

A POWDER X-RAY DIFFRACTOMETER STUDY
OF THE PHLOGOPITE-BIOTITE SERIES

by

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B.A.Sc., University of British Columbia
(1950)

M.A.Sc., University of British Columbia
(1952)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF
PHILOSOPHY
at the
MASSACHUSETTS INSTITUTE OF
TECHNOLOGY
June, 1955

Signature of Author
Department of Geology and Geophysics, May 16, 1955

Certified by
Thesis Supervisor

Accepted by
Chairman, Departmental Committee on Graduate Students

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Submitted to the Department of Geology and Geophysics
on May 16, 1955 in partial fulfillment of the
requirements for the degree of Doctor of Philosophy.

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% 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 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_0 . Tetrahedrally coordinated Al may cause a slight increase. In metamorphic biotites c_0 is larger than in igneous ones. The b_0 parameter shows little or no change with iron content but is smaller in fluorine-rich specimens. The a_0 parameter seems to show about the same variation as b_0 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.

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PART I. A Powder X-Ray Diffractometer Method
of Determination of the Iron-Magnesium Ratio in the
Phlogopite-Biotite Series

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 ferromagnesian 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, e.g., Hess (1952), where the iron content has been 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 (1941). The triangular plot of FeO, MgO, and TiO₂ 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 (1941a). Hall's plot of refractive index (δ) 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 and 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 .022. This value is about half of the change in γ produced by complete substitution of iron for magnesium.

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 (Brindley, editor, 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, 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). The procedure used is outlined in the Appendix. It was hoped that a situation exists where iron and magnesium make a large contribution to intensity in one reflection and practically

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 F 4.0 O	.12	40.9	3.1	-27.2	-35.7	-24.5	-4.8	11.7
	3.0 Si 1.03 Al	.28	-7.4	36.5	20.5	26.6	-28.0	-13.9	29.5
	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
	$F_{\text{calc}} \%$		8.0	-4.0	22.8	4.4	-24.5	18.0	18.3
	$ F_{\text{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 ⁺² 0.02 Fe ⁺³ 0.03 Ti	0	32.4	31.8	29.9	27.8	25.6	23.5	21.3
	1.5 OH 0.5 F 4.0 O	.12	40.0	3.0	-26.2	-33.4	-22.7	-4.3	10.5
	2.97 Si 0.95 Al 0.08 P	.28	-7.5	-36.1	20.4	26.5	-28.1	-13.8	29.3
	6.0 O	.34	-29.3	-20.5	40.5	-21.0	-8.5	22.0	-14.0
	0.9 K 0.04 Na	.5	-16.05	15.25	-13.7	12.3	-12.1	10.0	-8.9
	Total		19.6	-6.6	58.9	12.2	-45.8	37.4	38.2
	$F_{\text{calc}} \%$		9.0	-3.0	26.9	5.6	-20.9	17.1	17.5
	$ F_{\text{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

No.	<u>z</u>	001	002	003	004	005	006	007	
B19	0.9 Mg 1.15 Fe 0.03 Mn 0.2 Fe 0.3 Ti 0.3 Al	0	49.4	47.7	44.7	40.8	37.1	33.9	31.3
	1.8 OH 0.5 F 3.7 O	.12	39.8	3.0	-26.3	-33.4	-22.8	-4.4	10.5
	2.6 Si 1.4 Al	.28	-7.4	-36.0	20.5	26.4	-27.6	-13.7	29.1
	6.0 O	.34	-29.3	-20.5	40.4	-21.0	-8.5	22.1	-14.0
	0.74 K 0.06 Na 0.09 Ca	.50	-15.1	14.3	-12.9	11.7	-10.5	9.4	-8.7
	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
	F		4.5	0.4	6.0	3.7	4.6	3.6	3.6
B 7	0.68 Mg 1.46 Fe ⁺² 0.355 Fe 0.225 Ti 0.07 Al	0	53.87	52.06	48.56	44.22	40.13	36.48	33.32
	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 0.7535 K	.5	-14.82	14.06	-12.7	11.42	-11.17	9.3	-8.34
	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
	Δ F		6.5	0.9	0.1	4.0	6.4	2.4	5.5

No.	<u>z</u>	001	002	003	004	005	006	007
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	.12	41.0	3.1	-26.8	-35.1	-24.4	- 4.7	11.5
4.0 O								
3.0 Si	.28	- 7.4	-36.0	20.3	26.5	-27.8	-13.8	29.3
1.0 Al								
6.0 O	.34	-29.5	-20.5	39.9	-21.0	- 8.7	22.7	-14.4
0.925 K	.5	-16.9	16.2	-14.6	13.0	-11.8	10.6	- 9.5
0.09 Na								
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
F _{obs} %		8.5	2.5	26.7	14.5	15.5	20.5	15.3
Δ F		7.0	2.8	3.5	4.7	4.8	2.5	2.2

none in another. Such is not the case. Although the contribution to intensity increases greatly with increase in iron content, the contributions to various $00l$ 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 for substitution of Mg by Fe 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 (\underline{F} 's) of (004) to (005) against atomic proportion of iron $\left[100 \times \left(\frac{\text{Fe}}{\text{Mg}+\text{Fe}+\text{Al}}\right)\right]$. A line drawn through the points representing the analyzed specimens is straight. This is to be expected because \underline{F} is a summation, one of whose terms contains the scattering factor (\underline{f}). The second curve (Fig. 2) shows the ratio of uncorrected intensities for FeK radiation against molecular % of Fe, as above. This form is more readily used but because of a shift in glancing angles with compositions is less accurate than Fig. 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 ($\underline{f} \approx \underline{f}$ for Fe) tend to cancel those of Al and Li ($\underline{f} \approx \underline{f}$ for Mg), and inasmuch 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 1/2" 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 labelling the specimen and ease in removal if the mount is to be reversed in the goniometer. 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 $1/8^{\circ}$ 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% is obtainable by three 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. 4). 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 (see discussion of spectrographic techniques in the Appendix). X-ray determinations on specimens from localities where similar material had been analyzed also gave satisfactory agreement (e.g. Specimens B 18, B 26, B 7).

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}) and b are given in Table 2 and Fig. 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

Table 2. $\underline{c}_0 \sin \beta$, \underline{b}_0 , and \underline{a}_0 for Biotites

Spec. No.	$\underline{c} \sin \beta$	\underline{b}_0	\underline{a}_0	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	9.239		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

Spec. No.	<u>c</u> sin β	<u>b</u> .	<u>a</u> .	Fe/Fe+Mg+Al
BeF 19	10.092 \AA ^o	9.257 \AA ^o		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

because the ionic radius of Fe^{+2} ($.74 \text{ \AA}$, Ahrens, 1952) is larger than that of Mg^{+2} ($.67 \text{ \AA}$). 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*, 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.

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 \AA (see Fig. 4) and a rough measure of F content may be made as indicated in Fig. 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 $c \sin$ but lacking analyzed material positive tests could not be made.

A test on metamorphic biotites from Vermont** 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

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

**Loaned by Professor G.J.F. MacDonald of the Department of Geology and Geophysics, Massachusetts Institute of Technology.

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.

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 and 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 that of the rock magma 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 $\text{FeO}+\text{MnO}$, $\text{Fe}_2\text{O}_3+\text{TiO}_2$, and 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.

PART II. Appendix

Review of the Literature

In a recent publication Heinrich et al (1953) have made a thorough review of the literature on biotites and the reader is referred to this work for complete information. A 13-page bibliography is given which includes most of the important papers up to 1952. The form used by Heinrich et al will be followed here in order that the interested reader may more easily investigate features of the work not described here in detail. Heinrich's project on the natural history of micas was for the purpose of investigating physical properties, crystal structure and composition of natural micas as related to geological occurrence and genesis.

Micas are important both economically and petrologically. Their wide distribution and their mode of occurrence render them of great use in establishing the environment in which they and their parent rock originated.

The structure of micas was first studied using x-rays by Mauguin (1927, 1928a, b), who determined their unit cells and symmetry and discussed isomorphous replacement. He calculated the cell contents and found that the number of oxygen, hydroxyl, and fluorine atoms always totals twelve in the structural unit.

Pauling (1930) outlined the general structural scheme of micas, in particular the sequence of basal layers.

Jackson and West (1930, 1933) in their structural analysis showed this scheme to be correct.

Details of the mica structure may be found in many papers and textbooks (Bragg, 1937; Evans, 1948; Wells, 1950; Hendricks and Jefferson, 1939). The basic structural unit is the grouping of SiO_4 tetrahedra by sharing three oxygen atoms to form a continuous hexagonal sheet. In most micas one-quarter or more of the silicon is replaced by aluminum giving a sheet with the composition $(\text{Si}_3\text{AlO}_{10})^{-5}$. These sheets are paired, with the vertices of the tetrahedra pointing toward each other and offset one-half the diameter of a tetrahedron. Octahedrally coordinated magnesium, iron, and aluminum atoms link the tetrahedral sheets. The holes between adjacent oxygen atoms at the vertices of the tetrahedra are occupied by OH groups or by F atoms. The structure forms a tightly bound double sheet which is linked to the next sheet by loosely held potassium or sodium in twelve-fold coordination. These planes mark the eminent basal cleavage.

The general formula for mica according to Berman (1937) is



where W = K with subordinate Na, Ba, Ca,

X = Mg, Fe^{+2} , Mn^{+2} , Li

Y = Al, Fe^{+3} , Ti (subordinate)

Z = Si/Al 5/3 to 7/1.

The atoms represented by W have twelve-fold coordination, those represented by X and Y have octahedral (six-fold) coordination, those represented by Z have tetrahedral (four-fold) coordination. Table 3 gives a schematic representation of the various types of mica.

Polymorphism in the micas was first noted by Mauguin who found the c axis of biotite half that of muscovite. Hendricks and Jefferson gave a complete account of the polymorphic variations of which they found seven. Axelrod and Grimaldi (1949) found another polymorph (3-layer monoclinic muscovite) and Levinson (1953) described a new variation named by him "lithian muscovite".

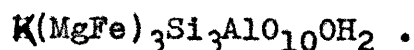
Heinrich's x-ray work consisted mainly of identifying different polymorphs of mica by means of 0-level Weissenberg photographs. Powder methods were used only where crystal development was poor, crystals were minute, or extinctions were poor. Polymorphs of phlogopite and biotite cannot, according to Heinrich, be distinguished by the powder method.

The classification of micas is a large topic and is described by Heinrich in detail. The historical development of classifications is outlined and a classification is given based on chemistry and structure. The species of mica are muscovite, paragonite, roscollite, lepidolite, taeniolite, zinnwaldite, phlogopite, and biotite, of which for this study only phlogopite and biotite need be considered.

TABLE 3
COMPOSITION OF MICAS

TALC		Mg	Mg	Mg	Si	Si	Si	Si	O ₁₀	OH ₂
PHLOGOPITE	K	Mg	Mg	Mg	Si	Si	Si	Al	O ₁₀	OH ₂ ^{1/2} (F)
PHLOGOPITE - BIOTITE	K,Na	MgFe	MgFe	FeAl	Si	Si	Si+Al	Al	O ₁₀	OH ₂
SIDEROPHYLLITE	K	Fe	Fe	Al	Si	Si	Si+Al	Al	O ₁₀	OH ₂
PYROPHYLLITE		Al	Al		Si	Si	Si	Si	O ₁₀	OH ₂
MUSCOVITE (PARAGONITE)	K(Na)	Al	Al		Si	Si	Si	Al	O ₁₀	OH ₂
MUSCOVITE - PHENGITE	K,Na	AlMgFe	AlMgFe		Si	Si	Si	Al+Si	O ₁₀	OH ₂
POLYLITHIONITE - PROTOLITHIONITE	K,Rb	LiFe	LiFe	AlLi	Si	Si	Si	Si+Al	O ₁₀	F ₂
MARGARITE	Ca	Al	Al		Si	Si	Al	Al	O ₁₀	OH ₂
CLINTONITE	Ca	Mg	Mg	Mg+Al	Si	Si+Al	Al	Al	O ₁₀	OH ₂

Phlogopite has the formula

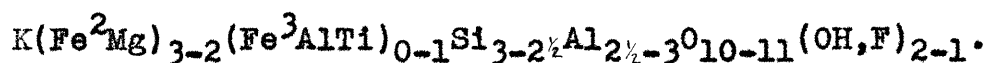


Sodium can substitute for K up to nearly $K/Na = 1/1$ (Harada, 1936); and minor Rb, Cs, Ba, and Ca may also proxy for K. In the octahedral position Mg^{+2} greatly predominates but Fe^{+2} and small amounts of Mn, Fe^{+3} , and Ti may be present. Very few phlogopites contain any octahedral Al.

The Si/Al ratio is 6/2 or greater. There is no compositional boundary between ferroan phlogopite and magnesian biotite. If a division is required Heinrich suggests that where the ratio of Mg/Fe is greater than 4/2 the mineral should be classed as a phlogopite. The following are synonyms for phlogopite: aspidolite, hydrophlogopite, magnesia mica, octophyllite, pholidolite, and rhombic mica.

One-layer monoclinic (1 M) phlogopite is the most common type. Others are: two-layer monoclinic (2 M), and three-layer hexagonal (3 H). Varieties of phlogopite, in addition to the three polymorphs are: manganophyllite and titanian phlogopite.

Biotite has the general formula



Some Na, Ca, Ba, Rb, and Cs may substitute for K. Manganese substitutes for some Fe^2 , F for OH, and Mg may be almost absent. Total F and OH may be very low (Walker and Parsons, 1926). Synonyms for biotite are: annite, euchlorite, haughtonite,

heterophyllite, hexagonal mica, iron mica, lepidomelane, meroxene, odenite (or odinite, odite, oderite), rhombenglimmer, titanmica, uniaxial mica, and waddoite. Hypothetical end members are: eastonite - $K_2Mg_5Al_4Si_5O_{20}(OH)_4$, annite - (hydroxy and fluor) $KFe_3AlSi_3O_{10}(OH,F)_2$, siderophyllite - (hydroxy and fluor) $KFe_3^2(Al,Fe^3)Si_3O_{10}(OH,F)_2$

The most common polymorph of biotite is the one-layer monoclinic (1 M) type. Others are: two-layer monoclinic (2 M), three-layer hexagonal (3 H), six-layer triclinic (6 T) probably 1 M or 2 M, twenty-four-layer triclinic (24 T), and eighteen-layer triclinic (18 T). In addition to the above polymorphs the following varieties are listed: calcian biotite (14.3% CaO), validity doubtful, manganian biotite, ferroan and ferrian biotite, lithian biotite, and titanian biotite.

Heinrich found, in a study of 80 phlogopite crystals by the Weissenberg method, that 75 have a one-layer monoclinic structure, three have the two-layer monoclinic, and two the three-layer hexagonal polymorph. He attempted to correlate polymorphism with paragenesis of both phlogopites and biotites but found no evident relationship.

New structural data are given for several biotites. Neither the 6-layer nor the 24-layer triclinic forms were found. A study of 80 pegmatitic biotites from 15 pegmatites in the southeastern United States shows that about 50 have crystallized as the 2-layer monoclinic polymorph, 15 as the 3-layer hexagonal polymorph, but only 1 as the 1-layer

monoclinic polymorph. Biotites from Bancroft and the Wilberforce district in Ontario are predominantly 1-layer forms as are most other biotites.

The optical properties for phlogopite are given as follows:

Refractive indices:

$$\alpha = 1.530 - 1.573$$

$$\beta = 1.557 - 1.617$$

$$\gamma = 1.558 - 1.618$$

Birefringence:

$$\gamma - \alpha = 0.028 - 0.049$$

$$2v = 0 - 12, \text{ optically } \ominus$$

Dispersion: $r < v$ weak to distinct

$$x \wedge c = 0^\circ - 4^\circ \quad y = b \quad z \wedge a = 0^\circ - 5^\circ$$

Optic plane \parallel to (010); \perp to (010) only in 2-layer forms (rare).

Indices and birefringences increase with Fe^{+2} and Mn content, but change more rapidly for similar increments of Ti and Fe^{+3} . Titaniferous phlogopites have indices as high as $\alpha = 1.599$, $\gamma = 1.643$.

Color varies from colorless to nearly black. The depth of color increases with an increase of Fe^{+2} and particularly with increasing Fe^{+3} and Ti. The latter is at least partially responsible for the reddish tints of some phlogopites.

Asterism in phlogopite is caused principally by rutile inclusions oriented along the principal crystallographic directions. The inclusions may be randomly or zonally distributed. Color zoning has been observed and may be progressive or oscillatory. Most zoned phlogopite tends to be darker in the core and to contain more rutile inclusions.

The optical properties of biotite are:

Refractive indices:

$$\alpha = 1.565 - 1.625$$

$$\beta = 1.605 - 1.675$$

$$\gamma = 1.605 - 1.675$$

Birefringence:

$$\gamma - \alpha = 0.040 - 0.060$$

$$2v = 0 - 25^\circ, \text{ optically } \ominus$$

Dispersion: $r > v$ or $r < v$

$$x \wedge c = 8^\circ - -2^\circ \quad y = b \quad z \wedge a = 0^\circ - 9^\circ$$

Optical plane \parallel to (010), less commonly

(only in 2-layer polymorphs) \perp to (010).

Indices vary as described for phlogopite. In some rare ferrian biotites γ may reach 1.73 and $\gamma - \alpha = 0.80$.

Color varies from green to brown to reddish-brown to black. Titanium, ferric oxide, and manganese produce reddish-brown to black color, ferrous oxide a blue-green color.

Zoning has been observed, but perhaps because of the darker colors has been less widely recognized than zoning

in other micas. Pegmatitic biotites examined show no zoning, and after studying over 100 specimens Heinrich concludes that zoning in biotite is very uncommon.

Igneous phlogopite occurs in ultramafic rocks, in lamprophyres, in potassic rocks, and in a few rare extrusive rocks. Metamorphic phlogopite occurs in marbles and magnesium-rich gneisses. Hydrothermal phlogopite occurs in veins with apatite and calcite in pegmatite and pyroxenite in Quebec and Ontario.

Biotite occurs in most intrusive rocks and is most abundant in the salic types. It may be primary or deuteric; in the latter case from the action of late fluids on hornblende, augite, or magnetite. Biotite phenocrysts are widespread in intermediate to salic extrusives. In metamorphic rocks biotite is a stable mineral over a broad pressure-temperature range over a wide range of rock composition.

Heinrich has shown by means of a triangular plot a systematic variation of composition of biotites according to source rock composition, which is chiefly an enrichment in iron towards the more salic rocks. Chapman and Williams (1935) have observed that in the transition from gabbro to granite biotite will show a decrease in Si, Ti, Al, and particularly Mg with a corresponding increase in Fe. Inoue (1950) reports a similar variation for nepheline syenite and nepheline pegmatite, as well as an enrichment of Mn in biotites of nepheline syenites. In a complex ranging in composition from pyroxene-mica diorite to porphyritic grano-

diorite, Nockolds and Mitchell (1948) find that the biotites show a progressive decrease in Si, Ti, and Mg and an increase in Al, Fe^{+3} , and Fe^{+2} on progressing from the diorite to the granodiorite. The trace elements Ga, Mn, and Rb increase in late biotites, whereas Cr, V, Cu, Ni, Co, and Sr decrease. Barium remains constant in early biotites and decreases in the late stages; Li increases rapidly in the early biotites and later remains about constant.

The position of Ti in the biotite structure is not known although Serdiuchenko (1948) in a discussion of its role concludes that at low temperature and in an acid medium, Ti proxies for Mg, whereas at high temperature, and in a more alkaline medium Ti may proxy for Si. Jakob (1937) maintains, however, that Ti is not found in the tetrahedral positions. Prider (1940) discusses a titaniferous phlogopite in which some of the Ti must be grouped with Si and Al to fill the tetrahedral positions. Machatschki (1930) states that Ti may not replace Si at low temperature, because of the difference in ionic radius, but may at high although there appears to be a great tendency for titanium oxides to exsolve. As Bragg (1937) points out it seems unlikely that, as Ti in other minerals shows octahedral coordination exclusively, it should be tetrahedrally coordinated in micas.

Obviously the problem is not solved. Serdiuchenko's conclusions may not be valid if the tetrahedral sites do not have to be completely filled or if the analyses he used are inaccurate.

An important paper by Nockolds (1947) describes a trend of variation in chemical composition in mica with respect to variation in rock type which was discerned as a result of a study of Caledonian igneous rocks from western Scotland.

The changes in chemical composition were plotted on triangular diagrams using Al_2O_3 , MgO , and total iron as FeO as the apices. Of all the analyses available only about 70 were used, the rest being discarded for any of the following reasons:

(1) Many old analyses and even some modern ones made on impure material do not conform to the structural formula of the mica group.

(2) Many analyses were made by inaccurate methods giving results not in conformity with the mica structure.

(3) In many instances no mention was made of the associated minerals or of the mode of origin of the rock.

(4) In many analyses F is not given.

1. Biotites from Calc-Alkali Igneous Rocks.

Those associated with highly aluminous minerals are rich in Al_2O_3 (e.g., muscovite, topaz, spodumene).

Those associated with hornblende, pyroxene, or olivine are low in Al_2O_3 .

Those which occur alone are intermediate.

The boundary lines are roughly parallel to lines of equal alumina content and the conclusion is reached that the ratio $\text{Al}/\text{Mg}+\text{Fe}$ in biotites from calc-alkalic igneous rocks is determined by their paragenesis whereas the Fe/Mg ratio depends not on paragenesis but on the degree of differentiation in the rock magma from which it formed, or upon the amount of contamination of the magma by assimilation of country rock.

In other words, the $\text{Al}/\text{Mg}+\text{Fe}$ ratio mirrors the environment, Fe/Mg the composition of the rock as a whole. Thus the $\text{Al}/\text{Mg}+\text{Fe}$ ratio gives information about the texture, paragenesis, mode of origin and presence or absence of certain other minerals, whereas the Fe/Mg ratio gives information about the rock composition, the extent of differentiation, the possibility of contamination, the probable composition of other ferromagnesian minerals, and the probable temperature of crystallization. These ratios, of course, must be used in connection with other petrologic data but may be of considerable assistance in the study of both igneous and metamorphic rocks.

A further classification of rocks may be made using the Mg/Fe ratio in biotites just as the Na/Ca ratio is used in feldspars.

Nockolds considered each paragenesis in turn,
i.e., association with topaz and spodumene,
association with muscovite,
biotite occurring alone,

association with hornblende,
 association with pyroxene and/or olivine.

A graph of the variation in metal content in various positions in the biotite structure shows significant changes only in Al (octahedral), Mg, and Fe. The Al content in the octahedral site increases steadily as the paragenetic sequence proceeds from mafic to salic environments.

The Fe/Mg ratio shows greatest variation but Nockolds states that this variation depends not on paragenesis but on the extent of differentiation in the rock. (If biotite occurs alone or with muscovite the rock is more highly differentiated than if it is associated with hornblende or pyroxene.)

In paragenesis (1) (associated with topaz etc.), the silica to alumina ratio in the tetrahedral position is much higher (a very siliceous melt, i.e., pegmatitic stage). For the same reason the Fe/Mg ratio is greatly increased. This is no doubt related to impoverishment of Mg in the magma by crystallization of magnesium-rich minerals.

2. Biotite Micas from Alkali Igneous Rocks.

Very few analyses were available for this phase of Nockolds' study. The results are similar to those in calc-alkaline rocks but are not so well defined. Aluminum increases in lower-temperature rocks. This may be due to the fact that the composition of the rocks does not reflect this temperature change because the rocks already represent extreme

differentiation or extreme contamination. It is noted that the Mg content is not high except in the case labelled P by Nockolds. This is biotite from Fitzroyite of Western Australia. This rock, although it contains no mafics except biotite, does show pseudomorphs of olivine and minor diopside and thus must have been high in magnesia originally.

Nockolds' Table V shows extremely erratic Fe/Mg ratios for different mineral associations. Nepheline syenite may form at least in some instances by contamination of a magma by limestones or other silica deficient rocks. Quite possibly those biotites high in magnesium were formed in nepheline syenites rich in magnesium by contamination from dolomites rather than limestones and the biotite merely reflects the Mg/Fe ratio in the nepheline syenite as a whole.

Previous attempts have been made to distinguish micas on the basis of x-ray data. These are described in detail by Brown (Brindley, editor, 1951). Isomorphous replacement may alter both the unit cell dimensions and the reflection intensities. According to Brown the only reflections of known relationship to structure are the (001) series and the (060) reflection. Intensity calculations can be made only for the (001) series because of the effect on the other reflections of different polymorphs.

Isomorphous replacements occur between Si and Al in the tetrahedral layers, among Al, Mg, Fe⁺², Fe⁺³, Ti, and Li in the octahedral (also K, Na, Ba, Ca, Rb, Cs in K layer) and among F, OH, O in OH layer.

Nagelschmidt (1937) distinguished two main types, the muscovite type and the phlogopite-biotite type. The b dimension of the unit cell for muscovite is given by Bragg (1937) as 9.02. This gives a spacing of 1.503 for (060) compared to 1.53 to 1.55 for phlogopite-biotite (a b distance of 9.18 to 9.30).

Brown derived a formula for the calculation of the b axis from the chemical constitution of a mica, and has made calculations of the intensities of basal reflections for various substitutions. The substitution of 3Mg^{+2} for 2Al^{+3} increases b₀ from 8.90 (for pyrophyllite) to 9.10 (for talc). Assuming increase per ion to be linear and proportional to the ionic diameter, the following table can be constructed which gives the effect of substituting each ion for one Al^{+3} in the octahedral layer:

<u>Ion</u>	<u>Increase per ion (kX units)</u>
Mg^{+2}	.066
Li^{+}	.066
Fe^{+3}	.032
Fe^{+2}	.083
Ti^{+4}	.022

Brown finds better correlation by treating all iron as Fe^{+2} and Li as Al. His formula is $\underline{b}_0 = (8.90 + 0.12 \text{Al}^{3+ \text{ IV}} + .066 \text{Mg}^{2+ \text{ VI}} + .083 \text{Fe}^{\text{VI}} + 0.022 \text{Ti}^{4+ \text{ VI}} \text{ kX})$ where $\text{Al}^{3+ \text{ IV}} =$ number of Al^{3+} ions in tetrahedral coordination,

$Mg^{2+ VI}$ = number of Mg^{2+} ions in octahedral coordination,
 Fe^{VI} = number of iron ions in octahedral coordination,
 $Ti^{4+ VI}$ = number of Ti^{4+} ions in octahedral coordination.

In calculating basal intensities, Brown found that the substitution of Al^{+3} for Si^{+4} makes very little difference, and only those in the octahedral make a large difference. Li^+ and Ti^{+4} rarely occur in quantity and are omitted from the calculations. Al^{+3} and Mg^{+2} have similar scattering curves as have Fe^{+3} , Fe^{+2} , and Mn.

Brown proposed that a guess at the content of the octahedral layer could be made by comparing calculated and observed values of intensity. He recommended that for dioctahedral micas the second-order reflection be compared with the first and third, and that for trioctahedral micas, the third and fifth should be compared. In the first case aluminous muscovites will have a second-order reflection of about the same strength as the first and third and iron muscovites a weaker second-order reflection. Magnesian biotites will have third- and fifth-order reflections of the same intensity but iron biotites will have a stronger third order than fifth order.

As shown in the body of this report these principles are not violated by the present study but are so amended that it is best not to make use of the graphs as given by Brown.

Analytical Data

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, b), Heinrich (1946), and Nockolds (1948). 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 supposed "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, 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

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 ₂ O ₃	12.35	12.60	16.65	16.32	15.89
Fe ₂ O 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 ₂ O	0.06	0.31	0.45	0.87	0.58
K ₂ O	10.88	9.91	7.50	7.92	9.02
Li ₂ O					1.01
Rb ₂ O					0.19
Cs ₂ O					0.12
F	9.30	2.66	2.04		3.88
Cl					0.24
H ₂ O+		2.84	3.48	3.87	1.92
H ₂ O-		0.33	0.47		
P ₂ O ₅		0.13			
Ign. loss at 640° C	<u>0.15</u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
	103.78	100.51	100.78	100.43	101.37
Less O for F	<u>3.92</u>	<u>1.12</u>	<u>0.89</u>	<u>--</u>	<u>1.68</u>
	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.

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.

Spectrographic Techniques

To supplement chemically analyzed material as a check on the x-ray method six specimens were analyzed spectrochemically for iron and magnesium. The working curve (Fig. 5) uses the ratio of intensities of the iron line at 2929 Å to the sum of the magnesium line at 2779 Å and the same iron line. This ratio is plotted against the atomic ratio of iron to magnesium plus iron. The curve was set up using three chemically analyzed specimens of which enough material was available. The spread of points is about the same as for the x-ray method if all trials are taken into account. However, if results of poor burns, which are generally a long way from the average value, are omitted, precision is increased to $\pm 5\%$. At least three and preferably six arcings were necessary to be sure of the correct average value. The chief cause of inaccuracies is thought to be the nature of the burn, and considerable attention was devoted to

improving its characteristics. In the early stages of the work an internal standard consisting of a mixture in the ratio of 1:2 of calcium carbonate and carbon was used. In spite of preheating the electrodes, the burn was erratic and not infrequently the entire sample jumped out of the electrode shortly after arcing started. Omitting the internal standard improved the burn somewhat but much greater success was attained by the use of an air jet (Stallwood, 1954). A slightly revised model (Stallwood, personal communication) was built in the Geology Shop and installed on a medium Hilger spectrograph. The Institute's compressed air supply was used with a large carboy serving as a water-settling tank and receiver. Pressures were measured on a mercury manometer. The jet was held in place by a laboratory clamp which was attached to the electrode support of the spectrograph by a converted flood-lamp holder. This gave freedom of movement of the jet for ease in adjustment and also insured that once adjusted the jet was moved with the electrode system. Although Stallwood recommended an air pressure equivalent to 6 inches of mercury, this was found to be excessive. Three and a half to four inches appears to be sufficient to cool the lower electrode without causing loss of sample by too strong an air current.

As a final attempt to improve the burn, tests were made using fused borax as a diluent. This appeared to reduce the number of sample losses by "popping". Precision was not greatly affected.

The following arcing conditions were used: quartz optics over a wavelength range of 2600-4100 Å, slit height 12 mm., slit width 0.06 mm., Eastman Kodak 1-N plates, a 7-step rotating sector - steps 1:2:4:8:16:32:64, 1/8 inch diameter impure graphite electrodes with a 1 mm. diameter and 3 mm. deep cavity, and anode excitation 6 amp. current arced to completion (20-25 seconds). The analysis lines are Fe 2929 and Mg 2779. This procedure which was developed by Dennen and Fowler (1954) is applicable to the following major elements in rocks and minerals: Al, Mn, Si, Ti, Ca, Na, K, Fe, and Mg. The procedure has the advantage that sensitive lines of all of these elements as well as some less common elements all appear on one plate.

Crystal-Structure Analysis

A brief note on crystal-structure analysis procedure is included to aid in future work along the lines established here.

In order to select a pair of reflections useful for determination of change in composition of an isomorphous mineral series, it is necessary to have a rough idea of the crystal structure and of the contributions to various reflections by each atom of the structure. Several works are devoted to crystal-structure analysis or contain useful information on the subject and the reader is directed to them for complete

information: (see Lipson and Cochran (1953), Lonsdale (1936 and 1948), Buerger (1942), Henry, Lipson, and Wooster (1951), Bijvoet, Kolkmeier, and MacGillavry (1951), and Bragg (1937).)

Atomic parameters for micas are given by Jackson and West (1930) and by Hendricks (1939). Hendricks' values for biotite have been used in the calculation of structure amplitudes (see Table 1 and Fig. 3). Although complete agreement is not shown, the structure is roughly correct so that the contribution to any basal reflection by each atom can be determined.

An example of the calculation process is given in Table 5. All multiplication was performed by slide rule which gives only three-place accuracy. This does not matter in this study, nor does it matter that the values for F_{obs} and F_{calc} show poor agreement. The important feature is that the calculation of F for each group of like atoms shows their contribution to intensity of x-ray reflections of any set of planes considered. The best possible choice of planes can then be made for the determination of composition of an isomorphous series. The procedure for calculation of structure amplitudes is in the general case long and tedious. The structure amplitude (F), or as it is sometimes termed, the "structure factor", may be obtained as the sum of the contributions of the atoms in the unit cell given by the equation

Table 5. Structure Amplitudes for Basal Reflections

Specimen B23 - Synthetic Fluorophlogopite,



<u>00l</u>	Atoms	<u>z</u>	<u>f</u>	<u>nf</u>	cos 2 <u>lz</u>	<u>F(+)</u>	<u>F(-)</u>	<u> F_{calc} %</u>	<u> F_{obs} %</u>
001	3.0 Mg	0	10	30	1	30			
	2.08 F	.12	9.5	19.8	.729	14.2			
	4.0 O	.12	9.3	37.2	.729	26.7			
	3.0 Si	.28	9.9	29.7	-.187		5.5		
	1.03 Al	.28	9.9	10.2	-.187		1.9		
	6.0 O	.34	9.3	55.8	-.536		29.9		
	1.0 K	.5	17.4	17.4	- 1		17.4		
						<u>70.9</u>	<u>54.7</u>		
						16.2		8.05	5.25
002			9.8	29.3	1	29.3			
			8.7	18.2	.063	1.1			
			8.0	32.0	.063	2.0			
			9.7	29.1	-.930		27.2		
			9.7	10.0	-.930		9.3		
			8.0	48.0	-.426		20.5		
			16.5	16.5	1	<u>16.5</u>			
						<u>48.9</u>	<u>57.0</u>		
								8.1	4.0
									2.5
003			9.2	27.5	1	27.5			
			7.7	16.0	-.637		10.2		
			6.7	26.8	-.637		17.0		
			9.5	28.5	.536	15.3			
			9.4	9.7	.536	5.2			
			6.7	40.2	.992	39.9			
			14.9	14.9	- 1		14.9		
						<u>87.9</u>	<u>42.1</u>		
						45.8		22.8	20.6

001	Atoms	<u>z</u>	<u>f</u>	<u>nf</u>	cos 2 <u>lz</u>	<u>F(+)</u>	<u>F(-)</u>	<u> F_{calc} %</u>	<u> F_{obs} %</u>
004	3.0 Mg	0	8.6	25.7	1	25.7			
	2.08 F	.12	6.7	14.0	-.992		13.9		
	4.0 O	.12	5.5	22.0	-.992		21.8		
	3.0 Si	.28	9.15	27.4	.729	20.0			
	1.03 Al	.28	8.9	9.1	.729	6.6			
	6.0 O	.34	5.5	33.0	-.637		21.0		
	1.0 K	.5	13.25	13.25	1	<u>13.25</u>			
						<u>65.55</u>	<u>56.7</u>		
						8.85		4.4	11.0
005			7.9	23.6	1	23.6			
			5.7	11.9	-.809		9.6		
			4.6	18.4	-.809		14.9		
			8.7	26.1	-.809		21.1		
			8.3	8.5	-.809		6.9		
			4.6	27.6	-.309		8.5		
			12.0	12.0	1	<u>12.0</u>			
						<u>23.6</u>	<u>73.0</u>		
						-49.4		24.5	25.9
006			7.2	21.5	1	21.5			
			4.8	10.0	-.187		1.9		
			3.9	15.6	-.187		2.9		
			8.2	24.6	-.426		10.5		
			7.8	8.0	-.426		3.4		
			3.9	23.4	.969	22.6			
			10.8	10.8	1	<u>10.8</u>			
						<u>54.9</u>	<u>18.7</u>		
						36.2		18.0	19.3
007			6.6	19.7	1	19.7			
			4.1	8.5	.536	4.6			
			3.3	13.2	.536	7.1			
			7.7	23.1	.967	22.4			
			7.2	7.4	.967	7.1			
			3.3	19.8	-.729		14.4		
			9.7	9.7	1	<u>9.7</u>			
						<u>60.9</u>	<u>24.1</u>		
						36.8		18.3	15.5

$$F_{hkl} = \sum_n f_{hkl_n} \cos 2\pi(hx_n + ky_n + lz_n) + i \sum_n f_{hkl_n} \sin 2\pi(hx_n + ky_n + lz_n)$$

where \underline{n} is the number of atoms per unit cell,

\underline{x} , \underline{y} , and \underline{z} are the atomic parameters,

\underline{f} is the atomic scattering factor of the \underline{n} th atom,

\underline{h} , \underline{k} , and \underline{l} are the Miller indices of the

reflection in question.

If only basal reflections are considered, terms involving \underline{h} and \underline{k} disappear. Also if the crystal is centrosymmetrical an atom having coordinates \underline{xyz} is always accompanied by one at $\overline{\underline{xyz}}$ and wave contributions occur in pairs of equal magnitude and opposite sign (Buerger, 1941). Thus in the case of biotite

$$\underline{F}_l = \sum_n \underline{f}_{l_n} \cos 2\pi \underline{lz}$$

for $00\underline{l}$ reflections.

The values of \underline{f} for each atom vary with the glancing angle and the wavelength of the x-ray beam. For routine work a large-scale graph should be prepared from data available in the Internationale Tabellen zur Bestimmung von Kristallstrukturen, Vol. 2, page 568 (1935). The abscissa chosen should be the glancing angle (or its sine) for the wavelength of the target used. Values for $\cos 2\pi \underline{lz}$ are obtained from the tables designed by Buerger (1941).

The product of the atomic scattering factor and the function $\cos 2\pi \underline{lz}$ is the structure amplitude (\underline{F}) of each atom

for the reflection in question. Their algebraic sum gives \underline{F} for each $00l$ reflection. These calculated \underline{F} 's may then be compared with the observed \underline{F} 's to determine how well the atomic parameters were chosen. If necessary a temperature factor is taken into account.

Observed intensities are converted to observed \underline{F}^2 by making the Lorentz and polarization corrections and if necessary absorption and extinction corrections. The Lorentz-polarization correction for powders is given (Internationale Tabellen, etc. 1935) as

$$L.p = \frac{1 + \cos^2 2\theta}{\sin^2\theta \cos \theta} .$$

A large graph prepared from the tables is convenient for routine work. \underline{F} is determined as the square root of the corrected intensity.

List of Specimens

- B 1. Biotite from granite, Chester, Nova Scotia, (M.I.T. No. R 1710).
- B 2. Biotite from gabbro, Tahawus, New York.
- B 3. Biotite from Capilano quartz diorite, Vancouver, B.C.
- B 7. Biotite from Miask, Ural Mountains (Herzog's No. 20).
- B 8. Phlogopite, Hadderspell Twp, Quebec (Whiting's No. 18).
- B 9. Siderophyllite. Brooks Mountain, Alaska (Whiting's No. 28).
- B11. Biotite from alnoite, Stovanset, Alno, Sweden, (Whiting's No. 72?).
- B12. Biotite, unknown, (M.I.T. Mineralogy collection).
- B13. Phlogopite, west of Dent, Clearwater County, Idaho. (U.S.G.S., A. Hietanen, Personal Communication).
- B14. Biotite, associated with wohlerite, Brevig, Norway (M.I.T. Mineralogy collection).
- B15. Biotite, Renfrew, Ontario. (M.I.T. Mineralogy collection).
- B16. Biotite, Asbestos mine southwest of Mt. Lincoln, Belchertown, Mass. (No. 3836, M.I.T. Petrology collection).
- B18. Phlogopite, Burgess, Ontario, (M.I.T. Mineralogy collection).
- B19. Biotite from "G 1" granite, Westerly Rhode Island (M.I.T. No. R 3042).
- B20. Biotite from granite, Brattleboro Quadrangle, Vermont (M.I.T. No. R 3041).

- B21. Biotite from granite, West Nictaux, Nova Scotia
(M.I.T. No. R 2095).
- B22. Biotite from granite, Albany Cross (M.I.T. No. R 2096).
- B23. Synthetic Fluor-Phlogopite, Electrotechnical Laboratory,
Norris, Tennessee (R.A. Hatch, Personal Communication).
- B24. Biotite, Kings Mountain, North Carolina (Ref. F.L.
Hess and R.E. Stevens, Amer. Mineral., 22, 1937, p. 1045).
- B25. Biotite from Nordmarkite (?), Brome Mountain Quarry,
Iron Hill Road, Quebec (M.I.T. No. R 3067).
- B26. Phlogopite from dolomite, Simplon Tunnel (Ref. J. Jakob,
Z. Krist., Bd. 69, 219, 1928).
- B27. Biotite from essexite, Mt. Johnson, Quebec (M.I.T.
No. 3068).
- B28. Synthetic phlogopite from Geophysical Laboratory,
Washington (950° C, 15,000 psi water vapor pressure, 5
hrs.) (Ref. Geochimica et Cosmochimica Acta, 6, 1954, 157).
- B31. Muscovite - labelled annite from Cape Ann granite,
Rockport, Mass. (M.I.T. Mineralogy collection) - (contains
admixed hematite).
- B32. Biotite from syenite, Kingston Mills, Ontario (M.I.T.
No. R 3082).
- B33. Biotite from foot of Mt. Megantic, Quebec (M.I.T. No.
R 3065).
- B34. Phlogopite, Sebastopol, Ontario (M.I.T. Economic Geology
collection).
- 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.

Acknowledgments

Laboratory work was conducted under the supervision of Professor H.W. Fairbairn to whom the author is deeply indebted for suggesting the problem and for sustained interest and advice during its development. Professor W.H. Dennen guided the spectrographic work. Professor M.J. Buerger, Dr. Theodor Hahn, and Mr. Nobukazu Niizeki gave valuable assistance. Technical work by Mr. Kenneth Harper and Mr. John Annese of the Geology Shop helped solve the mechanical problems. Specimens were kindly supplied by Mr. R.E. Stevens and Dr. A. Hietanen of the U.S. Geological Survey, by Dr. H.S. Yoder of the Geophysical Laboratory in Washington, D.C., and by Professor G.J.F. MacDonald of the Department of Geology and Geophysics of the Massachusetts Institute of Technology.

The author owes a debt of gratitude to his wife, Evelyn, for assistance in the preparation of the manuscript.

This research was supported by the Office of Naval Research under Contract No. N5ori-07857 with the Massachusetts Institute of Technology.

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Biographical Sketch .

John Arthur Gower was born on April 19, 1921 in Victoria, British Columbia, Canada, the third child of Leonard Elvins and Margaret Gower.

He received his Elementary and High School education in Victoria. After obtaining his Junior Matriculation in 1939 he commenced work in the Dominion Bank but resigned his position as teller in June, 1942, to join the Royal Canadian Air Force.

As a Radar Mechanic in the Air Force he was sent Overseas in June of 1943 after extensive training at the Universities of British Columbia and Toronto and at Air Force training schools. He served with an R.A.F. squadron on active duty in various parts of England and Ireland. He was repatriated to Canada in December 1945 and received his Honourable Discharge as L.A.C. in Vancouver.

In January, 1946 he enrolled at Victoria College for the accelerated First Year course given to Veterans. In September 1946 he began his engineering training at the University of British Columbia, Vancouver, B.C., where he received the degrees of B.A.Sc. in May, 1950 and M.A.Sc. in May, 1952 in the field of Geological Engineering. He was accepted by the Graduate School of the Massachusetts Institute of Technology in September, 1952, for work leading to a Ph.D. degree in Geology.

While a graduate student at the University of British Columbia he received the F.J. Nicholson Scholarship for the year 1951-52 and for his final year at the Massachusetts Institute of Technology he was awarded a Geology Scholarship. During the academic year 1950-51 he was a Teaching Assistant in Mineralogy and during 1951-52 he was appointed Senior Teaching Assistant in the Geology Department at the University of British Columbia. For his first two years of graduate work at the Massachusetts Institute of Technology he assisted Professor H.W. Fairbairn in Petrography and Optical Crystallography.

His summer field work in Geology includes five seasons with government surveys and three with private companies. His present employer is Kenneco Explorations (Canada) Limited with headquarters in Toronto, Ontario.

In June, 1948 he married the former Evelyn F. Wells of Victoria, British Columbia.

He is enrolled as an "Engineer-in-Training" with the B.C. Association of Professional Engineers and is a member of the Mineralogical Society of America.

A paper entitled "A magnesium borate from Isere, France and Swift River, Yukon Territory, with x-ray powder data for some anhydrous borates" by R.M. Thompson and J.A. Gower was published in the American Mineralogist, 39 (1954), pages 522-524.

An abstract of his Master's thesis, "The Seagull Creek Batholith and its Metamorphic Aureole, Y.T.", was published in the Canadian Mining Journal, 74, June 1953, page 100.

Fig. 1 Change in Ratio of Structural Amplitudes of (004) to (005) with Change in composition of Octahedral Atoms

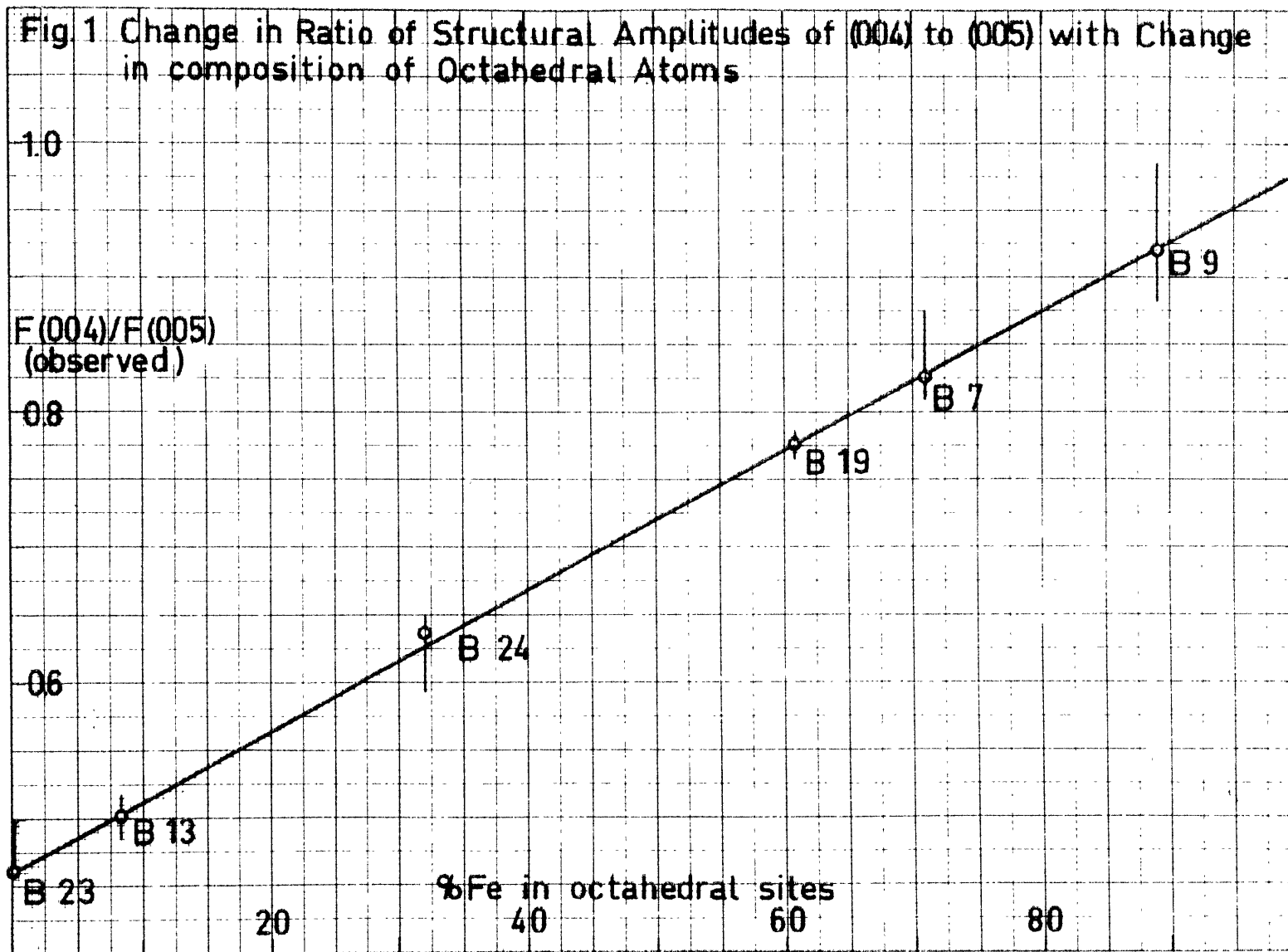


Fig. 2 Change in Ratio of observed Intensities
with Iron Content of Biotite

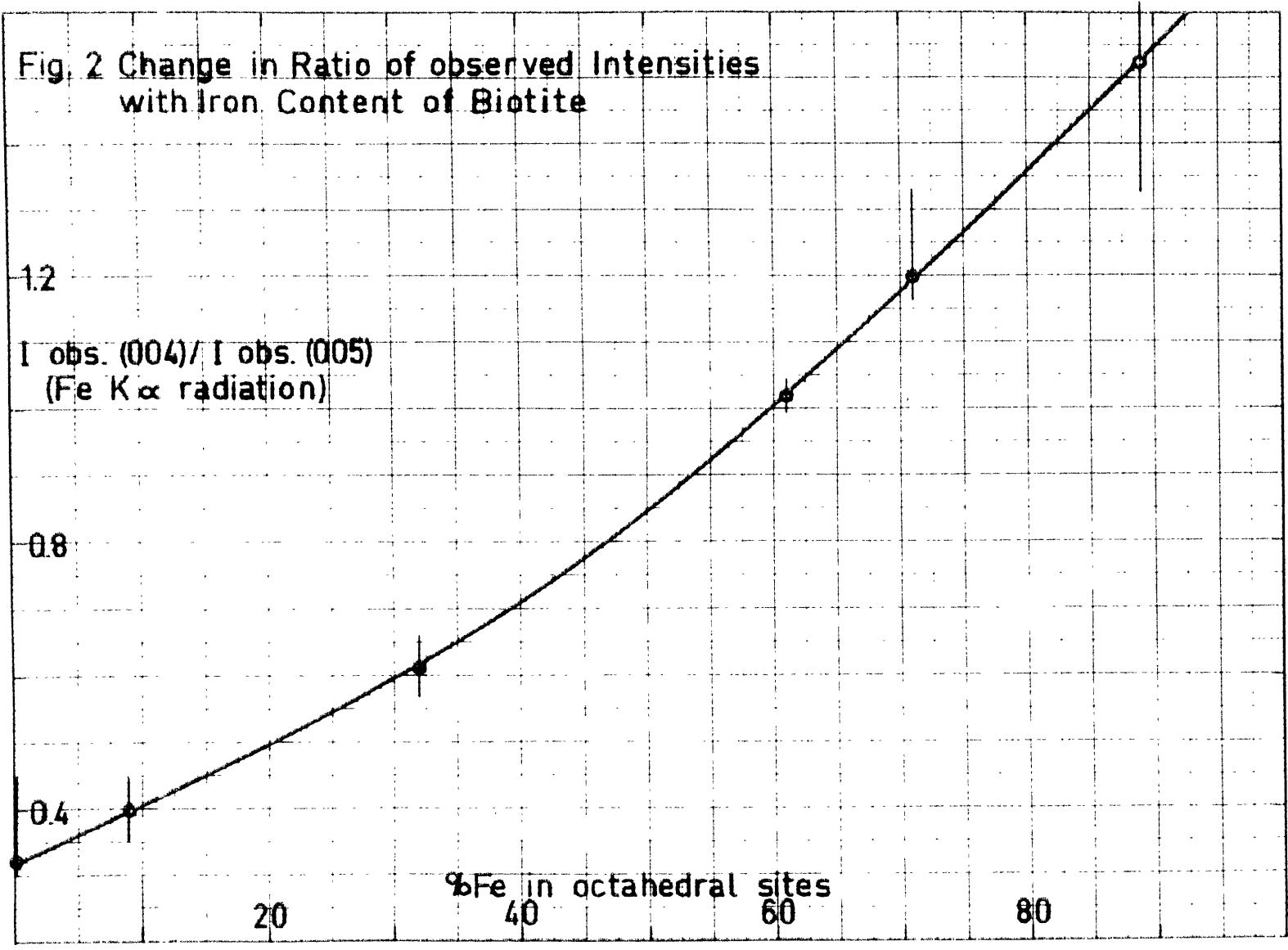
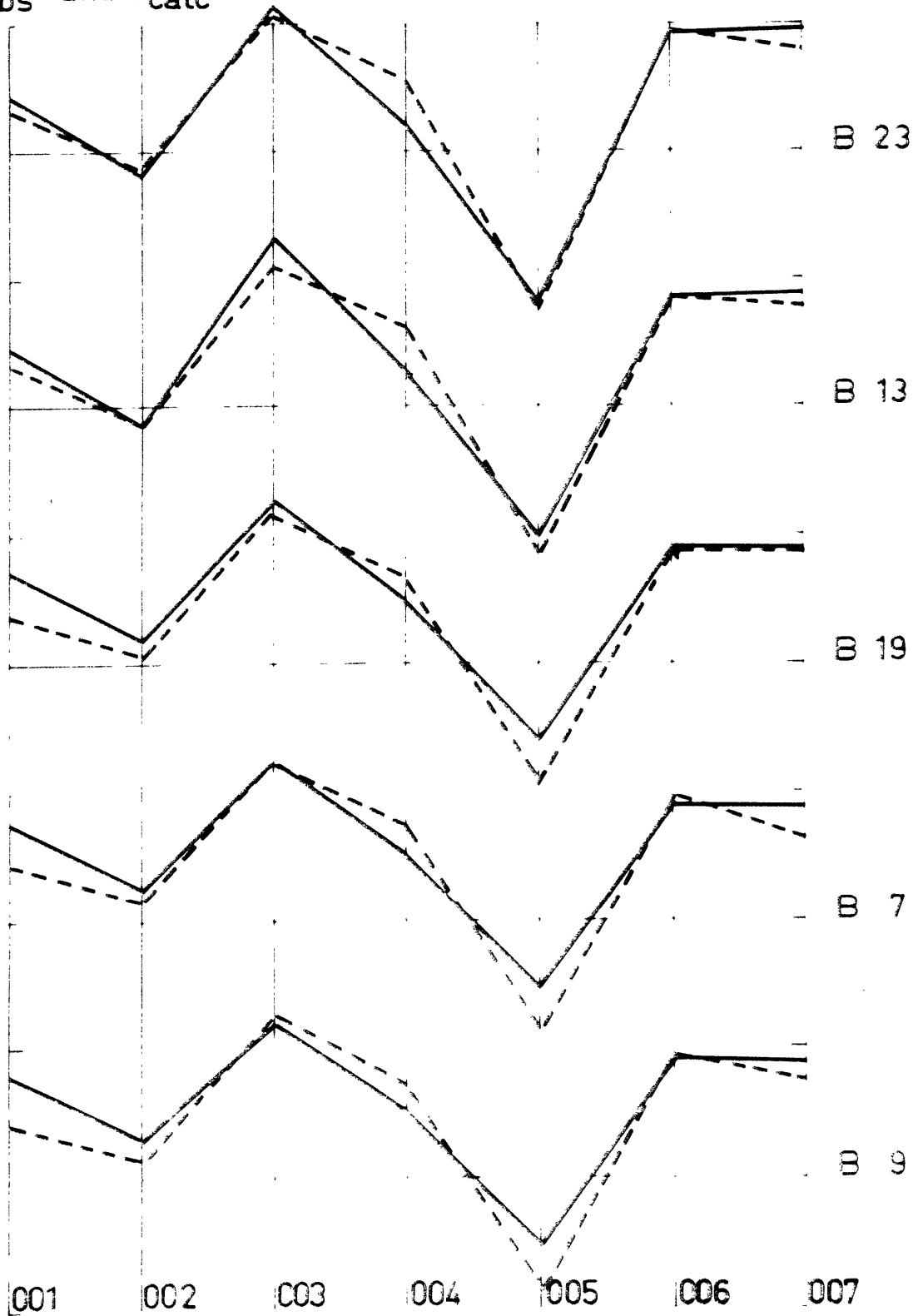


Fig. 3
 F_{obs} and F_{calc} for Basal Reflections ---obs —calc



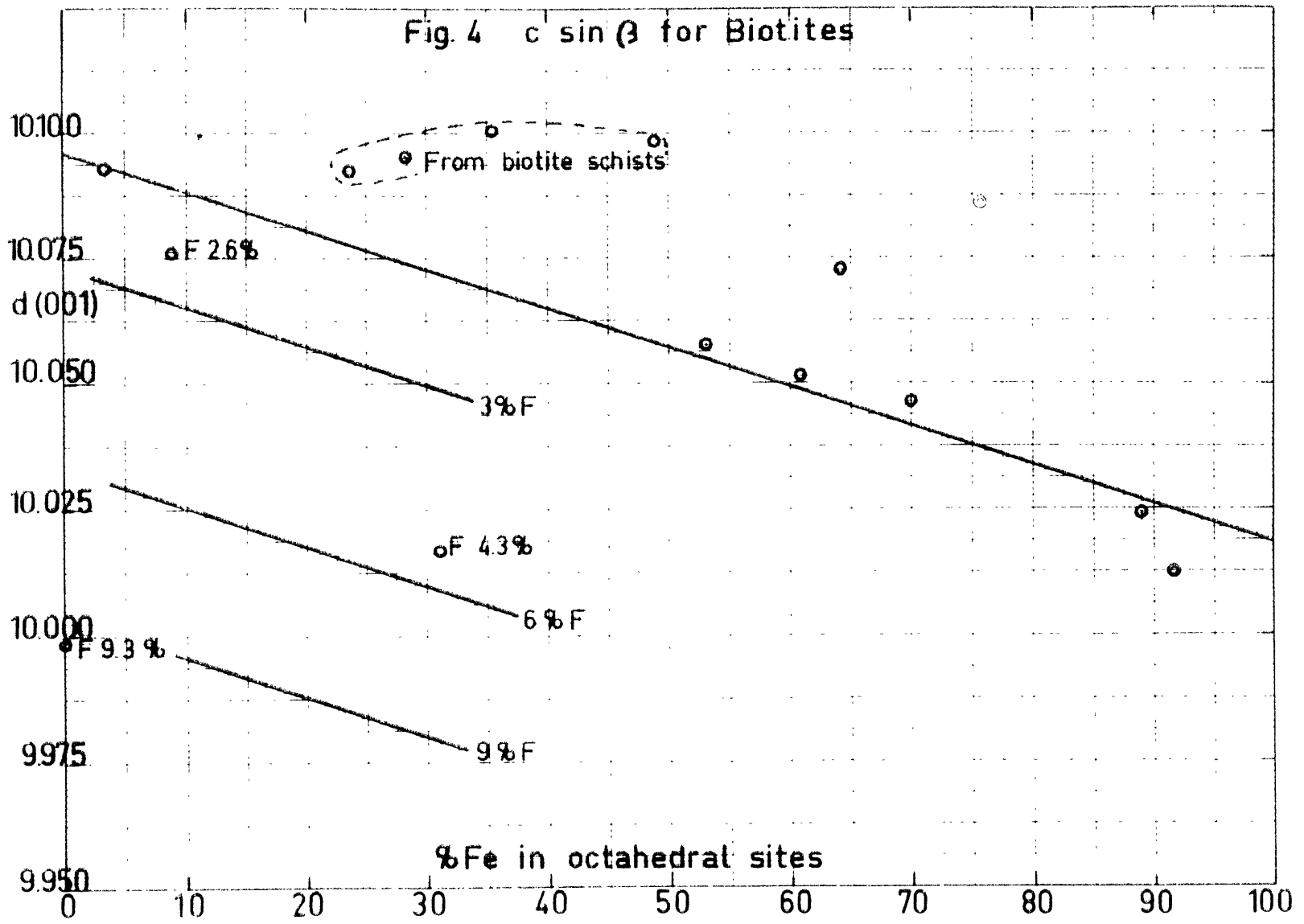
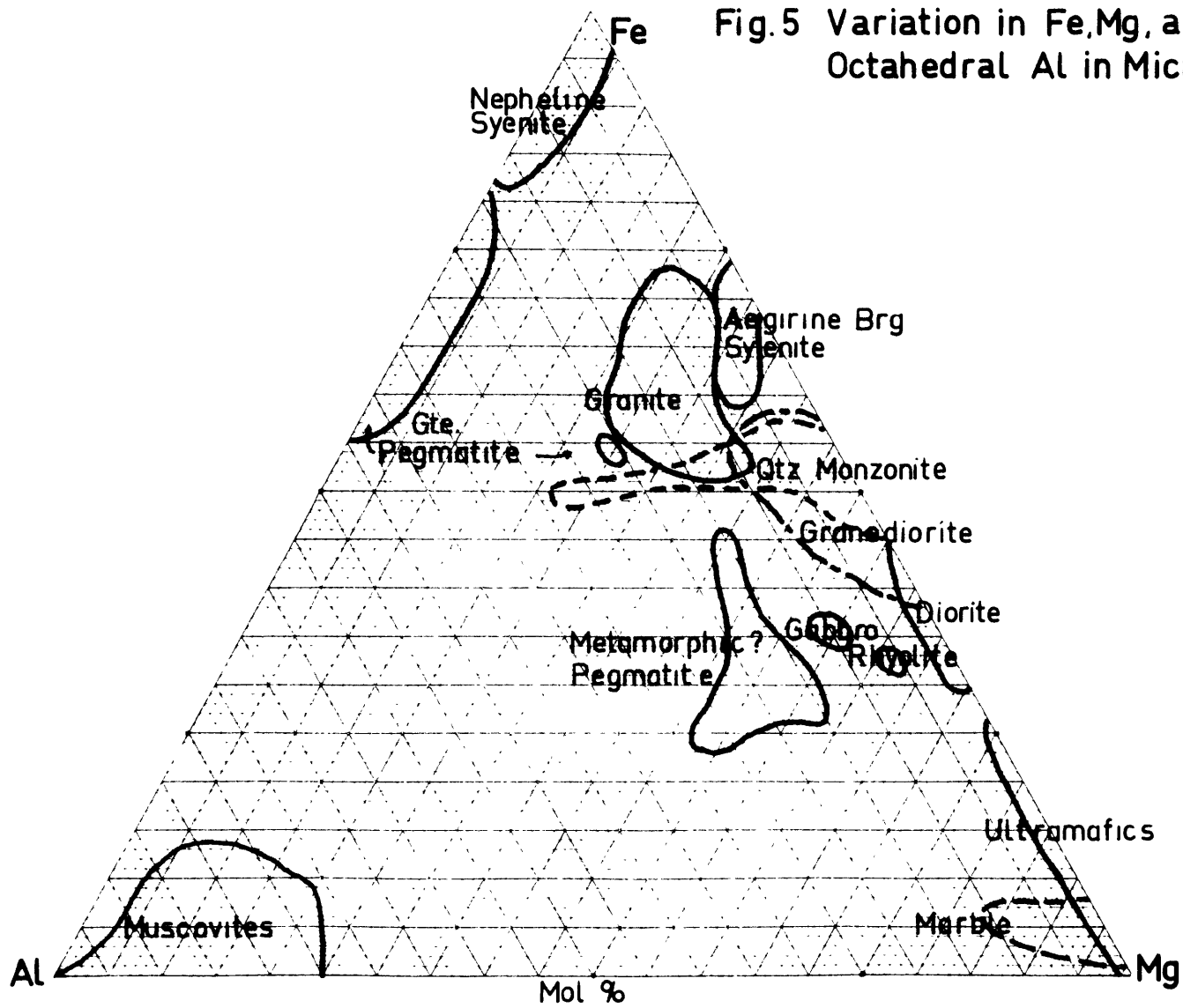


Fig.5 Variation in Fe,Mg, and Octahedral Al in Micas



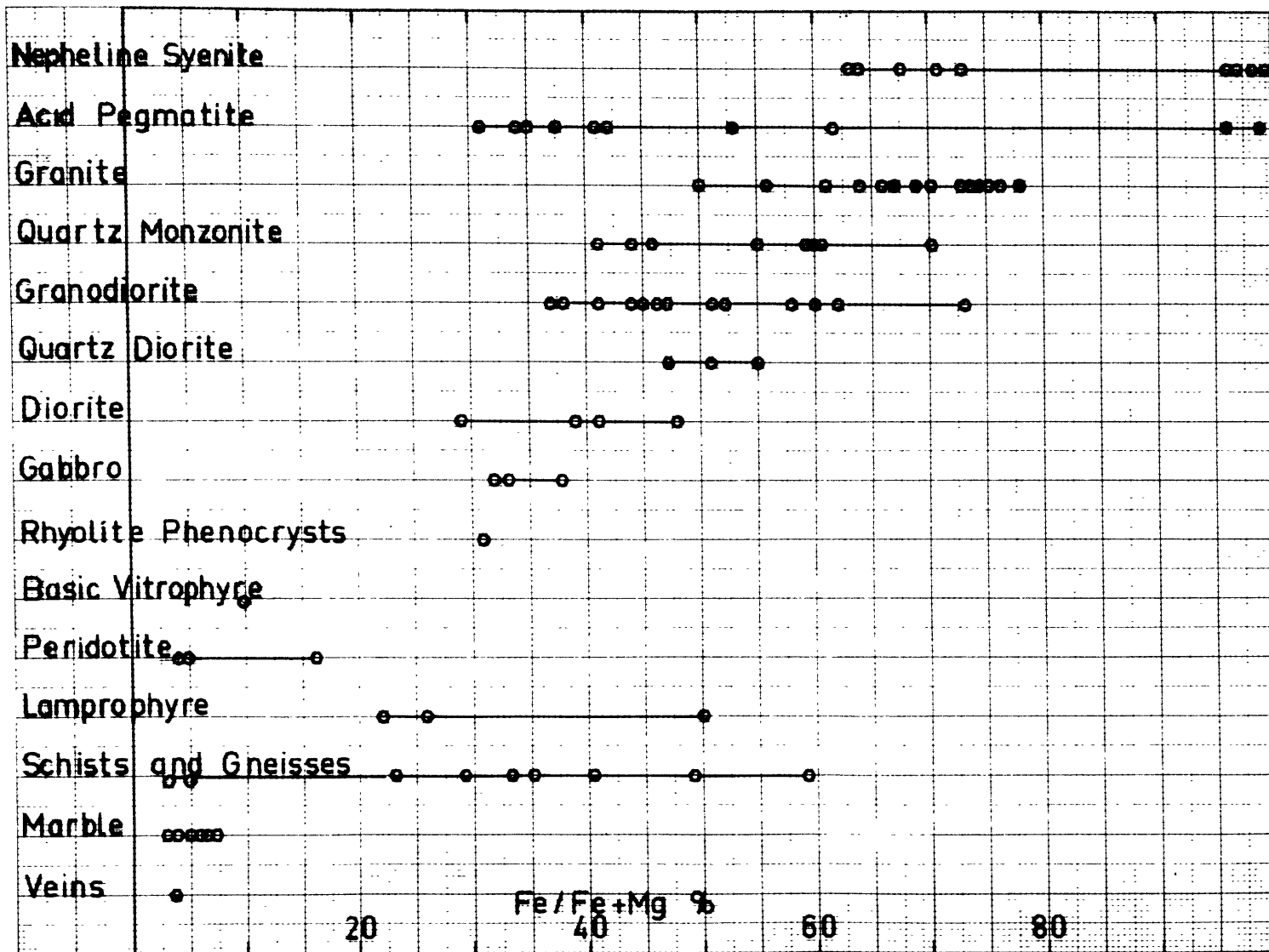


Fig 6 Variation in Iron Content of Biotites with Rock Type

Fig. 7 Variation in Spectral Intensities with Composition of Biotite

