THE AMERICAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

VOL. 9 AUGUST, 1924 No. 8

NOTES ON BIOTITE

FRANK F. GROUT, *University of Minnesota*

In the study of Minnesota rocks biotite is encountered in abundance and wide distribution. In one case it is closely related to magnetite in an iron ore prospect. These points seemed to warrant a careful test of the material. A study was planned, following somewhat the methods of Hirshi[1] and Seidel,[2] on the variation of this group of minerals with the occurrence in several kinds of rock, but adding data on the indices of refraction. This study is incomplete, but the optical data and analyses seem to warrant a few preliminary notes. Out of fourteen samples tested, thirteen had gamma and beta higher than are on record in the text books and compilations available; viz., 1.638.[3]

The recent popularity of the immersion method for determining indices of refraction makes it desirable to arrange the data for biotite in a form to use in estimating the compositions from indices. No attempt is here made at extreme accuracy of optical determination, or completeness of analysis. Such work is hardly possible on small grains of biotite constituting perhaps two per cent of a granite, especially when the biotites so commonly show a zoned structure and some variation even in a single crystal flake.[4] The index data are believed to be accurate to the second decimal for such material as the average of that analysed.

---

[1] Hirshi, H., Beiträge zur Kenntnis der gesteinbildenen Biotit. Inaugural dissertation, *Zurich.* (1901)

[2] Seidel, P., *Ibid.* (1906)

[3] Rosenbusch and others give a compilation from Kohlrausch, Zimanyi, Linck and Michel-Lévy and Lacroix.

Larsen records in U. S. Geol. Survey, *Bull.* **679**, several values with beta not over 1.638.

[4] Previously noted by Hirshi, *op. cit.*

METHODS

The several biotites analyzed were separated by hand picking, Thoulet's solution, panning, rolling on paper, and the use of a magnet. Commonly the treatment with heavy solution was made two or three times. The separate was well washed and in a check test it was found that no potash was added by the treatment. The sample was ground only to 40 mesh to avoid oxidation of the iron. Combined water was determined in a hard glass tube by Penfield's method and without prolonged blasting. The results may be a trifle low. Fluorine was not estimated in most samples. Other methods are approximately those of Hillebrand in Bulletin 700 of the U. S. Geological Survey.

The indices were compared by the Becke method with oils standardized on a goniometer, and checked by oils tested by the Geophysical Laboratory at Washington, and by oils from A. C. Hawkins, at Rochester. The optic angle was not measured, but always inspected to determine whether there was enough variation to serve as an easy method of distinction. All showed a small angle, and all good hexagonal plates had their optic planes parallel to the pinacoid (010). Pleochroism is strong in all samples. Color is stated for each.

THE SOURCES AND ANALYSES OF SAMPLES OF BIOTITE

From the fourteen biotites collected for the purpose, four have been analyzed by the writer and two others tested for iron and titanium. Tests are being conducted on the others, but none show a greater range in indices of refraction.

1. Green biotite poikilitically enclosed in feldspar in a basic segregation of the Kekequabic granite, Minnesota.
2. Brown biotite constituting about 2 per cent of the Vermilion granite, Minnesota.
3. Brown biotite constituting about 5 per cent of the granite at the quarry north of Mora, Minnesota.
4. Brown biotite (associated with hornblende) constituting about 5 per cent of the granite at Rockville, Minnesota.
5. Orange brown biotite from peridotite at the base of the Duluth gabbro, Minnesota.
6. Brown biotite from biotite schist, altered from Knife Lake slate by the Vermilion granite, Minnesota.

Partial Analyses of Minnesota Biotites

	1	2	3	4	5	6
SiO_2	38.32	37.12	35.67	36.06		
Al_2O_3	12.12	17.06	14.56	17.21		
Fe_2O_3	7.44	4.05	3.03	1.14	8.63	.64
FeO	7.72	14.80	23.23	23.75	12.96	17.60
MgO	16.55	10.21	9.24	6.16		
CaO	1.89	2.36	1.13	1.74		
Na_2O	.38	.68	.49	none		
K_2O	9.10	5.40	8.06	7.27		
H_2O+	1.20	3.10	1.02	1.28		
H_2O-	.20	.30	.23	.22		
TiO_2	1.67	2.23	3.32	2.73	4.34	1.50
ZrO_2	n.d.	n.d.	.05	1.65		
Cr_2O_3	n.d.	n.d.	.03	n.d.		
MnO	.11	.48	n.d.	.36		
F	n.d.	n.d.	.16	n.d.		
	96.70	97.79	100.22	99.57		
Sp. G.	3.021	3.107	3.125	3.125		
Indices						
Gamma	1.630±3	1.640±2	1.655±2	1.664±4	1.648±5	1.639±3
Alpha	1.580±3	1.597±5	1.605±4	1.610±5	1.584±6	1.596±4

FURTHER DATA

These analyses when compared with any compilation (such as Doelter's Handbuch der Mineralchemie, Dana's System of Mineralogy, or Osann's Beiträge zur chemischen Petrographie), show no exceptional features but the indices of refraction are nevertheless higher than might be expected. The increase of indices with increase of iron has been long understood, but these biotites are not unusually ferruginous.

Three similar records of high indices of refraction in biotites have been found in the literature. A. N. Winchell found the index of biotite in the Duluth gabbro to be above that of apatite; that is, probably above 1.638.[5] Tsuboi noted a green biotite in Japan as "unusual," because its indices were, gamma = 1.672 and alpha = 1.614.[6] Eskola found some biotites in Massachusetts with indices reaching a maximum of 1.660.[7]

With these several records showing the need of extending the limits of the index data for the group, it became of interest to see

---

[5] Winchell, A. N., The gabbroid rocks of Minnesota: *Am. Geol.*, **26**, 172, (1900).

[6] Tsuboi, S., *Jour. Geol. Soc. Tokyo*, **26**, 7-9, (1919).

[7] Eskola, P., Gneiss and limestone contact phenomena: *Jour. Geol.*, **30**, 269, (1922).

how far the series could be carried in the direction of increasing iron, and decreasing magnesia. Several samples in the laboratory of the University of Minnesota were from localities where the rocks and biotite had been analyzed. These were tested in oils like the others, and while the correlation of these optical data and the analyses is less accurate, the general nature of the curve seems to be indicated with fair certainty.

7. Biotite from quartz syenite, Wausau, Wis. Analysis in *Wis. Geol. and Nat. Hist. Survey, Bull.* **16**, 295, (1907). Gamma = 1.677 ± 5. Alpha = 1.612 ± 3. Fe_2O_3 = 7.87. FeO = 26.01. MgO = .76.

8. Lepidomelane from litchfieldite, Litchfield, Maine. Average of two analyses in *U. S. Geol. Survey, Bull.* **220**, 77, (1903). Gamma = 1.672 ± 5. Alpha = 1.618 ± 5. Fe_2O_3 = 21.86. FeO = 13.61. MgO = .95. The iron and titanium content of this sample was checked by work on the same sample as that tested for indices. The only notable difference was slightly more ferrous and less ferric oxide.

9. Biotite from pegmatitic granite, Rockport, Mass. Analysis in Rosenbusch, Elemente der Gesteinslehre, p. 73, (1898). Gamma = 1.677 ± 3. Alpha = 1.623 ± 5. Fe_2O_3 = 8.06. FeO = 30.35. MgO = .05.

10. Biotite from miaskite, Miask, Urals. Averages of two analyses in Iddings, Rock Minerals, p. 450, (1911). Gamma = 1.672 ± 5. Alpha = 1.614 ± 4. Fe_2O_3 = 6.24. FeO = 24.35. MgO = 5.22.

11. Biotite from quartz monzonite, Butte, Montana. Analysis in *Journal of Geology,* **7**, 743, (1899). Gamma = 1.655 ± 5. Alpha = 1.592 ± 5. Fe_2O_3 = 5.22. FeO = 13.72. MgO = 12.13.

12. Phlogopite from orendite, Leucite Hills, Wyoming. Analysis in *U. S. Geol. Survey, Bull.* **150**, 188. Gamma = 1.585 ± 10. Alpha = 1.550 ± 5. Fe_2O_3 = 2.73. FeO = .90. MgO = 22.40.

13. No biotite from Vesuvius is available here, and the optical data and analyses available in the literature may have been obtained from different flows. They are not consistent with other data.

14. Larsen in *U. S. Geological Survey, Bulletin* **679**, records a biotite with gamma = 1.574, and alpha = 1.541. These are about the lowest on record.

15. The maximum amount of iron oxide in biotite is theoretically, after Clarke, 43.84%. Doelter cites one containing 40.07% by actual test.

16. The texts usually quote for phlogopite the indices, gamma = 1.606 and alpha = 1.562 after Michel-Lévy and Lacroix. It may be suspected that this sample contained some iron oxides.

The variations in indices of refraction are plotted in figure 1, in comparison with the percentages of iron oxides. This combination of the two oxides was selected because, in the first place, the former notes on the subject suggest variation "with iron." In the second place, the variation of magnesia with the sum of the iron oxides is a fairly regular curve, while its variation with one of the iron oxides alone is much more erratic. It is noteworthy that in the compilations of biotite analyses, a high iron content, say above 25 per cent, means a low magnesia content, usually below 5 per cent. In those biotites having less than 5 per cent magnesia, however, the sum of iron oxides may vary from 20 to nearly 40 per cent.[8]

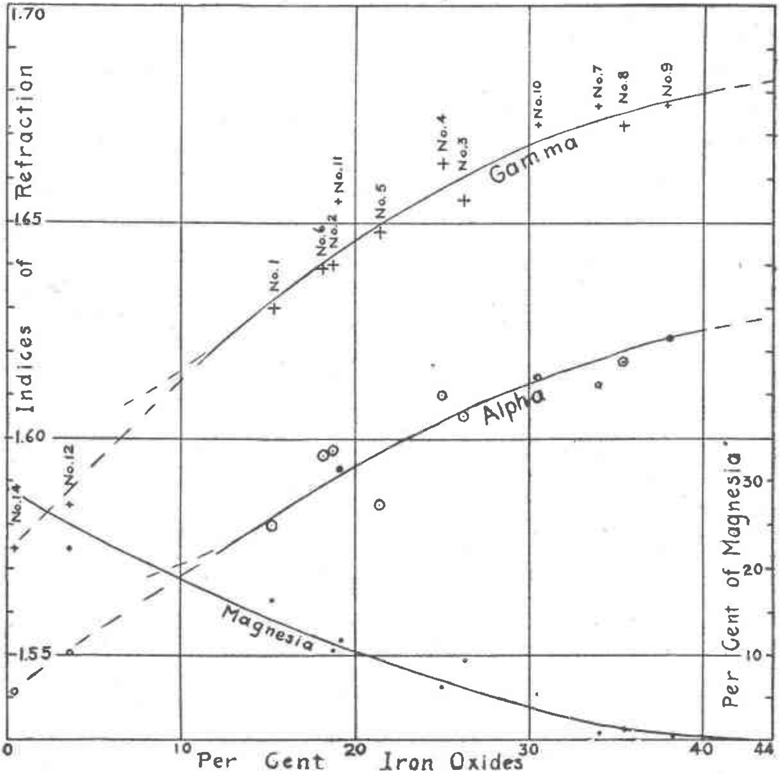

FIG. 1. The relation of iron oxides and magnesia in biotites to their indices of refraction. Crosses for the index gamma. Circles for the index alpha. Dots for the per cent magnesia. The larger crosses and circles indicate freshly determined and well correlated data. The smaller symbols are for optical tests made on biotite analyzed elsewhere.

This, of course, raises the question of the isomorphous relations of these elements and the possible oxidation of the ferrous iron in biotite. It is not the purpose of this note to discuss the structure

---

[8] Doelter, C., Mineralchemie, vol. 2, part 2, 680-705, (1917).

of the biotite group, but attention should be called to one of the theories. If the molecules suggested by Clarke[9] are accepted, the theoretical maximum of ferrous oxide is around 30 per cent. The biotites from Wausau, Rockport, Litchfield, and Miask all have more than enough iron to satisfy this maximum, so that some iron must be present in the original mineral as ferric oxide,—not as an oxide isomorphously replacing magnesia.

If the curves are approximately correct, it should be noted that most of the biotites of which analyses are given in the literature,[10] should have indices higher than the indices given in the texts and reference works.[11]

NOTES ON COLOR: The color of biotite seems to vary with several constituents, but a green is at least suggestive of a considerable content of ferric oxide. Yellow orange and red orange biotites were mentioned by Dr. L. V. Pirsson (personal communication) as probably titaniferous. Not having found a record of such a correlation I call attention to analysis 5 of the table and

---

[9] Clarke, F. W., The constitution of the natural silicates: *U. S. Geol. Survey, Bull.* 588, 52, (1914).

[10] Doelter gives 209 analyses in the work cited.

[11] Since the above data were fairly well outlined my attention was called by Dr. A. N. Winchell to a paper by Dr. W. Kunitz, about to appear in the *Neues Jahrbuch, etc.* His curves are similar and his study covers other micas besides biotite. His analyses, however, show some peculiarities both in average amounts of certain elements and in the selection of material for study. All his analyses show high water content, suggesting some hydration. (In Doelter's compilation not one tenth of the analyses show over 5 per cent water.) All analyses by Kunitz are low in potash and alumina. He has selected no biotites with less than 9 per cent magnesia, and only six of his samples contain over 4 per cent iron oxides. The curves here given may therefore be considered as an extension of his study at the ferruginous end. Furthermore much of his work is based on values of alpha, whereas the value of gamma is much more readily obtained by the rapid immersion methods using cleavage flakes.

The ferruginous end of the series is extrapolated by Kunitz to a maximum value for alpha = 1.629. He also suggests that the oxidation of ferrous iron to ferric may raise the indices slightly above the curve shown. On the contrary, with very low magnesia I find a maximum slightly below 1.625, even when ferric oxides constitute 8 or 10 per cent of the mineral. I feel certain, therefore, that the curve bends a little down at the right. In fact the data available indicate much more definite and uniform values at this end than at the magnesian end of the series, where there may be some doubt whether fluorine and hydrogen have similar effects on the indices; and whether a magnesian biotite is really different from phlogopite.

Kunitz shows larger optic angles in places in the biotite series than I have been able to find.

add the following data for three orange red samples. Biotites from contact ores of Parry Sound, Ontario, and from Thompkins Cove, Hudson River, New York, had about 3 per cent of TiO_2; that from olivine gabbro at Duluth, Minnesota, had about 6 per cent TiO_2. The most titaniferous biotite analyzed (color unknown) is probably one from shonkinite at Katzenbuckel,[12] containing 12.02 per cent. It should be added, however, that the manganiferous biotites are also red brown.

NOTE ON SPECIFIC GRAVITY: From Doelter's data[13] and a few new cases, a curve was drawn for average specific gravity variations with total iron oxide content. The iron determines the gravity with an error probably less than .01 in nearly all cases. The curve ranges from 2.70 with no iron, to 3.3 with 40 per cent iron oxides, and is nearly straight. The accuracy of such work, however, is probably less than that based on indices of refraction. No further work was therefore attempted.

[12] Rosenbusch, H., Gesteinslehre, p. 201. (Stuttgart, 1910).

[13] *Op. cit.*

FURTHER NOTES ON ATOMIC VOLUME ISOMORPHISM

EDGAR T. WHERRY, *Washington, D. C.*

In two previous notes on this subject,[1] the writer has pointed out how certain peculiar isomorphous replacements can be explained by the atomic volume relations, but values were there given for but few of the elements. Several requests for data on others having been received, a more complete list is here presented. Radii are stated in 10^{-8} cm., and volumes, based on the assumption that the atomic domains are spheres, are derived from them by the formula $V = 4/3\pi r^3$. For some purposes it will be better to consider the domains to be polyhedrons,[2] and then other formulas will apply, but these are to be discussed elsewhere.

In deriving dimensions from compounds, some of the constituents must be assumed to have a definite, fixed diameter; and since most of the best X-ray measurements have been made on oxides and halides, it is customary to apply this assumption to

[1] *Am. Min.*, 8, 1-8, 94-95, (1923).

[2] *Am. Min.*, 9, 45-54, (1924).