

*Chemical data on a silica-poor argillaceous hornfels and its constituent minerals.*

By F. H. STEWART, B.Sc., Ph.D.

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THE hornfels discussed here was collected from Sparcraigs, near Whitecairns, eight miles to the north of Aberdeen, very close to the eastern contact of the basic igneous intrusion of Belhelvie. The Highland Schists of the district are very poorly exposed, but at this locality there are a few small isolated outcrops of high-grade hornfels, nearly all silica-poor types, with garnet, spinel, hypersthene, cordierite, plagioclase, and biotite as their chief mineral constituents. The actual contact is obscured, but the igneous rock, an olivine-gabbro, is exposed at about twenty yards from the hornfels.

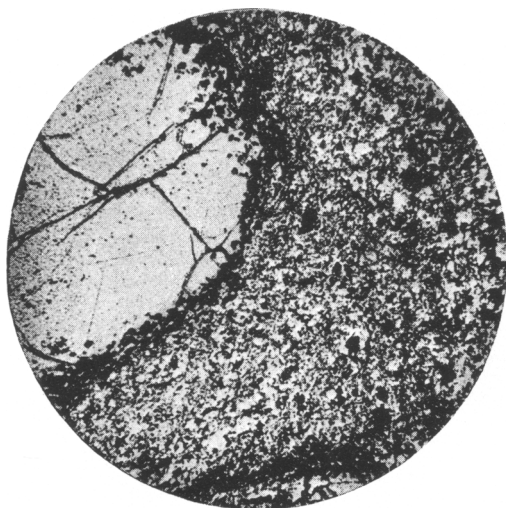


FIG. 1. Garnet-spinel-cordierite-plagioclase-biotite-hornfels.  
Sparcraigs, Belhelvie, Aberdeenshire.  $\times 15$ .

The hornfels on which this work has been done forms a fairly homogeneous band, about a foot in thickness, associated with closely related types. Fresh deep-red garnets, up to five millimetres in diameter, are scattered fairly evenly through the rock, and are set in a dark fine-grained base. The constituent minerals are garnet, spinel, cordierite, plagioclase, biotite, magnetite, and pyrrhotine, with a very little sillimanite and some orthoclase. In slice (fig. 1), the garnet forms large porphyroblasts, their rims crowded with small biotite flakes and iron-ore grains, with a few irregular grains of spinel. The interiors are relatively free from inclusions, but may contain patches of biotite flakes and

iron-ore crystals. A few small idioblastic garnets occur in the groundmass. Deep-green spinel forms irregular microporphyroblastic grains, up to 0.4 mm. in diameter, distributed evenly through the slice, and often associated with iron-ore. The finer-grained groundmass is composed chiefly of abundant biotite, cordierite, and plagioclase, with small grains of spinel and ore. The cordierite is often sector-twinned, and shows few haloes. It is optically positive. The plagioclase is andesine-labradorite, about  $Ab_1An_1$ , and is often untwinned. Some orthoclase has been observed in this groundmass, and a few tiny sillimanite needles.

An analysis of this rock is given in table I, with the measured mineral proportions. As it was found impossible to measure the relative proportions of cordierite and plagioclase, the plagioclase percentage was calculated from the values for CaO and  $Na_2O$  in the analysis. This was deducted from the measured percentage of the colourless constituents, and the remainder was allotted to cordierite, the small amount of orthoclase being neglected.

The garnet, spinel, cordierite, and biotite of this hornfels have been separated and analysed, and the analyses and atomic proportions are shown in tables II-V, with the optical properties of the minerals. The garnet was separated by hand-picking and by the centrifuge. The spinel was separated by centrifuging with

TABLE I. Garnet-spinel-cordierite-plagioclase-biotite-hornfels, Sparcraigs, Belhelvie, Aberdeenshire. (Analyst, F. H. Stewart.)

				Measured mineral proportions.							
SiO <sub>2</sub>	...	...	40.77	Na <sub>2</sub> O	...	...	1.09	Garnet	...	...	11
TiO <sub>2</sub>	...	...	2.13	K <sub>2</sub> O	...	...	2.73	Spinel and ore	...	...	6
Al <sub>2</sub> O <sub>3</sub>	...	...	25.90	H <sub>2</sub> O +	...	...	0.97	Biotite	...	...	42
Fe <sub>2</sub> O <sub>3</sub>	...	...	1.02	H <sub>2</sub> O -	...	...	0.26	Cordierite	...	...	21
FeO	...	...	17.52	P <sub>2</sub> O <sub>5</sub>	...	...	0.02	Plagioclase (calculated)	...	...	20
MnO	...	...	0.24	Total	...	...	99.67				100
MgO	...	...	4.95								
CaO	...	...	2.07								

TABLE II. Garnet from silica-poor hornfels, Sparcraigs, Belhelvie, Aberdeenshire. (Analyst, F. H. Stewart.)

	Wt. %.	Molecular ratios.	No. of metal atoms to 12 oxygens.	
SiO <sub>2</sub>	36.56	0.6087	Si	2.948
TiO <sub>2</sub>	0.51	0.0064	Ti	0.031
Al <sub>2</sub> O <sub>3</sub>	21.07	0.2067	Al	2.001
Fe <sub>2</sub> O <sub>3</sub>	0.47	0.0029	Fe <sup>'''</sup>	0.028
FeO	33.51	0.4665	Fe <sup>''</sup>	2.259
MnO	1.81	0.0255	Mn	0.124
MgO	3.97	0.0982	Mg	0.476
CaO	1.61	0.0287	Ca	0.139
Total	99.51		O	12.000
Almandine	77.85			
Pyrope	13.26			
Spessartine	4.24	<i>n</i>	...	1.801 ± 0.002 (Na)
Grossular	3.04	Sp. gr.	...	4.12
Andradite	1.61			

Clerici solution, but it was found impossible to free the material from composite garnet-spinel grains, and the analysis has been recalculated after subtraction of the garnet impurity (see table III). The cordierite and biotite were separated by the centrifuge and the Evans's electromagnetic separator (Min. Mag., 1939, vol. 25, p. 474), and the analysed material was practically free from impurities.

The refractory nature of the spinel made the determination of FeO rather difficult. The normal method was used (Washington, 1930, pp. 213-216), the mineral being decomposed by HF and H<sub>2</sub>SO<sub>4</sub>. Ten determinations were made, using 0.05 gram of material for each. In all cases there was incomplete decomposition, and the residues were filtered, washed, and treated again. In each determination there was complete decomposition after the third treatment. The values obtained varied between 37.51 and 35.79, with an average value of 36.50 %.

TABLE III. Spinel (hercynite) from silica-poor hornfels, Sparcraigs, Belhelvie, Aberdeenshire. (Analyst, F. H. Stewart.)

	Wt. %.	Wt. % recalculated after subtraction of garnet impurity.	Molecular ratios.	No. of metal atoms to 4 oxygens.
SiO <sub>2</sub>	2.69	—	—	—
TiO <sub>2</sub>	0.63	0.64	0.0080	Ti ... 0.014
Al <sub>2</sub> O <sub>3</sub>	50.56	53.02	0.5201	Al ... 1.824
Fe <sub>2</sub> O <sub>3</sub>	6.62	7.12	0.0446	Fe <sup>III</sup> ... 0.156
FeO	36.50	36.83	0.5127	Fe <sup>II</sup> ... 0.899
MnO	0.16	0.02	0.0003	Mn ... 0.001
MgO	2.48	2.37	0.0588	Mg ... 0.103
CaO	0.10	—	—	O ... 4.000
Total	99.74	100.00		
<i>n</i>	> 1.80			
Sp. gr.	4.21.			

The only impurity was garnet, the composition of which was calculated (on the basis of 2.69 % SiO<sub>2</sub>) from the analysis in table II.

TABLE IV. Cordierite, from silica-poor hornfels, Sparcraigs, Belhelvie, Aberdeenshire. (Analyst, F. H. Stewart.)

	Wt. %.	Molecular ratios.	No. of metal atoms to 18 oxygens.
SiO <sub>2</sub>	47.69	0.7940	Si ... 4.987
TiO <sub>2</sub>	trace	—	Al ... 4.007
Al <sub>2</sub> O <sub>3</sub>	32.52	0.3190	Fe <sup>III</sup> ... 0.049
Fe <sub>2</sub> O <sub>3</sub>	0.63	0.0039	Fe <sup>II</sup> ... 0.703
FeO	8.04	0.1119	Mn ... 0.004
MnO	0.04	0.0006	Mg ... 1.178
MgO	7.56	0.1875	Ca ... 0.058
CaO	0.52	0.0093	O ... 18.000
Na <sub>2</sub> O	0.53	0.0085	Na <sub>2</sub> O ... 0.053
K <sub>2</sub> O	0.42	0.0045	K <sub>2</sub> O ... 0.028
H <sub>2</sub> O +	1.85	0.1027	H <sub>2</sub> O ... 0.837
H <sub>2</sub> O -	0.55	0.0305	
Total	100.35		
$\alpha$	1.538	± 0.002 (sodium-light)	$\gamma - \alpha$ ... 0.009
$\beta$	1.542		2V ... 84°, positive
$\gamma$	1.547		Sp. gr. ... 2.64

TABLE V. Biotite, from silica-poor hornfels, Sparcraigs, Belhelvie, Aberdeenshire. (Analyst, F. H. Stewart.)

	Wt. %	Molecular ratios.	No. of metal atoms to 12 (O,OH,F).	
SiO <sub>2</sub> ... ..	34.87	0.5806	Si ... ..	2.665
TiO <sub>2</sub> ... ..	5.12	0.0641	Al ... ..	1.782
Al <sub>2</sub> O <sub>3</sub> ... ..	19.79	0.1941	Ti ... ..	0.294
Fe <sub>2</sub> O <sub>3</sub> ... ..	1.72	0.0108	Fe''' ... ..	0.099
FeO ... ..	17.79	0.2477	Fe'' ... ..	1.137
MnO ... ..	0.02	0.0003	Mn ... ..	0.001
MgO ... ..	7.42	0.1841	Mg ... ..	0.845
CaO ... ..	0.54	0.0096	Ca ... ..	0.044
Na <sub>2</sub> O ... ..	0.67	0.0108	Na ... ..	0.099
K <sub>2</sub> O ... ..	8.18	0.0868	K ... ..	0.797
H <sub>2</sub> O+ ... ..	2.89	0.1604	OH ... ..	1.472
H <sub>2</sub> O- ... ..	0.29	0.0161	F ... ..	0.101
F ... ..	0.42	0.0110		
Total ... ..	99.72			
Less O for F ... ..	0.18			
	99.54			

α ... ..	1.603	} ±0.002 (sodium-light)	α	Light yellow
β ... ..	1.660		β	} Brown with reddish tinge
γ ... ..	1.661		γ	
γ-α ... ..	0.058			

In each of these four minerals FeO and MgO may replace each other, and it is very interesting to note the selective distribution of these constituents. The FeO:MgO ratios are shown in table VI, with the weight percentages.

TABLE VI.

	Wt. % FeO.	Wt. % MgO.	Weight FeO:MgO.	Molecular FeO:MgO.	Wt. % Fe <sub>2</sub> O <sub>3</sub> .
Spinel ... ..	36.83	2.37	15.54	8.72	7.12
Garnet ... ..	33.51	3.97	8.44	4.75	0.47
Biotite ... ..	17.79	7.42	2.40	1.35	1.72
Cordierite ... ..	8.04	7.56	1.06	0.60	0.63

The FeO:MgO ratio in the spinel is remarkably high, and if we included Fe<sub>2</sub>O<sub>3</sub>, which is given in column five, it would be considerably higher still in relation to the ratios in the other minerals. A dark-green spinel from an aluminous xenolith in tholeiite from Mull (Thomas, 1922, p. 247) is considerably more magnesian, but contains quite a large amount of Fe<sub>2</sub>O<sub>3</sub> (4.26 %).

The above results are comparable to those obtained by Folinsbee (1941a, p. 52) from the minerals of an injection-gneiss near Great Slave Lake. He found that the garnet, cordierite, and biotite of this rock had the following compositions:

Garnet ... ..	24.0 % Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> ,	74.0 % Fe <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>
Biotite ... ..	39.9 % KMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> ,	60.1 % KFe <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>
Cordierite ... ..	61.0 % Mg <sub>2</sub> Al <sub>4</sub> Si <sub>5</sub> O <sub>13</sub> ,	39.0 % Fe <sub>2</sub> Al <sub>4</sub> Si <sub>5</sub> O <sub>13</sub>

The garnet and cordierite were analysed, and the composition of the biotite was obtained by 'optical analysis'. The ratios agree fairly well with those of the Belhelvie minerals, although the garnet is more magnesian, and the biotite

slightly less so, while the cordierite has almost the same ratio as the Belhelvie cordierite.

It may be noted that practically all the MnO of the Sparcraigs hornfels is contained in the garnet:

Wt. % MnO	...	...	Garnet.	Spinel.	Cordierite.	Biotite.
			1.81	0.02	0.04	0.02

This is of interest in view of the fact that Tilley (1926) has suggested that high manganese content promotes the formation of garnet in pelitic contact-zones. The manganese content of this garnet is, of course, comparatively low, and it is considered that other factors have played their part in promoting its formation in this particular case. The writer hopes to discuss this question in a later communication.

The  $TiO_2$ , as would be expected, is chiefly contained in the biotite, which differs from most analysed biotites in the combination of high  $TiO_2$  and high  $Al_2O_3$ . Only two analyses of biotite from thermally metamorphosed rocks have been found in the literature—one from the Oslo district (Lang, 1886, p. 318), and the other from a cordierite-biotite-hornfels from Japan (Tsuboi, 1938, p. 128). These analyses show high  $Al_2O_3$ , but comparatively low  $TiO_2$  content. The FeO:MgO molecular ratios are: Oslo, 1.52; Belhelvie, 1.35; Japan, 0.96.

The cordierite of this rock is peculiar in being an optically positive variety. Twelve records and six analyses of positive cordierites have been found in the literature, and five of these analyses are given in table VII. The sixth (Chacko, 1916) is not quoted, as it shows 5.65 %  $Fe_2O_3$ .

TABLE VII. Optically positive cordierites.

	A.	B.	C.	D.	E.	F.
SiO <sub>2</sub> ... ..	48.37	50.09	50.15	47.96	48.19	47.69
TiO <sub>2</sub> ... ..	—	—	0.38	nil	0.01	trace
Al <sub>2</sub> O <sub>3</sub> ... ..	29.22	31.78	33.07	31.52	33.45	32.52
Fe <sub>2</sub> O <sub>3</sub> ... ..	2.20	0.78	1.52	1.03	0.55	0.63
FeO ... ..	7.07	9.71	2.22	3.24	8.40	8.04
MnO ... ..	0.42	nil	0.12	1.09	0.18	0.04
MgO ... ..	9.54	6.69	11.01	12.16	7.95	7.56
CaO ... ..	1.92	—	0.29	nil	0.17	0.52
Na <sub>2</sub> O ... ..	—	—	0.14	0.33	0.22	0.53
K <sub>2</sub> O ... ..	—	0.07	0.08	trace	0.02	0.42
H <sub>2</sub> O ... ..	1.84	1.43	1.46	2.80	0.68	2.40
Total ... ..	100.58	99.55	100.44	100.13	99.82	100.35
Sp. gr. ... ..	2.598	2.65	2.588	—	2.631	2.64
2V <sub>γ</sub> ... ..	81–95°	88° 31'	88° 6'	76°	85–95°	84°
α ... ..	—	1.543	1.527	1.534	1.544	1.538
β ... ..	—	1.548	1.532	—	1.550	1.542
γ ... ..	—	1.553	1.538	1.543	1.556	1.547
γ–α ... ..	—	0.010	0.011	0.009	0.012	0.009

A. Madura district, Madras, India (Krishnan, 1924).

B. Santavuori, Ilmajoki, Finland (Pehrman, 1932).

C. Attu, Finland (Pehrman, 1932).

D. Cape Denison, Antarctica (Tilley, 1940).

E. Great Slave Lake (Folinsbee, 194').

F. Sparcraigs, Belhelvie.

These analyses show a wide variation in chemical composition. C and D are highly magnesian types, and agree with the suggestions of Shibata (1936, pp. 223-224) and Winchell (1937, pp. 1176-1177) that iron-poor cordierites may be optically positive, although their optic axial angles give points which lie rather above the curves in the diagrams given by these authors. The other cordierites of table VII, however, are much richer in iron, and on the basis of the diagrams of Shibata and Winchell they should have negative axial angles of about 45-50°. The analyses can all be closely matched by analyses of negative cordierite, and the total variation ranges of the oxides are roughly the same in both cases. The optically positive cordierites show a tendency to have lower refractive indices and birefringence than negative types of similar MgO:FeO ratio, and Folinsbee (1941b) suggests that this is due to a low alkali and high alkali-earth content in the positive types. However, it seems rather unlikely that an increase in alkali-content would have the effect of raising the indices and birefringence in a ferromagnesian mineral like cordierite, and from an examination of the available data the writer cannot agree with this suggestion. A comparison of the analyses E and F, which have very similar FeO: MgO ratios, points rather in the opposite direction, but the low water-content of analysis E is perhaps the deciding factor in this case. Folinsbee has suggested that the variation of the optic axial angle may largely depend on the content of alkalis and lime, and gives diagrams to show that the optic axial angle decreases with increase of alkalis and with decrease of lime. He finally obtains a curve showing a marked decrease of optic axial angle with increase of  $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO}$ . When analyses D and F of table VII are plotted on this diagram, it is found that their axial angles are 25-30° too high, and in view of the small number of points plotted, and the fact that they are considerably scattered, the shape of the curve depends almost entirely on one isolated point at the alkali-rich end. The writer considers that the data are insufficient for determination of the true relations.

It appears, then, that no single replacement series can account for the anomalous variation of the optic axial angle. There are so many variables in the cordierite formula that the scarcity of complete and reliable analyses makes it impossible to solve the problem at present.<sup>1</sup>

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#### References

- 1886 Lang (H. O.). *Nyt Mag. Nat.*, vol. 30, p. 318.
- 1916 Chacko (I. C.). *Geol. Mag.*, dec. 6, vol. 3, pp. 462-464. [M.A. 1-66.]
- 1922 Thomas (H. H.). *Quart. Journ. Geol. Soc. London*, vol. 78, p. 247. [M.A. 2-304.]
- 1924 Krishnan (M. S.). *Min. Mag.*, vol. 20, pp. 248-251.
- 1926 Tilley (C. E.). *Min. Mag.*, vol. 21, pp. 47-50.

<sup>1</sup> The effects of the Water-content, and of an isomorphous substitution of silicon and magnesium for aluminium, on the optical properties of cordierite, have been discussed in a recent paper by Thiele (1940). Several new analyses are given and these are quoted by Folinsbee (1941b). Unfortunately Thiele's paper is not available to the writer, but from an examination of the published analyses of cordierite it is considered that here again the data are insufficient to throw much light on the subject.

- 1930 Washington (H. S.). The chemical analysis of rocks. 4th edition, pp. 213-216. New York.
- 1932 Pehrman (G.). Acta Acad. Aboensis, Math. Physica, vol. 6, no. 11, 12 pp. [M.A. 5-383.]
- 1936 Shibata (H.). Japanese Journ. Geol. Geogr., vol. 13, pp. 205-227. [M.A. 6-479.]
- 1937 Winchell (A. N.). Amer. Min., vol. 22, pp. 1175-1179. [M.A. 7-208.]
- 1938 Tsuboi (S.). Japanese Journ. Geol. Geogr., vol. 15, p. 128. [M.A. 7-183.]
- 1940 Thiele (E.). Chemie der Erde, vol. 13, pp. 64-91. [M.A. 8-162.]
- 1940 Tilley (C. E.). Rept. Australasian Antarct. Exp., ser. A, vol. 4, pp. 339-344.
- 1941 $\alpha$  Folinsbee (R. E.). Amer. Min., vol. 26, pp. 50-53. [M.A. 8-225.]
- 1941 $\beta$  — Amer. Min., vol. 26, pp. 485-500. [M.A. 8-227.]
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