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X-RAY MEASUREMENT OF THE IRON-MAGNESIUM RATIO IN BIOTITES*

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ABSTRACT. The iron-magnesium ratio in biotite may be determined by measuring the intensity ratio of (004) to (005). This ratio is highly sensitive to iron-magnesium substitution and is virtually unaffected by other substitutions such as Na for K, F for OH, and Al for Si. The intensity method gives adequate precision and appears to be accurate to about 5 percent or less of the magnesium-iron content.

Unit cell measurements are of limited value in the determination of composition. Iron-rich biotites have a shorter c_o parameter than magnesium members, in spite of the fact that iron has a larger ionic radius than magnesium. Fluorine produces a marked decrease in c_o. Tetrahedrally coordinated Al may cause a slight increase. In metamorphic biotites c_o is larger than in igneous ones. The b_o parameter shows little or no change with iron content but is smaller in fluorine-rich specimens. The a_o parameter seems to show about the same variation as b_o but the reflections in some specimens are too weak to be identified with certainty by powder methods.

A new form of analysis plot has been used which shows more extensive solid solution with muscovite than has been previously supposed.

ACKNOWLEDGMENTS

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INTRODUCTION AND STATEMENT OF THE PROBLEM

For many years the composition and abundance of feldspars have been used to classify igneous rocks. The feldspars are useful minerals for this purpose because of the ease with which variations in composition may be determined. However, feldspars tell only half the story of a rock. They say nothing of the ferromagnesian content and of the variation in relative amount of iron and magnesium.

The amounts of the various ferromagnesian minerals in a rock may be easily determined petrographically. The relative amount of iron and magnesium in any of the ferromagnesians is not so easily determined, although in olivine, pyroxene, and to a certain extent amphibole, a rough estimate of the iron content may be made on the basis of optical properties. X-rays have also been useful in certain instances (Hess, 1952), where the iron content has been

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related to the size of the unit cell. The commonest ferromagnesian in salic rocks and the ferromagnesian most widely distributed is biotite, and it would be desirable because of this to have some simple method of determining the Fe/Mg ratio in biotites.

It has further been shown (Nockolds, 1947) that the ratio of magnesium to iron in igneous rock micas reflects very closely the magnesium-iron ratio of the rock as a whole. This is understandable because the known properties and compositions of phlogopites and biotites indicate a complete solid-solution series between magnesium-rich and iron-rich members (Winchell, 1935).

To determine the ratio of magnesium to iron, various techniques have been described in the literature. Winchell and Winchell (1951) give curves showing changes in optical properties with change of composition. These can be used to give a rough approximation of composition, but in some cases the data are not reliable, especially for replacement in other than the Mg-Fe sites.

The relation of color to composition has been studied by Hall (1941a). The triangular plot of FeO, MgO, and TiO_2 with respect to color shows that although color is most certainly controlled by iron and titanium content it is of limited value as a diagnostic feature. Blue-green biotites are low in titanium and rich in iron. Red or red-brown biotites may be rich in titanium but may have any Mg-Fe ratio. The plot might be more useful if the Fe/Mg content were known precisely. The color would then perhaps give an indication of titanium content. A further complication, not evaluated by Hall, is the effect of manganese, which presumably also produces a reddish-brown color. According to Hall biotites do not in general contain sufficient manganese to have any effect upon the color. Geological occurrence would no doubt be of assistance in predicting manganese content. The effect of change in oxidation state of the iron is not known because of the lack of ferric-iron biotites, but for the analyzed specimens used by Hall it apparently has little effect on color.

The relation between refractive index and composition has also been studied by Hall (1941b). Hall's plot of refractive index (γ) versus total iron shows that although iron causes an increase in refractive index, other elements affect it so much that correlation between iron content and refractive index is not possible. Titanium, manganese, and both ferric and ferrous iron raise the refractive index. Fluorine lowers the refractive index.

Hall questions Winchell's (1935) diagram relating chemical composition to optic properties because titaniferous biotites have much higher indices than even siderophyllite. The effect of 1% TiO_2 on refractive index is calculated by Hall to be + .0046, somewhat lower than the amount (.01) given by Kunitz (1936).

The conclusion reached by Hall is that no sure information can be obtained as to the chemical composition of a biotite from its refractive index alone, since a biotite high in iron and low in titanium may have the same index as one low in iron and high in titanium.

Heinrich (1946, 1953) states that the effect of ferric iron in raising refractive indices in biotite is approximately twice that of ferrous iron and about the same as that of titanium. Observations on synthetic fluor-phlogopite prepared by the Electro-technical Laboratory at Norris, Tennessee show that

replacement of all OH by F (about 9% by weight) lowers γ by 0.22. This value is about half of the change in γ produced by complete substitution of iron for magnesium.

TABLE 1

Structure Amplitudes (F) for Basal Reflections

No.			z	001	002	003	004	005	006	007
B23	3.0	Mg	0	30.0	29.3	27.5	25.7	23.6	21.5	19.7
	2.08		.12	40.9	3.1	-27.2	-35.7	-24.5	- 4.8	11.7
	4.0	O								
	3.0	Si	.28	- 7.4	36.5	20.5	26.6	-28.0	-13.9	29.5
	1.03	Al								
	6.0	O	.34	-29.9	20.5	39.9	-21.0	- 8.5	22.6	-14.4
	1.0	K	.5	-17.4	16.5	-14.9	13.2	-12.0	10.8	- 9.7
	Total			16.2	- 8.1	45.8	8.8	-49.4	36.2	36.8
	F_{calc} %			8.0	- 4.0	22.8	4.4	-24.5	18.0	18.3
	$\|F_{obs}\|$%			5.2	2.5	20.6	11.0	25.9	19.3	15.5
	ΔF			2.8	1.5	2.2	6.6	1.4	1.3	2.8
B13	2.7	Mg								
	0.2	Fe++		32.4	31.8	29.9	27.8	25.6	23.5	21.3
	0.02	Fe+++								
	0.03	Ti								
	1.5	OH								
	0.5	F	.12	40.0	3.0	-26.2	-33.4	-22.7	- 4.3	10.5
	4.0	O								
	2.97	Si								
	0.95	Al	.28	- 7.5	-36.1	20.4	26.5	-28.1	-13.8	29.3
	0.08	P								
	6.0	O	.34	-29.3	-20.5	40.5	-21.0	- 8.5	22.0	-14.0
	0.9	K	.5	-16.05	15.25	-13.7	12.3	-12.1	10.0	- 8.9
	0.04	Na								
	Total			19.6	- 6.6	58.9	12.2	-45.8	37.4	38.2
	F_{calc} %			9.0	- 3.0	26.9	5.6	-20.9	17.1	17.5
	$\|F_{obs}\|$%			6.26	3.45	21.9	12.4	23.7	16.95	15.25
	ΔF			2.74	0.45	5.0	6.8	2.8	0.15	2.25
B19	0.9	Mg								
	1.15	Fe								
	0.03	Mn	0	49.4	47.7	44.7	40.8	37.1	33.9	31.3
	0.2	Fe								
	0.3	Ti								
	0.3	Al								
	1.8	OH								
	0.5	F	.12	39.8	3.0	-26.3	-33.4	-22.8	- 4.4	10.5
	3.7	O								
	2.6	Si	.28	- 7.4	-36.0	20.5	26.4	-27.6	-13.7	29.1
	1.4	Al								
	6.0	O	.34	-29.3	-20.5	40.4	-21.0	- 8.5	22.1	-14.0
	0.74	K								
	0.06	Na	.50	-15.1	14.3	-12.9	11.7	-10.5	9.4	- 8.7
	0.09	Ca								
	Total			37.4	8.5	66.4	24.5	-32.3	47.3	47.2
	F_{calc} %			14.2	3.2	25.2	9.3	-12.3	17.9	17.9
	$\|F_{obs}\|$%			18.7	3.6	19.2	13.0	16.9	14.3	14.3
	ΔF			4.5	0.4	6.0	3.7	4.6	3.6	3.6

TABLE 1 (*Continued*)

No.			z	001	002	003	004	005	006	007
B 7	0.68	Mg								
	1.46	Fe++								
	0.355	Fe	0	53.87	52.06	48.56	44.22	40.13	36.48	33.32
	0.225	Ti								
	0.07	Al								
	2.01	OH								
	4.0	O	.12	39.80	3.02	−26.0	−32.7	−22.3	− 4.27	10.32
	2.575	Si								
	1.425	Al	.28	− 7.4	−36.2	20.4	26.5	−28.0	−13.75	29.2
	6.0	O	.34	−29.2	−20.45	40.5	−21.0	− 8.5	22.05	−13.95
	0.025	Ca								
	0.130	Na	.5	−14.82	14.06	−12.7	11.42	−11.17	9.3	− 8.34
	0.7535	K								
	Total			42.25	12.49	69.76	28.44	−29.84	49.81	50.55
	F_{calc} %			14.9	4.4	24.6	10.1	10.6	17.5	17.9
	F_{obs} %			8.4	3.5	24.7	14.1	17.0	19.9	12.4
	ΔF			6.5	0.9	0.1	4.0	6.4	2.4	5.5
B 9	2.05	Fe								
	0.03	Mg								
	0.35	Li	0	58.2	54.4	49.9	45.4	41.4	37.8	34.2
	0.07	Mn								
	0.5	Al								
	2.0	OH								
	4.0	O	.12	41.0	3.1	−26.8	−35.1	−24.4	− 4.7	11.5
	3.0	Si								
	1.0	Al	.28	− 7.4	−36.0	20.3	26.5	−27.8	−13.8	29.3
	6.0	O	.34	−29.5	−20.5	39.9	−21.0	− 8.7	22.7	−14.4
	0.925	K								
	0.09	Na	.5	−16.9	16.2	−14.6	13.0	−11.8	10.6	− 9.5
	Total			45.4	17.2	68.0	28.8	−31.3	52.6	51.1
	F_{calc} %			15.5	5.3	23.2	9.8	−10.7	18.0	17.5
	$\lvert F_{obs}\rvert$%			8.5	2.5	26.7	14.5	15.5	20.5	15.3
	ΔF			7.0	2.8	3.5	4.7	4.8	2.5	2.2

Optical spectrographic techniques may be used for semi-quantitative determinations of Mg and Fe, as well as for estimating relative amounts of Ti, Mn, Cs, Rb, Li, and many other trace elements. An important disadvantage lies in the fact that in studying rock biotites it is sometimes impossible to obtain a completely pure specimen. Admixed iron oxide, chlorite, amphibole, and intergrown crystals of zircon, rutile, sphene, and apatite would introduce large and unknown errors. These would exist not only in spectrographic analyses but also in standard chemical analyses. X-ray techniques obviate this last difficulty because small amounts of admixed minerals do not affect the structure of the mineral being studied.

THE METHOD

Development.—A common method of mineral identification using X-rays involves determination of lattice constants. For minerals in an isomorphous series such determinations are diagnostic if the lattice constants change markedly for the ion pair concerned but do not change for other compositional changes or for any other reasons. The changes in unit cell dimensions

are discussed later, but it is sufficient to say now that they are of limited use in determining the magnesium-iron content of biotites.

Another possible method is to measure changes in intensity of X-ray reflections with changes in magnesium-iron content. Brown (in Brindley, 1951) has calculated the variation in basal reflection intensities with variation in magnesium-iron content of biotites, and has suggested a method by which magnesium biotite may be distinguished from iron biotite using X-ray powder photographs.

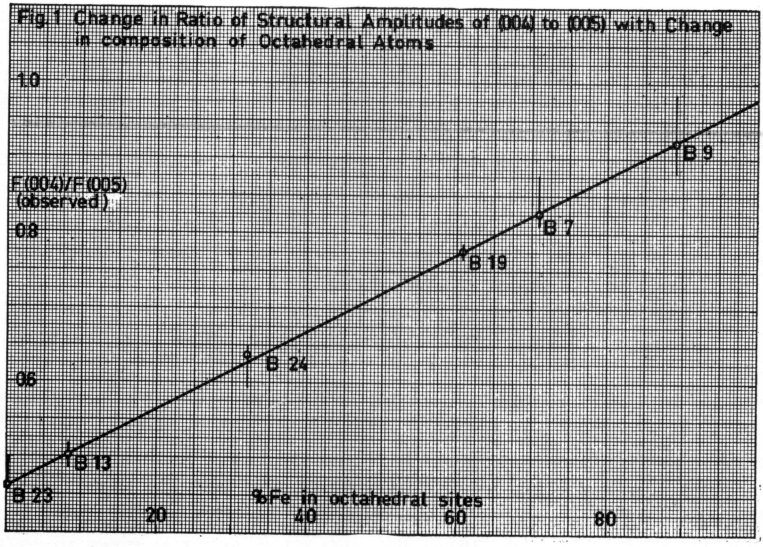
Because of varying degrees of preferred orientation in powder mounts and of different forms of layer stacking in the crystal structure it is desirable to use only basal reflections in the measurement of relative intensities, even though apparently one-layer monoclinic forms predominate (Heinrich and others, 1953).

In order to determine the best pair of reflections to use for a precise determination of iron and magnesium content, the contribution of each atom to the amplitude of basal reflections has been calculated (table 1 and fig. 3). It was hoped that a situation exists where iron and magnesium make a large contribution to intensity in one reflection and practically none in another. Such is not the case. Although the contribution to intensity increases greatly with increase in iron content, the contributions to various 00*l* reflections change only slightly relative to one another.

One significant feature is that the (005) reflections are opposite in phase to (004) reflections, whereas the Mg-Fe contribution to each of these is in the same phase. This means that as Fe is substituted for Mg the intensity of the (004) reflection increases and that of (005) decreases. Substitution for Si by Al, or for OH by F has practically no effect on intensities. Substitution of Na for K might interfere because of the difference in atomic number, and thus in scattering effect. Quite fortuitously the phases of the structure amplitude for K in (004) and (005) are opposite so that substitution of Na for K has a similar effect on both reflections and thus produces very little change in the ratio.

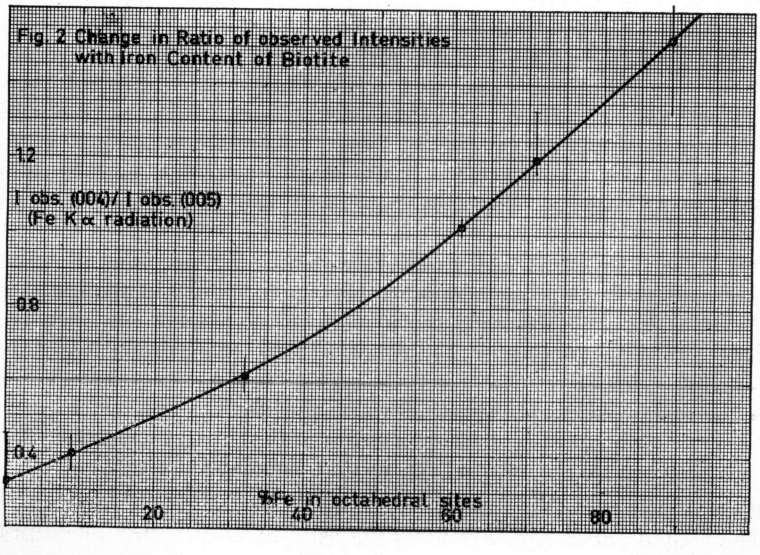
Replacement of Mg or Fe by other cations is not extensive, although it may be enough to interfere with the curve. Manganese has almost the same scattering factor as Fe; Al has almost the same scattering factor as Mg. Lithium, having a very small scattering factor, would act in the same direction as Mg but more strongly. Where these elements are greatly enriched, other minerals in the rock will frequently indicate their presence—e.g., spodumene, topaz, and muscovite. Where Al is abnormally low, olivines and pyroxenes may be associated with the biotite.

Two types of working curve were prepared. The first (fig. 1) is a plot of the ratio of structure amplitudes (F's) of (004) to (005) against atomic proportion of iron $\left[100 \times \left(\frac{\text{Fe}}{\text{Mg+Fe+Al}} \right) \right]$. A line drawn through the points representing the analyzed specimens is straight. This is to be expected because F is a summation, one of whose terms contains the scattering factor (f). The second curve (fig. 2) shows the ratio of uncorrected intensities for



FeKα radiation against molecular percent of Fe, as above. This form is more readily used but because of a shift in glancing angles with compositions is less accurate than figure 1.

Limitations.—The use of the curves (figs. 1 and 2) is limited to biotites which contain principally magnesium and iron in the octahedral positions. The ratio actually measured depends on the relative amounts of Fe, Mn, Ti, Al (octahedral), Li, and Mg in the structure. However, the effects of Mn and Ti ($f \approx f$ for Fe) tend to cancel those of Al and Li ($f \approx f$ for Mg), and inas much as high concentrations of these elements may frequently be detected



optically some adjustment could be made to the observed ratio to correct for them.

A rare alkali biotite (Hess and Stevens, 1937) serves as a test of such a variety. In spite of the unusual composition of the mica the observed ratio, Fe/Mg+Fe %, falls very close to the curve (fig. 1).

Reproducibility.—A high degree of precision is attainable if a great deal of care is exercised in preparation of the specimen. The source of greatest error lies in not having the surface of the powder perfectly flat and in the plane of the holder. An uneven surface produces irregularly shaped peaks which may give large errors in intensity ratios.

The observed extent of these errors is indicated by vertical lines (figs. 1 and 2) through the points representing the best values for the analyzed specimens.

Sample preparation and measuring techniques.—The method found to give the highest degree of precision is that described by McCreery (1949). The mica is first reduced to powder by filing the edges of cleavage pieces or, if the grains are too small to file, by grinding in acetone with 120 grade carborundum in an iron mortar. Impurities may be removed by heavy liquids and by magnetic separation. Although −400 mesh material gives the flattest surface coarser sizes (up to −270 mesh) are satisfactory especially if the mica is not well crystallized. A greater degree of preferred orientation is produced and basal reflections will thus have greater intensity.

The powder is packed gently into a drilled ½″ diameter hole in a thin section slide, backed by another slide. A third slide is placed on top and the whole turned over. The original backing slide is carefully lifted off so that the surface of the powder is not disturbed. The completed mount is then bound at one end with plastic tape or drafting tape. The latter was found more satisfactory both because of ease in labeling the specimen and ease in removal if the mount is to be reversed in the gonimeter. An internal standard may be mixed with the powder if desired.

A North American Philips X-ray diffractometer and Brown recorder were used in all the work. Both copper and iron radiation were used, but iron was preferred because of improved patterns for iron-rich biotites. Preliminary traverses were made at 50 kv and 10 Ma at 1° per minute using 1° slits and a time constant of 2 seconds. This revealed any impurities, such as chlorite, amphiboles, or pyroxenes, and gave the approximate 2θ angles for all reflections.

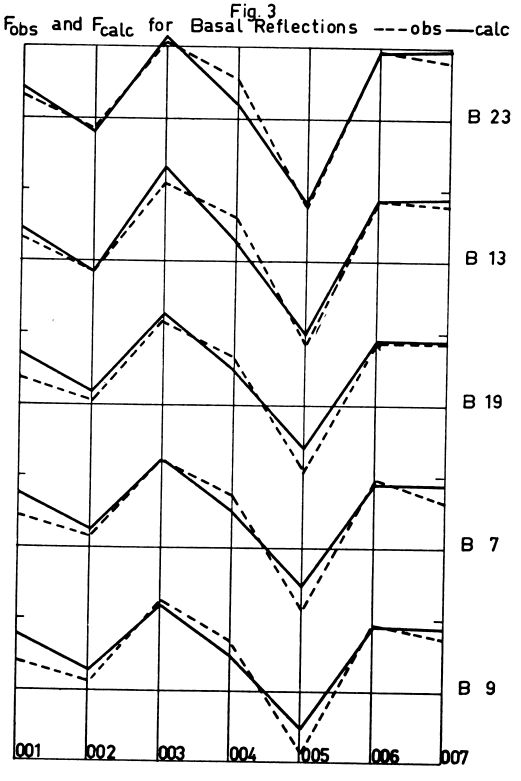
The (004) and (005) peaks were traversed at ⅛° per minute. Accuracy was improved by measuring a number of sample mounts a few times each rather than measuring the same mount many times. If the specimen is well crystallized 1° slits may be used, but if not, 4° slits are necessary to give peaks large enough to measure.

Areas under peaks are measured with a planimeter, with which precision of 1 percent is obtainable by these repetitions of each measurement.

Accuracy.—The accuracy of the method could not be fully investigated because of insufficient analyzed material. However, a spectrochemical method gives a rough check. A curve of line-intensity ratio versus iron concentration

was plotted using the available analyzed specimens and the indicated iron content of several biotites was compared to that given by the X-ray method (fig. 7). Adequate correlation was obtained where spectrochemical determinations gave good reproducibility (about 1% spread in measured Fe/Mg+Fe ratio), but some difficulty was experienced in developing a technique for arcing biotites. X-ray determinations on specimens from localities where similar material had been analyzed also gave satisfactory agreement (specimens B 18, B 26, B 7).

Fig. 3

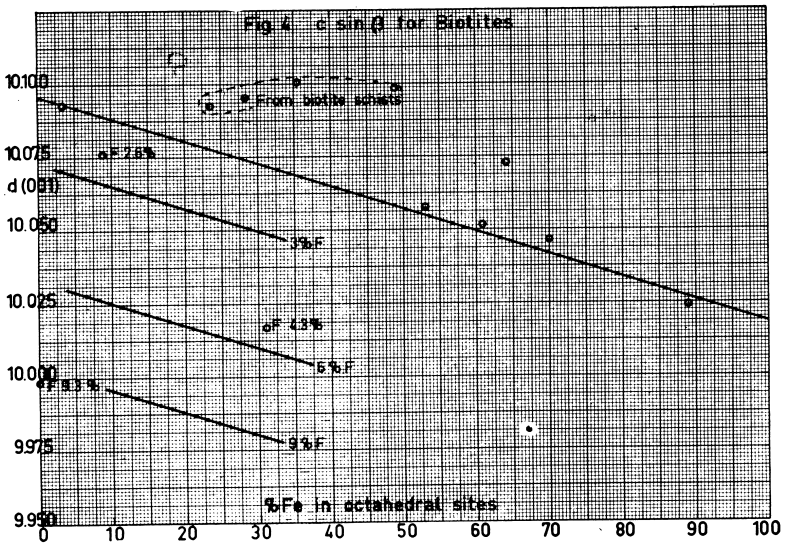


UNIT CELL DETERMINATIONS

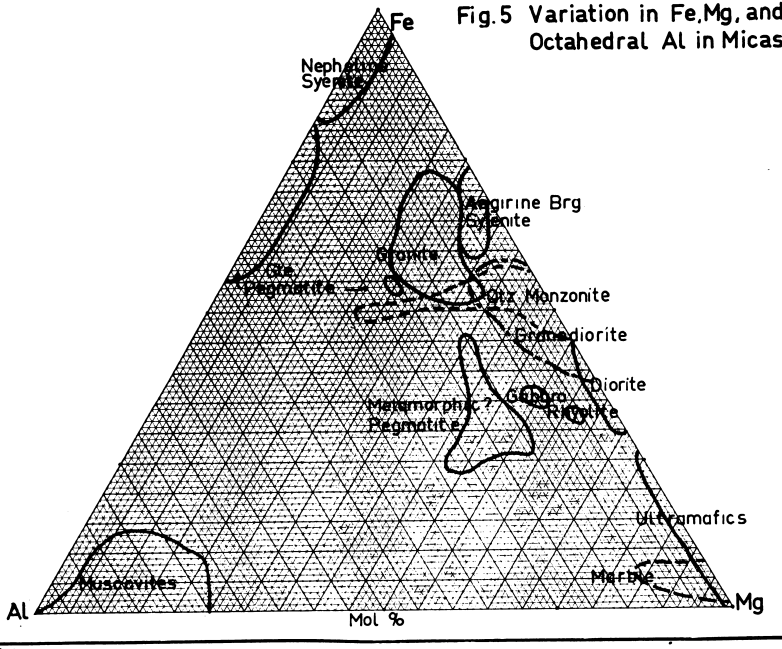
Unit cell sizes were measured by using (004), (005), (060), and where possible (200).

The powdered sample was mixed with an internal standard of finely powdered (-400 mesh) silicon and X-rayed as described above. Results for $c \sin \beta (d_{001})$, b, and a are given in table 2 and figure 4.

For the chemically analyzed specimens and for those checked spectrochemically a decrease in $c \sin \beta$ is noted with increase of iron content. At first sight this seems anomalous because the ionic radius of Fe^{+2} (.74 Å, Ahrens, 1952) is larger than that of Mg^{+2} (.67 Å). However, similar changes are shown by chlorite (von Engelhardt, 1942). This phenomenon may have the



following explanation. Iron has more than twice the polarizing power of magnesium,[1] and may so polarize the OH layer as to reduce the distance between apical oxygen atoms and thus partially collapse the structure. No great increase in b was found such as was found in chlorite by von Engelhardt.



[1] Using $\frac{ze}{r^2}$, polarizing power for Mg = 335 and Fe = 720 (see Evans, 1948, p. 181, and Ahrens, 1953).

The effect of F was studied in a few analyzed phlogopites. Complete replacement of OH by F reduces $c \sin \beta$ by about 0.1 Å (see fig. 4) and a rough measure of F content may be made as indicated in figure 4.

In iron-biotites where more aluminum commonly substitutes in both octahedral and tetrahedral layers, the effect of F is obscured—as for example in B 9, which is rich in both F and Al. Aluminum apparently increases $c \sin \beta$, but lacking analyzed material positive tests could not be made.

A test on metamorphic biotites from Vermont[2] indicate that they have a larger d_{001} spacing than do igneous. This may be caused by a high percentage of aluminum, a low confining pressure during crystal growth, a partial substitution of water for potassium, or some other cause. A granite with "cold" contacts from the same area contains a biotite with a larger-than-normal d_{001} spacing. Further work is required on this phase of the subject.

TABLE 2

$c_o \sin \beta$, b_o, and a_o for Biotites

Spec. no.	$c_o \sin \beta$	b_o	a_o	Fe/Fe Mg Al
B 1	10.057 Å	9.250 Å		59 %
2	10.032	9.223		33
3	10.081	9.245		50
7	10.046	9.250		71
8	10.010	9.232		1
9	10.024	0.239		89
11	10.073	9.242	5.23	55
12	10.053	9.237	5.28	59
13	10.076	9.235	5.23	9
14	10.012	—		92
15	10.037	9.231	5.26	47
16	10.103	9.254		30
18	10.051	9.213	5.22	11
19	10.051	9.243	5.28	61
20	10.072	9.253	5.24	68
21	10.072	9.250	5.24	54
22	10.065	9.255	5.26	81
23	9.985	9.179	5.22	0
24	10.017	—		32
25	10.087	9.247	5.28	76
26	10.093	9.238		3
27	10.042	9.231		55
31	9.915	9.066	5.14	Muscovite
34	10.066	9.216		51
BeF 19	10.092	9.257		23
Be 74	10.103	9.257		35
G 43	10.095	9.251		29
BeF 14	10.096	9.254	5.26 ?	53
BH 9 3	10.095	9.260		48
E 15 4	10.097	9.251		43

[2] Lent by Professor G.J.F. MacDonald of the Department of Geology and Geophysics, Massachusetts Institute of Technology.

RELATION OF PHYSICAL PROPERTIES AND COMPOSITION TO ENVIRONMENT

Several studies have been made of the variation in composition of biotites with respect to variation in their parent rock type (Nockolds, 1947; Heinrich, 1946, 1953). A few of the more significant conclusions are outlined below.

In a study of Caledonian igneous rocks from Western Scotland, Nockolds (1947) found that in calc-alkali igneous rocks those biotites associated with highly aluminous minerals are rich in Al_2O_3, those associated with hornblende, pyroxene, or olivine are low in Al_2O_3, and those which occur alone are intermediate. He concludes that the Al/Mg+Fe ratio is determined by the paragenesis of the rock, but the Fe/Mg ratio depends on the degree of differentiation of the source magma, or upon the amount of contamination by assimilation of country rock. In other words the Al/Mg+Fe ratio reflects the environment, whereas the Fe/Mg ratio reflects the composition of the rock as a whole.

The explanation of this relationship may be as follows: Aluminum can enter into limited substitution with Mg and Fe in the octahedral positions of biotites. In aluminum-rich rocks, then, the biotites can take only part of the aluminum, and separate aluminum-rich minerals will be formed—such as muscovite, spodumene, and topaz. In aluminum-poor rocks the available aluminum will be used by biotite and the associated minerals will be non-aluminous, e.g., pyroxene, olivine, and to a certain extent amphibole. Substitution of Mg for Fe in biotites is complete, however, and the ratio of Mg to Fe in any biotite is probably close to that of the rock as a whole at the time of formation of the biotite.

Heinrich (1946) studied the relation of the chemical variation of biotites to geologic occurrence. He plotted ratios of FeO+MnO, $Fe_2O_3+TiO_2$, and

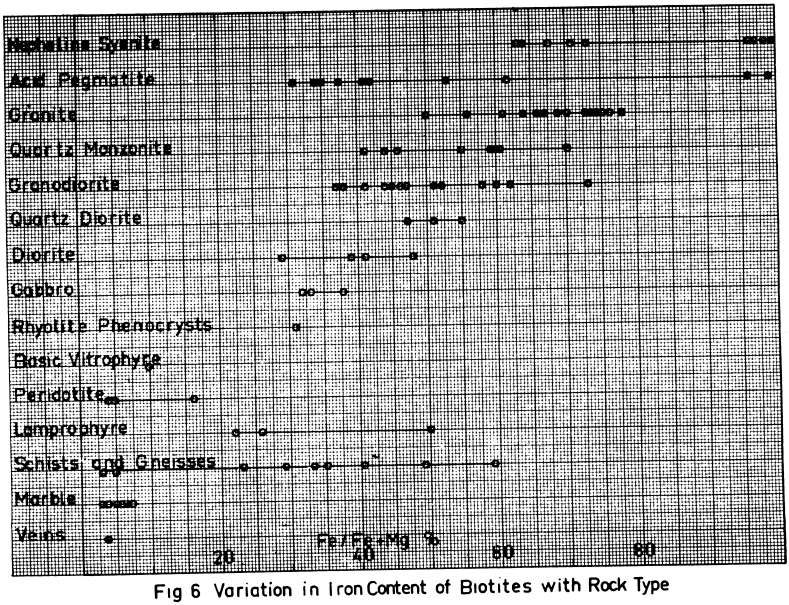


Fig 6 Variation in Iron Content of Biotites with Rock Type

MgO in biotites from eight rock types and found that the ratios fell into restricted fields. The ratio of FeO to Fe_2O_3 does not vary greatly with rock type but the ratio of total Fe to Mg varies from close to zero to a very large figure equivalent to the sequence of Bowen's fractional crystallization series.

The explanation of this may lie in the relative bonding energies of magnesium to oxygen and iron to oxygen. Because of its greater ionization potential magnesium tends to form a stronger bond with oxygen than does iron, so that magnesium silicates have in general a higher melting point than their iron analogues (Ahrens, 1953).

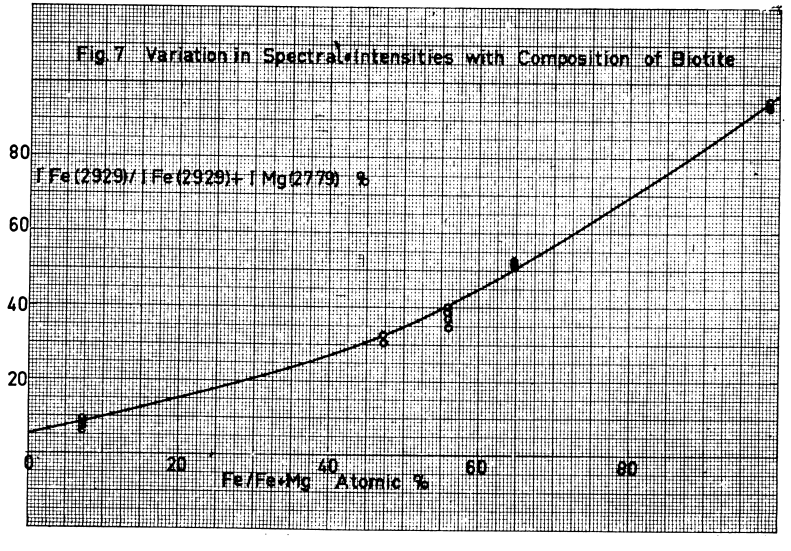
CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

The foregoing method of determining the extent of magnesium-iron substitution in biotites by X-ray diffractometry makes use of a ratio of X-ray intensities that is very sensitive to changes in the amounts of magnesium and iron and relatively insensitive to other compositional changes. The chief disadvantage of the method is that manganese, lithium, aluminum, and titanium, which may substitute in the octahedral sites, are not detected.

Careful measurements of cell dimensions indicate that these are of little value in determining composition but do show systematic changes for which explanations can be suggested.

The intensity method is rapid and reasonably accurate. It may find considerable use in studying changes in the magnesium-iron content of rocks in metamorphic zones, and in more precise classification of igneous rocks than is at present possible by petrographic methods.

Further research, using similar methods of determining iron/magnesium ratios, is recommended for other minerals. In fact the method may be applied to any solid-solution series in which the substituting elements have a large difference in atomic number (and thus in atomic scattering factor). Some of



the more obvious series are: olivines, amphiboles, pyroxenes, carbonates, chlorites, montmorillonites, epidotes, garnets, spinels, and tourmalines.

APPENDIX

Chemical analyses were available for only five of the specimens studied. These are presented in table 4. Hundreds of biotite analyses are to be found in the literature. Compilations have been made by Doelter (1917), Hall (1941a, 1941b), Heinrich (1946), and Nockolds (1947). Many of them show poor agreement with ideal structural formulae and may have been made on impure material or by inaccurate methods. One hundred of the more reliable have been plotted on a triangular diagram (fig. 5) showing ratios of Fe, Mg, and octahedral Al. The diagram shows the biotite-phlogopite field, the muscovite-ferrimuscovite-picrophengite field, and a supposel "forbidden" field. However, some biotites apparently contain enough octahedrally coordinated aluminum to invade this field. It is noteworthy that all of these are associated with aluminous minerals such as topaz, spodumene, muscovite, and beryl. The source rocks for various biotites are indicated on the plot and occupy fairly definite,

TABLE 4
Chemical Analyses

	B 23	B 13	B 19*	B 7	B 9
SiO_2	42.50%	42.19%	34.10%	33.07%	37.01%
TiO_2		0.61	4.90	3.84	0.02
Al_2O_3	12.35	12.60	16.65	16.32	15.89
Fe_2O_3	0.04	0.33	3.86	5.97	Trace
FeO		2.91	17.75	22.46	30.16
MnO		0.02	0.59		1.01
MgO	28.36	25.61	7.91	5.85	0.22
CaO	0.14	0.06	1.08	0.26	0.10
Na_2O	0.06	0.31	0.45	0.87	0.58
K_2O	10.88	9.91	7.50	7.92	9.02
Li_2O					1.01
Rb_2O					0.19
Cs_2O					0.12
F	9.30	2.66	2.04		3.88
Cl					0.24
H_2O+		2.84	3.48	3.87	1.92
H_2O-		0.33	0.47		
P_2O_5		0.13			
Ign. loss at 640° C	0.15				
	103.78	100.51	100.78	100.43	101.37
Less O for F	3.92	1.12	0.89	—	1.68
	99.86	99.39	99.89	100.43	99.69

* This specimen contains 8% chlorite ($n_Y = 1.630$, $n_Z - n_X = 0.00$) for which adjustment is made.

although overlapping, fields. A greater tolerance for octahedral aluminum is indicated in iron-rich varieties. To show the iron-magnesium ratios directly the data are also presented in a more simplified plot (fig. 6) showing the range in iron-magnesium ratios for biotites of each major rock type.

The desirability of determining the iron-magnesium ratio is clearly shown. Each rock type contains biotites of limited compositional range. It is important to know not only that the biotite composition falls in the range given but also what the composition is in terms of iron and magnesium. Mineral association and optics will indicate unusual enrichments of rare alkalies, fluorine, and aluminum but will not give iron and magnesium content. The X-ray intensity method does this satisfactorily enough to be of some use in petrologic studies.

List of Specimens

B1 Biotite from granite, Chester, Nova Scotia.
B2 Biotite from gabbro, Tahawus, New York.
B3 Biotite from Capilano quartz diorite, Vancouver, B.C.
B7 Biotite from Miask, Ural Mountains.
B8 Phlogopite, Hadderspell Twp, Quebec.
B9 Siderophyllite, Brooks Mountain, Alaska.
B11 Biotite from alnoite, Storanset, Alno, Sweden.
B12 Biotite, unknown.
B13 Phlogopite, west of Dent, Clearwater County, Idaho (U.S.G.S., A. Hietanen, personal communication).
B14 Biotite, associated with wohlerite, Brevig, Norway.
B15 Biotite, Renfrew, Ontario.
B16 Biotite, Asbestos mine southwest of Mt. Lincoln, Belchertown, Mass.
B18 Phlogopite, Burgess, Ontario.
B19 Biotite from "G 1" granite, Westerly, Rhode Island.
B20 Biotite from granite, Brattleboro Quadrangle, Vermont.
B21 Biotite from granite, West Nictaux, Nova Scotia.
B22 Biotite from granite, Albany Cross, Nova Scotia.
B23 Synthetic fluor-phlogopite, Electrotechnical Laboratory, Norris, Tennessee (R. A. Hatch, personal communication).
B24 Biotite, Kings Mountain, North Carolina (ref. Hess and Stevens, 1937, p. 1045).
B25 Biotite from Nordmarkite (?), Brome Mountain Quarry, Iron Hill Road, Quebec.
B26 Phlogopite from dolomite, Simplon Tunnel (ref. Jakob, 1928, p. 219).
B27 Biotite from essexite, Mt. Johnson, Quebec.
B28 Synthetic phlogopite from Geophysical Laboratory, Washington (950°C, 15,000 lb/in^2 water vapor pressure, 5 hrs.) (ref. Yoder and Eugster, 1954, p. 157).
B31 Muscovite—labeled annite from Cape Ann granite, Rockport, Mass.
B32 Biotite from syenite, Kingston Mills, Ontario.
B33 Biotite from foot of Mt. Megantic, Quebec.
B34 Phlogopite, Sebastopol, Ontario.

Metamorphic Biotites from Vermont

BeF 19 With garnet, staurolite (with chlorite alteration), quartz.
Be 7 4 With kyanite, staurolite, chlorite.
G 4 3 Chlorite-biotite.
BeF 14 Biotite porphyroblasts with chlorite rims, quartz, muscovite, and paragonite.
BH 9 3 Garnet zone—with orthoclase.
E 15 4 Garnet zone—no feldspar.

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