

The composition and paragenesis of the hornblendes of the Glen Tilt complex, Perthshire.

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I. *Introduction.*

THE south-eastern margin of the Glen Tilt complex¹ consists of a long strip of diorites with a number of small associated patches of rocks of appinitic type. Xenoliths, both of hornblendite and hornblende-schist, the latter belonging to the Perthshire series of the Dalradian, are found enclosed within the dioritic rocks, which range petrographically from diorite to quartz-mica-diorite. In all these rocks hornblende is the most important ferromagnesian constituent always predominating over pyroxene in the basic members and frequently persisting to the exclusion of biotite in the intermediate rocks of the intrusion. The hornblendes were examined chemically because of the difficulty of estimating their composition even from a thorough optical investigation. As they play such an important role in the complex it is considered that they may give some indication of the history and mode of formation of the rocks in which they occur. Such a chemical investigation of a series of related hornblendes will also indicate the possible range of composition of common amphiboles within the diorites and related rocks of a single complex.

Nine complete analyses of the hornblendes have been made, five from the appinites and diorites, one from a hornblendite xenolith, one from a

¹ The geology of Upper Strathspey, Gaich and the Forest of Atholl. Mem. Geol. Surv. Scotland, Sheet 64, 1913.

hornblende-schist xenolith, one from an injected hornblende-schist, and finally one from unaltered hornblende-schists of the Perthshire series.

Although a number of methods were tried in the separation of the hornblendes from the rest of the rock constituents, the following procedure was found to be the most efficient. In the case of the larger hornblendes from the appinites, and injected and xenolithic hornblende-schists, in which the crystals measured at least 0.25 by 0.25 cm. (analyses 2, 4, 8, 9), they were first drilled as cleanly as possible from the other rock constituents using a dental drill. This provided a highly concentrated fraction before crushing for the separation of included impurities and small adhering particles. All iron-ore was then removed from the crushed material by an electromagnetic separator and practically all the quartz and felspar by repeated fractional separations in bromoform. The heavier impurities, such as occasional grains of pyroxene and sphene were removed by continuous separation in methylene iodide. Finally, by adjusting a solution of methylene iodide and benzene until its specific gravity was just greater than that of the hornblende, and then just less than the hornblende, most of the composite grains were removed. In the case of the smaller hornblendes (analyses 1, 3, 5, 6, 7) the whole rock was crushed and many more separations were required to obtain a pure concentrate. In both groups, however, this fraction was never completely free from a number of composite grains. The most satisfactory method of removing the latter was to pick these unwanted grains out with a camel-hair brush under a biological dissecting or low-powered binocular microscope, and each grain was examined separately before being finally passed for analysis. The analyses were made on fractions weighing between 1.5 and 2.5 grams according to the difficulty or ease of obtaining a pure concentrate. This depended almost entirely on the grain-size required to obtain the maximum number of monomineralic grains, which varied from 0.25 to 0.50 mm. according to the texture of the rock in which the hornblende occurred.

II. *The Hornblende Analyses.*

The analyses of the hornblendes are given in table I together with their optical properties and specific gravity. The values for $2V$ and $\gamma:c$ were measured on the universal stage, and the specific gravity was obtained by matching small grains with methylene iodide diluted with benzene and measuring the specific gravity of the liquid with a hydrostatic balance.

TABLE I. Analysis of hornblendes. (Analyst W. A. Deer.)

	1.	2.	3.	4.	5.	6.	7.	8.	9.
SiO ₂ ...	42.11	43.01	48.92	45.50	48.32	48.96	44.23	44.15	47.14
TiO ₂ ...	2.76	2.87	1.21	1.73	1.43	1.07	1.81	3.73	1.74
Al ₂ O ₃ ...	10.05	12.01	5.88	9.66	6.43	7.85	14.62	10.59	9.44
Fe ₂ O ₃ ...	2.82	3.35	6.50	6.06	5.45	3.62	5.11	5.02	3.66
FeO ...	15.14	9.07	7.79	6.90	7.90	8.25	8.94	8.89	8.38
MnO ...	0.24	0.19	0.17	0.18	0.13	0.12	0.21	0.17	0.11
MgO ...	11.48	14.00	14.32	14.61	14.82	15.69	10.78	12.30	14.44
CaO ...	11.34	11.79	11.37	11.24	11.99	11.90	10.81	11.80	10.53
Na ₂ O ...	1.01	1.08	1.20	1.20	0.99	1.04	1.51	1.26	1.15
K ₂ O ...	1.43	1.01	0.71	0.92	0.67	0.53	0.61	1.10	1.30
H ₂ O + 105° ...	2.02	1.40	1.37	1.73	1.61	0.63	1.42	0.95	2.00
H ₂ O - 105° ...	0.06	0.06	0.18	0.19	0.06	0.08	0.08	0.11	0.53
F ...	—	0.84	0.27	trace	trace	1.41	0.22	0.84	—
	100.46	100.68	99.89	99.92	99.80	101.15	100.35	100.91	100.42
Less O for F ...	—	0.36	0.11	—	—	0.61	0.09	0.36	—
	100.46	100.32	99.78	99.92	99.80	100.54	100.26	100.55	100.42
Sp. gr. ...	3.205	3.170	3.159	3.164	3.159	3.160	3.174	3.176	3.162
2V ...	66°	70°	78°	77°	76°	75°	70°	71°	74°
γ:c ...	15°	15°	19°	18°	20°	19°	18°	17°	18°
α ...	1.662	1.650	1.643	1.651	1.653	1.651	1.659	1.654	1.651
β ...	1.673	1.664	1.655	1.660	1.663	1.662	1.670	1.665	1.661
γ ...	1.680	1.672	1.664	1.669	1.671	1.670	1.677	1.673	1.669
γ-β ...	0.007	0.008	0.009	0.009	0.008	0.008	0.007	0.008	0.008
γ-α ...	0.018	0.022	0.021	0.018	0.018	0.019	0.018	0.019	0.018

Pleochroism.

Hornblende from:	Pleochroism.		
	α	β	γ
1. Typical Glen Tilt diorite ...	pale yellow-green	greenish-yellow	brownish-green
2. Coarse appinite (large phenocrysts) ...	pale yellow-brown straw	brown-yellow yellow-green	dark yellow-brown green
3. Coarse appinite (small) ...	pale yellow-brown	light yellow-brown	brownish-yellow
5. Quartz-orthoclase-plagioclase-hornblende-rock ...	yellow-green	pale brown	brown
6. Hornblendite xenolith ...	straw	yellow-green	brownish-green
7. Hornblende-schist ...	pale yellow-green	pale green	green
8. Injected hornblende-schist	pale brown	brown	dark brown
9. Hornblende-schist xenolith	pale brown	brown	dark brown

The hornblende from the typical Glen Tilt diorite shows the greatest amount of individuality both chemically and optically. It is distinguished from the hornblendes of the appinites by a very high percentage of ferrous iron and an extremely low Fe₂O₃/FeO ratio, and this high iron content is shown by the high specific gravity. Furthermore, it is the only hornblende that combines low silica with a moderately low alumina percentage, and finally the Na₂O/K₂O ratio is very much less than in the other varieties. This distinct chemical constitution has resulted in the refractive indices being higher than those of the other hornblendes of the complex. This hornblende has been consistently developed in all the diorites without quartz or biotite, and in composition closely resembles a number of hornblendes from diorites and gabbros.¹

¹ W. Kunitz, Neues Jahrb. Min., Abt. A. 1930, Beil.-Bd. 60, p. 245. [M.A. 4-200.]

The hornblendes of the appinites and related quartz-orthoclase-plagioclase-hornblende-rock show a wide range of composition and vary with the formation-stage of the rock in which they occur. In the typical coarse appinite two distinct generations of hornblende occur. Brammall¹ has described from Malvern polyvarietal hornblendes from appinitic types which seem to be a feature of rocks of this nature. The earlier is a large brown hornblende set in a finer-grained matrix containing the later well-formed idiomorphic green hornblendes. The presence of two distinct amphiboles in this appinite is sufficient to suggest that one is unstable. The large brown hornblendes are usually completely surrounded by plagioclase and are invariably rimmed by a narrow zone of green hornblende. In many cases this conversion of the brown to the green type has been very much more extensive and the brown hornblendes show large areas of peripheral and sometimes internal replacement. This conversion from the brown to the green hornblende is frequently accompanied by the ejection of small granules of sphene, and the analyses show the brown to be more titaniferous than the green hornblende. Their compositions are seen to be well contrasted, low silica and high alumina in the earlier-formed brown hornblende being replaced by high silica and low alumina in the green. There is also a marked change in the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio, and the difference in titania has already been noticed.

The hornblendes occurring as medium size phenocrysts in the appinite containing pyroxene (analysis 4) have a similar habit to the large brown hornblende of the coarse appinites. Peripheral conversion to a green hornblende is again common, but in this case there is only a little sphene ejected. Small green hornblendes are also present in the finer matrix and appear to be identical in optical properties and habit with the analysed small green hornblende of the coarse appinite (analysis 3). The instability of these phenocrystal hornblendes is again marked by their readiness to be converted to a green hornblende which is stable in the assemblage in which they occur. The main feature of their composition is their intermediate position between those of the brown and green hornblendes of the coarse appinite in the silica/alumina replacement ratio.

In the hornblende from the quartz-orthoclase-plagioclase-hornblende-rock the stage has been reached in which the hornblende has become almost univarietal in a rock of appinitic type. The grain-size of the rock is also significant. It is one of uniform granular texture in which there is practically no distinction in the size of the hornblendes. Although there

¹ A. Brammall and J. G. C. Leech, read before Min. Soc., March 1936.

are some larger individuals showing pale brown cores with broad rims of green hornblende, no attempt was made to separate the green and the brown varieties and the analysis (no. 5) represents the composite composition of both hornblendes. Some of the smaller hornblendes are also pale brown in colour. In spite of this composite nature, the analysis shows a striking comparison with the small green hornblende of the typical appinite. Silica is high and alumina low, the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio is closely similar, and the TiO_2 , MgO , and CaO show equally close percentages.

The hornblende from the hornblendite is seen to possess the characters of an amphibole of late formation, and shows close affinities with the small later-formed green hornblende of the appinites, and the mineral from the quartz-orthoclase-plagioclase-hornblende-rock. Compared with the average hornblendite¹ the analysis shows high silica and low alumina. The feature of the average hornblendite analysis is one of early hornblende formation, and is closely comparable with both the analyses of the earlier-formed phenocrystal hornblende of the appinites, and the brown hornblende of the injected schists. From these facts it seems probable that the analysis of the hornblende of the hornblendite xenoliths does not represent its original composition, but shows that it has since been converted to a form in equilibrium with the assemblage of the enclosing rock. The magma from which the hornblende² crystallizes for the formation of a hornblendite is undoubtedly basic in composition, and hornblendite analyses show that the hornblendes are similar in type to the earlier hornblendes of the Glen Tilt complex. This conversion of the Glen Tilt hornblendite amphibole to a new variety stable in this more acid assemblage is also shown where the hornblende detached from the xenoliths, and incorporated within quartz-diorite, is seen to be in equilibrium with the enclosing rock.

The green hornblende from the hornblende-schist (the one analysed was taken from the central unaffected portion of a large xenolith) presents quite a different composition from the other hornblendes. This is to be expected as it is in no way genetically connected with the rocks of the complex, and arises as a metamorphic product of regional movements prior to the emplacement of the intrusion. It is rich in alumina

¹ R. A. Daly, *Igneous rocks and the depth of the earth*. New York, 1935. Average hornblendite: SiO_2 42.80, TiO_2 1.62, Al_2O_3 10.55, Fe_2O_3 6.62, FeO 9.16, MnO 0.24, MgO 12.48, CaO 11.67, Na_2O 1.89, K_2O 1.00, H_2O 1.73, P_2O_5 0.24.

² The hornblende of some hornblendites is not primary but results from the alteration of pyroxene; e.g. the davainite at Garabal Hill (B. K. N. Wyllie and A. Scott, *Geol. Mag.*, 1913, vol. 50, p. 503).

and correspondingly poorer in magnesia than the igneous hornblende, and shows the highest $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio. The conversion of this hornblende under two different conditions has been examined. In many localities where the hornblende-schists form the contact-rock, or occur as large xenoliths within the granite, large porphyroblastic hornblendes are seen to grow within the body of the schist and especially in proximity to the narrow permeating veins of volatile-rich emanations from the granite. These porphyroblastic hornblendes lose their green colour, develop a pale brown tint, and are sieved with many inclusions of feldspar. As these are expelled the hornblende develops a stronger brown colour and becomes more and more idiomorphic. The chemical changes involved in this conversion from the green hornblende of the schist to the newly-formed brown variety show, from the recalculated analyses compared on the basis of equal volumes, an increase of TiO_2 1.9, MgO 1.5, CaO 1.0, K_2O 0.5, F 0.6 %; and a decrease of Al_2O_3 4.0, Na_2O 0.25, H_2O 0.45 %; while SiO_2 , Fe_2O_3 , and FeO remained unchanged. These recalculated analyses are given under A, B, C in table II.

TABLE II. Recalculated analyses of hornblendes.

	A.	B.	C.	D.	E.
SiO_2	43.91	44.12	44.07	46.95	44.58
TiO_2	3.71	1.80	3.72	1.73	1.82
Al_2O_3	10.53	14.58	10.57	9.40	14.73
Fe_2O_3	5.00	5.10	5.01	3.65	5.15
FeO	8.84	8.92	8.88	8.34	9.01
MnO	0.17	0.21	0.17	0.11	0.21
MgO	12.24	10.76	12.28	14.38	10.87
CaO	11.73	10.79	11.77	10.48	10.90
Na_2O	1.25	1.50	1.26	1.15	1.52
K_2O	1.09	0.60	1.10	1.29	0.61
$\text{H}_2\text{O}+105^\circ\text{C.}$	0.94	1.41	0.95	1.99	1.42
$\text{H}_2\text{O}-105^\circ\text{C.}$	0.11	0.08	0.11	0.53	0.08
F	0.83	0.22	0.84	—	0.22
	100.35	100.09	100.73	100.00	101.12
Less O for F	0.35	0.09	0.35	—	0.09
	100.00	100.00	100.38	100.00	101.03

A. Analysis 8 recalculated to 100 %.

B. Analysis 7 recalculated to 100 %.

C. Analysis 8 allowance made for the differences in specific gravity.

D. Analysis 9 recalculated to 100 %.

E. Analysis 7 allowance made for the differences in specific gravity.

It is interesting to compare the composition of the brown hornblende developed in the hornblende-schist permeated by granite veins and that

developed from hornblende-schist xenoliths enclosed in the diorite. These schist xenoliths develop a marginal zone rich in large brown hornblende phenocrysts. The formation of this new hornblende results from the instability of the schist amphibole under magmatic conditions, and detached clots of this newly formed hornblende, which do not readily lose their individuality when immersed in the diorite, indicate their comparative stability in the new environment. The diorite penetrates along the laminae of the schist, and the newly formed brown hornblendes tend to be aligned along these planes as well as around the xenolithic margins. The conversion of the small, green schist hornblende to the brown takes place very rapidly as the margins or veins are approached, the transition usually being completed within 0.5 cm. The composition of this hornblende shows a greater change than the brown hornblende of the permeated schists, but its most significant feature is that, taken as a whole, it shows a closer resemblance to the hornblende of the diorite than the other hornblendes of the complex. The green hornblende of the schist and the analyses of the newly-developed brown hornblende have been recalculated to 100.00% and compared on the basis of equal volumes. From the recalculated analyses (B, D, E, table II) the following additions of material are seen: SiO_2 2.35, MgO 3.5, K_2O 0.6, H_2O 0.6%; and the following losses Al_2O_3 5.3, Fe_2O_3 1.5, FeO 0.75, Na_2O 0.35, and CaO 0.4%.

If the three analyses are considered together and the brown hornblende developed around the schist xenoliths regarded as the most advanced type, i.e. more stable in a diorite environment, the majority of the oxides show a progressive change. The most important movement of the oxides is a marked decrease in alumina which is counterbalanced by a corresponding increase in the magnesia percentage. Other oxides showing a progressive change are FeO , Fe_2O_3 , Na_2O , MnO decreasing, and K_2O increasing. Silica, titania, and lime appear to have no simple relationship. Although there is a gradual increase in the sum of the water and fluorine content, their mutual replacement does not appear to be at all systematic.

III. *The Hornblendes, their Composition and Genetical Relationships.*

The hornblende analyses have been plotted on a trilinear diagram (fig. 1) in order to demonstrate graphically the difference between the earlier and later formed hornblendes and their relations with the hornblendes from the schist and hornblendite. The diagram emphasizes the difference between the large brown 'phenocrystal' hornblendes, whether

occurring in the permeated schist, schist xenoliths, or the typical appinitic development, and the smaller green hornblendes either of the finer matrix of the appinites or that from the quartz-orthoclase-plagioclase hornblende-rock. This rock is considered from the available evidence

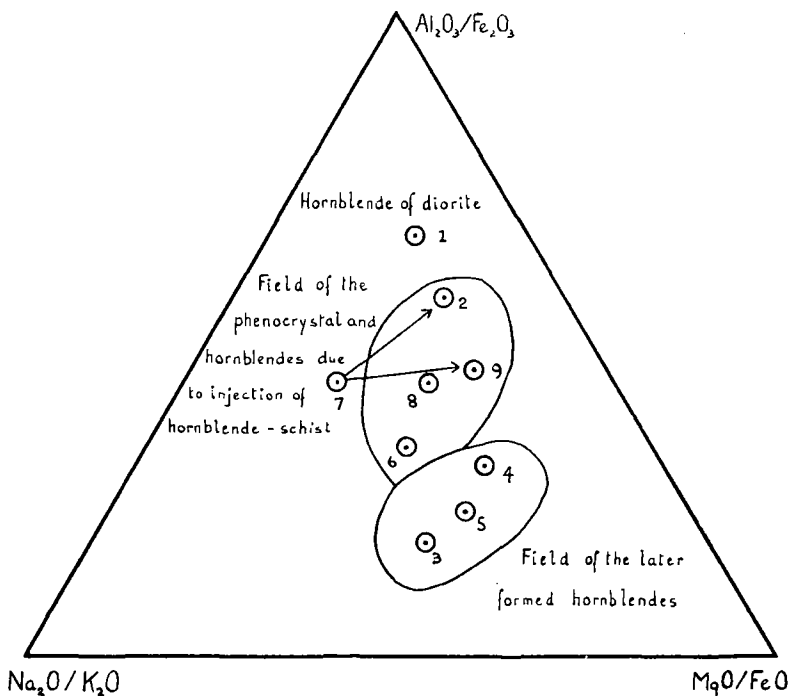


FIG. 1. Trilinear diagram showing the variation in the molecular ratios $Al_2O_3/Fe_2O_3-Na_2O/K_2O-MgO/FeO$ of the earlier- and later-formed hornblendes. The figures refer to the numbers in table I.

to be derived from the hornblendite. From table I the two hornblendes from these two rocks are seen to be closely comparable, and the diagram shows that only a small movement towards the field of the later-formed hornblendes is necessary to convert the hornblendite amphibole to a variety stable in the new environment of the quartz-orthoclase-plagioclase-hornblende-rock. The intermediate chemical position of the hornblende from the medium-grained appinite between the fields of the brown and green hornblende is clearly seen and the aluminous nature of the hornblende from the schist and its brown injection derivatives, altering with a progressive increase in the MgO/FeO ratio, is demonstrated.

Finally, the isolated character of the green hornblende from the ordinary diorite and its lack of genetic relationship with the other hornblendes is fully emphasized. The hornblendes show that the differences in chemical composition between the green and brown varieties, except the earlier-formed greenish-brown hornblende of the diorite, are a consistently higher silica percentage and lower alumina, total alkalis, and titania in

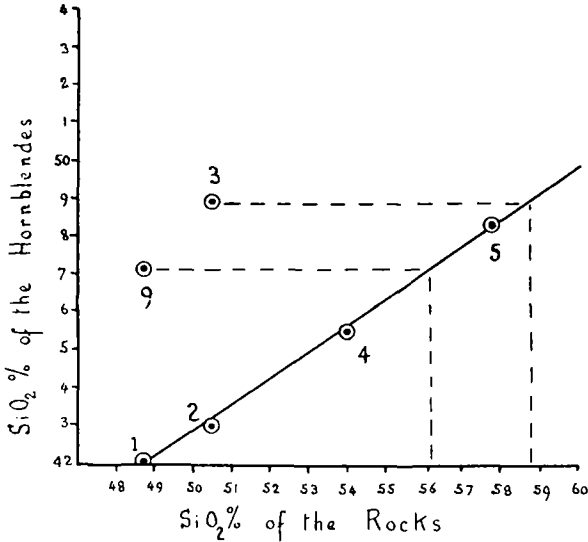


FIG. 2. Diagram showing the relationship between the silica percentage of the hornblendes and of the rocks in which they are contained.

the green, while the total iron is approximately the same in both hornblendes. These results are in agreement with the averages of the main constituents in green and brown hornblendes presented by Graham.¹

It will be seen from the analyses that the silica percentage of the hornblendes tends to increase as the rock becomes richer in silica. A diagram showing the relationship of the silica percentage of the hornblende and the parent rock is shown in fig. 2. Although there is no rigid relationship between the silica percentage of the hornblende and the rock in which it is formed there is no doubt that an increase in the acidity of the parent rock tends to favour the development of a hornblende richer in silica. Of the plotted analyses which fall off the line showing this relationship only that of the small green hornblende of the typical

¹ W. A. P. Graham, Amer. Min., 1926, vol. 11, p. 121. [M.A. 3-294.]

appinite has been precipitated from even a 'partial' magma, and from a general examination of the rock is inferred to be of later formation, developed at a stage comparable with that of the quartz-orthoclase-plagioclase-hornblende-rock. The brown hornblende of the typical appinite results from the alteration of the original hornblende, whereas the green hornblende is a direct product of the hybridizing 'magma' and the xenolithic rock either hornblendite or hornblende-schist. The small green hornblende is in equilibrium with this later fraction of the rock, that is, with the feldspar, but is at a more advanced stage than that represented by the bulk analysis of the rock. This conclusion is strengthened by the diagram, which shows that the hornblende would be more closely related to a rock of approximately 58% silica. It was suggested in discussing the 'reaction' hornblende of the schist xenolith enclosed in the quartz-mica-diorite, that the more extensive change, compared with the newly-developed hornblende in the injected schist, was due to an attempt to produce a hornblende in equilibrium with the quartz-mica-diorite. From the above diagram it is seen that the silica percentage of the rock should contain between 55% and 56% silica, and this is very close to the actual composition of the analysed quartz-mica-diorite.¹ The silica percentage of the brown porphyroblastic hornblende developed in the injected schists indicates possible stability within the silica variation of the appinites. This is not surprising in view of the fact that at least some of the appinite types are derived from the alteration of hornblende-schists. Graham (*loc. cit.*, p. 119), in discussing the chemical composition of hornblendes from eight different rock families, showed that the silica is high and the alumina low in typical hornblendes from granites. This has also been noticed in the late-stage hornblende from the Cairnsmore complex.²

A significant feature of the hornblendes of the Glen Tilt rocks is the almost constant percentage of total iron oxides, and except for the hornblende from the diorite (anal. 1) the extreme variation is from 11.87 to 14.29%. It is well known that the MgO/FeO ratio is higher in the solid phase than in the liquid phase with which it is in equilibrium, and consequently that differentiation will proceed in the direction of a low MgO/FeO ratio. This differentiation trend has not been effective in the development of the Glen Tilt hornblendes, and although analyses 3, 4,

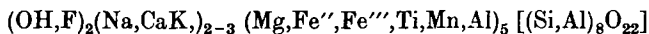
¹ SiO₂ 56.73% for the quartz-mica-diorite of the Glen Tilt complex. A description of the diorites and associated rocks of this complex will be published later.

² W. A. Deer, Note on a pegmatitic hornblende from the Cairnsmore complex. *Geol. Mag.* London, 1937, vol. 74, pp. 359-361. [M.A. 7-25.]

and¹ 6 do show a slightly higher total iron content than the rest there is no decrease in the MgO/FeO ratio. This fall in the ratio MgO/FeO has been observed by Hurlbut¹ in the hornblendes from the Bonsall tonalite, California. Basing his results on the refractive indices of hornblendes in altered gabbro xenoliths, now of dioritic composition, immersed in tonalite, he states that the 'data show a close relation between the various hornblendes, but indicate that the hornblendes of the inclusions are higher in magnesia and lower in iron than those of the tonalite'. The absence of this trend in the hornblendes of Glen Tilt is no doubt to be correlated with their development in rocks not formed under conditions of ordinary crystallization-differentiation. The majority have not formed from a magma of the composition now represented by the rock in which they occur, and it has also been shown that some are not in equilibrium with the assemblage in which they occur.

IV. *Crystal Chemistry of the Hornblendes.*

Although Warren has confirmed the early work of Schaller² giving the formula of tremolite as $H_2Ca_2Mg_5(SiO_3)_8$ the statement of Bowen and Posnjak³ that the amphibole question is probably finally solved seems to be somewhat premature. The hornblende analyses have been calculated according to Warren's⁴ formula



derived from a study of the crystal-structure of tremolite,⁵ and extended to include the common hornblendes, that is, on a basis of 24(O,OH,F) atoms to the unit cell. The formulae derived from these calculations are listed below. This type formula had also been developed by Kunitz⁶ for certain amphiboles, but this agreement between the earlier chemical study and the later X-ray investigation is not so well maintained by the general amphibole formula proposed by Machatschki,⁷ $XY_3(Si,Al)_4(O,OH,F)_{12}$, in which X represents Ca^{++} and Na^+ , with a little K^+ , and perhaps Mn^{++} , and Y represents Mg^{++} , Fe^{++} , Al^{+++} , and Mn^{+++} .

¹ C. S. Hurlbut, *Amer. Min.*, 1935, vol. 20, p. 622. [M.A. 6-223.]

² W. T. Schaller, *Bull. U.S. Geol. Surv.*, 1916, no. 610, p. 136. [M.A. 1-258.]

³ N. L. Bowen and E. Posnjak, *Amer. Journ. Sci.*, 1931, ser. 5, vol. 22, p. 201. [M.A. 5-103.]

⁴ B. E. Warren, *Zeits. Krist.*, 1930, vol. 72, pp. 493-517. [M.A. 4-278.]

⁵ B. E. Warren, *Zeits. Krist.*, 1929, vol. 72, p. 42. [M.A. 4-201.]

⁶ W. Kunitz, *Neues Jahrb. Min., Abt. A*, 1930, Beil.-Bd. 60, pp. 200, 206. [M.A. 4-200.]

⁷ F. Machatschki, *Zeits. Krist.*, 1929, vol. 71, p. 222. [M.A. 4-202.]

TABLE III. Calculation of formulae of hornblendes nos. 1-9.

	Wt. %.	No. of metal atoms on basis of 24(O,OH,F).		Wt. %.	No. of metal atoms on basis of 24(O,OH,F).			
		Hornblende no. 1.			Hornblende no. 2.			
SiO ₂ ...	42.11	6.314	} 8.00	43.01	6.288	} 8.00		
Al ₂ O ₃ ...	10.05	1.776		{ 1.686 0.090	12.01		2.062	{ 1.712 0.350
TiO ₂ ...	2.76	0.311	} 5.21	2.87	0.314	} 5.21		
Fe ₂ O ₃ ...	2.82	0.319			3.35		0.368	
FeO ...	15.14	1.896			9.07		1.109	
MnO ...	0.24	0.031	} 2.39	0.19	0.023	} 2.34		
MgO ...	11.48	2.565			14.00		3.049	
CaO ...	11.34	1.822	} 2.02	11.79	1.845	} 1.75		
Na ₂ O ...	1.01	0.294			1.08		0.306	
K ₂ O ...	1.43	0.274	} 2.02	1.01	0.188	} 1.75		
H ₂ O+ ...	2.02	2.018			1.40		1.364	
H ₂ O- ...	0.06	—		0.06	—			
F ...	—	—		0.84	0.386			
	100.46			100.68				
Less O for F ...	—			0.36				
	100.46			100.32				
		Hornblende no. 3.			Hornblende no. 4.			
SiO ₂ ...	48.92	7.155	} 8.00	45.50	6.630	} 8.00		
Al ₂ O ₃ ...	5.88	1.010		{ 0.845 0.165	9.66		1.654	{ 1.370 0.284
TiO ₂ ...	1.21	0.133	} 5.11	1.73	0.189	} 5.17		
Fe ₂ O ₃ ...	6.50	0.715			6.06		0.663	
FeO ...	7.79	0.952			6.90		0.840	
MnO ...	0.17	0.021	} 2.25	0.18	0.022	} 2.26		
MgO ...	14.32	3.120			14.61		3.171	
CaO ...	11.37	1.780	} 1.46	11.24	1.754	} 1.68		
Na ₂ O ...	1.20	0.339			1.20		0.338	
K ₂ O ...	0.71	0.132	} 1.46	0.92	0.172	} 1.68		
H ₂ O+ ...	1.37	1.335			1.73		1.681	
H ₂ O- ...	0.18	—		0.19	—			
F ...	0.27	0.123		trace	—			
	99.89			99.92				
Less O for F ...	0.11			—				
	99.78			99.92				

TABLE III (continued).

	Wt. %.	No. of metal atoms on basis of 24(O,OH,F).		Wt. %.	No. of metal atoms on basis of 24(O,OH,F).		
Hornblende no. 5.				Hornblende no. 6.			
SiO ₂	48.32	7.044	} 8.00	48.96	7.068	} 8.00	
Al ₂ O ₃	6.43	1.101		{ 0.956	7.85		1.332
			{ 0.145			{ 0.400	
TiO ₂	1.43	0.156	} 5.10	1.07	0.117	} 5.29	
Fe ₂ O ₃	5.45	0.597					
FeO	7.90	0.964					
MnO	0.13	0.016					
MgO	14.82	3.218					
CaO	11.99	1.871	} 2.28	11.90	1.840	} 2.23	
Na ₂ O	0.99	0.280					
K ₂ O	0.67	0.124	} 1.57	1.04	0.291	} 1.25	
H ₂ O+	1.61	1.565					
H ₂ O-	0.06	—					
F	trace	—		1.41	0.642		
	99.80			101.15			
Less O for F ...	—			0.61			
	99.80			100.54			
Hornblende no. 7.				Hornblende no. 8.			
SiO ₂	44.23	6.436	} 8.00	44.15	6.491	} 8.00	
Al ₂ O ₃	14.62	2.498		{ 1.564	10.59		1.829
			{ 0.934			{ 0.320	
TiO ₂	1.81	0.198	} 5.14	3.73	0.411	} 5.09	
Fe ₂ O ₃	5.11	0.559					
FeO	8.94	1.087					
MnO	0.21	0.026					
MgO	10.78	2.337					
CaO	10.81	1.685	} 2.22	11.80	1.858	} 2.42	
Na ₂ O	1.51	0.424					
K ₂ O	0.61	0.114	} 1.48	1.10	0.207	} 1.34	
H ₂ O+	1.42	1.377					
H ₂ O-	0.08	—					
F	0.22	0.105		0.84	0.406		
	100.35			100.91			
Less O for F ...	0.09			0.36			
	100.26			100.55			

TABLE III (continued).

	Wt. %:	No. of metal atoms on basis of 24(O,OH,F).	
Hornblende no. 9.			
SiO ₂	47.14	6.813	} 8.00
Al ₂ O ₃	9.44	1.597	
TiO ₂	1.74	0.188	} 5.13
Fe ₂ O ₃	3.66	0.397	
FeO	8.38	1.013	
MnO	0.11	0.013	
MgO	14.44	3.109	
CaO	10.53	1.629	} 2.19
Na ₂ O	1.15	0.321	
K ₂ O	1.30	0.240	} 1.93
H ₂ O+	2.00	1.927	
H ₂ O--	0.53	—	
F	—	—	

100.42

In his work on the crystal-structure and chemical composition of the monoclinic amphiboles Warren (loc. cit., 1930, pp. 508-509) stated that the excess in the value of the (Na,Ca,K) group greater than 2.0, as determined for tremolite, depends on the amount of aluminium replacing silicon in the tetrahedral chains, and that in those hornblendes where approximately one quarter of the silicon is replaced by aluminium the value of the (X) group (Na,Ca,K) becomes nearly 3.0. Although this is the case with some hornblendes (e.g. those chosen by Warren and included in his table, p. 506) it is far from being a general rule as seen by a number of recent hornblende analyses.¹ This is clearly the case of the Glen Tilt minerals, for although they show a very slight general tendency to increase the value of the (X) group from 2.0 towards 3.0 with increasing replacement of silicon by aluminium there is no close relationship between these two factors. In the general case the value of the (X) group does not appear to be dependent so much on the silicon/aluminium replacement as on the percentage of alkalis in the hornblende composition. The amount of lime in the constitution, not only of common hornblende but also of tremolite and actinolite, tends to be almost constant, so that any increase in the percentage of total alkalis is effective in increasing the value of the (X) group, and this is the case of those

¹ J. D. W. Wiseman. Quart. Journ. Geol. Soc. London., 1934, vol. 90, pp. 368-369, 382-384 [M.A. 6-224]; S. R. Nockolds, Geol. Mag. London, 1935, vol. 72, p. 310; and others.

analyses chosen by Warren. The Glen Tilt hornblendes show a relatively constant and moderately low amount of total alkalis, but a considerable range of alumina, with a consequently small variation in the value of the (X) group for very larger difference of silicon/aluminium replacements.

The distinction between the earlier- and later-formed hornblendes of the complex is seen in the varying values of the replacements listed below:

		Hornblendes.								
		1.	2.	3.	4.	5.	6.	7.	8.	9.
A.	1.69	1.71	0.85	1.37	0.96	0.93	1.56	1.51	1.19	
B.	0.09	0.35	0.16	0.28	0.14	0.40	0.93	0.32	0.41	
C.	0.39	0.34	0.25	0.26	0.28	0.23	0.22	0.42	0.19	

- A. Aluminium replacing silicon.
 B. Aluminium replacing magnesium.
 C. Excess of (X) group over 2.

The table indicates the very rough correlation between the increasing value of the (X) group with the increasing replacement of silicon by aluminium. The isolated position of the hornblende from the normal diorite is seen in the very high replacement of silicon by aluminium, and the low replacement of magnesium. It emphasizes the sympathetic decrease in the MgO and FeO in the conversion of the green hornblende from the schist to the brown hornblendes of the injected schists, and the convergence of these towards the structure and composition of the later-formed hornblendes. This is especially marked in the 'reaction' hornblende developed at the margin of the schist xenolith in the quartz-mica-diorite (no. 9).

There are only two relationships which the hornblende composition must satisfy: the first is the hornblende crystal-structure; the second, that the total positive and negative valencies must balance. The occupation of the vacant AA' positions of Warren (loc. cit., 1930, p. 512) in the tremolite structure by alkalis is of course insufficient in itself to balance the negative valency excess caused by the replacement of silicon by aluminium. This was demonstrated graphically by plotting the amount of aluminium replacing silicon against the excess of the value of the (X) group over 2.0 from a large number of analyses from Doelter,¹ Kunitz (loc. cit., pp. 244-245), and others, and in only two cases was the balance obtained, solely by the increase of the (X) group. A selection of the formulae obtained from these analyses showing the replacement values

¹ C. Doelter, *Handbuch der Mineralchemie*, 1914, vol. 2, pt. 1, pp. 610-620.

is given below. The deficiency of positive ions is, however, further compensated by the replacement of divalent magnesium by sesquioxides and tetravalent titanium. This is usually slightly offset by the replacement of divalent calcium by univalent alkalis when the value for Ca^{++} is less than 2.0.

- I. $(\text{OH})_{1.8} (\text{Ca}, \&c.)_2 \text{Na}_{0.3} \text{Mg}, \&c._{4.5} (\text{Fe}''', \text{Ti}, \text{Al})_{0.7} [(\text{Si}_{7.1} \text{Al}_{0.9} \text{O}_{22})]$.
- II. $(\text{OH})_{1.6} (\text{Ca}, \&c.)_2 \text{Na}_{0.7} \text{Mg}, \&c._{4.4} (\text{Fe}''', \text{Ti}, \text{Al})_{0.8} [(\text{Si}_{6.3} \text{Al}_{1.7} \text{O}_{22})]$.
- III. $(\text{OH})_{1.4} (\text{Ca}, \&c.)_2 \text{Na}_{0.7} \text{Mg}, \&c._{4.1} (\text{Fe}''', \text{Ti}, \text{Al})_{1.1} [(\text{Si}_{6.3} \text{Al}_{1.7} \text{O}_{22})]$.
- IV. $(\text{OH})_2 (\text{Ca}, \&c.)_2 \text{Na}_{0.5} \text{Mg}, \&c._{4.5} (\text{Fe}''', \text{Ti}, \text{Al})_{0.7} [(\text{Si}_{6.4} \text{Al}_{1.6} \text{O}_{22})]$.
- V. $(\text{OH})_2 (\text{Ca}, \&c.)_2 \text{Na}_{0.4} \text{Mg}, \&c._{4.3} (\text{Fe}''', \text{Ti}, \text{Al})_{0.9} [(\text{Si}_{6.4} \text{Al}_{1.6} \text{O}_{22})]$.
- VI. $(\text{OH})_2 (\text{Ca}, \&c.)_2 \text{Na}_{0.7} \text{Mg}, \&c._{4.2} (\text{Fe}''', \text{Ti}, \text{Al})_{1.0} [(\text{Si}_{6.4} \text{Al}_{1.6} \text{O}_{22})]$.
- VII. $(\text{OH})_{2.1} (\text{Ca}, \&c.)_2 \text{Na}_{0.3} \text{Mg}, \&c._{3.2} (\text{Fe}''', \text{Ti}, \text{Al})_{1.7} [(\text{Si}_{6.3} \text{Al}_{1.7} \text{O}_{22})]$.
- VIII. $(\text{OH})_{1.9} (\text{Ca}, \&c.)_2 \text{Na}_{0.5} \text{Mg}, \&c._{4.1} (\text{Fe}''', \text{Ti}, \text{Al})_{0.9} [(\text{Si}_{6.7} \text{Al}_{1.3} \text{O}_{22})]$.
- IX. $(\text{OH})_{1.5} (\text{Ca}, \&c.)_2 \text{Na}_{0.5} \text{Mg}, \&c._{3.9} (\text{Fe}''', \text{Ti}, \text{Al})_{1.3} [(\text{Si}_{6.4} \text{Al}_{1.6} \text{O}_{22})]$.
- X. $(\text{OH})_{1.8} (\text{Ca}, \&c.)_2 \text{Na}_{0.2} \text{Mg}, \&c._{4.2} (\text{Fe}''', \text{Ti}, \text{Al})_{0.9} [(\text{Si}_{7.0} \text{Al} \text{O}_{22})]$.

Nos. I-VI are from Kunitz's hornblende analyses (loc. cit., p. 245) nos. 4-9 respectively.

No. VII. Doelter, p. 620. Hornblende from diorite. Schwarzenberg, Vosges.

No. VIII. Doelter, p. 619. Hornblende from hornblende-gabbro. Beaver Creek, California.

No. IX. Doelter, p. 619. Hornblende from anorthite-diorite-schist. Kremstal, Austria.

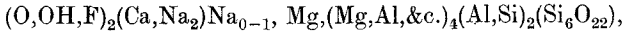
No. X. Doelter, p. 614. Hornblende from quartz-diorite. Mount Hoffman, California.

The value of the (Y) group in the common hornblende is consistently higher than the value 5 for the tremolite structure, and it seems likely that some of the vacant AA' positions may be occupied by ions of the (Y) group. This high value of the (Y) group is significant and also appears to be related to the value of the hydroxyl-fluorine group. Warren (loc. cit., 1930, p. 516) has commented on the possibility that in cases in which there has been a large replacement of magnesium by sesquioxides and titanium the (OH,F) group may be partly replaced by oxygen. In such cases the value of the (Y) group is usually considerably greater than 5.0 and the value of (OH,F) well below 2.0.¹ The replacement of OH^- and F^- by O^{--} then becomes necessary to maintain the

¹ E. S. Larsen, J. Irving, F. A. Gonyer, and E. S. Larsen (3rd), Amer. Min., 1937, vol. 22, p. 898. [M.A. 7-31.] Three analyses of hornblendes from the Tertiary volcanic rocks of the San Juan region, Colorado, support this suggestion. The authors state that if Fe'' is replaced by Fe''' some replacement, such as OH by O, must take place, a fact which is confirmed by the analyses, the formulae of which are given below:

1. $(\text{OH}, \text{F})_{0.6} (\text{Ca}, \text{Na})_{2.4} (\text{Mg}, \text{Fe}'', \text{Fe}''', \text{Mn}, \text{Ti}, \text{Al})_{5.25} [(\text{Si}, \text{Al})_8 \text{O}_{22}]$.
2. $(\text{OH}, \text{F})_{1.2} (\text{Ca}, \text{Na})_{2.4} (\text{Mg}, \text{Fe}'', \text{Fe}''', \text{Mn}, \text{Ti}, \text{Al})_{5.25} [(\text{Si}, \text{Al})_8 \text{O}_{22}]$.
3. $(\text{OH})_{0.8} (\text{Ca}, \text{Na})_{2.5} (\text{Mg}, \text{Fe}'', \text{Fe}''', \text{Mn}, \text{Ti}, \text{Al})_{5.4} [(\text{Si}, \text{Al})_8 \text{O}_{22}]$.

chemical valency which is upset by the introduction of additional ions in the (Y) group. This becomes more obvious in the case of the basaltic hornblendes and the anhydrous amphiboles which show characteristically a very low value for the (OH,F) group, and a consistently large replacement of magnesium by titanium and ferric iron. This oxygen/hydroxyl replacement is accepted by Berman and Larsen,¹ who write the hornblende formula, showing the limits of replacement as:



but the restriction of the minimum value for silicon to 6.0 does not appear to hold in the case of some basaltic hornblendes.²

V. The Relationship of the Optical Properties and Chemical Composition.

The study of the Glen Tilt amphiboles shows that the hornblendes remain the most difficult series of the common rock-forming minerals to estimate chemically from their optical properties. Nevertheless, some indication of their constitution can be obtained from the optical properties and especially from the refractive indices. The most important factor effecting the refractive indices is the magnesia/ferrous iron ratio. Billings³ has shown that the optical properties of ferromagnesian hornblende and magnesian hornblende are largely determined by this ratio. With increasing ferrous iron the refractive indices as well as the specific gravity increase, and these changes are accompanied by a decrease in the optic axial angle. These optical effects are also described by Marchet⁴ in the hornblendes from the Waldviertel, Austria. Ford's⁵ investigations and Wiseman's study (loc. cit., p. 384) of hornblendes under conditions of progressive metamorphism conform to this general rule. Barnes⁶ also observed that the conversion of green hornblende to brown hornblende on heating was accompanied by a decrease in the extinction-angle ($\gamma : c$). This is seen in the relationship of the green and brown hornblendes of the Glen Tilt complex.

¹ H. Berman and E. S. Larsen, *Amer. Min.*, 1931, vol. 16, p. 142. [M.A. 5-216.]

² Y. Kawano, *Proc. Imp. Acad. Tokyo*, 1934, vol. 10, pp. 349-352. [M.A. 6-190.]

Analysis of basaltic hornblende:

SiO₂ 38.30, TiO₂ 6.06, Al₂O₃ 12.87, Fe₂O₃ 7.98, FeO 6.96, MnO 0.12, MgO 11.79, CaO 10.47, Na₂O 3.11, K₂O 1.30, H₂O+ 1.10, F 0.05, giving the formula: (OH,F)_{1.1}(Ca,Na,K)_{2.8}(Mg,Fe'',Fe''',Mn,Ti)_{5.1}[(Si_{5.7}Al_{2.3})O₂₂].

³ M. Billings, *Amer. Min.*, 1928, vol. 13, p. 292. [M.A. 4-39.]

⁴ A. Marchet, *Min. Petr. Mitt. (Tschermak)*, 1925, vol. 38, p. 494. [M.A. 3-82.]

⁵ W. E. Ford, *Amer. Journ. Sci.*, 1914, ser. 4, vol. 37, p. 179.

⁶ V. E. Barnes, *Amer. Min.*, 1930, vol. 15, p. 393. [M.A. 4-391.]

The ratio of ferric to ferrous iron does not appear to be as important as the MgO/FeO ratio in the common hornblendes (compare Ford's diagram, p. 192). This ratio, however, becomes increasingly important in the case of the basaltic and oxyhornblendes. The ferric/ferrous iron ratios of the Glen Tilt hornblendes have been plotted on Barnes' diagram (loc. cit., p. 413) showing the relationship between ferrous and ferric iron in analysed samples of common, basaltic, and heated hornblendes. They all fall in the common hornblende field, although in numbers 3 and 4 the ferrous/ferric ratio approaches unity. The ratio Fe''/Fe''' does not appear to become important in effecting the optical properties until the Fe'''/Fe'' ratio is at least 2/1. The most difficult oxides to estimate from the optical properties are silica and alumina. This is illustrated by analyses 2, 5, 6, in which the values for α and γ are very similar but in which the silica and alumina percentages vary considerably. On the whole, increasing refractive index in hornblendes of diorites indicates an increase in alumina and a decrease in silica (see Ford's diagrams 1 and 2, p. 183). The increase of refractive index in the hornblendes of granites is usually due to a large increase in iron and not the increase in the silica/alumina ratio that accompanies it. Lime is very constant in value in all the common hornblendes and has no obvious influence on the refractive index.

VI. *The Colour of the Hornblendes.*

The question of the colour of the hornblendes still remains an unsolved problem. Although it is quite evident that the ratio $\text{Fe}_2\text{O}_3/\text{FeO}$ becomes important in the heated oxyhornblendes,¹ the change from green to brown hornblende is quite independent of this ratio in naturally occurring minerals. The $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio is increased in the green hornblendes of Glen Tilt, and in two recent analyses of green hornblende from the Purcell sills, British Columbia,² the ratio approaches 2:1. Graham (loc. cit., p. 121) has also stressed the relative unimportance of the state of the iron oxidation and its influence on the optical properties of hornblende. In a general study of green minerals MacCarthy³ has shown that although the majority of green minerals are distinctly ferrous, that this is by no means always true, and a fair number of ferric minerals are evident.

¹ V. E. Barnes, loc. cit., p. 413; W. A. P. Graham, loc. cit., p. 122; A. Belovsky, Neues Jahrb. Min., 1891, p. 291.

² H. M. A. Rice, Amer. Min., 1935, vol. 20, p. 308. [M.A. 6-119.]

³ G. R. MacCarthy, Amer. Min., 1926, vol. 11, p. 321. [M.A. 4-251.]

The most noticeable increase in the conversion of the green hornblende of the schist to a deep brown hornblende in the permeated portions of the schist is the increase in titania. Winchell¹ and Graham (loc. cit., p. 121) have already suggested that the differences of green and brown hornblendes lies in the amount of titanium occurring as TiO_2 and Ti_2O_3 . The correlation between a brown colour and a high titanium content is supported by the general characteristics of basaltic hornblendes. The specific increase or decrease of titanium is not, however, the only deciding factor. This is seen in the brown 'reaction' hornblende, of the hornblende-schist xenoliths immersed in the quartz-mica-diorite in which the change from green to brown hornblende is unaccompanied by any increase in the percentage of titania. In the greenish-brown hornblendes of the appinites the large range of tint developed with a corresponding difference in chemical composition, the increase in the brown component does appear to be accompanied by an increase in the titanium percentage. This increase in the greenish-brown hornblendes has been noticed by Nockolds,² but in those hornblendes of the Glen Tilt complex with a well-developed deep green colour this correlation does not hold. This suggests that the colour problem of the hornblendes does not rest simply on the percentage of any one constituent, but rather on the type of ions in the hornblende structure, and is probably dependant on the state of the titanium oxidation as Ti''' or Ti'''' .

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¹ A. N. Winchell, Amer. Journ. Sci., 1924, ser. 5, vol. 7, p. 303. [M.A. 2-304.]

² S. R. Nockolds, personal communication.
