THE BIOTITE SYSTEM

A. N. WINCHELL, University of Wisconsin, Madison, Wis.

Ten years ago the writer published the results of certain studies in the mica group and presented diagrams showing the approximate relations between variations in composition and in optic properties in certain parts of the group. At that time in dealing with biotites, the most difficult problem was to determine the correct end-member molecules, especially with respect to ferric iron and titanium; but they were both finally considered as proxying for magnesium. Since that time the writer has shown that ferric iron probably proxies for magnesium in chlorite; Kunitz has demonstrated that ferrous iron in biotite can be changed artificially to the ferric state without destroying the crystal; Barnes has shown that the same change can be produced (and reversed) in hornblende, and that the change is accomplished by eliminating hydrogen and not by adding oxygen. Therefore the idea that ferric iron proxies for magnesium in biotites is no longer an assumption based chiefly on a study of the analyses, but is at least a reasonable theory. During the last few years, Machatschkis and Jakob have adopted the view that titanium also probably proxies for magnesium, at least in large part.

It seems desirable to re-examine the data for the biotite system and revise the diagrams, partly because of new data (36 new analyses) and partly because a square diagram must be so constructed that if the molecules at the corners are A, B, C, and D, (A and C being at diagonally opposite corners), 50A+50C must equal 50B+50D, since the central point of the square represents equal parts of A and C, and also represents equal parts of B and D. Therefore, it is incorrect to use $\text{H}_4\text{K}_2(\text{Mg},\text{Fe})_6\text{Al}_3\text{Si}_6\text{O}_{24}$ and $\text{H}_4\text{K}_2(\text{Mg},\text{Fe})_6\text{Al}_4\text{Si}_5\text{O}_{24}$ at the corners; it is necessary to use $5\{\text{H}_4\text{K}_2(\text{Mg},\text{Fe})_6\text{Al}_3\text{Si}_6\text{O}_{24}\}$ and $6\{\text{H}_4\text{K}_2(\text{Mg},\text{Fe})_6\text{Al}_4\text{Si}_5\text{O}_{24}\}$. A

7 Dr. N. L. Bowen kindly called the writer’s attention to this method of testing a square diagram.
comparison of the diagram (Fig. 2) now presented with that published ten years ago shows that this change has very little effect on the position of the lines representing optic properties, although the point representing any given analysis is shifted somewhat toward the left margin.

Fig. 1. Variations in composition in the biotite system.

REFERENCES FOR BIOTITE ANALYSES, FIG. 1

In calculating biotite analyses, lime has been omitted, since Jakob and Kunitz have shown that micas contain little, if any, lime. It may be that biotite (as originally formed) contains some ferric iron, but it seems probable that biotites contain much ferric iron only as a result of oxidation of ferrous iron in the crystal by natural processes, and, for simplicity, all ferric iron has been calculated as if it were ferrous iron (that is, Fe₂O₃ is considered to be equal to two FeO). Manganese monoxide is also calculated as ferrous oxide. Since the studies of Jakob and Machatschkilr indicate that titanium proxies chiefly for magnesium, in spite of the marked difference in valence, it has been calculated with ferrous iron, as it was in the study made ten years ago. Fluorine is cal-

culated as equivalent to hydroxyl. Soda is calculated as equivalent to potassa. In all these cases the basis of calculation is, of course, molecular proportion and not weight percentage.

Fig. 2. Variations in composition and optic properties in the biotite system.

REFERENCES FOR FIG. 2

2. G. Schaubberger: *Cent. Min.*, 1927, A, p. 89. \((-)2V = 21^\circ \pm; N_e = 1.697, N_p = 1.616\).
5. F. F. Grout: *loc. cit.*, No. 8 = Doelter's 115. \(N_e = 1.672, N_p = 1.618\).
There are some analyses of biotite which can not be calculated according to these rules into $\text{H}_4\text{K}_2(\text{Mg},\text{Fe})_6\text{Al}_2\text{Si}_8\text{O}_{24}$ and $\text{H}_4\text{K}_2(\text{Mg},\text{Fe})_5\text{Al}_3\text{Si}_6\text{O}_{18}$ without large discrepancies, which may be due to seriously impure samples or unreasonably large errors in the analyses. On the other hand many of the best analyses give small discrepancies. In practically all analyses of biotite the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio lies between 1:3 (as in the first formula) and 2:5 (as in the
second formula). Basing the calculation of the two molecules on this ratio, there will result an excess or deficiency of MgO (including FeO, MnO, Fe₂O₃ and TiO₂). Ordinarily there will also be certain discrepancies in K₂O and H₂O. In Figure 1 no analyses have been used which gave a discrepancy greater than 55 mols of MgO (corresponding with 2.2 weight per cent MgO), and this discrepancy is less than 40 mols except in analyses numbered 12, 14, 17a, 19, 26, 30, 33, 39, 46, 47, 51, 60, 72, 74, and 87. Discrepancies in H₂O (+F) are not considered very important for present purposes. Discrepancies in (K₂O+Na₂O) are surprisingly large in some cases, but they are less than 32 mols (or about two per cent Na₂O by weight) except in Nos. 19, 23, 28, 40, 44, 45, 49, and 87.

If the theory here presented as to the composition of biotite is correct, then much (or all?) of the ferric iron in biotite was originally ferrous iron, and has been oxidized by natural processes. This is most clearly evident when analyses containing high tenors of ferric iron are considered; to calculate these analyses into the molecules used in this discussion it is necessary to consider the ferric iron as equivalent to ferrous iron, a condition well illustrated in analyses 1, 4, 5, 11, 12, 16, 19, 20, 38, and 46; each of these analyses has more than ten per cent of Fe₂O₃ by weight.

In Figure 2 at first only those analyses (accompanied by measures of refractive indices) were plotted which could be calculated into the molecules used in this study with a discrepancy less than 55 mols of MgO (or 2.2 per cent by weight); then it was discovered that analyses with a greater MgO discrepancy gave equally good agreement between measured and indicated optic properties, except in numbers 14 and 21, in which the refractive indices, as measured, are clearly abnormal, since they indicate a birefringence of .091 and .096, respectively, whereas no other biotites of similar composition are known to have a birefringence greater than .05 to .06. Those added to the figure in this way are numbers 4, 7, 13, 14, 19, 20, 21, 25, and 26.

In Figure 2, showing the relations between composition and optic properties, No. 1 (Grout's lepidomelane from Wausau, Wis.) has an index which corresponds with about 15 per cent less Fe than reported in the analysis, but the sample, optically measured, is only from the same locality (and not necessarily from the same sample) as that which was analyzed.

No. 31 (Orcel's phlogopite from Utah) has an index and a bire-
fringence which correspond with about ten per cent more Fe than shown by the analysis. This may be due to the fact that the sample is variable in color (and therefore doubtless in composition and properties) and the palest part was used for the analysis.

No. 38 (H. S. Washington's phlogopite from Italy) also has an index and birefringence indicating about 10–15 per cent more Fe than shown by the analysis, but the indices were measured only approximately as shown by the record ($N_e = 1.61–1.62$, $N_p = 1.56–1.57$).

In all other cases discrepancies between the diagram and measures of the minimum index of refraction are less than 0.01.

The birefringence has not been measured in samples 6, 12, 20, 27, 32, and 37. Samples in which the measured birefringence differs from that indicated by the diagram by more than 0.01 are No. 2 (Schauberger's biotite from Brevik, Norway—$N_e - N_p = 0.081$) and No. 8 (Eckermann's biotite from Mansjö Mt., Sweden—$N_e - N_p = 0.0424$).

It is clear that some variations between indicated and actual optical properties must be expected, since the diagram makes no attempt to show the effects upon the optical properties of variations in tenor of water, or fluorine, or soda, and makes no distinction between titanium, manganese, ferrous iron, and ferric iron, in spite of the fact that Kunitz has shown that oxidation of ferrous iron in biotite raises the index, $N_e$, for example, from 1.667 to 1.718 for a change from 6.51 Fe₂O₃ and 17.83 FeO in natural biotite to 24.89 Fe₂O₃ in the same mineral after heating.