

*The composition and paragenesis of the biotites of the  
Carsphairn igneous complex.*

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THE Cairnmore of Carsphairn igneous complex (1) is the smallest of the larger Caledonian intrusions of the Southern Uplands of Scotland. The intrusion is composite, consisting of a central granite, followed by successive zones of granite-tonalite hybrid, tonalite, and basic hybrids. The complex began with the intrusion of a gabbro. When this was crystallized, but still at a high temperature, the tonalite was emplaced. This intrusion of tonalite produced a series of hornblende-hybrids. The hybridization of the original gabbro attendant on the injection of the tonalite is the result of a 'partial magma' of potash-felspar, quartz, and volatiles. The final intrusion of granite took place while the tonalite was still incompletely crystallized, and resulted in the formation of a zone of acid hybrid rocks. The three biotites that have been analysed occur in the granite, tonalite, and hornblende-hybrid respectively. The analyses were made in order to determine what changes in composition take place with an increase in the acidity of the parent rock, and whether any characteristic feature is maintained indicating their connexion as members within the complex.

The analyses are tabulated below and, although no striking differences of composition are shown, a number of the oxides exhibit a progressive change from the biotite of the granite to that of the tonalite. FeO, Al<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>O increase in the granite biotite, and MgO, TiO<sub>2</sub>, and MnO decrease. The other important constituents SiO<sub>2</sub>, K<sub>2</sub>O, and (OH,F) remain fairly constant.

R. W. Chapman and C. R. Williams (2) in a study of the White Mountain magma series in New Hampshire found, in passing from the biotite of the gabbro to the biotite of the granite, a systematic decrease in SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO, and an increase in Fe<sub>2</sub>O<sub>3</sub>, FeO, and MnO. The main difference is the opposed tendency of the

$Al_2O_3$  in the biotites from the two localities. But in their most important feature, the increase of the FeO/MgO ratio, they are in very good agreement. Correlated with this increased ratio, the refractive indices rise in the biotites of the granites. Similarly, C. S. Hurlbut (3)

Analyses of biotites and their parent rocks. (Analyst, W. A. Deer.)

	I.	II.	III.	IV.	V.	VI.
SiO <sub>2</sub> ...	34.64	34.33	34.96	70.40	60.10	59.97
Al <sub>2</sub> O <sub>3</sub> ...	16.30	14.80	15.29	14.89	16.29	16.86
Fe <sub>2</sub> O <sub>3</sub> ...	3.22	2.48	2.90	0.50	1.49	1.31
FeO ...	19.94	19.07	18.30	1.75	3.93	4.98
MgO ...	8.23	11.62	10.42	0.83	2.83	3.20
CaO ...	1.03	1.56	1.11	1.61	4.85	4.52
Na <sub>2</sub> O ...	0.80	0.65	0.41	3.88	3.92	3.89
K <sub>2</sub> O ...	7.90	8.16	7.99	4.85	3.41	1.89
H <sub>2</sub> O + 105° ...	2.88	2.32	3.07	0.52	1.32	0.87
H <sub>2</sub> O - 105° ...	0.64	0.18	0.41	0.28	0.24	0.13
TiO <sub>2</sub> ...	3.48	3.63	3.99	0.68	1.17	1.21
P <sub>2</sub> O <sub>5</sub> ...	nil	nil	nil	0.08	0.31	0.23
MnO ...	0.31	0.35	0.39	trace	n.d.	0.02
Li <sub>2</sub> O ...	0.25	0.36	0.33	n.d.	n.d.	n.d.
F <sub>2</sub> ...	1.69	2.38	1.17	n.d.	n.d.	n.d.
CO <sub>2</sub> ...	n.d.	n.d.	n.d.	0.03	0.15	1.20
	101.31	101.89	100.74	100.30	100.01	100.28
Less O for F	0.73	1.01	0.49			
	100.58	100.88	100.25			

I, Biotite from granite. II, Biotite from tonalite. III, Biotite from hornblende-hybrid. IV, Granite. V, Tonalite. VI, Hornblende-hybrid. [The rock analyses, IV-VI, are quoted from Quart. Journ. Geol. Soc. London, 1935, vol. 91, p. 72.]

The refractive indices (all  $\pm 0.002$ ) and pleochroism of the biotites are given below:

	I (from granite).	II (from tonalite).	III (from hornblende-hybrid).
$\alpha$ ...	1.595	1.598	1.596
$\beta$ ...	1.652	1.651	1.646
$\gamma$ ...	1.656	1.652	1.650
$\gamma - \alpha$ ...	0.061	0.054	0.054
$\alpha$ ...	pale yellow.	medium yellow.	pale yellow.
$\beta$ ...	{ mottled, dark	{ medium yellow	{ yellowish-brown.
$\gamma$ ...	{ yellow-brown.	{ brown.	{ medium reddish-brown.

has shown that the biotites of altered gabbro xenoliths have a lower FeO/MgO ratio than the biotite of the enclosing tonalite. Comparing the refractive indices of the biotites of the tonalite with those of the changing gabbro xenoliths, he found six out of ten had a higher

refractive index than the corresponding biotite in the gabbro xenolith. The other four had the same refractive indices.

There is little doubt that the biotite compositions are closely related to their mode of origin, as suggested by A. F. Hallimond (4, p. 27). The difference between the two biotites of the more basic rocks and that of the granite is marked by the latter being richer in  $Al_2O_3$  and poorer in  $MgO$ . This distinction between biotites of basic and of acid rocks has also been stated by Hallimond: 'As the content of RO oxides increase in the rock the mica becomes more phlogopitic.'

The variation of the Cairnsmore biotites expressed as mixtures of standard mica species displays their tendency to increase the phlogopitic molecule as the basicity of the rock increases. The calculation is based on the hexasilicate constitution of the mica suggested by Hallimond, and the results are tabulated below.

	Molecular proportions %						Mol. ratio
	Pr.	Lp.	Ph.	Pr.	Bi.		RO/R <sub>2</sub> O <sub>3</sub> .
I. ...	9.4	55.6	35.0	9.5	90.5		2.81
II. ...	11.0	39.0	50.0	11.0	89.0		3.65
III. ...	11.6	45.9	42.5	11.5	88.5		3.09

Pr. = Protolithionite,  $2H_2O.(K,Na)_2O.Li_2O.3RO.2Al_2O_3.6SiO_2$ .

Lp. = Lepidomelane,  $2H_2O.(K,Na)_2O.4FeO.3(Al,Fe)_2O_3.6SiO_2$ .

Ph. = Phlogopite,  $2H_2O.(K,Na)_2O.6(Mg,Ca).Al_2O_3.6SiO_2$ .

Bi. = Biotite species (Lp. and Ph.).

From the above table the biotite from the hornblende-hybrid is seen to be intermediate between that of the granite and the tonalite, notwithstanding that the hybrid is a more basic rock than the tonalite, and, in fact, owes its present assemblage to the intrusion of the tonalite. The biotite of the two more acid rocks has been precipitated directly from the magma liquid, but the biotite of the hybrid has been formed by the destabilization of hornblende with the change in the conditions of phasal equilibrium and its subsequent conversion to biotite. In this way it could be argued that the composition of the biotite arising from the hornblende depends almost entirely on that of the original metasilicate. But if this was the case there is little doubt that the resulting biotite would be considerably richer in the phlogopite molecule than the calculation shows it to be, and certainly richer than the biotite of the tonalite. The intermediate position of the biotite of the hybrid is a reflection of the influence of the acid 'partial magma' (1, p. 68) responsible for the production of the hornblende-hybrids. In this way the phasal equilibrium is pushed beyond that of the tonalite and depends on

the potash available during the hybridization process. In a similar way the ratio  $RO/R_2O_3$  shows the biotite of the hybrid to be the product of a condition of more acid phasal equilibrium. The Cairnsmore biotites confirm A. Brammall's observation that 'Increase in the ratio  $RO/R_2O_3$  implies, in general, retrogression towards the field of the basic rocks' (5, p. 185).

Number of metal atoms on basis of 12(O,OH,F) in analysed biotites (I-III).

	I.		II.		III.	
	Mol. prop.	Metal atoms.	Mol. prop.	Metal atoms.	Mol. prop.	Metal atoms.
SiO <sub>2</sub> ...	0.5745	2.663	0.5693	2.631	0.5798	2.672
Al <sub>2</sub> O <sub>3</sub> ...	0.1595	1.478	0.1448	1.344	0.1496	1.379
Li <sub>2</sub> O ...	0.0084	0.083	0.0120	0.111	0.0110	0.101
TiO <sub>2</sub> ...	0.0434	0.201	0.0453	0.209	0.0498	0.230
Fe <sub>2</sub> O <sub>3</sub> ...	0.0202	0.187	0.0155	0.143	0.0182	0.168
FeO ...	0.2775	1.286	0.2654	1.227	0.2547	1.173
MnO ...	0.0044	0.020	0.0049	0.023	0.0055	0.025
MgO ...	0.2041	0.946	0.2882	1.332	0.2584	1.191
CaO ...	0.0184	0.085	0.0278	0.128	0.0198	0.091
Na <sub>2</sub> O ...	0.0129	0.120	0.0105	0.097	0.0066	0.061
K <sub>2</sub> O ...	0.0839	0.778	0.0866	0.800	0.0847	0.781
H <sub>2</sub> O +	0.1599	1.483	0.1288	1.191	0.1704	1.570
F <sub>2</sub> ...	0.0450	0.417	0.0620	0.586	0.0310	0.286

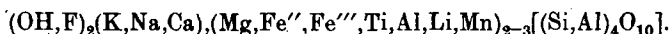
I. (OH,F)<sub>1-9</sub>(Mg,Fe'',Fe''',Ti,Li,Mn,Al)<sub>2-9</sub>[(Si,Al)<sub>4</sub>O<sub>10</sub>](K,Na,Ca)<sub>1-9</sub>.

II. (OH,F)<sub>1-9</sub>(Mg,Fe'',Fe''',Ti,Li,Mn)<sub>3</sub>[(Si,Al)<sub>4</sub>O<sub>10</sub>](K,Na,Ca)<sub>1-9</sub>.

III. (OH,F)<sub>1-9</sub>(Mg,Fe'',Fe''',Ti,Li,Mn,Al)<sub>2-9</sub>[(Si,Al)<sub>4</sub>O<sub>10</sub>](K,Na,Ca)<sub>0-9</sub>.

The complete structure of biotite has not yet been determined by X-ray analysis, but the partial analyses of L. Pauling (6) and C. Mauguin (7), together with the work of W. W. Jackson and J. West (8) on the structure of muscovite, J. W. Gruner (9) on the structure of talc and pyrophyllite, and R. C. McMurchy (10) on the structure of chlorite, along with the chemical study on the brittle micas by G. Koch (11), leaves little doubt that the biotite formula<sup>1</sup> can be written structurally as  $KX_nY_4O_{10}(OH,F)_2$ , in which X represents cations of co-ordination number 6, and Y cations of co-ordination number 4, with  $2 \leq n \leq 3$ .

This formula, written so as to cover the usual replacements within the various groups, becomes



<sup>1</sup> This formula,  $(OH,F)_2KX_nY_4O_{10}$ , given by Pauling, must not be confused with Machatschki's formula (12)  $(OH,F)_2WY_z[z_4O_{10}]$ , in which z = cations with ionic radius  $0.4 \pm 0.1 \text{ \AA}$ . (Si,Al); Y = cations with ionic radius  $0.75 \pm 0.15 \text{ \AA}$ . (Fe'',Fe''',Al,Ti,Mn,Li); W = cations with ionic radius  $1.3 \pm 0.1 \text{ \AA}$ . (K).

Four molecules, each containing twelve oxygen atoms, are present in the unit cell. Two of these oxygen atoms belong to (OH) groups and are replaceable by fluorine so that in fluorine-bearing biotites the value of O + F is twelve.

The three biotites from Cairnsmore have been calculated on the basis of twelve oxygen atoms in the unit cell, in order to compare them with the above structural formula. These are given on p. 498 together with the corresponding formulae.

Similar formulae for five biotites from the Dartmoor granites, deduced from the analyses given by Brammall and Harwood (5), are as follows :

1.  $(\text{OH}, \text{F})_{1.9}(\text{Mg}, \text{Fe}''', \text{Fe}'', \text{Ti}, \text{Mn}, \text{Li}, \text{Al})_{2.7}[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{K}, \text{Na}, \text{Ca})_{0.9}$
2.  $(\text{OH}, \text{F})_{2.3}(\text{Mg}, \text{Fe}''', \text{Fe}'', \text{Ti}, \text{Mn}, \text{Li}, \text{Al})_{2.6}[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{K}, \text{Na}, \text{Ca})_{0.9}$
3.  $(\text{OH}, \text{F})_{2.2}(\text{Mg}, \text{Fe}''', \text{Fe}'', \text{Ti}, \text{Mn}, \text{Li}, \text{Al})_{2.7}[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{K}, \text{Na}, \text{Ca})_{0.9}$
4.  $(\text{OH}, \text{F})_{1.6}(\text{Mg}, \text{Fe}''', \text{Fe}'', \text{Ti}, \text{Mn}, \text{Li}, \text{Al})_{2.9}[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{K}, \text{Na}, \text{Ca})_{1.0}$
5.  $(\text{OH}, \text{F})_2(\text{Mg}, \text{Fe}''', \text{Fe}'', \text{Ti}, \text{Mn}, \text{Li}, \text{Al})_{2.7}[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{K}, \text{Na}, \text{Ca})_{1.0}$

It will be seen that these analyses agree well with the structural formula, and also give some indication of the structural range of biotite. C. Mauguin (7, p. 881) has stated that the number of the X group with co-ordination number 6 (Mg, &c.) in biotites is 3, and that the number of metal plus silicon atoms is 8. 'In margarite and muscovite the total number of metal and silicon atoms is 7, in lepidolite, phlogopite, and biotite it is 8.' L. Pauling (6, p. 128) suggested, as indicated in the structural formula, that the value of the X group can vary within the limits 2-3. This second suggestion is seen to be the more correct from the above analyses, in which the value for the X group varies from 2.6 to 3, and the total number of metal and silicon atoms varies between 7.5 and 8. Whether this X group value can vary between the minimum 2 and 3 in a complete range seems unlikely, but any value between  $n = 2.5$  and 3 is possible. The increase in the value of the X group towards 3 indicates an increase in the phlogopite molecule of the biotite [see table of analyses].

From the above formulae some of the other points suggested by L. Pauling are confirmed. Within the limited variation of the lime content of the biotites,  $\text{Ca}^{++}$  can replace  $\text{K}^+$  as well as  $\text{Na}^+$ . This had already been suggested by A. N. Winchell (13) from a purely chemical study. Nor is it surprising, as the structural layers in the brittle micas are held together by  $\text{Ca}^{++}$  ions instead of  $\text{K}^+$  ions. Further, it is well known that calcium can replace sodium and potassium in the amphibole structure (14). In calculating the formulae,

$Mn^{++}$  has been placed in the X group according to W. Vernadsky (15) and others, but in virtue of its intermediate ionic radius between the X group and the (K,Na,Ca) group it may be able to enter into this second group in those biotites which are below the unity value (e.g. Cairnsmore, anal. no. III; Dartmoor, anal. nos. 1, 2, 3).  $Li^+$ , as suggested by its ionic radius, replaces  $Mg^{++}$  in the X group. This becomes obvious in the case of the lithium-micas, lepidolite and zinnwaldite.

In the Cairnsmore biotites the amount of aluminium replacing silicon is nearly constant and has an average of 1.34 in the  $Y_4$  group. Those from the Dartmoor intrusion are rather less constant and have an average of 1.32. These values indicate a close approximation to a 1:2 replacement of silicon by aluminium within the tetrahedral groups in biotite of granites and intermediate rocks.

The constant deficiency of the (OH,F) group below the value 2 in the analyses of the Cairnsmore biotites is probably due to the difficulty of the accurate determination of fluorine. W. Kunitz (16) has suggested that some of the water may have been reduced by FeO during the ignition giving a somewhat low value for  $H_2O (+105^\circ)$ . This effect is too small, however, to account for the observed differences of the analytical and structural value in some cases (e.g. Dartmoor, no. 4). This discrepancy in the value of  $H_2O (+F)$  has been noted by Winchell (17) in calculating many recent analyses.

The structural formulae show the essential similarity of the three Cairnsmore biotites and distinguish them from those of the Dartmoor biotites. The distinction of the biotites from acid and intermediate rocks is shown by the position of the aluminium in the structure. In the acid rocks part of the aluminium replaces magnesium, in the intermediate the whole is replacing silicon.<sup>1</sup>

In conclusion, the following points are emphasized:

(1) The biotite FeO/MgO ratio is progressively increased as the rock becomes more acid; i.e. the micas change away from phlogopite towards an iron-rich lepidomelane.

<sup>1</sup> The biotites from the White Mountain magma series (Chapman and Williams, 1935, p. 512) do not conform with this suggestion. In each of the biotites from the granite, monzodiorite, and gabbro, part of the aluminium is replacing magnesium. The two latter analyses, however, do not fit the structural formula for biotite.

1.  $(OH,F)_{1.6}(Mg,Fe'',Fe''',Ti,Mn,Al)_3[(Si,Al)_4O_{10}](K,Na,Ca)_{0.9}$ .
2.  $(OH,F)_{0.8}(Mg,Fe'',Fe''',Ti,Mn,Al)_{2.3}[(Si,Al)_4O_{10}](K,Na,Ca)_{1.0}$ .
3.  $(OH,F)_{0.8}(Mg,Fe'',Ti,Mn,Al)_{3.3}[(Si,Al)_4O_{10}](K,Na,Ca)_{0.9}$ .

(2) The ratio  $RO/R_2O_2$  increases in the biotites of the more basic rocks.

(3) Aluminium replaces magnesium in the Y group, as well as silicon in the tetrahedra, in the biotites of the more acid rocks.

(4) There is a close relationship between the biotite and the rock in which it occurs when the mineral has been precipitated directly from a magma liquid. This relationship does not apparently hold when the assemblage is the result of hybridization unless equilibrium has been established.

(5) The biotites of the complex show a characteristic similarity and differ from those of other intrusions, for example, the Dartmoor complex and the White Mountain magma series.

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