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LAYER CHARGE RELATIONS IN THE DIOCTAHEDRAL AND TRIOCTAHEDRAL MICAS*

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ABSTRACT

In theoretical formulas for dioctahedral and trioctahedral micas, the entire composite-layer charge originates in the tetrahedral layers owing to substitution of one-fourth of the Si by Al; the octahedral layer is neutral. But formulas calculated for published analyses of a great number of dioctahedral and trioctahedral micas show that these ideal charge relations are altered by the proxying of other cations for the octahedral cation theoretically present. Cations carrying a lower positive charge than the cation ideally presumed to occupy the octahedral sites, as Mg or Li for Al in dioctahedral micas, or Li for Mg or Fe^{+2} in trioctahedral micas, do not proxy for that cation in sufficient number to compensate for the difference in charge; consequently, not all the negative octahedral charges are neutralized, and the layer is left with a negative charge which necessitates an equivalent decrease in the tetrahedral negative charge by increase in Si and decrease in Al. In such micas, part of the total composite layer charge originates in the octahedral layer, part in the tetrahedral layer, and the total charge is the sum of two negative charges.

The additional charges carried by cations having a higher charge than the octahedral cations for which they proxy, as Al or Fe^{+3} for Mg in trioctahedral micas, may be accommodated in two ways: (a) by a positive charge on the octahedral layer, which is compensated for by an equivalent increase in the negative tetrahedral charge by greater substitution of Al for Si, or (b) by nonoccupancy of octahedral sites, the negative charges associated with these sites being then available to neutralize the additional positive charges carried by the proxying cations. Formulas of natural trioctahedral micas show that in most of them accommodation has been made in both ways to varying degrees; in very few has accommodation been made entirely in one way. In most trioctahedral micas, therefore, the total charge is made up of a positive octahedral charge and a negative tetrahedral charge greater than 1.00 by an equivalent amount.

INTRODUCTION

In the ideal formulas for the prototypes of the dioctahedral and trioctahedral trisilicic micas, muscovite and phlogopite, the octahedral layer is neutral, and the entire inherent charge on the composite layer originates in the tetrahedral layer owing to the proxying of trivalent aluminum for quadrivalent Si. The octahedral layer is neutral. This octahedral-tetrahedral charge relation can be shown by a notation above the respective groups in the structural formulas:

$$\overset{.00}{\mathrm{Al}_{2.00}}(\overset{-1.00}{\mathrm{Si}_{3.00}\mathrm{Al}_{1.00}})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.00}\ \mathrm{K}^{+1.00}_{1.00}$$

$$[\overset{.00}{\mathrm{Mg}_{3.00}}(\overset{-1.00}{\mathrm{Si}_{3.00}\mathrm{Al}_{1.00}})\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.00}\ \mathrm{K}^{+1.00}_{1.00}$$

However, very few, if any, natural muscovites and phlogopites have the exact composition specified in these ideal formulas. Almost all muscovites

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contain a little magnesium, and almost all phlogopites contain a little octahedral aluminum, Al(VI). Both muscovites and phlogopites may contain some iron, trivalent, bivalent, or both. Some also have titanium, or manganese, and more rarely, vanadium and chromium. These cations occupy octahedral sites and proxy for the ion specified in the ideal formulas.

If the proxying cation has the same charge as the cation for which it proxies, there is no change in the number of positive charges carried by the octahedral cations, and the neutrality of the octahedral layer is not affected. But if the proxying cation has a different charge than the cation for which it proxies, the octahedral layer acquires either a positive or a negative charge, depending on whether the proxying cation carries a higher or a lower charge than the proxied cation. The effect of such substitutions, based on calculated formulas of published analyses, was studied in detail for dioctahedral micas (Foster, 1956), trioctahedral micas (Foster, in press), and for lithium micas (Foster, in press). The present paper represents a correlation of the results of these studies with respect to layer charge relations.

THE EFFECT OF SUBSTITUTIONS IN DIOCTAHEDRAL MICAS

Although two octahedral sites are ideally occupied by trivalent cations (as two Al in the ideal formula of muscovite) formulas calculated from published analyses of dioctahedral micas show that some of the octahedral sites are occupied by quadrivalent cations, such as Ti, and divalent cations, such as Fe^{+2}, Mg and Mn, or even univalent cations, such as Li.

Replacement by quadrivalent cations

Quadrivalent cations proxying for trivalent cations, ion for ion, increase the number of positive octahedral charges and necessitate layer charge adjustments. Thus substitution of 0.25 Ti^{+4} for 0.25 Al^{+3}(VI)* in muscovite:

$$[(\overset{+.25}{Al_{1.75}Ti_{.25}})(\overset{-1.25}{Si_{2.75}Al_{1.25}})O_{10}(OH)_2]^{-1.00}\overset{+1.00}{K}_{1.00}$$

induces a positive charge of 0.25 on the octahedral layer and necessitates an equivalent increase in the negative charge on the tetrahedral layer by decrease in Si content and increase in Al content, in order to preserve a composite layer charge of 1.00. However, no analysis of a dioctahedral mica has come to hand in which Ti alone or so much Ti replaces Al. In most calculated formulas of dioctahedral micas the amount of Ti is much lower than 0.25, and usually divalent cations more than compensate for the effect of Ti.

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* Al(VI) indicates octahedral Al; Al(IV) indicates tetrahedral Al.

Replacement by bivalent cations

Most commonly the cations proxying for Al in the dioctahedral micas in addition to Fe^{+3}, are the bivalent cations, Fe^{+2}, Mg, and Mn^{+2}. A bivalent cation proxying for a trivalent octahedral cation, ion for ion, decreases the number of positive octahedral charges, and some of the negative charges associated with the octahedral layer are left unneutralized. Thus the layer has a negative charge, which necessitates adjustment in the tetrahedral layer. In order to preserve a composite-layer charge of 1.00, the negative charge on the tetrahedral layer must decrease by an amount equivalent to the negative charge on the octahedral layer, that is, there must be an increase in Si and a decrease in Al(IV), in accordance with the equation, $R^{+2}+\mathrm{Si}=\mathrm{Al(VI)}+\mathrm{Al(IV)}$. For example, in the following formula,

$$[\underbrace{\overset{-.30}{(\mathrm{Al}_{1.70}\mathrm{Fe}^{+2}_{.08}\mathrm{Mg}_{.22})}}_{2.00}\overset{-.72}{(\mathrm{Si}_{3.28}\mathrm{Al}_{.72})}\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.02}\mathrm{K}^{+1.01}_{1.01},$$

0.30 R^{+2} cations can be considered as having replaced 0.30 Al(VI) cations and 0.28 Si cations as having replaced 0.28 Al(IV) cations, $0.30\ R^{+2}+0.28\ \mathrm{Si}=0.30\ \mathrm{Al(VI)}+0.28\ \mathrm{Al(IV)}$. The total composite-layer charge is a sum of two negative charges. Because bivalent cation replacement in the octahedral layer is more general and usually greater than quadrivalent cation (Ti) replacement, most formulas calculated from analyses of dioctahedral micas are characterized by (*a*) negative octahedral charge, (*b*) a tetrahedral charge less than −1.00, (*c*) a Si occupancy greater than 3.00, and (*d*) Al(IV) occupancy less than 1.00.

If half the trivalent octahedral cations ideally occupying the octahedral layer in muscovite are replaced by R^{+2} cations, the octahedral layer would have a charge of −1.00, and the tetrahedral layer would be entirely occupied by Si cations, and neutral.

$$[\overset{-1.00}{(\mathrm{R}^{+3}_{1.00}\mathrm{R}^{+2}_{1.00})}\overset{.00}{\mathrm{Si}_{4.00}}\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.00}\mathrm{K}^{+1.00}_{1.00}.$$

Schaller (1950) postulated such trisilicic-tetrasilicic series to explain the composition of high-silica sericites, and selected leucophyllite as the tetrasilicic end member. However, from available analyses, leucophyllite is not a mica, but a hydrous mica, with an H_2O content of 6.30 per cent and a K_2O content of only 3.39 per cent; interlayer cations occupy only 0.46 sites and the composite layer charge is only (−0.43), not (−1.00). The only representative of a true tetrasilicic dioctahedral potassium mica found among published analyses is a celadonite from near Reno, Nevada (analysis 5, Table 1), whose analysis yields the formula,

$$[\underbrace{(Al_{.07}Fe^{+3}_{.93}}_{1.00}\overset{-.98}{\,}\underbrace{Fe^{+2}_{24}Mg_{.77})}_{1.01}\overset{.00}{Si_{4.00}}O_{10}(OH)_2{}^{-.98}(K,Na)^{+.98}_{.98}$$

In this formula the octahedral R^{+3} cations occupy one site, the R^{+2} cations 1.01 sites, and Si occupies exactly 4.00 sites. The tetrahedral layers are neutral and the entire composite layer charge originates in the octahedral layer.

TABLE 1. ANALYSES OF DIOCTAHEDRAL MICA REPRESENTING STEPS IN THE TRISILICIC-TETRASILICIC SERIES

	1	2	3	4	5
SiO_2	46.77	49.16	52.58	49.53	55.61
Al_2O_3	34.75	30.81	23.56	5.84	.79
Fe_2O_3	.71	—	—	20.06	17.19
FeO	.77	1.43	5.76	5.95	4.02
MgO	.92	2.22	2.43	2.92	7.26
MnO	—		—	—	.09
CaO	.13	.15	.65	.56	.21
Na_2O	.47	.48	—	.46	.19
K_2O	10.61	10.90	9.52	9.31	10.03
TiO_2	.21	.04	—	—	—
H_2O^-	4.48	.15	5.94	4.91	.48
H_2O^+		4.73			4.40
F	.16	—	—	—	—
	100.11	100.07	100.44	99.54	100.27
0=F	.07				
Total	100.04				

1. Sultan Basin, Snohomish Co., Washington; Axelrod and Grimaldi (1949), p. 565. Total includes 0.13% BaO.
2. Amelia, Virginia; Glass (1935), p. 756, no. 5.
3. Wildschapback-Thal, Baden, Germany; Dana (1892), p. 618, no. 45.
4. Urals, Russia; Hendricks and Ross (1941), p. 692, no. 5.
5. Reno, Nevada, 23 mi. E.; Wells (1937), p. 102, O.

The entire range of R^{+2} replacement is represented among natural dioctahedral micas, as shown by the analyses and formulas in Tables 1 and 2. The change in the seat of the composite layer charge from the tetrahedral to the octahedral layers is illustrated by means of histograms in Fig. 1. Formulas calculated from many published analyses of dioctahedral micas indicate that, throughout the series, octahedral occupancy remains constant at about 2.00 sites (in the half-cell formula) and that replacement of R^{+3} by R^{+2} is ion for ion. In general, the trisilicic end of the series is characterized by Al as the predominant trivalent octahedral cation, whereas the tetrasilicic end of the series is characterized by Fe^{+3}.

Replacement by univalent ions

In attempting to explain muscovites having as much as 3.3 per cent of Li_2O, Levinson (1953, p. 93) concluded that, because of similarity in atomic radii, Al = 1.43 Å, Li = 1.51 Å, substitution of Li for Al is possible but not necessary, as Li could occupy vacant octahedral positions. Li occupying vacant octahedral sites in muscovite would cause a positive charge on the octahedral layer, which would in turn have to be compensated for by an equivalent increase in the negative charge on the tetrahedral layer by decrease in silicon and increase in aluminum, and the number of octahedral sites occupied would be greater than 2.00 by an amount equal to the number of sites occupied by Li. However, formulas calculated for analyses of lithian muscovites exhibit quite the contrary layer-charge relations, being characterized by a negative octahedral charge and by a decrease in the negative tetrahedral charge equivalent to the negative octahedral charge, as illustrated in the following formulas,

TABLE 2. FORMULAS FOR DIOCTAHEDRAL MICAS REPRESENTING STEPS IN THE TRISILICIC-TETRACILICIC SERIES (CALCULATED FROM ANALYSES IN TABLE 1)

1. Muscovite $[\underbrace{\overset{-.10}{(\mathrm{Al}_{1.84}\mathrm{Fe}^{+3}_{.04}\mathrm{Fe}^{+2}_{04}\mathrm{Mg}_{.09})}}_{2.01}\overset{-.89}{(\mathrm{Si}_{3.11}\mathrm{Al}_{.89})}\mathrm{O}_{10}(\mathrm{OH})_2]^{-.99}(\mathrm{K}_{.90}, \mathrm{Na}_{.06}, \mathrm{Ca}/2_{.01})^{+1.00}_{.98}$

2. Sericite $[\underbrace{\overset{-.30}{(\mathrm{Al}_{1.70}\mathrm{Fe}^{+2}_{.08}\mathrm{Mg}_{.22})}}_{2.00}\overset{-.72}{(\mathrm{Si}_{3.28}\mathrm{Al}_{.72})}\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.02}(\mathrm{K}_{.93}, \mathrm{Na}_{.06}, \mathrm{Ca}/2_{.01})^{+1.02}_{1.00}$

3. $[\underbrace{\overset{-.49}{(\mathrm{Al}_{1.45}\mathrm{Fe}^{+2}_{.33}\mathrm{Mg}_{.25})}}_{2.03}\overset{-.43}{(\mathrm{Si}_{3.57}\mathrm{Al}_{.43})}\mathrm{O}_{10}(\mathrm{OH})_2]^{-.92}(\mathrm{K}, \mathrm{Ca}/2)^{+.92}$

4. Glauconite $[\underbrace{\overset{-.72}{(\mathrm{Al}_{.18}\mathrm{Fe}^{+3}_{1.12}\mathrm{Fe}^{+2}_{.37}\mathrm{Mg}_{.32})}}_{1.99}\overset{-.33}{(\mathrm{Si}_{3.67}\mathrm{Al}_{.33})}\mathrm{O}(\mathrm{OH})_2]^{-1.05}(\mathrm{K}_{.88}, \mathrm{Na}_{.07}, \mathrm{Ca}/2_{.02})^{+1.03}_{.99}$

5. Celadonite $[\underbrace{\overset{-.98}{(\mathrm{Al}_{.07}\mathrm{Fe}^{+3}_{.93}\mathrm{Fe}^{+2}_{.24}\mathrm{Mg}_{.77})}}_{2.01}\overset{.00}{\mathrm{Si}_{4.00}}\mathrm{O}_{10}(\mathrm{OH})_2]^{-.98}(\mathrm{K}_{.92}, \mathrm{Ba}_{.03}, \mathrm{Ca}/2_{.02})^{+1.01}_{.99}$

1. $[\underbrace{\overset{-.10}{(\mathrm{Al}_{1.89}\mathrm{Fe}^{+3}_{.01}\mathrm{Li}_{.20})}}_{2.10}\overset{-.91}{(\mathrm{Si}_{3.09}\mathrm{Al}_{.91})}\mathrm{O}_{10}(\mathrm{OH})_2]^{-1.01}(\mathrm{K}_{.88}, \mathrm{Na}_{.07}, \mathrm{Rb}_{.05}, \mathrm{Cs}_{.01})^{+1.01}_{1.01}$

$$2.\quad \underbrace{\Big[\overset{-.13}{(Al_{1.73}\overset{+2}{Fe}_{.07}Mg_{.01}Mn_{.02}Li_{.48})}}_{2.31}\overset{-.89}{(Si_{3.11}Al_{.89})}O_{10}(OH)_2\Big]^{-1.02}(K_{.86}, Na_{.08}, Rb_{.06}, Cs_{.01})^{+1.01}_{1.01}$$

$$3.\quad \underbrace{\Big[\overset{-.20}{(Al_{1.58}\overset{+3}{Fe}_{.01}\overset{+2}{Fe}_{.02}Mg_{.01}Mn_{.12}Li_{.73})}}_{2.47}\overset{-.84}{(Si_{3.16}Al_{.84})}O_{10}(OH)_2\Big]^{-1.04}(K_{.82}, Na_{.10}, Rb_{.08}, Cs_{.01})^{+1.01}_{1.01}$$

which were calculated from the analyses given in Table 3. Also significant in these formulas is the number of sites occupied by octahedral cations, which exceed 2.00 by an amount considerably less than the number of sites occupied by Li. These layer-charge relations and octahedral occupancies indicate that Li has not simply occupied vacant octahedral sites, but has replaced Al(VI) at a ratio of less than three Li for one Al(VI). If three Li had replaced one Al(VI), there would have been no change in the layer-charge relations but a somewhat greater increase in octahedral occupancy. Assuming that the "primary" muscovites from which the lithian muscovites whose formulas appear above were derived to have had an octahedral occupancy of 2.00, the Li/Al(VI) replacement ratios in these formulas are two Li for one Al(VI), 2.8 Li for one Al(VI) and 2.8 Li for one Al(VI), respectively. These ratios are characteristic of the replacement ratios found in other lithian muscovites studied.

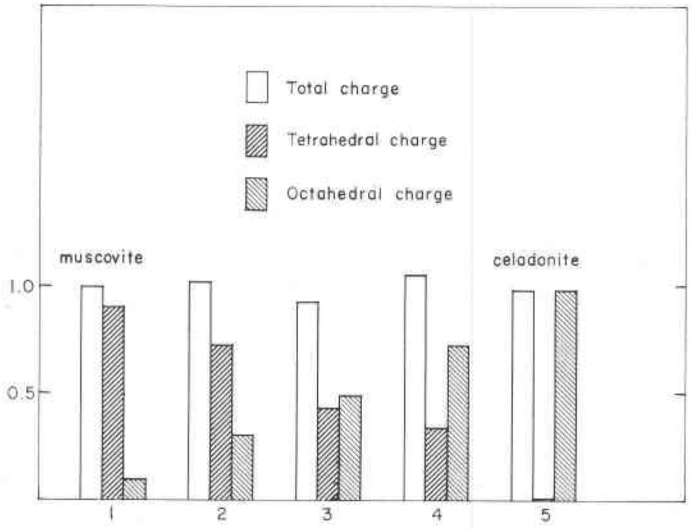


FIG. 1. Histograms of formulas of dioctahedral micas representing steps in the trisilicic-tetrasilicic series. (Numbers below histograms refer to formulas in Table 2.)

The micas whose formulas are given above were found by Levinson to have normal muscovite structures. From his study, Levinson concluded that the muscovite structure can accommodate up to about 3.3 per cent Li_2O. Micas having between 3.4 to 4.0 per cent Li_2O he found to have a combination of forms, 2-layer muscovite and 6-layer lepidolite, and those with more than 4.0 per cent Li_2O he found to have lepidolite structures. Correlation of these findings with calculated formulas of analyses of lithium-bearing micas, some the same ones as were studied by Levinson, showed that those having a combination of muscovite and lepidolite forms had octahedral occupancies of about 2.50 to 2.60, and an Li occupancy of about 0.90 to 1.05. Thus the muscovite structure persists to an octahedral occupancy of about 2.50 sites, halfway between the 2.00 sites of typical dioctahedral micas and the ideal three sites of trioctahedral micas.

TABLE 3. ANALYSES OF LITHIAN MUSCOVITES

	1	2	3
SiO_2	46.17	46.30	47.00
Al_2O_3	35.57	33.08	30.60
Fe_2O_3	.15	.00	.26
FeO	.08	1.20	.41
MgO	.00	.14	.13
MnO	.04	.28	2.04
CaO	.00	.00	Trace
Li_2O	.76	1.80	2.70
Na_2O	.56	.63	.77
K_2O	10.37	10.09	9.52
Rb_2O	1.1	1.37	1.93
Cs_2O	.3	.41	.18
H_2O^-	.12	.34	.25
H_2O^+	4.06	3.06	2.18
F	.76	2.06	4.09
	100.04	100.76	102.06
O=F	.32	.87	1.72
Total	99.72	99.89	100.34

1. Varuträsk, Sweden; Berggren (1941), p. 264, J.
2. Varuträsk, Sweden; Berggren (1940), p. 185, E.
3. Manitoba, Canada; Stevens (1938), p. 615, no. 1 (U. S. Nat. Museum no. 97635).

The composition of lepidolites can be interpreted in the same way as that of the lithian muscovites, with similar Li/Al(VI) replacement ratios and charge relations. However, they are not a continuation of that series, as they have a different structural form, being trioctahedral, not dioctahedral micas.

THE EFFECT OF SUBSTITUTIONS IN TRIOCTAHEDRAL MICAS

In the trioctahedral micas the most common substitutions are trivalent cations, Al and Fe^{+3}, or bivalent cations, Fe^{+2} or Mn, for bivalent Mg in the ideal phlogopite formula. Proxying bivalent cations, of course, have no effect on the layer-charge relations, but proxying trivalent cations tend to give a positive charge to the octahedral layer, which necessitates adjustments in the tetrahedral layer.

Replacement by trivalent cations

In Winchell and Winchell (1951), p. 373, the formulas for eastonite and siderophyllite (recast in the form used in this paper) assume that Al proxies for

$$[\overset{+.50}{(Al_{.5}Mg_{2.5})}\overset{-1.5}{(Si_{2.5}Al_{1.5})}O_{10}(OH)_2]^{-1.00}K^{+1.00}_{1.00}, \quad \text{and}$$

$$[\overset{+.50}{(Al_{.5}Fe^{+2}_{2.5})}\overset{-1.50}{(Si_{2.5}Al_{1.5})}O_{10}(OH)_2]^{-1.00}K^{+1.00}_{1.00},$$

for Mg or Fe^{+2} ion for ion. A substitution of 0.5 Al for 0.50 Mg or Fe^{+2} thus increases the number of positive octahedral charges by 0.5. This amount of positive charge on the octahedral layer necessitates an equivalent increase in the negative charge on the tetrahedral layers, so that the amount of Si present must decrease by 0.5 and the amount of Al must increase by the same amount. Octahedral occupancy remains constant at 3.00. However, Holzner (1936) noticed that in formulas calculated from analyses of biotites octahedral occupancy is usually between 2.89 and 2.49. 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 two types, with most biotites approximating the ratio of two of phlogopite to one of muscovite, which yields a formula for biotite of

$$[\underbrace{\overset{.00}{(Al_{.67}Mg_{2.00})}}_{2.67}\overset{-1.00}{(Si_{3.00}Al_{1.00})}O_{10}(OH)_2]^{-1.00}K^{+1.00}_{1.00}.$$

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 ideal formulas. The 0.67 additional positive charges carried by the 0.67 trivalent cations in the octahedral layer are neutralized by the 0.66 negative charges associated with the 0.33 unoccupied octahedral sites.

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

$$n\mathrm{R}^{+3}(\mathrm{VI}) + n\mathrm{R}^{+3}(\mathrm{IV}) = n\mathrm{R}^{+2} + n\mathrm{Si}^{+4}.$$

In the other way of accommodating octahedral cations, the proxying of trivalent for bivalent cations is in a 2:3 ratio. There is, consequently, no increase in the total number of positive charges present in the octahedral layer, nor is there any change in the layer charge relations, nor in the composition of the tetrahedral layers as compared to the ideal formulas for muscovite and phlogopite, but there is a decrease in the number of octahedral sites occupied equivalent to one-half the number of octahedral trivalent cations. These relations are expressed in the following equation,

$$2n\mathrm{R}^{+3}(\mathrm{VI}) = 3n\mathrm{R}^{+2} + n\ \textit{Oct. Sites}.$$

In the first type of accommodation for trivalent octahedral cations 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 close to 1.00.

Structural formulas calculated for more than 200 published analyses of phlogopites, biotites, siderophyllites, and lepidomelanes, show that few natural trioctahedral micas accommodate the additional charges carried by trivalent octahedral cations entirely by either one of these ways or the other. Almost all the formulas studied showed the characteristics of both equations. Part of the additional positive charges are neutralized by an increase in negative tetrahedral charge, and a part are neutralized by negative charges associated with unoccupied octahedral positions, as in the following formula,

$$[\underbrace{\overset{+.31}{(\mathrm{Al}_{.35}\overset{+3}{\mathrm{Fe}}_{.36}\overset{+2}{\mathrm{Fe}}_{1.08}\mathrm{Mg}_{1.01})}}_{2.80}\overset{-1.27}{(\mathrm{Si}_{2.73}\mathrm{Al}_{1.27})}\mathrm{O}_{10}(\mathrm{OH})_2]^{-.96}(\mathrm{K, Ca/2})^{+.96}_{.89}.$$

In this formula the octahedral trivalent cations carry 0.71 more positive charge than the same number of divalent cations would carry. Of this additional charge, 0.31 forms a positive charge on the octahedral layer which is approximately neutralized by the increased negative charge on the tetrahedral layer, and the other 0.40 are neutralized by the 0.40 charges associated with the 0.20 unoccupied octahedral sites. The degree to which accommodation for the additional positive charges carried by trivalent (and quadrivalent) cations is made by one method or the other varies greatly. In general, however, there seems to be a tendency to greater accommodation by the first method mentioned above in trioctahedral micas of low octahedral trivalent cation content, with increasing tendency to accommodation by the second method as the octahedral trivalent cation content increases. This is shown in Table 4 by average formulas (calculated from more than 150 analyses) for trioctahedral micas arranged in order of increasing octahedral trivalent (and quadrivalent) cation content. In trioctahedral micas having very low octahedral trivalent cation content, 0.10 sites, for example, all the additional positive charges form a positive charge on the octahedral layer, and are neutralized by an equivalent increase in the negative tetrahedral

TABLE 4. AVERAGE FORMULAS FOR TRIOCTAHEDRAL MICAS, IN ORDER OF INCREASING OCTAHEDRAL TRIVALENT (AND QUADRIVALENT) CATION CONTENT

Octahedral trivalent ion content	Average formula
0.00–0.20	$[\overset{+.10}{\underbrace{(Al_{.05}Fe^{+3}_{.05}Fe^{+2}_{.05}Mg_{2.85})}_{3.00}}\overset{-1.10}{(Si_{2.90}Al_{1.10})}O_{10}(OH)_2]^{-1.00}K^{+1.00}_{1.00}$
0.21–0.40	$[\overset{+.15}{\underbrace{(Al_{.15}Fe^{+3}_{.10}Fe^{+2}_{.35}Mg_{2.35})}_{2.95}}\overset{-1.15}{(Si_{2.85}Al_{1.15})}O_{10}(OH)_2]^{-1.00}K^{+1.00}_{1.00}$
0.41–0.60	$[\overset{+.20}{\underbrace{(Al_{.10}Ti_{.10}Fe^{+3}_{.20}Fe^{+2}_{.90}Mg_{1.55})}_{2.85}}\overset{-1.20}{(Si_{2.80}Al_{1.20})}O_{10}(OH)_2]^{-1.00}K^{+1.00}_{1.00}$
0.61–0.80	$[\overset{+.25}{\underbrace{(Al_{.20}Ti_{.15}Fe^{+3}_{.25}Fe^{+2}_{1.25}Mg_{.90})}_{2.75}}\overset{-1.25}{(Si_{2.7}Al_{1.25}}O_{10}(OH)_2]^{-1.00}K^{+1.00}_{1.00}$
0.81–1.00	$[\overset{+.25}{\underbrace{(Al_{.25}Ti_{.15}Fe^{+3}_{.30}Fe^{+3}_{1.25}Mg_{.75})}_{2.70}}\overset{-1.25}{(Si_{2.75}Al_{1.25})}O_{10}(OH)_2]^{-1.00}K^{+1.00}_{1.00}$

charge, and there is full octahedral occupancy, as shown in the first formula. In the second average formula 0.15 of the 0.25 additional positive charges carried by trivalent octahedral cations form a positive charge on the layer, and are neutralized by an equivalent increase in the negative tetrahedral charge and 0.10 are neutralized by the negative charges associated with 0.05 unoccupied octahedral sites. In the third formula two-fifths of the 0.50 additional positive charges are neutralized by the first method and three-fifths by the second method. And in the fifth formula 0.60 of the 0.85 additional positive charges are neutralized by the second method, and only 0.25 by the first method. It must be understood, of course, that in some of these micas, whatever their octahedral trivalent cation content, adjustment by one method or the other is emphasized and these average formulas show only the average trend.

Because of the neutralization of some of the additional positive charges carried by trivalent (and quadrivalent) octahedral cations by negative charges associated with unoccupied octahedral sites, octahedral occupancy in most trioctahedral micas is somewhat less than 3.00 sites. Thus they are not truly trioctahedral, nor are they truly octaphyllites, as they generally have fewer than 8 cations for 12 anions.

Replacement by univalent cations

The ferrous lithium micas, protolithionites and zinnwaldites, are, like siderophyllite, characterized by high Fe^{+2} and very low Mg content. These similarities in compositional characteristics suggest siderophyllite as the prototype from which the ferrous lithium micas are derived, just as muscovite can be considered the prototype from which the lithian muscovites are derived. Starting with siderophyllite, formulas calculated from published analyses of protolithionite and zinnwaldite show a general increase in Si, and a general decrease in Al(IV) and Fe^{+2} with increase in Li. The relative amounts of Al(VI) and Fe^{+3} vary considerably but the total amount of octahedral R^{+3} cations remains quite constant. This is illustrated by the analyses shown in Table 5 and by the formulas calculated from these analyses shown in Table 6.

Li replacing Fe^{+2} in a 2:1 ratio in an isomorphous series of this sort would cause no change in the layer-charge relations but would increase octahedral occupancy by an amount equal to one-half the Li added. The gradual change in the layer charges in these formulas from siderophyllite to cryophyllite, from an octahedral charge of $+0.25$, with a tetrahedral charge of -1.32, to an octahedral charge of -0.42, indicates that Li has replaced Fe^{+2} in a less than 2:1 ratio. The ratio varies from one formula to the next, but the overall Li:Fe^{+2} ratio is 1.4:1. Thus the proxying Li cations carry fewer positive charges than the Fe^{+2} cations they proxy,

TABLE 5. ANALYSES OF SIDEROPHYLLITES, AND FERROUS LITHIUM MICAS SHOWING CHANGE IN COMPOSITION WITH INCREASE IN Li_2O CONTENT

	1	2	3	4	5	6
SiO_2	32.52	38.00	41.78	45.87	48.40	52.17
Al_2O_3	19.07	27.00	22.76	22.50	21.62	16.39
Fe_2O_3	10.08	—	.98	.66	.24	4.11
FeO	17.83	18.50	14.24	11.66	7.19	5.99
MgO	.70	.12	.55	—	—	Tr.
MnO	.21	.64	—	1.75	1.97	.32
Li_2O	.39	1.44	2.42	3.28	4.18	4.99
CaO	.73	1.30	—	—	.06	Trace
Na_2O	.21	1.37	.67	.42	1.12	.63
K_2O	8.53	8.15	10.51	10.46	10.45	10.48
TiO_2	.21	.64	—	—		
H_2O^+	3.17	3.00	1.41	.91	.64	1.46
H_2O^-	3.21	.04			.24	
F	2.36	1.66	6.48	7.94	2.24	7.02
	99.22	101.86	101.80	105.53	100.83	103.56
O=F	.99	.70	2.72	3.33	1.04	2.95
Total	98.23	101.16	99.08	102.20	99.79	100.61

1. Ebisu mine, Naegi District, Japan; Shibata, 1952, p. 162, no. 6.
2. Volhynia, Russia; Tsyganov, 1954, p. 386, no. 9.
3. Altenburg, Saxony, Germany; Kunitz, 1924, p. 413.
4. Zinnwald, Erzgebirge, Bohemia; Dana, 1892, p. 626, no. 1. Total includes 0.08 per cent P_2O_5.
5. Lingwu, Hunan, China; Meng and Chang, 1935, p. 56. Total includes 2.48 per cent B_2O_3.
6. Cape Ann, Rockfort, Mass.; Clarke, 1886, p. 358, B.

and the octahedral layer becomes increasingly deficient in positive charges, necessitating changes in the charge and composition of the tetrahedral layers, increase in Si and decrease in Al(IV).

Cryophyllite has the lithium content of a lepidolite and may be termed a "ferroan" lepidolite. Further replacement of Fe^{+2} by Li in the ratio found in these formulas produces a formula close to polylithionite, with some Fe^{+3} proxying for Al(VI).

Thus lepidolites may be interpreted, compositionally, as if derived from muscovite, by substitution of Li for Al(VI), or from siderophyllite, by substitution of Li for Fe^{+2}. In either substitution the substitution ratio is such that the substituting Li cations carry fewer positive charges than the cations replaced, with the result that increase in Li content is accompanied not only by decrease in Al(VI) or Fe^{+2}, as the case may be,

TABLE 6. FORMULAS CALCULATED FROM ANALYSES GIVEN IN TABLE 5, SHOWING CHANGE IN COMPOSITION AND IN LAYER CHARGE RELATIONSHIP WITH INCREASE IN Li CONTENT

	Formula	% Li₂O
1. Siderophyllite	$[\overset{+.25}{\underbrace{(\text{Al}_{.52}\text{Ti}_{.01}\overset{+3}{\text{Fe}}_{.62}\overset{+2}{\text{Fe}}_{1.22}\text{Mg}_{.09}\overset{+2}{\text{Mn}}_{.02}\text{Li}_{.13})}_{2.61}}\overset{-1.32}{(\text{Si}_{2.68}\text{Al}_{1.32})}\text{O}_{10}(\text{OH})_2]^{-1.07}\text{K}(\text{Na}, \text{Ca}/2)^{+1.06}_{.99}$	0.39
2. Protolithionite	$[\overset{+.06}{\underbrace{(\text{Al}_{1.06}\text{Ti}_{.03}\overset{+2}{\text{Fe}}_{1.12}\overset{+2}{\text{Mn}}_{.04}\text{Mg}_{.01}\text{Li}_{.42})}_{2.68}}\overset{-1.24}{(\text{Si}_{2.76}\text{Al}_{1.24})}\text{O}_{10}(\text{OH})_2]^{-1.15}\text{K}(\text{Na}, \text{Ca}/2)^{+1.15}_{1.04}$	1.44
3. Protolithionite	$[\overset{-.15}{\underbrace{(\text{Al}_{1.04}\overset{+3}{\text{Fe}}_{.05}\overset{+2}{\text{Fe}}_{.87}\text{Mg}_{.06}\text{Li}_{.71})}_{2.73}}\overset{-.93}{(\text{Si}_{3.07}\text{Al}_{.93})}\text{O}_{10}(\text{OH})_2]^{-1.08}\text{K}(\text{Na})^{+1.08}_{1.08}$	2.42
4. Zinnwaldite	$[\overset{-.16}{\underbrace{\text{Al}_{1.08}\overset{+3}{\text{Fe}}_{.04}\overset{+2}{\text{Fe}}_{.68}\overset{+2}{\text{Mn}}_{.10}\text{Li}_{.92})}_{2.82}}\overset{-.79}{(\text{Si}_{3.21}\text{Al}_{.79})}\text{O}_{10}(\text{OH})_2]^{-.95}\text{K}(\text{Na})^{+.94}_{.94}$	3.28
5. Zinnwaldite	$[\overset{-.40}{\underbrace{(\text{Al}_{1.11}\overset{+3}{\text{Fe}}_{.01}\overset{+2}{\text{Fe}}_{.42}\overset{+2}{\text{Mn}}_{.12}\text{Li}_{1.16})}_{2.82}}\overset{-.65}{(\text{Si}_{3.35}\text{Al}_{.65})}\text{O}_{10}(\text{OH})_2]^{-1.05}\text{K}(\text{Na})^{+1.07}_{1.07}$	4.18
6. Cryophyllite	$[\overset{-.57}{\underbrace{(\text{Al}_{.90}\overset{+3}{\text{Fe}}_{.21}\overset{+2}{\text{Fe}}_{.24}\overset{+2}{\text{Mn}}_{.02}\text{Li}_{1.38})}_{2.85}}\overset{-.42}{(\text{Si}_{3.58}\text{Al}_{.42})}\text{O}_{10}(\text{OH})_2]^{-.99}\text{K}(\text{Na})^{+1.00}_{1.00}$	4.99

TABLE 7. ANALYSES OF LEPIDOLITES SHOWING CHANGE IN COMPOSITION WITH INCREASE IN Li_2O CONTENT

	1	2	3
SiO_2	49.19	51.07	57.03
Al_2O_3	24.81	22.05	15.55
FeO	0.24[a]	0.23[a]	0.12[a]
MgO	0.05	0.09	0.22
MnO	2.51	0.76	0.72
Li_2O	5.10	5.89	6.84
CaO	Trace	Trace	Trace
Na_2O	0.52	0.82	0.44
K_2O	10.25	9.70	10.65
Rb_2O	1.78	1.38	1.35
Cs_2O	0.19	0.09	0.40
TiO_2	0.08	0.06	0.03
H_2O^-	1.21	—	0.49
H_2O^+		0.96	0.74
F	6.89	7.13	9.00
	102.82	100.23	103.72[b]
O=F	2.90	3.00	3.79
	99.92	97.23	99.93

[a] Total Fe reported as FeO.

[b] Includes 0.14 per cent Nb_2O_5.

1. Ohio City, Colo.; Winchell, 1942, p. 115, no. 10, 6-layer lepidolite structure.
2. Calgoorie, Western Australia; Stevens, 1938, p. 615, no. 14. 6-layer hexagonal lepidolite structure.
3. Antsongombato, Madagascar, Stevens, 1938, p. 615, no. 16. 1-layer lepidolite structure. Total includes 0.14 per cent Nb_2O_5.

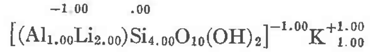
but also by decrease in Al(IV), and by increase in Si and in the number of octahedral positions occupied, or, otherwise expressed, increase in Li content is accompanied by increase in negative octahedral charge and by decrease in negative tetrahedral charge as illustrated in the following formulas calculated from the analyses in Table 7.

1. $$\Big[\overset{-.35}{\underbrace{(Al_{1.32}\overset{+2}{Fe}_{.01}\overset{+2}{Mn}_{.14}Li_{1.39})}_{2.86}}\overset{-.67}{(Si_{3.33}Al_{.67})}O_{10}(OH)_2\Big]^{-1.02}K(Na, Rb, Cs)^{+1.03}_{1.03}$$

2. $$\Big[\overset{-.52}{\underbrace{(Al_{1.25}\overset{+2}{Fe}_{.01}Mg_{.01}\overset{+2}{Mn}_{.04}Li_{1.61})}_{2.92}}\overset{-.52}{(Si_{3.48}Al_{.52})}O_{10}(OH)_2\Big]^{-1.04}K(Na, Rb, Cs)^{+1.02}_{1.02}$$

3. $$\Big[\overset{-.87}{\underbrace{(Al_{1.05}\overset{+2}{Fe}_{.01}Mg_{.02}\overset{+2}{Mn}_{.04}Li_{1.84})}_{2.96}}\overset{-.17}{(Si_{3.83}Al_{.17})}O_{10}(OH)_2\Big]^{-1.04}K(Na, Rb, Cs)^{+1.04}_{1.04}$$

The general trend is, therefore, toward an end member in which the entire composite layer charge is on the octahedral layer, and in which the tetrahedral layers are completely occupied by Si and neutral, as in the hypothetical end member polylithionite,



$$\left[\overset{-1.00}{(Al_{1.00}Li_{2.00})}\overset{.00}{Si_{4.00}}O_{10}(OH)_2\right]^{-1.00}K^{+1.00}_{1.00}$$

In the few analyses of lithian biotites available, Li_2O does not exceed 1.5 per cent, equivalent to about 1.5 formula sites. The data are so meager as to permit no conclusions as to replacement ratios or layer charge relations.

CONCLUSION

A study of formulas calculated from published analyses of dioctahedral and trioctahedral micas shows that substitution of octahedral cations having a different valence from the cation ideally present produces changes in the octahedral-layer charge which is accompanied by layer charge and compositional adjustments. If the substituting cation carries less charge than the cation substituted, the deficiency in charge is not entirely compensated by increase in the number of cations substituted, the octahedral anions are not entirely neutralized, and the octahedral layer has a negative charge. This is accompanied by decrease in the negative charge on the tetrahedral layers, that is, increase in Si and decrease in tetrahedral Al. In such micas, as in most dioctahedral and in lithium micas, Si occupies more than 3.00 formula sites and tetrahedral Al less than 1.00 formula sites. The total composite layer is the sum of two negative charges.

If the substituting cation has a higher charge than the octahedral cation substituted, the excess in charge is seldom entirely compensated by decrease in the number of cations substituted, and there are not enough octahedral anions to neutralize all the positive charges present. Thus the octahedral layer has a positive charge, and the tetrahedral layer has a negative charge greater than 1.00 by about an equivalent amount, with a lower Si content and a higher Al(IV) content than in the ideal formula. In such micas, phlogopites, biotites, siderophyllites and lepidomelanes, Si occupies fewer than 3.00 formula sites and Al(IV) occupies more than 1.00. The total layer charge is the algebraic sum of a positive and a negative charge.

As most natural dioctahedral and trioctahedral micas exhibit such substitutions, they differ in layer charge relations and in layer composition from the ideal formulas for such micas to a greater or lesser degree, depending on the degree and ratio of substitution.

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