

OPTICAL AND CHEMICAL VARIATIONS IN MINERALS FROM A SINGLE ROCK SPECIMEN

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ABSTRACT

Refractive indices of mafic silicates from a single pyroxene amphibolite specimen in the Sterling Lake magnetite region, southeastern New York, show considerable ranges in biotite. In a small, apparently homogeneous piece of drill core, β of biotite ranges from 1.600 to 1.620, γ' of hornblende from 1.650 to 1.665, and γ of orthopyroxene from 1.698 to 1.708.

Three fractions of biotite were separated from this drill core. The fractions had measurable chemical differences as determined spectrographically, titrimetrically and by fluorescent x-ray analysis.

Geologic history and environment had a bearing on the optical and chemical variations. The amphibolite was replaced by gneiss and pegmatite. Iron and other elements released from the mafic silicates migrated to the ore zone as a result of a geochemical gradient with the major culmination in a marked depression (the ore zone). This depression, where dip and strike diverge from that of the adjacent amphibolite, was a site of pressure difference during stress. The geochemical gradient probably existed until deformation ceased.

The results presented raise many questions. Are ranges in chemical composition and refractive index a general phenomenon, are they found only where a geochemical or pressure gradient exists, and are they indications of disequilibrium? Much additional work is necessary before it will be possible to answer such questions.

INTRODUCTION

In mineralogic and petrologic studies it is generally assumed that the refractive indices of a few grains from a small piece of rock adequately represent the optical properties of the phases present unless zoning is observed. In other words, there is an assumption that in a small piece of rock the mineral phases are constant in optical properties and therefore in chemical composition. However, in the course of a series of studies over the past ten years by the senior author and his students, it has become apparent that this may not be a valid assumption.

As an example of our findings we present the results obtained from the study of pyroxene amphibolite which forms the host rock at the Scott magnetite deposit, Sterling Lake, in southeastern New York. At this deposit the mafic silicates from a series of apparently homogeneous amphibolite drill core specimens $1\frac{1}{8}$ by $2\frac{1}{2}$ inches in size were studied. It was discovered that significant ranges in any particular refractive index exist for each mafic mineral species. For example, in one piece of drill core the β index of biotite ranges from 1.600 to 1.620, the γ' index of hornblende from 1.650 to 1.665, and the γ index of orthopyroxene from 1.698 to 1.708. These results were mentioned by Hagner and Collins (1955) and reported in more detail by Collins (1955).

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It was decided to investigate the ranges over which differences in optical and chemical properties exist in the minerals of the pyroxene amphibolite. The results of this preliminary report illustrate that biotite, hornblende, augite, and orthopyroxene from a small piece of drill core each has a measurable range in optical properties. Three fractions of biotite were separated magnetically and proved to have, in addition to optical differences, measurable chemical differences as determined spectrographically, titrimetrically, and by fluorescent α -ray analysis. Work done to date suggests that such differences may be a general phenomenon.

PETROGRAPHY OF A PYROXENE AMPHIBOLITE

The mafic silicates studied are from a pyroxene amphibolite layer about 800 feet thick that constitutes the host rock of the magnetite ore body at the Scott mine. This rock has been replaced in varying degree by granitic gneiss, pegmatite, and magnetite.

The principal minerals of the amphibolite are plagioclase, biotite, hornblende, augite, orthopyroxene, and magnetite. Where the rock has been replaced by gneiss or pegmatite it contains microcline and quartz in varying amounts, depending upon the amount of replacement. Plagioclase (An_{20-38}) is the most abundant mineral except in some thin layers rich in mafic silicates. Orthopyroxene is pleochroic from colorless to pale green to reddish yellow. It is commonly partly or completely altered to uralite or bastite, sometimes with chlorite and granular magnetite. Augite is colorless to pale green in thin section and non-pleochroic. In places it is altered in part to hornblende or biotite. Hornblende is the common green to brownish-green variety and is pleochroic from yellow to yellow-green or blue-green; locally it is altered in part to chlorite. Biotite is pale reddish brown in thin section and in places is somewhat bleached and altered to chlorite and magnetite. Magnetite, in small amount, is present as primary disseminated grains and in places as very minor secondary grains after the mafic silicates.

REFRACTIVE INDICES OF THE MAFIC SILICATES

Refractive indices were determined for each mafic silicate at intervals along several drill cores; the results from one core are shown in Table 1. Index measurements were made by the Becke method using sodium light at room temperature; maximum error is estimated to be ± 0.002 . Care was taken to avoid altered grains and those with inclusions of other minerals. Many grains of each mineral were measured in order to be certain that *all* grains were above one oil at one extreme and below another at the other extreme.

TABLE 1. REFRACTIVE INDICES OF COEXISTING MAFIC SILICATES IN PYROXENE AMPHIBOLITE

No.	Biotite Determined	Difference	Hornblende γ' Determined	Difference	Orthopyroxene γ Determined	Difference	Augite β Determined	Difference
576	1.638-1.653	.015	1.688-1.698	.010	1.698-1.716	.018	1.688-1.693	.005
596	1.625-1.660	.035	none	—	1.683-1.697	.014	1.688-1.697	.009
606	1.630-1.650	.020	1.683-1.692	.009	1.703-1.717	.014	1.688-1.697	.009
626	1.625-1.650	.025	1.682-1.687	.005	none	—	1.678-1.692	.014
636	1.620-1.635	.015	1.675-1.690	.015	none	—	1.688-1.693	.005
646	1.625-1.650	.025	1.673-1.687	.014	none	—	1.693-1.698	.005
667	1.628-1.635	.007	none	—	1.702-1.712	.010	1.683-1.688	.005
686	1.618-1.642	.024	none	—	1.687-1.703	.016	1.688-1.698	.010
709	1.628-1.638	.010	1.668-1.673	.005	none	—	1.683-1.687	.004
722	1.617-1.627	.010	1.663-1.668	.005	1.677-1.707	.030	1.683-1.687	.004
733	1.600-1.620	.020	1.650-1.665	.015	1.698-1.708	.010	1.678-1.692	.014
743	none	—	1.648-1.668	.020	1.698-1.708	.010	1.683-1.692	.009
753	1.615-1.640	.025	1.668-1.682	.014	none	—	1.683-1.687	.004
763	1.615-1.635	.020	1.668-1.672	.004	1.658-1.702	.044	1.688-1.692	.004
773	1.618-1.630	.012	1.663-1.673	.010	1.698-1.708	.010	1.687-1.692	.005
793	1.613-1.628	.015	1.668-1.673	.005	1.683-1.712	.029	1.698	.000
803	1.632-1.647	.015	1.678-1.688	.010	none	—	none	—
812	1.628-1.643	.015	1.673-1.682	.009	none	—	1.688-1.693	.005
833	1.638-1.652	.014	1.673-1.683	.010	1.687-1.717	.030	1.688-1.702	.014
844	1.640-1.660	.020	none	—	none	—	1.688-1.697	.009
853	1.632-1.642	.010	1.673-1.687	.014	none	—	altered	—
863	none	—	1.673-1.687	.014	none	—	altered	—

The γ of orthopyroxene, β of biotite and augite, and the γ' of hornblende were measured. Hornblende fragments resting on {100} do not give good α or β values, but γ' measured at extinction on the cleavage fragment, closely approximates the true γ value. For biotite, since β and γ are so nearly equal, the β value was read directly from basal cleavage flakes. Table 1 gives the refractive indices of coexisting mafic silicates along a portion of one drill core, namely S-15. This core penetrated a magnetite ore zone at a depth of 722 to 777 feet along the core axis.

As can be seen from Table 1, all mafic silicates of the 22 specimens, except the augite of S-15-793, show ranges of index values. For biotite, the highest minus the lowest index within a single rock specimen varies from .007 to .035; for hornblende, .005 to .020; orthopyroxene, .010 to .044; and for augite, .004 to .014. These ranges of refractive index are considerably higher than the maximum error expectable from measurement.

BIOTITE FRACTIONS

In order to obtain some idea of the variations in optical and chemical properties, biotite was selected for further study because of ease of separation and reliability of β measurement. A piece of pyroxene amphibolite core $1\frac{1}{8}$ inches in diameter and $2\frac{1}{2}$ inches long was taken at a depth of 771 feet along the core axis; inclination of the hole is 52° . Specimen S-9-771

was selected because of the relatively large amount of biotite available at this footage.

The amphibolite was crushed, ground in a porcelain mortar to pass through an 80 mesh screen on to a 100 mesh screen; this material was washed to remove adhering dust. A preliminary separation of biotite was made by floating in distilled water and catching on filter paper. The dried biotite was split into three fractions with a Frantz isodynamic magnetic separator by varying the input current while the optimum setting of the side and forward slopes was kept constant (Fig. 1). This scheme of separation

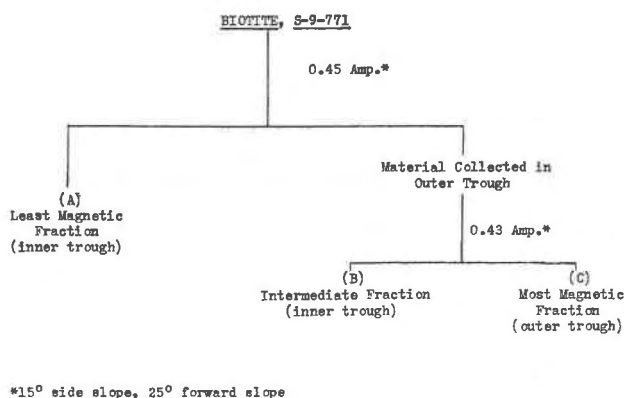


FIG. 1. Diagrammatic illustration of biotite separation into three fractions.

ration is an arbitrary one and the intermediate fraction (B) overlaps the least magnetic fraction (A) on the one hand and the most magnetic one (C) on the other.

The three biotite fractions obtained in this manner were 90–95 per cent pure. Purification to 99+ per cent was accomplished by hand picking grains under a binocular microscope. Examination of the purified fractions with a petrographic microscope showed them to be similar in appearance, without inclusions of magnetite or other minerals, and almost unaltered.

ANALYSIS OF THE BIOTITE FRACTIONS

X-ray Powder Diffraction. X-ray powder diffraction, using a Straumanis camera, Fe radiation and a Mn filter, was employed in order to verify that there were no major differences in crystal structure of the biotite fractions. The results are qualitative, nevertheless the precision was sufficient to show that there is no change in position or relative intensity of corresponding lines in the patterns of the three fractions.

Spectrographic Analyses. Spectrographic analyses were made to determine the amount and possible variation in amounts of elements in the biotite fractions (Table 2). The analyses were made by Oiva Joensuu using chemically analyzed biotite from the Grout Laboratory of the University of Minnesota as standards. All of the specimens were arced in duplicate. The error for major constituents is ± 5 per cent of the amount present; trace elements were determined to within ± 10 per cent. Anhydrous K_2SO_4 was used as a buffer for the arcing. Specimens as well as the standard were mixed with K_2SO_4 (containing 1 per cent Co_3O_4 as an internal standard) and graphite 1:1:4 and burned with a blower arc. For V_2O_3 and ZrO_2 the detection limit is less than 30 ppm; for Cr_2O_3 and Y_2O_3 less than 20 ppm; Sc_2O_3 less than 10 ppm; NiO, Yb_2O_3 , CuO, BeO less than 5 ppm; and for CoO, less than 4 ppm.

Of the major constituents, TiO_2 , Fe, MnO, and MgO increase in amount from the least magnetic fraction to the most magnetic; Al_2O_3

TABLE 2. SPECTROGRAPHIC ANALYSIS OF BIOTITE FRACTIONS

Analyst: Oiva Joensuu

Element or Oxide	Amount Present in %		
	Fraction A	Fraction B	Fraction C
Major Constituent			
SiO_2	35.	35.	36.
TiO_2	2.6	2.7	3.0
Al_2O_3	14.5	15.5	13.7
Fe	13.0	13.2	13.5
MnO	0.22	0.23	0.28
CaO	0.5	0.22	0.35
MgO	13.5	14.5	15.0
Minor Constituent		Amount Present in ppm	
V_2O_3	380	320	390
BeO	2	2	2
CuO	90	35	90
Yb_2O_3	5	5	5
Y_2O_3	30	30	30
Sc_2O_3	20	20	20
NiO	250	220	300
CoO	85	90	90
Cr_2O_3	120	140	140
BaO	800	850	1100
ZrO_2	150	50	70

and CaO were erratic in behavior. The constituents present in minor amounts show no systematic increase or decrease from fraction A to fraction C except for BaO which increases.

Fluorescent X-Ray Analysis for Iron. Fluorescent *x*-ray analysis for iron was employed to obtain semi-quantitative information on the amount of total iron in the biotite fractions. Analyses were made with a General Electric Fluorescent *x*-ray spectrometer using tungsten radiation and a lithium fluoride crystal. In order to achieve precision, the time in seconds to make 16,384 counts of secondary *x*-ray radiation characteristic of the excited iron atoms was recorded for each specimen. During the analysis, many checks were made to establish that the *x*-ray unit was generating radiation in a constant manner. The time in seconds should be inversely proportional to the percentage of iron in the sample, and counts per second is directly proportional to iron. In addition, specimens were ground to minus 325 mesh and checked for coarse grains, pressed to obtain a smooth surface, repacked four times in the holder, and each was run four times to ascertain whether the manner of packing was a source of error.

The results shown in Table 3 comprise a completely random design

TABLE 3. FLUORESCENT X-RAY ANALYSES OF BIOTITE FOR IRON

Fraction	Packing	No. of Sec. for 16,384 Counts				Mean	Counts/Sec.
A	1	49.3	49.6	49.8	50.0	49.62	
	2	51.4	51.9	51.0	51.4	51.42	
	2	50.4	50.6	51.2	51.1	50.82	
	4	51.9	51.1	50.9	51.9	51.45	
Fraction Mean: 50.83 322.32							
B	1	49.3	49.1	49.2	49.0	49.15	
	2	47.6	47.9	47.7	48.3	47.87	
	3	48.6	49.0	49.0	49.1	48.92	
	4	49.0	49.0	48.7	48.6	48.82	
Fraction Mean: 48.69 336.46							
C	1	47.7	48.1	48.1	47.5	47.85	
	2	49.6	49.2	49.5	49.7	49.50	
	3	47.7	47.5	47.2	47.3	47.42	
	4	48.7	48.6	48.7	48.7	48.67	
Fraction Mean: 48.36 338.77							

with subsamples, an experimental design which can be studied by analysis of variance techniques. Results of analysis of variance are listed in Table 4. Details of this type of experimental design and a worked example are clearly presented by Steel and Torrie (1960), so it is not necessary to elaborate in this paper.

The analysis of variance F-test shows that the variation among packings within fractions exceeds variation among replications of the same packing ($F = 28.41$, significant at the 99% confidence level). Collectively, the magnetic fractions differ greatly ($F = 11.76$, significant at the 99%

TABLE 4. ANALYSIS OF VARIANCE OF FLUORESCENT X-RAY DETERMINATION OF IRON

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F
Among packings	11	80.29		
Magnetic fractions	(2)	58.07	29.035	11.76 ¹
Fraction A vs B and C	(1)	57.19	57.19	23.16 ¹
Fraction B vs C	(1)	0.88	0.88	0.36 n.s.
Among packings within fractions (experimental error)	(9)	22.22	2.469	28.41 ¹
Among replications within packings (instrumental error)	36	3.13	0.0869	
Total	47	83.42		

¹ Significant at 99% confidence level.

n.s. Not significant.

level), but breaking the analysis of fractions into single degrees of freedom reveals that fraction A differs greatly from B and C combined ($F = 23.16$, significant at the 99% level), whereas there is not a significant difference between fractions B and C. This comparison of fractions A, B and C is shown graphically in Fig. 2.

Results in Table 4 can be used to improve the design of future experiments of this type. Variation within packings (instrumental error of x-ray unit) is so much less than the variation among packings within a fraction (used as total experimental error for comparing fractions A, B, and C), that it is more efficient to use research time in preparing more packings per fraction and less replications of a single packing. Future experiments on three fractions probably should have 2 replications per packing and 8 packings per fraction, if sufficient sample material is available. Such a design would be more sensitive in detecting small differences among fractions A, B and C. One might even diminish the total work to 3 fractions,

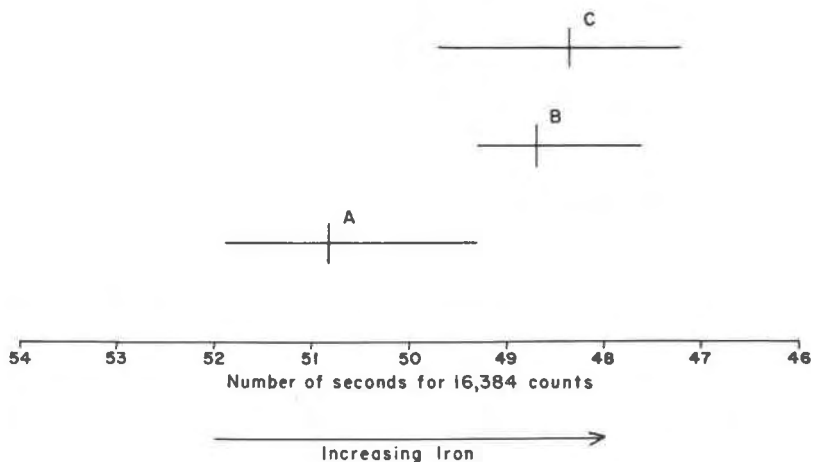


FIG. 2. Ranges and mean values from *x*-ray determination of iron from fractions A, B and C.

6 packings per fraction, and 2 replications of each packing (36 *x*-ray measurements); this would not appreciably affect the sensitivity of the experiment.

Titrimetric Determination of Iron. As a check on the fluorescent *x*-ray and spectrographic methods, the biotite fractions were analyzed by an adaptation (Clemency and Hagner, 1961) of the automatic derivative spectrophotometric titration method of Malmstadt and Roberts (1956). This method has certain advantages over the classical wet chemical procedure of Washington (1930) in that results of higher precision and accuracy can be obtained in a much shorter time and on smaller specimens. Thus, a 0.1 gram specimen is sufficient for minerals containing 3 per cent or more total iron; the analysis takes an hour or less per specimen. The relative error is about 2 per cent.

The results are given in Table 5, and are in general accord with those

TABLE 5. TITRIMETRIC DETERMINATION OF IRON

Fraction	% Total Iron ¹	% Total Iron ²	Mean of Two Iron Determinations
S-9-771 A	11.55	11.26	11.41
S-9-771 B	12.14	11.80	11.97
S-9-771 C	12.43	12.05	12.24

¹ Calibrated with U.S.G.S. rock sample W-1. S. S. Leung, analyst.

² Calibrated with standard iron solution. C. V. Clemency, analyst.

obtained by spectrographic and fluorescent x -ray analysis for iron. Fractions A, B and C contain successively more iron. The determinations using rock sample W-1 for calibration are consistently greater than those calibrated with a prepared standard iron solution; the cause of this is unknown. However, analytical results are precise enough that the increasing iron trend from fractions A through C is considered valid.

Note that fraction A differs from B much more than B differs from C in Table 5. This relation is similar to that obtained from x -ray determination of the relative amounts of iron. It is a manifestation of the efficiency of separation of magnetic fractions resulting from a single passage of biotite through the magnetic separator.

Refractive Index Study. The β refractive index of biotite in fractions A, B and C was measured by the Becke method. Sodium light was used and the temperature of the room was checked frequently; the error is ± 0.002 . Grain mounts were prepared and close traverses were run across each mount so as to count essentially all grains. A series of measurements was made for each biotite fraction until all the mineral grains were above a certain index at one extreme and below another at the other extreme. Grains with an index exactly the same as an immersion oil were rare and were counted as being below the oil. It should be emphasized that with the technique used it is necessary to measure many grains in order to determine the range in refractive index.

Refractive index measurements for the three fractions are summarized in Fig. 3, which shows the percentage of biotite flakes with β less than specified values. For each index liquid specified, 63 to 584 grains were studied, and the proportion of grains with a refractive index less than the liquid was calculated. The proportions were determined from an average of 321 grains per index liquid per magnetic fraction. Cumulative percentage curves for each fraction are quite different, and the mean value of β increases from A to B to C. Figure 3 demonstrates that biotite from a single rock fragment can be physically (magnetically) separated into fractions with different optical and chemical properties, so the biotite is by no means homogeneous in character throughout the rock.

Some of the spread in index for a single fraction in Fig. 3 is due to the gap in indices of the oils. Possibly some is caused by very slight tilting of biotite flakes in the oils, although all grain mounts were "flattened" with a pencil eraser to ensure proper arrangement of cleavage flakes; the optic angles of interference figures were centered and small. Effect of tilting probably was insufficient to account for the spreads measured. Great care was taken in the selection of grains to be measured in order to avoid those that were altered or contained inclusions.

In each fraction the grains with lowest index have almost the same

value. This is believed to be due to the nature of the magnetic separation procedures; grains with relatively little magnetism adhere to grains or clusters of grains that are more magnetic and all move down the same trough together. Nevertheless, the average index for each biotite fraction increases from A to C.

Several years ago Cherkasov (1957) devised a technique of "focal screening" for measurement of refractive indices by the immersion

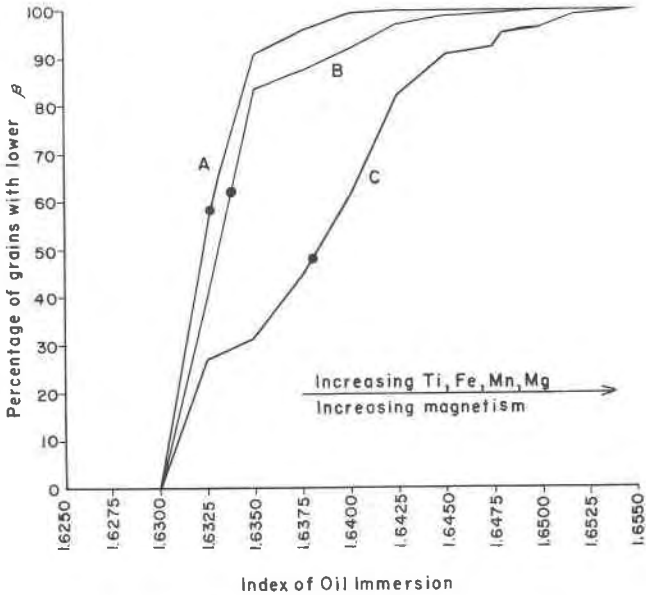


FIG. 3. Percentage of biotite grains with β lower than specified value. Dots indicate sample means.

method; recently Wilcox (1962) also described this procedure. Wilcox (1963) states that the focal screening technique "establishes at once the existence of a variation in index within an immersion mount. Used together with the spindle stage, it permits determination of the variation of a principal index around the profile of a single crystal fragment." Wilcox has also found variations of index "from crystal to crystal in a given igneous or metamorphic rock" and "within a given crystal."

The relationship between refractive index of biotite and chemical composition is a complex one. Hall (1941) showed that Mn, Ti, Fe^{2+} and Fe^{3+} raise the index and F lowers it. Also, a biotite low in iron and high in titanium may have the same index as one high in iron and low in titanium. Heinrich (1946) has pointed out that ferric iron raises the index of biotite about as much as titanium does and twice as much as ferrous iron does.

Taneda (1957) has also studied the relationship between optical properties and chemical composition in biotite and hornblende. A glance at the spectrographic analyses (Table 2) shows that the constituents with consistent increase in percentage from fraction A to C are MgO, Fe, TiO₂, MnO and BaO. The variation in refractive index and iron content is not proportional. Apparently several elements have affected the index values.

Inspection of Fig. 3 reveals that β of biotite fraction A has a distribution only moderately different from B, and these differ greatly from fraction C. Titrimetric and x-ray data indicate that fractions B and C are similar in iron content and are greatly different from fraction A. These relations might suggest that some element(s) other than iron are influencing index of refraction properties in sample S-9-771.

A number of investigators have emphasized that the indices of a mineral in a rock will differ when the mineral is associated with certain other minerals. In the biotite fractions from the Scott Mine, however, the effects of additional minerals on refractive index can be neglected since we are dealing with one piece of rock containing a widespread distribution of the same mineral phases, i.e., hornblende, pyroxene, plagioclase, and magnetite. The same is true of all the specimens in Table 1 for which refractive indices are given. It would be difficult or impossible, however, with the methods used, to determine the effects during recrystallization, if any, of contiguous grains on individual grains of biotite.

DISCUSSION AND CONCLUSIONS

We have demonstrated that biotite, hornblende, augite, and orthopyroxene from one small piece of drill core each has a measurable range in refractive index. Three fractions of biotite from the core, separated arbitrarily by magnetic means, have similar gross atomic structure but differ optically and chemically. Even allowing for appreciable errors in optical, spectrographic and titrimetric determinations, the data point to the existence of differences in fractions A to C.

We have not yet discovered whether the spread in refractive index and the differences in chemical composition are due to (1) microscopic compositional zoning, or to (2) compositional variations from one homogeneous crystal to another. If (2) is the case, it may reflect differences in chemical composition of biotite within different layers, a millimeter or so apart, of the pyroxene amphibolite.

Up to this point we have been concerned with a phenomenological factor of interest and importance which indicates that more care should be taken in petrographic investigations and in the characterization of the optical and chemical properties of the constituent minerals of rocks. Next

TABLE 6. SPECTROGRAPHIC ANALYSES OF MAFIC MINERALS AND TOTAL ROCK
Analyst O. Joensuu

Spec.	Biotite							Hornblende				
	70	169 ¹	325	576 ²	596 ³	646 ⁴	733 ⁵	70	325	576	636	733
SiO ₂	34.	35.5	36.	34.	35.	35.	35.	42.	43.	43.	50.	45.
TiO ₂	4.7	3.55	4.8	4.3	3.9	4.4	1.8	1.9	1.7	2.5	1.9	0.52
Al ₂ O ₃	13.5	14.0	13.5	14.5	13.1	14.5	14.	10.5	9.5	12.	12.	8.5
MnO	0.18	0.245	0.16	0.14	0.12	0.115	0.125	0.3	0.33	0.40	0.45	0.70
MgO	10.5	13.25	12.5	11.	12.9	12.	16.	8.5	11.5	10.	13.5	16.5
CaO	0.45	0.35	0.75	0.65	0.41	1.25	2.1	10.5	10.5	11.	10.5	12.
Na ₂ O				0.22		0.35	0.4			1.3	1.7	1.6
Fe ⁰	14.	14.	12.5	11.5	14.6	9.8	8.7	13.5	12.	14.	10.5	9.0
	(In parts)											
Cr ₂ O ₃	40	125	40	300	425	620	900	40	130	320	500	20
V ₂ O ₃	330	545	750	620	363	650	95	230	690	900	550	250
CoO	95	85		90	105	120	60	70	90	130	60	40
NiO	50	160	210	240	305	350	180	95	130	140	250	45
ZrO ₂	110	~55	120	100	238	130	80	120	210	120	60	80
Sc ₂ O ₃	20	43	20	<10	29	<10	15	220	190	160	160	100
Y ₂ O ₃	20	<30	20	<10	<30	<10	<10	290	210	300	40	400
Yb ₂ O ₃	5	<5	5		<5			25	20	30	75	35
CuO	85	30	40	15	128	20	60	65	35	15	12	70
B ₂ O ₇										x	x	x
La ₂ O ₃										x	x	x

¹ Average of two samples BeO 2 ppm, BaO 1050 ppm.

² K₂O 8.2%, BaO 0.17%, SrO and Li₂O 100 ppm.

³ Average of four samples. BeO 2 ppm, BaO 2000 ppm.

⁴ K₂O 8.5%, BaO 0.35%, SrO and Li₂O 100 ppm.

⁵ K₂O 8.0%, BaO 0.14%, SrO and Li₂O 100 ppm.

Nos. 733 and 729 are from the ore zone.

x=no lines visible, concentration below detection limit.

we would like to discuss some genetic implications of this phenomenon. Recently Wilson (1960) got anomalous results when he tried to correlate chemical compositions obtained from optical data with chemical analyses. He suggested that the main cause of inconsistencies was due to "variation in composition of grains in the rock under study" and that the olivine, orthopyroxene, and clinopyroxene in the metamorphic assemblage studied were in a non-equilibrium state. He attributed the "anomalous" departure of tie-line trends, derived chemically or optically, to the metamorphic history or status of the rocks. These conclusions are in accord with the results obtained by Hagner and Collins (1955).

The geologic history and environment of the Scott Mine pyroxene amphibolite undoubtedly had a bearing on the optical and chemical variations herein discussed. In places the amphibolite contains layers of gneiss, pegmatite and magnetite ore which have replaced it in varying degree. These layers occupy areas that probably were places of least normal pressure or potential "openings" at the time of replacement.

Augite					Orthopyroxene				Total Rock				
70	325	576	636	733	169	576	686	733	70	325	576	636	729
49.	51.	52.	53.	53.	52.	52.	54.	55.	45.	48.	52.	50.	53.
0.33	0.17	0.19	0.2	0.08	0.06	0.11	0.065	0.032	1.6	1.9	1.15	1.	0.33
4.7	2.1	2.7	3.1	1.7	2.1	2.0	1.7	1.2	13.5	14.5	15.5	17.	16.
0.4	0.45	0.65	0.55	0.37	1.25	1.2	0.82	0.85	0.35	0.25	0.26	0.2	0.18
10.	12.	12.5	13.5	13.5	19.	19.	25.	26.	5.0	5.3	5.8	8.	7.2
17.	21.	23.	22.	23.	0.25	1.1	0.75	0.95	7.8	9.5	6.5	9.	3.
		0.7	0.7	0.5		0.2	0.25	0.2			4.5	3.7	2.
8.7	7.2	8.2	6.8	7.	16.8	19.	14.	16.	14.5	11.2	8.5	7.3	7.6
per million)													
40	40	100	210	x	150	200	x	x	50	110	230	440	25
100	310	320	220	150	20	100	220	60	230	650	520	460	700
45	60	55	30	15	70	160	40	50	60	33	33	50	35
10	40	80	130	13	60	130	25	17	<10	30	66	210	30
100	100	60	80	90	50	90	70	50	200	210	90	110	50
260	220	270	110	80	40	75	65	25	30	110	65	60	30
110	90	120	15	270	20	25	35	20	90	50	70	40	60
12	9	11	x	20	40	x	x	x	10	5	5	x	x
25	8	15	20	15		20	25	30	350	90	25	<5	10
		x	x	x		x	x	x			x	x	x
		x	x	x		x	x	x			x	x	x

Gneiss was first introduced into these "openings" and replaced the amphibolite with release of iron which migrated to the ore zone. Later deformation was accompanied by, or succeeded by, the introduction of pegmatite and the development of more magnetite. During metamorphism and replacement, the bulk of the amphibolite in the tightest parts of the structure was not replaced, but iron was released from the mafic silicates and moved to the ore zone. This unreplaced amphibolite, from which specimens S-9-771 and the minerals in Tables 1 and 6 were separated, was "altered" only in the sense that incoming Mg, Ca, and certain ferrides were substituted for iron in the structure of the mafic silicates without any evidence of breakdown of mineral crystals. A change in condition, such as would result if "openings" developed in the system, could cause an aqueous phase to migrate towards the "openings" and escape. Differential pressure and loss of the aqueous phase would cause a change in equilibrium conditions under which certain minerals would not be stable. The high concentration of oxide minerals within the ore zone is evidence that oxidizing conditions existed there, or at least oxide minerals were more stable there than elsewhere (Hagner *et al.*, 1963).

Iron was probably first removed from the mafic silicates nearest the ore zone as a result of disequilibrium in the rock. As these minerals lost iron, mafic silicates further and further away also lost some of their iron to the

dispersed phase. The gradient thus established continued in existence until deformation ceased. The optical and chemical data here presented indicate that the composition of particular phases is not constant even over distances of a few millimeters or less. That a geochemical gradient did exist with the major culmination at the center of a marked depression (the ore zone) is indicated by the fact that the iron content of the mafic silicates decreases toward this zone; other chemical changes are also evident (Table 6). Ca, Mg, Cr, Ni and Co in the mafic silicates increase in amount toward the ore zone; V increases and then decreases. The ferrides drop within the ore zone except for the Cr content of biotite. These changes have been discussed more fully elsewhere (Hagner *et al.* 1963). That this depression was a site of pressure difference during stress is shown by the fact that the dip and strike of the ore zone diverge from that of the adjacent amphibolite. Locally the ore thins or is discontinuous where there are marked changes in strike, and the ore zone itself occupies a region where the dip differs by an average of 9 degrees from that of the immediately adjacent amphibolite. This could result in the formation of a pressure gradient during deformation and it is believed that such conditions might account for the optical and chemical differences described.

The results presented raise many questions the answers to which require additional research. It would be interesting to know if ranges in chemical composition and refractive index are a general phenomenon and if they are to be found only where a geochemical or pressure gradient exists. Are spreads in refractive index indications of disequilibrium and what is the true meaning of equilibrium with regard to rock systems? Refractive index appears to be a much more sensitive indicator of variations in mineral properties than is perhaps realized, even though differences in index of many complex minerals generally can be correlated only in a crude manner with chemical changes. It would be instructive to compare minerals formed under equilibrium conditions with minerals formed under disequilibrium conditions.

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