STUDIES IN THE MICA GROUP; THE BIOTITE-PHLOGOPITE SERIES.*

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ABSTRACT. The chemistry of the biotite-phlogopite series is discussed and examples are given of members with maximum percentages of the constituent elements in order to illustrate the variation in chemical composition. Several hundred analyzed biotites and phlogopites are grouped into eight classes according to geologic occurrence and their $Fe_2O_3+TiO_2-FeO+MnO-MgO$ ratios are plotted by groups on triangular diagrams. That each group occupies a restricted field in the diagrams illustrates the fixed relationships between chemical composition and geologic occurrence. However, biotites from extrusive rocks do not fit the diagrams. The relation beween the indices of refraction and chemical composition is shown by plotting γ against Wt. % $FeO+2(Fe_2O_3+TiO_2)$. Ferric iron and titanium appear to have an effect on the indices in the order of twice that of ferrous iron.

INTRODUCTION.

IN the spring of 1942 the writer began an investigation of the mica minerals in an attempt to correlate variations in chemical composition with geological occurrence, and to a lesser extent physical properties with chemical composition. An extensive survey of the literature was made to obtain a collection of analyses and related data that would be as complete as possible. During the fall of 1945 the analyses were studied and an attempt was made to present the results in a systematic manner. The writer is greatly indebted to the late Professor Harry Berman who suggested the study and contributed much to its early progress, to Professor E. S. Larsen for valuable discussions during its later progress, and to Professor C. S. Hurlbut for a critical reading of the manuscript.

Nearly 300 analyses of biotites and phlogopites were obtained from the literature, and eight unpublished analyses were made available to the writer by Professor E. S. Larsen. In some analyses the source of the material was not stated, and consequently the data were valueless for the first part of this study. In many cases optical and physical properties were not given for the analyzed micas, and these analyses could not

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be used for the second part of the study. Biotites that contain excessive water and correspondingly low potash were disregarded as being weathered. Analyses of the rarer members of the series, such as manganophyllites, manganphlogopite, barium biotites, and calciobiotite, were not used in plotting the triangular diagrams. The publication of the large number of tabulated analyses is not attempted, but the analyses and their sources are retained in the writer's files and are available for reference.

MEMBERS OF THE BIOTITE-PHLOGOPITE SERIES.

The general formula in the biotite-phlogopite series can be expressed by: $W_4(X,Y)_{8-12}Z_{16}O_{40}(O,OH,F)_8$ (Berman, 1937), where

W = K, minor Na,Ba,Ca
X = Mg, Fe″, Mn″
Y = Al, Fe‴,Ti^{IV}, Mn‴, and rarely Ti‴
Z = Si, Al in a ratio of 5:3 to 6:2

In Table I are presented a number of analyses which were chosen to indicate in a general way the maximum content of various constituents or pairs of constituents in members of the series.

Micas rich in either ferric iron or ferrous iron are common, but relatively few biotites contain both iron atoms in more than moderate amounts. Most biotites contain small amounts of Ti^{IV}, with a recorded maximum of about 12% TiO_2. Biotites that contain high percentages of TiO_2 are generally low in Fe_2O_3 but may be rich in either FeO or MgO. Analysis 5 is an example of a biotite with a moderate amount of ferrous iron and a high TiO_2 content. Analysis 6 is a phlogopitic biotite that has a high content of titanium associated with large amounts of MgO. Trivalent titanium has been reported to occur in biotite (Anal. 7), but it appears to be uncommon.

Except in the manganophyllites, manganese, either divalent or trivalent, is uncommon. In biotites small amounts of MnO are associated with a high content of either ferric or ferrous iron (Analyses 8 and 9). The highest content of divalent manganese is reported from a manganphlogopite (Analysis 10). Some manganophyllites contain both divalent and trivalent manganese; others have only divalent manganese; and in a few the manganese is chiefly in the divalent form.

The alkali metals are the minor variables in the series. Sodium substitutes for potassium in limited amounts in only a few biotites. Calcium and barium are present in very limited quantities. A maximum of about three atoms of sodium may occur either in iron-rich biotites or in phlogopites (Analyses 13 and 14). Barium appears to accompany only magnesium-rich biotites or phlogopites (Analyses 15 and 16). The highest content of calcium is reported from a micaceous mineral from an altered limestone block in a tuff at Vesuvius (Analysis 17).

CHEMICAL VARIATION WITH GEOLOGIC OCCURRENCE.

In determining the genetic grouping of the mica it is necessary to note whether it has formed as a normal constituent of the rock or whether it crystallized under atypical conditions. For example, biotite from a fayalitic nodule in a granite has formed under conditions different from those under which the ordinary granitic biotite developed and would be expected to show a consequent difference in chemical composition. Likewise biotite from a schist inclusion in pegmatite formed in an environment different from that of ordinary pegmatitic biotite. In each case the histories of the two types are different, and the micas cannot be placed in the same genetic group.

The biotite-phlogopite micas occur as primary constituents of many types of igneous rocks, both intrusive and extrusive, which range in composition from felsic to ultramafic. They also occur in pegmatites, metamorphosed limestones, and hydrothermal veins. Biotite is a common constituent of gneisses, schists and other metamorphic rocks. Undoubtedly the mineral forms under a wide variety of conditions. The chemical composition is a reflection not only of the elements and proportions thereof available for formation but also of the geologic environment under which the mineral crystallizes. Thus biotites from syenites differ from those in granites, and those, in turn, differ from biotites from more mafic rocks. Biotites from extrusive rocks are different in composition from those in the intrusive equivalents even though the rocks may be very similar in chemical composition. Schauberger (1927), in his study of biotites of the alkalic rocks of Bohemia concluded that the iron-rich biotites occur in the felsic rocks of the petrographic province and the magnesium-rich ones in the mafic rocks and that the composition of the biotites, with respect to iron and magnesium, was related to the Fe-Mg ratio in the parent rock and not to the absolute amounts of Mg and Fe present.

To express this variation in a quantitative way it was necessary to decide upon the fundamental chemical variants and then to group the occurrences systematically. After some experimentation a triangular diagram with the plots, $Fe_2O_3+TiO_2$, $FeO+MnO$, and MgO was chosen. The occurrences were grouped as follows:

1. Granitic pegmatites
2. Granites, quartz monzonites, granodiorites
3. Tonalites, diorites
4. Gabbros
5. Peridotites and other ultramafics
6. Syenites, nepheline syenites, and syenitic pegmatites
7. Gneisses and schists
8. Metamorphosed limestones

Very few analyses have been made of biotites from hydrothermal veins, and the general characteristics of this group could not be determined. Likewise relatively few biotites from extrusive rocks have been analysed.

BIOTITES FROM GRANITIC PEGMATITES.

It is recognized that granitic pegmatites may contain hydrothermal biotite, and every effort was made to include in this group only primary magmatic biotites. These biotites (Fig. 1) are characterized chiefly by a very high content of FeO, which has a maximum of about 30%. Both MgO and $Fe_2O_3+TiO_2$ are less than 10%, with MgO generally the smaller.

BIOTITES FROM GRANITES, QUARTZ MONZONITES, GRANODIORITES.

Many analyses have been made of biotites from granites and granodiorites. The FeO content ranges from about 12% to 25% (Fig. 2). The content of $Fe_2O_3+TiO_2$ generally is less than 10% and the MgO content may be as high as 12%. The few analyzed biotites from rhyolites and latites fall at a considerable distance outside of the general field.

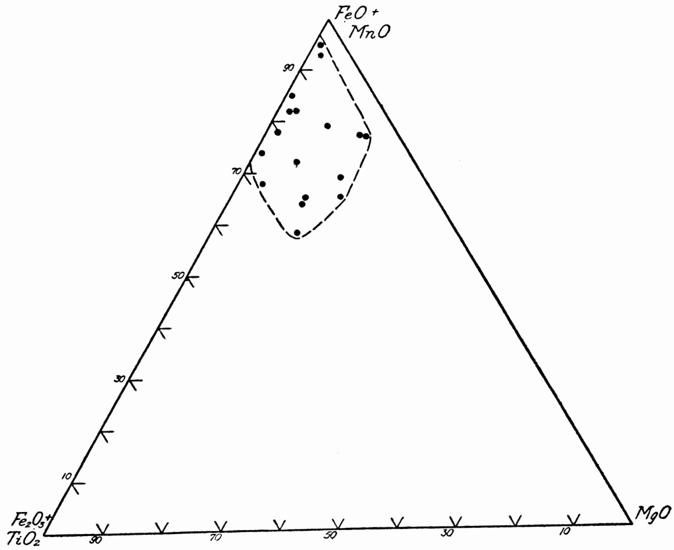

Fig. 1. Biotites from Granitic Pegmatites.

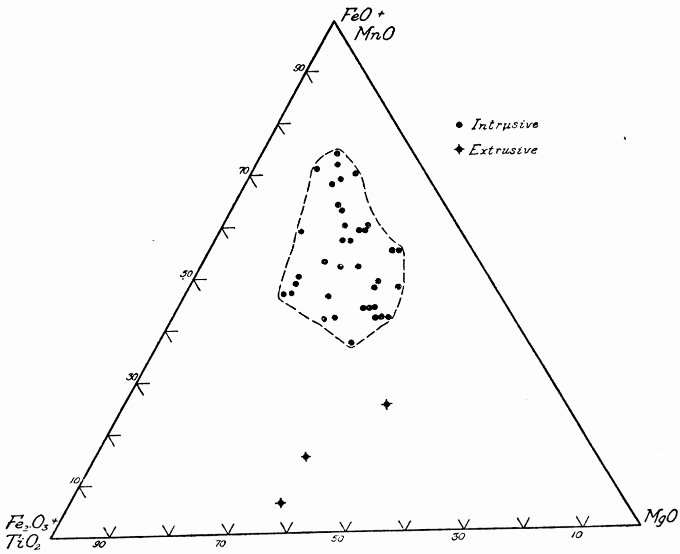

Fig. 2. Biotites from Granites, Quartz Monzonites, Granodiorites.

BIOTITES FROM TONALITES AND DIORITES.

Figure 3 shows the distribution in composition of biotites from tonalites and diorites. The field lies within the area of the granitic field (Fig. 2), but is restricted to the corner richest in

TABLE I.

No.	Name	Constituent	Formula	Occurrence	Locality	Reference
1.	lepidomelane	Fe''	$K_{4.0}\ Na_{0.5}\ Fe''_{9.5}\ Mn_{0.08}\ Fe'''_{2.3}\ Ti_{0.08}\ Mg_{0.04}\ Al_{6.4}\ Si_{11.3}\ O_{46.9}\ (OH)_{0.5}\ F_{0.6}$	Syenitic pegmatite	French River, Ontario	Univ. Toronto Studies, Geol. Ser., 22, 5-14, 1926
2.	lepidomelane	Fe'''	$K_{3.8}\ Na_{1.3}\ Ca_{0.3}\ Fe''_{2.0}\ Mn_{0.7}\ Fe'''_{6.1}\ Ti_{1.2}\ Mg_{2.0}\ Al_{2.6}\ Si_{11.3}\ O_{43.0}\ (OH)_{5.0}$	Syenitic pegmatite	Langesundfjord, Norway	Zeit. Kryst., 16, 191, 1890
3.	lepidomelane	Fe'' and Fe'''	$K_{3.2}\ Na_{1.0}\ Fe''_{3.7}\ Mn_{0.4}\ Fe'''_{4.6}\ Mg_{0.04}\ Al_{6.8}\ Si_{14}\ O_{47.5}\ (OH)_{0.5}$	Cancrinite-sodalite syenite		AMER. JOUR. SCI., 32, 353-361, 1886
4.	phlogopite	Mg	$K_{3.2}\ Na_{0.2}\ Fe''_{0.07}\ Mg_{13.0}\ Al_{3.9}\ Si_{13.4}\ O_{46.9}\ (OH)_{1.1}$	Metamorphosed limestone?	Edwards, N. Y.	AMER. JOUR. SCI., 36, 317-331, 1888
5.	wodanite	Ti'''' and Fe''	$K_{3.2}\ Na_{1.0}\ Ca_{0.3}\ Fe''_{2.7}\ Mn_{0.02}\ Fe'''_{0.7}\ Ti_{2.9}\ Mg_{6.4}\ Al_{3.5}\ Si_{12.1}\ O_{47.8}\ (OH)_{0.1}\ F_{0.1}$	Shonkinite	Katzenbuckel, Germany	Mitt. Baden. Geol. Land., Heidelberg, 8, 317-340, 1919
6.	phlogopitic biotite	Ti'''' and Mg	$K_{4.0}\ Na_{0.1}\ Ca_{0.2}\ Ba_{0.1}\ Fe''_{0.9}\ Fe'''_{0.7}\ Ti_{2.0}\ Mg_{8.8}\ Al_{3.9}\ Si_{12.1}\ O_{46.9}\ (OH)_{0.4}\ F_{0.7}$	Lamproite	West Kimberly area, Western Australia	Min., Mag., 25, 374-387, 1940
7.	biotite	Ti'''	$K_{3.8}\ Na_{0.9}\ Fe''_{7.8}\ Mn_{0.2}\ Ti''''_{0.4}\ Ti'''_{0.5}\ Mg_{3.3}\ Al_{4.4}\ Si_{11.5}\ O_{42.5}\ (OH)_{5.1}\ F_{0.3}$	Granitic pegmatite	Deroma, Holland, Southern Sweden	Schweiz. Min. Petro. Mitt., 17, 149-153, 1937
8.	biotite	Mn'' and Fe''	$K_{3.8}\ Na_{0.6}\ Ca_{0.6}\ Fe''_{5.8}\ Mn_{1.0}\ Fe'''_{2.7}\ Ti_{0.4}\ Mg_{2.4}\ Al_{4.3}\ Si_{10.6}\ O_{40.6}\ (OH)_{7.4}$	Miascite	Tscherenschanka, Ilmen Mtns., U.S.S.R.	Warsaw Univ. Nachr., 1909
9.	lepidomelane	Mn'' and Fe'''	$K_{3.2}\ Na_{1.6}\ Fe''_{2.3}\ Mn_{1.4}\ Fe'''_{6.0}\ Mg_{1.5}\ Al_{4.5}\ Si_{11.0}\ O_{42.6}\ (OH)_{5.4}$	Mariupolite	near Azov Sea, U.S.S.R.	Min. Mitt., 21, 238-246, 1902
10.	manganphlogopite	Mn'' and Mg	$K_{1.8}\ Na_{0.6}\ Ca_{0.3}\ Fe''_{0.6}\ Mn_{4.7}\ Ti_{0.1}\ Mg_{8.0}\ Al_{5.4}\ Si_{11.3}\ O_{43.6}\ (OH)_{4.4}$ *	Metamorphosed limestone?	Kasos mine, Totigi prefecture, Japan	Jour. Geol. Soc. Japan, 45, Suppl. to 532, 1938
11.	manganophyllite	Mn'' and Mn'''	$K_{3.5}\ Na_{0.4}\ Mn''_{2.3}\ Mn'''_{0.7}\ Fe'''_{1.0}\ Mg_{9.4}\ Al_{3.0}\ Si_{11.7}\ O_{40.5}\ (OH)_{7.5}$	Metamorphosed limestone	Harstigen, Varmland, Sweden	Zeit. Kryst., 61, 155-163, 1925
12.	manganophyllite	Mn'''	$K_{3.1}\ Na_{0.8}\ Fe'''_{0.9}\ Mn'''_{1.8}\ Mg_{9.8}\ Al_{4.7}\ Si_{10.7}\ O_{40.4}\ (OH)_{7.6}$	Metamorphosed limestone	Langban, Sweden	do
13.	phlogopite	Na	$K_{2.3}\ Na_{2.9}\ Ca_{0.03}\ Fe''_{0.2}\ Fe'''_{0.5}\ Ti_{0.07}\ Mg_{9.4}\ Al_{3.6}\ Si_{11.7}\ O_{46.6}\ (OH)_{1.4}$	Metamorphosed limestone	Tansen, Kankyohokudo, Korea	Jour. Fac. Sci., Imper. Univ. Hokkaido, 3, 315-323, 1936
14.	siderophyllite	Na	$K_{2.3}\ Na_{3.0}\ Ca_{0.4}\ Fe''_{4.8}\ Mn_{0.2}\ Fe'''_{3.4}\ Ti_{0.3}\ Mg_{1.1}\ Al_{6.1}\ Si_{9.7}\ O_{39.4}\ (OH)_{8.0}\ F_{0.6}$	Basic segregation, Baveno granite	Baveno, Italy	Perio. Min. Roma, 7, 61-76, 1936
15.	barytbiotite	Ba and Ca	$K_{1.9}\ Na_{0.2}\ Ca_{2.6}\ Ba_{0.6}\ Fe''_{0.1}\ Fe'''_{0.5}\ Mg_{11.1}\ Al_{6.4}\ Si_{8.8}\ O_{39.1}\ (OH)_{8.9}$	Metamorphosed limestone	Kaiserstuhl	Daub, R. Dissertation, Freiberg, 1912
16.	phlogopite	Ba	$K_{2.9}\ Na_{0.6}\ Ba_{0.3}\ Fe''_{0.2}\ Fe'''_{0.5}\ Mg_{11.9}\ Al_{4.7}\ Si_{11.5}\ O_{42.0}\ (OH)_{6.0}$	Metamorphosed limestone	Edwards, N. Y.	Zeit. Kryst, 3, 122-167, 1879
17.	calciobiotite	Ca	$K_{3.0}\ Na_{2.2}\ Ca_{4.3}\ Mn_{0.07}\ Fe'''_{0.4}\ Ti_{0.02}\ Mg_{4.2}\ Al_{6.2}\ Si_{10.5}\ O_{39.6}\ F_{4.8}\ F_{3.6}$	Altered limestone inclusion in tuff	Vesuvius, Italy	Zeit. Kryst., 57, 419 (abstract), 1922-23

* May be somewhat weathered; note low alkalies.

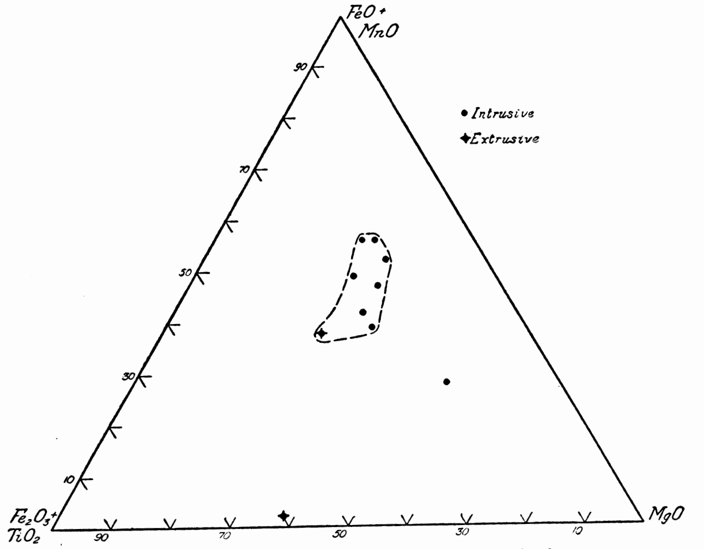

Fig. 3. Biotites from Tonalites and Diorites.

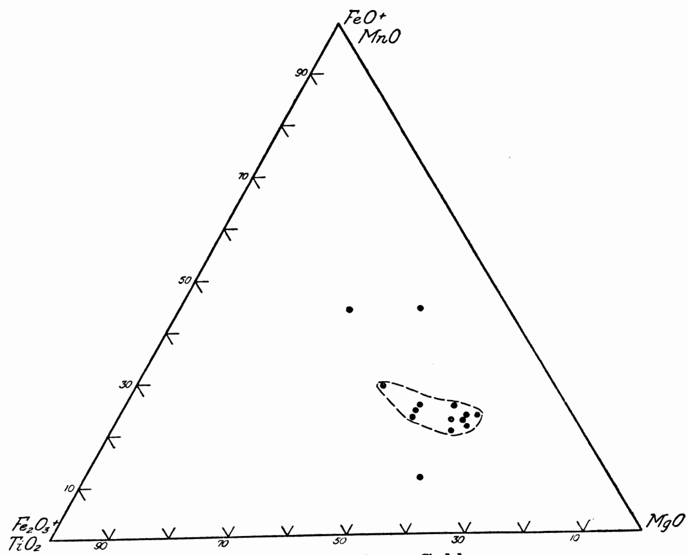

Fig. 4. Biotites from Gabbros.

MgO. In general the FeO content is lower, but the range of $Fe_2O_3+TiO_2$ is the same. One of two biotites from andesites falls within the field, but the other is at a considerable distance from it.

BIOTITES FROM GABBROS.

Most biotites from gabbros and other mafic intrusive rocks have an MgO content of 15-20% (Fig. 4). The ratio of FeO+MnO to $Fe_2O_3+TiO_2$ of many approximates 1:1. The maximum FeO content is about 10%, and the maximum Fe_2O_3 content is about 8%, but TiO_2 is high in those in which the ferric iron is low. Some of the basaltic biotites fall within the field of concentration, and others lie outside of it. The extrusive biotites of this group are more similar in chemical composition to their intrusive equivalents than in any other group.

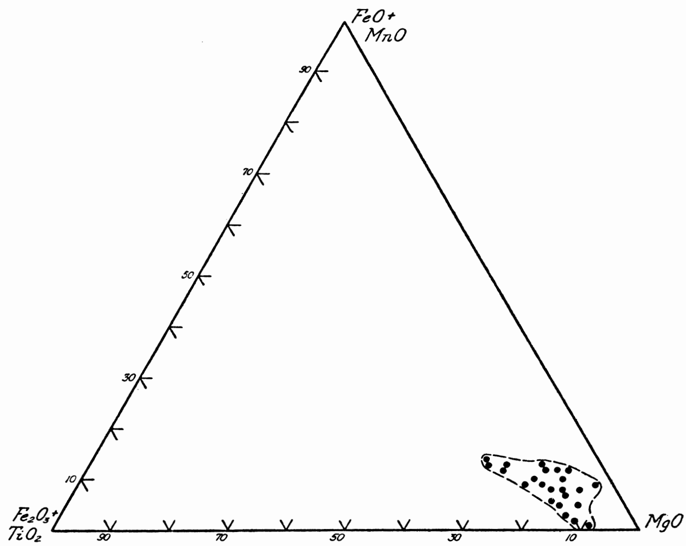

Fig. 5. Biotites and Phlogopites from Periodotites and other Ultramafics.

BIOTITES FROM ULTRAMAFIC ROCKS.

Micas of the ultramafic rocks are phlogopites or phlogopitic biotites that contain a maximum of about 6% Fe_2O_3 and 5% FeO. The content of TiO_2 is generally very low. The MgO maximum is nearly 30%. Many of these micas appear to be intermediate in composition between true phlogopites of the metamorphosed limestones and biotites from less mafic intrusive rocks.

BIOTITES FROM SYENITES, NEPHELINE SYENITES, AND SYENITIC PEGMATITES.

Biotites from syenitic rocks contain the highest percentages of Fe_2O_3. Included in this group are the lepidomelanes, a term that has been applied to biotites rich in either ferric or ferrous iron or both. The FeO content may also be very high, with a maximum of nearly 32%, but in general it is less than in bio-

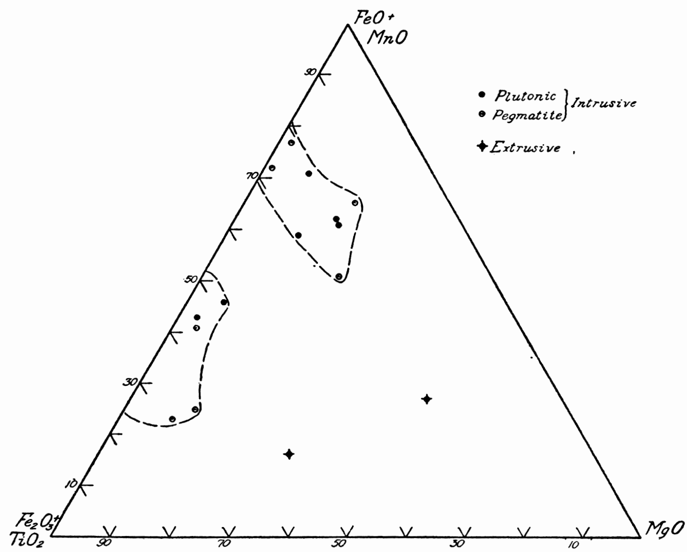

Fig. 6. Biotites from Syenites, Nepheline Syenites, and Syenitic Pegmatites.

tites from granitic pegmatites (Fig. 6). The percentage of MgO may be as much as 9%, but it rarely exceeds 7%. Biotites from the pegmatitic facies are apparently richer in either ferric or ferrous iron than those from the plutonic rocks, but biotites from the equivalent extrusive rocks appear to be much richer in MgO.

BIOTITES FROM GNEISSES AND SCHISTS.

Despite the variation in mineral content and texture of metamorphic rocks, most of these biotites have a closely restricted range in chemical composition (Fig. 7). The FeO maximum is 20%; Fe_2O_3 is generally less than 10%; and MgO is commonly less than 18%. The field occupied by this group includes the area occupied by the intermediate group (Fig. 3) but extends beyond it toward the field of the gabbroic biotites. Although both ortho- and paragneisses are included in the group, the biotites show no extreme variations in composition. A few biotites from amphibolites were plotted and fell into the area of the ultramafic biotites.

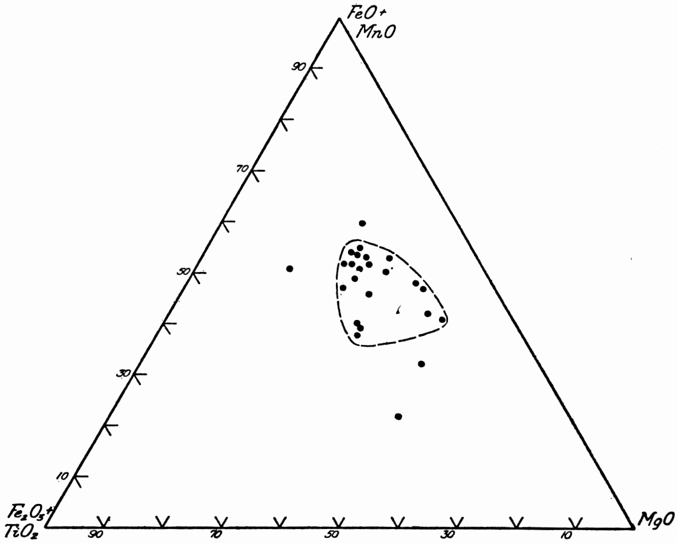

Fig. 7. Biotites from Gneisses and Schists.

PHLOGOPITES FROM METAMORPHOSED LIMESTONES.

The micas that occur in metamorphosed limestones are phlogopites very rich in magnesium with a maximum MgO content of about 30% (Fig. 8). Many of these contain very little iron, and the maximum content of the two iron oxides is less than 10%. A special group that is not plotted on the triangular diagrams is the manganophyllite sub-series, which includes the magnesium-manganese micas that are generally low in iron. These contain a maximum of 12% $MnO+Mn_2O_3$.

BIOTITES FROM PEGMATITIC FACIES.

The diagrams indicate that biotites from pegmatitic facies in the granitic and syenitic groups are richer in iron than those from the plutonic equivalents. In the other intrusive groups

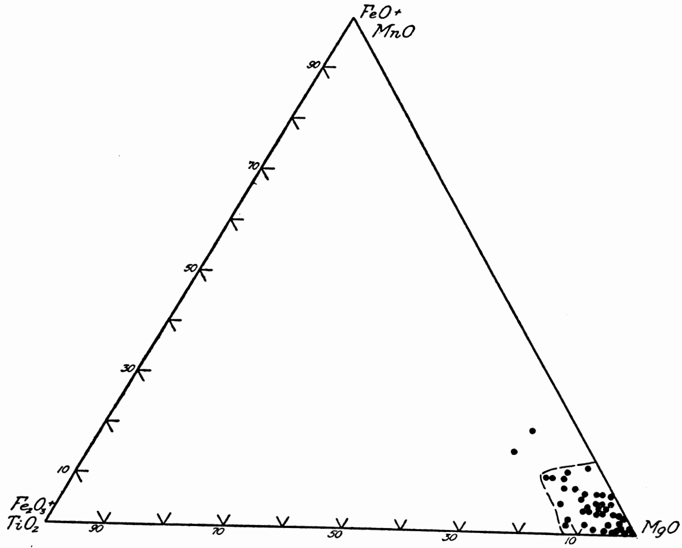

Fig. 8. Phlogopites from Metamorphosed Limestones.

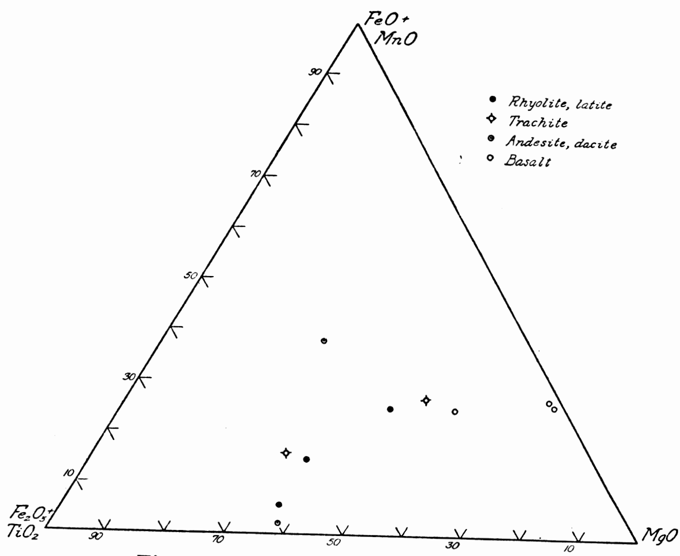

Fig. 9. Biotites from Extrusive Rocks.

the meager data that are available indicate that this relationship is probably also valid. Rubidium- and caesium-bearing biotites are known only from pegmatites.

BIOTITES FROM EXTRUSIVE ROCKS.

Except for basaltic biotites, the extrusive ones do not fit at all well the fields of their intrusive equivalents. Not enough analyses are available for a complete picture of the relationships between the two, but in general the extrusive ones are poorer in FeO. Biotites rich in $Fe_2O_3+TiO_2$ and with moderate amounts of MgO appear to be restricted to extrusive rocks (Fig. 9). In many of the extrusives the analyzed biotite occurs as phenocrysts, which may not have attained chemical equilibrium with the groundmass. Also oxidation of some of the iron to the ferric state may have taken place.

RELATION OF INDEX OF REFRACTION TO CHEMICAL COMPOSITION.

Several attempts have been made to show in a quantitative way the relation between the indices of refraction and the chemical composition of biotites (Grout, 1924; Kunitz, 1924; Winchell, 1935; Kunitz, 1936; and Hall, 1941). Grout plotted α and γ against the combined weight percentage of FeO and Fe_2O_3 and obtained a curve with a uniform slope up to about 28% of the oxides, after which point the curve flattens slightly. Twelve analyses were used. Kunitz plotted α against the weight percentages of the two theoretical "end-molecules," $K_2HAlMg(SiO_4)_3$ and $KH_2AlFe_3(SiO_4)_3$, and obtained a straight line with seven analyses.

The theoretical "end-molecules" used by Kunitz (1924) and Winchell (1935) have little significance in the structure of the biotite molecule, nor can the variation in chemical composition of the series be expressed adequately in terms of them. Kunitz (1936) showed that in those biotites in which the total iron remains nearly constant the index of refraction increases with increasing titania, a relationship which can be expressed as a straight line function. Hall (1941) calculated that 1% TiO_2 increases the refractive index by .0046. Hall plotted also γ against weight percent FeO and obtained two general fields, one of which (Field 1) contained the iron-titanium biotites and the other (Field 2) with lower indices which contained the iron-manganese biotites.

The writer plotted the γ indices of refraction of about 60 biotites and phlogopites against the weight percentages of

$FeO+Fe_2O_3$, but no simple relationship was evident. Next the indices were plotted against the weight percentages of MgO, but this result was even less satisfactory. A third trial consisted of plotting the indices on a triangular diagram of the type employed in Figures 1-9 and then contouring the result, but this scheme was unsuccessful.

A fairly well defined curve was obtained by plotting the indices against the combined weight percentages of FeO, Fe_2O_3, and TiO_2. This had the advantage of throwing nearer to the line many of the analyses in which Fe_2O_3 is low, for it is in these biotites that the higher percentages of TiO_2 occur. In

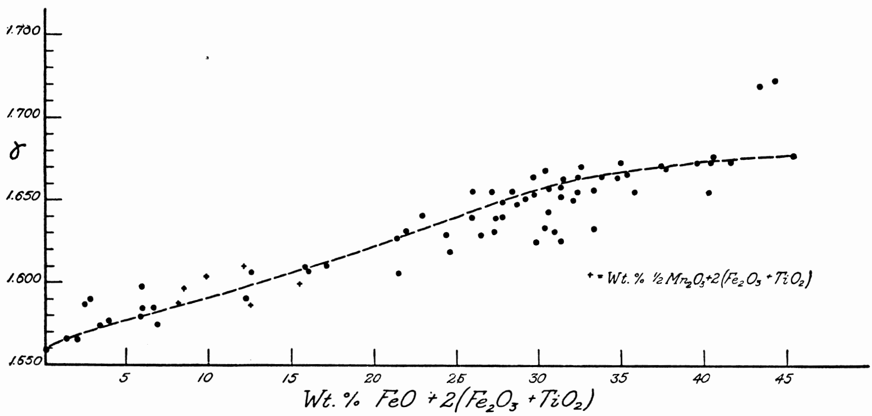

Fig. 10. The Relationship between Index of Refraction and Chemical Composition in the Biotite-Phlogopite Series.

general, however, the curve was unsatisfactory, especially for the biotites unusually rich in ferric iron.

It is likely that increments of Fe_2O_3 and TiO_2 have a greater effect upon the indices than have comparable additions of FeO. To test this idea the weight percentages of Fe_2O_3, and TiO_2 were weighted by various numbers. The best curve was obtained when a factor of 2 was used (Fig. 10). Thus it appears that the effect of the ferric iron and the titanium is about twice that of the ferrous iron. The γ indices of a few manganophyllites were also plotted against $\frac{1}{2}(Mn_2O_3 \text{ or } MnO)+2(Fe_2O_3+TiO_2)$. These plots fall reasonably close to the curve and indicate that the effect of the manganese is less than that of the ferrous iron.

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