similar in composition, as shown by these formulas calculated from their analyses (48 and 50, respectively, table 11).

$$(K_{0.89}, Na_{0.05}, Ca/2_{0.01})^{+0.97}_{0.96}$$

Both are Mg dominant biotites with very low octahedral Al and moderate Fe<sup>+3</sup> content. Both have a moderate octahedral positive charge, with an equivalent increase in the negative tetrahedral charge; and in both the deficiency in octahedral occupancy is moderate, which indicates about equal adjustments by methods A and B for the additional positive charges carried by trivalent and guadrivalent octahedral cations. In the third member of the group, a mica from monzonite in Thuringia, Mg and Fe<sup>+2</sup> occupy 1.01 and 1.02 octahedral positions, respectively. This biotite is also somewhat higher in Fe<sup>+3</sup> content than the other two from quartz monzonite, but it is similar to them in octahedral and tetrahedral Al content and in TiO<sub>2</sub> and MnO content. In this biotite one-third of the adjustment for additional positive octahedral cations is by method A and two-thirds is by method B.

The points representing these three biotites fall on the left boundary of the area occupied by biotites from granodiorite (gd), figure 12. Biotites from granodiorite.—The eight biotites from granodiorite occupy a large area (gd), in the upper part of the granite area (fig. 12). It also overlaps the line (Mg:Fe<sup>+2</sup>=1:1) between the Mg and Fe<sup>+2</sup> dominant biotites; thus both types of biotites are obtained from granodiorite. In these biotites, Mg and Fe<sup>+2</sup> together generally occupy from approximately 2.30 to 2.45 octahedral positions, but the relative proportions of the two cations present varies greatly, as illustrated in the following formulas calculated from analyses 44, 67, and 111, table 11,

$$\underbrace{[\underbrace{(Al_{0.00}Ti_{0.21}Fe_{0.17}^{+3}Fe_{0.01}^{+2}Mg_{1.56}Mn_{0.02}^{+2})}_{2.87}(Si_{2.74}Al_{1.21}Fe_{0.05}^{+3})O_{1^{0}}(OH)_{2}]^{-0.93}}_{(K_{0.94},Na_{0.06})_{0.93}^{+0.03}}$$

 $\underbrace{[\underbrace{(\mathrm{Al}_{0,11}\mathrm{Ti}_{0.18}\mathrm{Fe}_{0.17}^{+3}\mathrm{Fe}_{1.20}^{+2}\mathrm{Mg}_{1.09}\mathrm{Mn}_{0.02}^{+2})}_{2.77}(\mathrm{Si}_{2.75}\mathrm{Al}_{1.25})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.07}}_{(\mathrm{K}_{0.88},\mathrm{Na}_{0.08},\mathrm{Ca}/2_{0.05})_{1.01}^{+1.06}}$ 

 $\underbrace{(\underbrace{\mathrm{Al}_{0.12}\mathrm{Ti}_{0.22}\mathrm{Fe}_{0.06}^{+3}\mathrm{Fe}_{1.74}^{+2}\mathrm{Mg}_{0.55}\mathrm{Mn}_{0.04}^{+2}}_{2.83}(\mathrm{Si}_{2.74}\mathrm{Al}_{1.26})\mathrm{O}_{10}(\mathrm{OH})_2]^{-0.98}}_{(\mathrm{K}_{0.90},\mathrm{Na}_{0.02},\mathrm{Ca}/2_{0.03})_{0.96}^{+0.99}}$ 

These formulas also serve to illustrate the characteristics of biotites from granodiorite: their generally low octahedral Al content, their fairly low  $Fe^{+3}$  content, and their moderately high TiO<sub>2</sub> content. In these biotites, as in those from granite and quartz monzonite, adjustment for the additional charges carried by these trivalent and quadrivalent octahedral cations is made almost equally by method A and method B, except for two, as in the second formula above, in which adjustment is predominately by method B.

Biotites from diorite and quartz diorite.—The points representing biotites from diorite and quartz diorite occupy an elongated area (qd) on the middle right side of the granite area in figure 12, most of the area being below the Mg:Fe<sup>+2</sup>=1:1 line. This group also contains both Mg and Fe<sup>+2</sup> dominant individuals, but 5 of the 7 in the group are Fe<sup>+2</sup> dominant. However, in neither the Mg or Fe<sup>+2</sup> dominant individuals is the dominance extreme, as is illustrated by these formulas of analyses (53 and 101, table 11) which represent the Mg and Fe<sup>+2</sup> extremes of the group

$$[\underbrace{(Al_{0.94}Ti_{0.26}Fe_{0.04}^{+2}Fe_{1.16}^{+2}Mg_{1.34}Mn_{0.01}^{+2})}_{2.85}(Si_{2.74}Al_{1.26})\theta_{10}(OH)_{2}]^{-0.96}$$

$$(K_{0.86}, Na_{0.05}, Ca/2_{0.01})^{+.96}_{0.92}$$

 $\frac{+0.51}{[(\mathrm{Al}_{0.85}\mathrm{Ti}_{0.15}\mathrm{Fe}_{0.20}^{+3}\mathrm{Fe}_{1.36}^{+3}\mathrm{Mg}_{0.75}\mathrm{Mn}_{0.02}^{+2})(\mathrm{Si}_{2.45}\mathrm{Al}_{1.54})0_{10}(\mathrm{OH})_2]^{-1.03}}{2.83}$ 

 $(K_{0.88}, Na_{0.11}, Ca/2_{0.02})^{+1.03}_{-1.01}$ 

The Mg dominant members of the group contain considerable Fe<sup>+2</sup>, and the Fe<sup>+2</sup> dominant members contain considerable Mg although Fe<sup>+2</sup> may be more dominant in some Fe<sup>+2</sup> dominant members than Mg is in any of the Mg dominant members. These two formulas also illustrate the extremes of octahedral aluminum content in members of the group. The Fe<sub>2</sub>O<sub>3</sub> content of 5 of the 7 biotites in this group was less than 1 percent. The biotite represented by the formula for 101 above has the highest Fe<sub>2</sub>O<sub>3</sub> content, 3.49 percent. Adjustment for the additional positive charges carried by trivalent octahedral cations in these biotites is, in general, fairly evenly distributed between method A and method B.

The one point representing biotite from diorite falls not in the quartz diorite area (qd) but near the top of the granite area. This biotite is more dominantly magnesian than other biotites from diorite and quartz diorite, but is not unlike them in other compositional characteristics.

Biotites from nepheline syenite.—The biotites from nepheline syenite are definitely more ferroan than the biotites heretofore considered. The almost round area (ns) in figure 12 enclosing points representing biotites in this group lies well below the Mg-Fe<sup>+2</sup>=1:1 line, with the upper edge just touching the lower edge of the granodiorite area (gd). The formula calculated for analysis 109, table 11

$$\underbrace{[(\underline{Al_{0.08}Ti_{0.22}Fe_{0.35}^{+3}Fe_{1.46}^{+2}Mg_{0.68})(Si_{2.58}Al_{1.42})0_{10}(OH)_2]^{-0.97}}_{2.79}$$

$$(\underline{K_{0.79}, Na_{0.13}, Ca/2_{0.92})^{+0.98}}_{0.94}$$

fairly well represents the general characteristics of the members of this group, which are quite uniform in composition. Octahedral Al is very low. In some members there is not enough to complete the filling of the tetrahedral group, and some Fe<sup>+3</sup> must be allocated to this group for its completion. The  $Fe_2O_3$  content is generally fairly high, varying between 4 and 10 percent in the analyses at hand. Mn is considerably higher than in the biotites heretofore studied, several of the nepheline syenite biotites having between 2 and 3 percent MnO. TiO<sub>2</sub> content is quite variable. Although in a few biotites in this group adjustment for additional positive octahedral charges is made equally by the two methods, in most the adjustment is dominantly by method B. Thus, many of the formulas for this group are characterized by a low positive octahedral charge, with fewer octahedral positions occupied than in the biotites heretofore considered.

Biotites from gneiss and schist.—Points representing biotites from gneiss and schist occupy an area in figure 12 which lies athwart the lower part of the granodiorite (gd) area, the middle of the quartz diorite (qd) area, and the upper part of the nepheline syenite (ns) area. This location indicates that the biotites from gneiss and schist are somewhat higher in  $Fe^{+2}$  content than the biotites from granodiorite, but generally lower in  $Fe^{+2}$ content than biotites from nepheline syenite. The formula calculated for analysis 86, table 11, represents the general character of the biotites in this group:

$$[\underbrace{(\mathrm{Al}_{0.29}\mathrm{Ti}_{0.20}\mathrm{Fe}_{0.12}^{+3}\mathrm{Fe}_{1.18}^{+3}\mathrm{Mg}_{0.94}\mathrm{Mn}_{0.03}^{+2}}_{2.76}(\mathrm{Si}_{2.64}\mathrm{Al}_{1.36})0_{10}(\mathrm{OH})_2]^{-1.03}$$

$$(\mathrm{K}_{0.59},\mathrm{Na}_{0.16},\mathrm{Ca}/2_{0.02})^{+1.09}_{1.07}$$

These biotites are all Fe<sup>+2</sup> dominant, with moderate octahedral Al content and fairly low Fe<sup>+3</sup> content. Adjustment for additional positive octahedral cations is made about equally by methods A and B, with a moderate octahedral positive charge (0.30-.40), a moderate negative tetrahedral charge in excess of 1.00, and with an octahedral occupancy deficiency of about 0.2 position.

Biotites from pegmatite.—Of 14 analyses of micas from pegmatite, only 4 represented biotites; all the others represented Mg deficient trioctahedral micas, siderophyllites, lepidomelanes, and intermediates of these. Three of the four biotites from pegmatite are highly Mg dominant and are lower in  $Fe^{+2}$  than any of the biotites from granite or granodiorite. Thus, the points representing them in figure 12 fall outside the upper boundary of the granite area. The fourth biotite from pegmatite is highly  $Fe^{+2}$  dominant. The point representing it falls just outside the granite area on the lower right side of figure 12.

Trioctahedral micas from pegmatite.—Ten of the fourteen analyses of micas from pegmatites are very low in Mg (<1.5 percent MgO) and high in Fe<sup>+2</sup> content. They therefore represent the Mg deficient end of the Mg replacement system and occupy an area at the bottom of the triangular diagram shown in figure 12. Two of these analyses represent siderophyllites, with Al the greatly dominant trivalent octahedral cation, and with Fe<sup>+3</sup> very low or absent; five represent lepidomelanes, with Fe<sup>+3</sup> the greatly dominant trivalent octahedral cation, and with Al very low or absent. The other three analyses represent aluminian lepidomelanes, with significant amounts of both Fe<sup>+3</sup> and octahedral Al, but with Fe<sup>+3</sup> present in somewhat greater amounts than octahedral Al. The three micas from nepheline syenite pegmatite are, however, quite similar in composition, like biotites from nepheline syenite, and like

them are characterized by iron. The Mg content in the micas from nepheline syenite pegmatite is, however, very much lower. All three of these micas (124, 125, and 126) are lepidomelanes, with octahedral Al very low or absent. In one the Al is so low that there is not sufficient to complete the filling of the tetrahedral group, making it necessary to assign some  $Fe^{+3}$  to that group.

Li is reported in 7 of the 10 analyses of Mg deficient trioctahedral micas from pegmatites, the amount reported varying from 0.08 to 1.01 percent Li<sub>2</sub>O. No Li is reported in the three analyses from nepheline symite pegmatite. This failure to report Li does not mean, necessarily, that Li is not present. Li, if present, but not determined, is reported as Na. As Li is considered an octahedral cation and calculated as such, failure to determine Li if present causes a double error in the formula calculation, too few octahedral cations and too many interlayer cations, the amount of error depending on the amount of Li present. In one of the formulas calculated from the three analyses in which Li is not reported, 126, table 11, the higher interlayer cation content, 1.11, suggests the possible presence of Li. In the other two formulas calculated from analyses in which Li is not reported, the interlayer cation content is not high, but this does not rule out the possible presence of small amounts of Li.

Other Mg-deficient trioctahedral micas.—Of the 3 other analyses of Mg deficient trioctahedral micas at hand, 2 are of micas from greisen, and 1 is of mica from offshoot veins of trap dike. One of the two micas from greisen is a siderophyllite, with less than 1 percent of Fe<sub>2</sub>O<sub>3</sub>, the other is about halfway between siderophyllite and lepidomelane. The latter is reported to contain 0.39 percent Li<sub>2</sub>O. No Li is reported in the siderophyllite, but the high interlayer ion content is suggestive of its possible presence. The mica from offshoot veins from trap dike is an aluminian lepidomelane containing 0.59 percent Li<sub>2</sub>O.

The Mg-deficient trioctahedral micas show a greater tendency toward one-sided adjustment for the extra charges carried by trivalent and quadrivalent octahedral cations than do the biotites. Of the 13 Mg deficient trioctahedral micas here considered, 8 showed preferential adjustment, 75 percent or more, by method B. In three the adjustment is entirely by method B, except for compensation due to Li.

Li, with its single positive charge, compensates for as many extra charges carried by trivalent octahedral cations as the number of octahedral positions it occupies. This may be illustrated by referring to the formula for D63, table 12,

$$[\underbrace{(\mathrm{Al}_{0.46}\mathrm{Fe}_{0.68}^{+8}\mathrm{Fe}_{1.09}^{+2}\mathrm{Mg}_{0.07}\mathrm{Mn}_{0.03}^{+2}\mathrm{Li}_{0.18})}_{2.51}_{-1.02}_{(\mathrm{Si}_{2.98}\mathrm{Al}_{1.02})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.04}\mathrm{K}_{1.01}^{+1.01}}$$

In this formula Al and Fe<sup>+3</sup> carry 1.14 positive charges in excess of the number of positive charges that would be carried by the same number of bivalent cations. On the other hand, 0.18 Li carries only half as many positive charges as would be carried by the same number of bivalent cations. Thus the xLi cations compensate for  $x \mathbb{R}^{+3}$  cations, the number of extra positive charges carried by the trivalent cations is reduced by the number of positions occupied by Li, and the layer structure must adjust for 0.96 extra charges, not 1.14. This adjustment is made entirely by method B, that is, unoccupancy of octahedral positions, with the anionic charges associated with these unoccupied positions available for the neutralization of the extra charges. Octahedral occupancy is only 2.51, the 0.49 unoccupied positions contributing 0.98 negative charges for the neutralization of the 0.96 extra positive charges, and the octahedral layer is left with a residual charge of -0.02.

# DISCUSSION OF RELATION BETWEEN MICA COMPOSI-TION AND OCCURRENCE

This study of the relation between the composition and character of trioctahedral micas and their geologic occurrence indicates that igneous rocks such as granites, diorites, and nepheline syenites, and metamorphic rocks, such as gneiss and schist, yield trioctahedral micas in which both Mg and Fe<sup>+2</sup> are present in significant amounts, that is, biotites, but do not yield trioctahedral micas, like phlogopites, with very high Mg content and low Fe<sup>+2</sup> content, or micas like siderophyllites and lepidomelanes, with very low Mg content and high Fe<sup>+2</sup> content. Heinrich (1946, p. 842, 844) found that phlogopites occur in peridotites and other ultramafic rocks and in metamorphosed limestones. The data that are available on phlogopites for the present study indicate that some phlogopites are from contact zones of metamorphism. All the siderophyllites and lepidomelanes are from pegmatites or greisen. Thus the extreme types of trioctahedral micas, those with extremely high or extremely low Mg content, are from extreme types of rocks.

There is not a clear distinction in the composition of biotites from different kinds of rocks. This is illustrated by these three formulas, calculated from analyses 49, 50, and 51, table 11:

$$\begin{array}{c} \begin{array}{c} +0.27 & -1.27 \\ [\underline{(Al_{0.02}Ti_{0.19}Fe_{0.27}^{+3}Fe_{0.02}^{+2}Mg_{1.38}Mn_{0.02}^{+2})} (Si_{2.72}Al_{1.27})O_{10}(OH)_2]^{-1.00} \\ \hline \\ \underline{(K,Na)_{0.96}^{+0.01}} \\ \hline \\ \underline{(K,Na)_{0.96}^{+0.96}} \\ \underline{(K,Na)_{0.96}^{+2}Fe_{0.27}^{+2}Fe_{0.90}^{+2}Mg_{1.40}Mn_{0.08}^{+2})} (Si_{2.72}Al_{1.25})O_{10}(OH)_2]^{-0.97} \\ \hline \\ \underline{(K,Na,Ca/2)_{0.96}^{-0.97}} \\ \underline{(K,Na,Ca/2)_{0.96}^{-0.97}} \\ \hline \\ \underline{(Al_{0.07}Ti_{0.27}Fe_{0.28}^{+2}Fe_{0.28}^{+2}Mg_{1.28}Mn_{0.01}^{+2})} (Si_{2.25}Al_{1.24})O_{10}(OH)_2]^{-0.97} \\ \hline \\ \underline{(K,Na,Ca/2)_{0.96}^{-0.97}} \\ \hline \end{array}$$

2.78

These formulas are essentially identical, not only in the kinds and amounts of ions present, but in octahedral charge and occupancy, tetrahedral charge, and total charge. They are much more alike than many calculated formulas for biotites not only from the same kind of rock, but than some from the same rock at the same location. Yet 49 represents a biotite from granodiorite, 50 a biotite from monzonite, and 51 a biotite from granite. Thus biotites from different rocks may be very similar in composition and character. That they are not differentiated clearly in character is attested by the superimposing and overlapping of areas in figure 12. At 1 place at the middle right-hand side of the biotite area, the areas for 4 different rocks are superimposed.

Conversely, biotites from the same kind of rock may differ greatly in character and composition. This is particularly true of biotites from granites and to a lesser extent of biotites from granodiorite, diorite, and quartz diorite. The diversity in composition and character of biotites from granite is shown by the large area occupied by these biotites, which embraces practically the entire biotite area as shown in figure 11. This picture, however, is probably distorted to some extent by the loose usage of the term "granite" to cover monzonite, quartz monzonite, granodiorite, diorite, and quartz diorite.

The figures in Heinrich's study (1946, p. 836-848) of the relation between composition and geologic occurrence in the biotite-phlogopite series seem to indicate a more clear-cut differentiation between the composition of biotites and their parent rocks than was found in this study. However, he used a separate diagram for each of his rock groups. If the diagrams for his group 2 (granites, quartz monzonites, granodiorites), group 3 (tonalites, diorites), group 6 (syenites, nepheline syenites, but excluding nepheline syenite

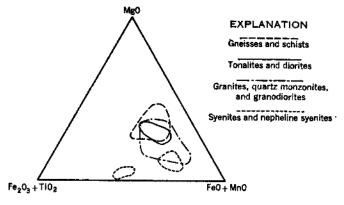


FIGURE 13.—Relation between the composition and the geologic occurrence of biotites. (After Heinrich, 1946, figs. 2, 3, 6, and 7 superimposed and reoriented.)

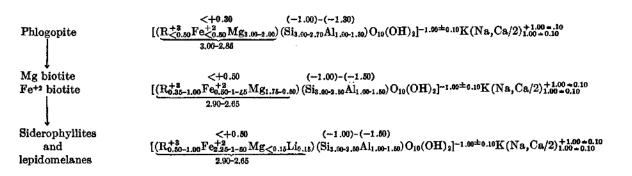
pegmatites), and group 7 (gneisses and schists), which include all the groups shown in figure 12 except pegmatites and greisen, are superimposed on each other, as in figure 13, it is found that the areas occupied by biotites from these different rocks overlap considerably. The tonalite-diorite area lies almost wholly within the granite, quartz monzonite, granodiorite area, and half of the gneiss-schist area overlies the same part of the same area. Thus at this 1 place the areas for 3 groups overlie each other. In figure 13 the triangular diagram of Heinrich has also been reoriented, so that MgO, FeO+MnO, and Fe<sub>2</sub>O<sub>3</sub>+TiO<sub>2</sub> occupy the same corners with respect to the viewer as do Mg,  $Fe^{+2}$ +Mn, and  $\mathbf{R}^{+3}$ +Ti in figure 12. The occupied areas in the two figures occur in the same general part of triangular diagrams-a very good agreement in view of the different methods used in plotting the biotite compositions; Heinrich's biotites being plotted on the basis of percentage by analysis, in which octahedral Al and the great equivalent difference between Mg and Fe<sup>+2</sup>

is ignored, and the biotites in figure 12 being plotted on the basis of octahedral positions occupied, including octahedral Al.

However, correlations of this sort can show only the broader aspects of the relation between biotite composition and the parent rocks; details of the relation are possible only in more localized studies.

# SUMMARY AND CONCLUSIONS

The composition of the trioctahedral micas can be interpreted as derived from phlogopite, Mg<sub>3.00</sub>(Si<sub>3.00</sub>Al)  $O_{10}(OH)_2 K_{1.00}$ , by the proxying of other cations, particularly Fe<sup>+2</sup>, Fe<sup>+3</sup>, and Al, for Mg. Phlogopite, in its ideal form may, therefore, be considered the prototype of the trioctahedral micas, just as muscovite, in its ideal form, is the prototype of the dioctahedral micas. In natural phlogopites the proxying of other cations for Mg is minor, and Mg is greatly predominant, occupying more than 70 percent of the octahedral positions. Progressively greater proxying of other cations, particularly Fe<sup>+2</sup>, for Mg leads successively to Mg biotites, in which Mg is still the dominant octahedral cation, but in which Fe<sup>+2</sup> is present in significant amounts. Fe<sup>+2</sup> biotites, in which Fe<sup>+2</sup> is the dominant octahedral cation, with Mg present in subordinate but significant amounts, and siderophyllites and lepidomelanes, in which Mg is essentially absent, occupying less than 5 percent of the octahedral positions. Thus, in order of decreasing Mg content, the trioctahedral micas, phlogopites, biotites, siderophyllites, and lepidomelanes form a complete system, from full octahedral occupancy by Mg at one end to nil Mg occupancy at the other end. These relations are expressed in the following equations, which show the range in composition of three principal groups.



Considered as derivatives of phlogopite as the prototype, all trioctahedral micas exhibit multiple proxying of other cations for Mg. The phlogopites are the only trioctahedral micas in which one kind of cation is greatly predominant in the octahedral group. Consequently, the low Mg end of the system is represented by siderophyllite and lepidomelane, not by annite, the  $Fe^{+2}$  analog of phlogopite.

The proxying of bivalent ions, like  $Fe^{+2}$  or  $Mn^{+2}$ , for Mg is ion for ion, and no layer charge adjustments are necessary, but the proxying of trivalent ions, like Al, or Fe<sup>+3</sup>, for Mg, because of their greater valence, requires layer charge adjustments. The two possible types of adjustment may be expressed by the following equations:

$$2nR^{+3} = nR^{+2} + nSi$$
 (A)  
$$2nR^{+3} = 3nR^{+2}.$$
 (B)

In the (A) type of adjustment  $nR^{+3}$  ions proxy for nMg ions in the octahedral layer, and an additional nAl ion proxies for nSi ions in the tetrahedral layers. Formulas for trioctahedral micas that have accommodated trivalent octahedral cations in this way are characterized by a positive octahedral charge equivalent to the number of trivalent octahedral cations present, a negative tetrahedral charge greater than 1.00 by an amount equivalent to the positive octahedral charge. that is, to the number of trivalent octahedral cations, and by full octahedral occupancy. In the (B) type of adjustment  $2nR^{+3}$  cations proxy for 3nMg ions. Formulas for trioctahedral micas that have accommodated trivalent octahedral cations in this way are characterized by a neutral octahedral layer, and a negative tetrahedral charge of 1.00 as in the ideal formula for phlogopite, but octahedral occupancy is deficient by an amount equivalent to one-half the number of trivalent octahedral cations. A few formulas for trioctahedral micas have the octahedral positive charge, the equivalently greater negative tetrahedral charge, and the full octahedral occupancy indicative of the (A) type of adjustment, and a few have the neutral octahedral group and deficient octahedral occupancy of the (B) type of adjustment, but most formulas for trioctahedral micas have characteristics of both types of adjustment—a positive octahedral charge, a negative tetrahedral charge greater than 1.00, and octahedral deficiency-indicating a combination of the two types of adjustment. The relative degree of adjustment by (A) or (B), and, consequently, the proxying ratio of trivalent for bivalent octahedral cations varies. However, the average proxying ratio in the 250 formulas included in this study is 0.73 Al for 1.00 Mg, a proxying ratio which is considerably closer to that of the (B) than to that of the (A) type of adjustment, indicating generally greater adjustment by (B) than by (A).

In general, the degree of adjustment by (B) increases with the octahedral  $R^{+3}$  content. This is reflected in a general decrease in the number of octahedral positions occupied with increase in octahedral  $R^{+3}$  content, with the average octahedral positive charge remaining about the same throughout the octahedral  $R^{+3}$  range. Thus most trioctahedral micas are not truly trioctahedral. Nor are they true octaphyllites, as the number of cations in the half cell is usually less than eight.

The trend of R<sup>+3</sup> proxying is, therefore, toward muscovite or other dioctahedral mica. However, the distribution of the formulas studied over the  $R^{+3}$  range, and the scarcity of formulas having more 0.90 octahedral positions occupied by  $R^{+3}$ , strongly indicates that the normal extent of  $R^{+3}$  proxying for Mg is approximately one-third of the occupied octahedral positions and that there is not a continuous series between the trioctahedral and dioctahedral micas.

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INTERPRETATION OF TRIOCTAHEDRAL MICAS

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Interlayer cations	Charge	<u>╡┽┥</u> ┽┽┽┽┽┽┽┽┽┽┼┧┼┼┽╡┼┧┽┼┼┼┼┼┼┼┼┼┼┼┼┼┼┼┼┼┼┼┼
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	V	998488889728588874888898898989898888888888888888888
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	ysis Beep 14-45)	

TABLE 11.—Analyses and data for writing formulas of trioctahedral micas used in correlation study. In order of decreasing MgO content] **41** 

TABLE 11.—Analyses and data for writing formulas of trioclahedral micas used in correlation study—Continued	[In order of decreasing MgO content]
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	AbOs	近其礼貌说说我说说我们说我说话我们我我们我说过我说说我说说,你们们说说我们我们就没有这些法律我们不可以是这些人们的问题。" 了我就说那么说我说我说我们我我们我我们我我们我的你的你们的你的我们就能是我我们就能能能能能能能能能能能。"
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Anal-	(see p. 44-45)	88888888888888888888888888888888888888

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

The following numbers are in terms of percentages.
The fullowing numbers are in terrahedral group.
Includes 2.08 BaO.
Includes 1.08 BaO.
Includes 0.30 CO., which is equivalent to all CaO and to 0.07 a find, a fincludes 0.32 BaO.
Includes 0.33 PaO.
Includes 0.33 PaO.
Includes 0.33 PaO.
Includes 0.34 BaO.
Includes 0.34 BaO.
Includes 0.34 BaO.
Includes 0.35 BaO.
Includes 0.36 BaO.
Includes 0.74 CryO.
Incl

 <sup>41</sup> Includes 0.57 Lat0 (0.11 octanedral positions), 0.04 BaO, and 0.04 to 25 Prot.
 <sup>42</sup> Includes 0.23 Prot.
 <sup>42</sup> Includes 0.23 Prot.
 <sup>41</sup> Includes 0.35 Lat0 (0.07 octahedral positions, 0.02 BaO, and 0.04 YaO.
 <sup>41</sup> Includes 0.35 Lat0 (0.13 octahedral positions).
 <sup>42</sup> Includes 0.35 Lat0 (0.13 octahedral positions).
 <sup>43</sup> Includes 0.48 Lat0 (0.13 octahedral positions).
 <sup>44</sup> Includes 0.48 Lat0 (0.15 octahedral positions).
 <sup>45</sup> Includes 0.48 Lat0 (0.15 octahedral positions).
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 <sup>47</sup> Includes 0.60 Lat0 (0.15 octahedral positions).
 <sup>48</sup> Includes 0.60 Lat0 (0.30 octahedral positions).
 <sup>48</sup> Includes 0.60 Lat0 (0.30 octahedral positions).
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 <sup>48</sup> Includes 0.60 Lat0 (0.00 octahedral positions).
 <sup>48</sup> Includes 0.60 Lat0 (0.30 octahedral positions).
 <sup>48</sup> Includes 0.60 Lat0 (0.00 octahedral positions).
 <sup>48</sup> Includes 0.60 Lat0 (0.00 octahedral positions). <sup>41</sup> Includes 0.12 Li<sub>2</sub>O (0.04 octahedral positions).
 <sup>41</sup> Includes 0.03 Fa0.
 <sup>41</sup> Includes 0.09 Ba0.
 <sup>41</sup> Includes 0.07 BaO.
 <sup>41</sup> Includes 1.05 ZrO.
 <sup>41</sup> Includes 0.14 Li<sub>2</sub>O (0.04 octahedral positions).
 <sup>41</sup> Includes 0.19 Li<sub>2</sub>O (0.06 octahedral positions).
 <sup>42</sup> Includes 0.19 Li<sub>2</sub>O (0.06 octahedral positions).
 <sup>43</sup> Includes 0.24 Fo0.
 <sup>44</sup> Includes 0.37 Li<sub>5</sub>O (0.11 octahedral positions).
 <sup>44</sup> Includes 0.37 Li<sub>5</sub>O (0.11 octahedral positions).
 <sup>45</sup> Includes 0.37 Li<sub>5</sub>O (0.11 octahedral positions). <sup>31</sup> Includes 0.08 Cr<sub>2</sub>O<sub>4</sub> (0.01 octahedral positions), and 0.11 Li<sub>5</sub>O (0.03 octahedral positions).
<sup>31</sup> Includes 0.38 Li<sub>3</sub>O (0.08 octahedral positions), 0.37 Rb<sub>3</sub>O, and trace CsO.
<sup>32</sup> Includes 0.33 BaO.
<sup>34</sup> Encludes 0.33 BaO.
<sup>34</sup> Encludes 0.35 BaO.
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<sup>31</sup> Encludes 0.03 BaO.
<sup>32</sup> Encludes 0.03 BaO.
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<sup>36</sup> Encludes 0.03 PaO.
<sup>37</sup> Encludes 0.03 EaO.
<sup>36</sup> Encludes 0.03 PaO.
<sup>36</sup> Encludes 0.03

# INTERPRETATION OF TRIOCTAHEDRAL MICAS

Locality and reference for analyses in table 11

- DeKalb, N.Y., Dana, E.S., 1892, The system of mineralogy, 6th ed., New York, John Wiley and Sons, p. 633, No. 11.
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- Mineralogie, Geologie, u. Paläontologie, Beilage-Band 50, p. 412, tuble 2, No. 2,
  Mansjö Mountain, Sweden, Eckermann, H. v., 1925, Tschermaks mineralog. petrog. Mitt., v. 38, p. 281.
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  U.S.S.R. (eract locality not given), Berkhin, S. I., 1954, Akad. Nauk SSSR Dokhady, v. 95, p. 146, No. 260.
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  Easton, Pa., Eyerman, J., 1904, Am. Geologist v. 34, p. 46, C.
  Easton, Pa., Eyerman, J., 1904, Am. Geologist v. 34, p. 46, A.
  Lake Baikal, U.S.S.R., Dana, E. S., 1892, The system of mineralogy, 6th ed., New York, John Wiley and Sons, p. 630, No. 1.
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TABLE 12.—Analyses and data for writing formulas of trioctakedral micas not used in correlation study [In order of decreasing MgO content]

**4**6

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

The following numbers are in terms of percentage.

Includes 0.07 LigO (0.02 octabedral positions).
 Includes 0.20 LigO (0.05 octabedral positions), 1.28 BaO, and 0.31 Cl.
 All the Al, Fe<sup>44</sup> and Tl and some Fe<sup>44</sup> are necessary to fill the terribodral group.
 All the Al and Fe<sup>44</sup>, and some Th are necessary to fill the tetra-terribodral group.
 All the Al and Fe<sup>44</sup>, and some Th are necessary to fill the tetra-hedral group.
 Includes 0.03 LigO (0.14 octabedral positions).
 All the Al and A Fe<sup>44</sup>, and some Th are necessary to fill the tetra-hedral group.
 Includes 0.03 LigO (0.14 octabedral positions).
 Includes 0.03 LigO (0.16 octabedral positions).
 Includes 0.04 LigO (0.03 octabedral positions).
 Includes 0.04 Crool, 100 BaO, 0.07 (1, and 0.09 S.
 Includes 0.04 Erol, 100 BaO, 0.07 (1, and 0.06 S.

<sup>\*\*</sup> Includes 0.37 Li<sub>2</sub>O (0.11 octahedral positions).
 <sup>\*\*</sup> Includes 0.17 Li<sub>2</sub>O (0.06 octahedral positions).
 <sup>\*\*</sup> Includes 0.17 Li<sub>2</sub>O (0.08 octahedral positions).
 <sup>\*\*</sup> Includes 0.18 Pi<sub>2</sub>O (0.03 octahedral positions).
 <sup>\*\*</sup> Includes 0.18 Pi<sub>2</sub>O.
 <sup>\*\*</sup> Includes 0.17 Li<sub>2</sub>O (0.10 octahedral positions).
 <sup>\*\*</sup> Includes 0.17 Li<sub>2</sub>O (0.25 octahedral positions).
 <sup>\*\*</sup> Includes 0.17 Li<sub>2</sub>O (0.26 octahedral positions).
 <sup>\*\*</sup> Includes 0.17 Li<sub>2</sub>O (0.26 octahedral positions).
 <sup>\*\*</sup> Includes 0.17 Li<sub>2</sub>O (0.26 octahedral positions).
 <sup>\*\*</sup> MgO+CaO=0.38. The formula values for the predominantly MgO is predominantly MgO is predominantly CaO. Assuming this value for the predominantly MgO malkes no charge in the formula values the number of positions occupied by Fe<sup>\*\*</sup> for 1.52, adds 0.03 positions occupied by Pi<sup>\*\*</sup> for 1.52, adds 0.03 positions occupied by Pi<sup>\*\*</sup> for 1.52, adds 0.03 positions occupied by Pi<sup>\*\*</sup> for 1.52, adds 0.03 positions octahedrage to 0.96. This analysis represents the compositions of the type lepidomelane.

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# INTERPRETATION OF TRIOCTAHEDRAL MICAS

### Locality and reference for analyses in table 12

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