Ferrian chlorospinel from Carneal, Co. Antrim

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with chemical analysis by
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Summary. A Tertiary dolerite plug at Carneal, Co. Antrim has been contaminated by Chalk with the production of calc-silicates and related minerals. In a larnite–spinel-rock the spinel is of the unusual ferrian variety. It has the composition $(Mg_{6\cdot82}Fe''_{0\cdot76}Mn_{0\cdot12}\ Ni_{0\cdot01}Zn_{0\cdot01})(Al_{11\cdot2}Fe'''_{4\cdot94}Ti_{0\cdot03})O_{32}$. The spinel, which is brown, has: *n*, $1{\cdot}86_2$; *D*, 3·97; *a*, 8·1905 Å. A chemical analysis and powder data are given, the implications of experimental data are briefly discussed, and the nomenclature is reviewed.

A TERTIARY dolerite plug discovered by Mr. H. E. Wilson and Mr. E. J. Cobbing of the Geological Survey of Northern Ireland (Institute of Geological Sciences) at Carneal, Co. Antrim (Robbie, 1960), intrudes Tertiary basalt lavas but was contaminated by Chalk with the production of a variety of unusual rock-types and rare mineral assemblages. In many characteristics the assemblages resemble those described in the classic series of researches on Scawt Hill by Tilley and his colleagues (especially Tilley, 1929, and Tilley and Harwood, 1931). Only brief mention of the mineralogy and petrology has so far appeared (Sabine, 1962, 1967). The main rock-types are: dolerite, pyroxene-rich dolerite, gabbro, pyroxenite, wollastonite-rock, and other calc-silicate and related rocks. Among the minerals present are: fayalitic olivine, sahlite, nepheline, and aegirine, and in the contact zone there are larnite, scawtite, spurrite, merwinite, wollastonite, gehlenite, ferrian spinel, magnetite, perovskite, gyrolite, tobermorite and related minerals, xonotlite, hydrogrossular, portlandite, calcite, and thomsonite. Some of the minerals display metasomatic replacement relationships.

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Among the scarcer of the extraordinary rock-types there are several specimens of larnite–spinel-rock, which represents metamorphosed and metasomatised Chalk. The rock consists of an aggregate of larnite prisms mainly 0·05–0·15 mm long with abundant idiomorphic spinel crystals. There are minor amounts of other calcium silicates and related minerals, and some magnetite. Some of the spinel occurs in crystal aggregates of rectangular outline suggesting that some of the mineral may be pseudomorphous after an earlier mineral.

The spinel is in crystals up to about 0·25 mm across, but mainly 0·05–0·15 mm. It is generally nearly opaque, but in thin section some is brown, about Dresden Brown, 17′.O–Y.k of Ridgway's colour code (1912). Most of the grains are equidimensional, many clearly octahedral, and some show twinning on the spinel law. The mineral is not appreciably affected by a small hand magnet. The spinel has n $1{\cdot}86_2$(Na), D (calculated from analysis and cell size) 3·97.

Within the rock sample from which material was separated for analysis, the homogeneous nature of the spinel was established by Mr. R. I. Lawson using an electron-probe X-ray microanalyser (Geoscan). The distribution of aluminium and iron showed the spinel to be of uniform elemental composition and that the full chemical analysis is in consequence representative of unzoned material. The homogeneity of the spinel was also confirmed by the sharpness of lines on X-ray powder films. An approximate electron-probe analysis for iron, without making corrections for absorption, enhancement, or atomic number effects, which in this case would not be large, gave Fe 23 % (average of two counts), compared with 23·4 % in the full chemical analysis.

The spinel was separated from the rock by Mr. J. Dangerfield by physical methods followed by hand-picking. Chemical separation was not attempted since there was a possibility that it might affect the analytical results. Small quantities of impurity, mainly larnite, remained in the separated mineral, and from point counts Mr. Dangerfield estimated these to amount to about 3·4 % by volume (equivalent to about 2·5 % by weight).

The difficulty of dissolving many spinels is well known, and Mr. G. A. Sergeant notes:

> For the main semi-micro gravimetric analysis and colorimetric determinations of titanium, manganese, and total iron, the mineral was brought into solution by treatment with hydrofluoric acid and repeated evaporation with perchloric and sulphuric acids. For the determination of ferrous iron, the mineral was dissolved by heating with phosphoric acid in the presence of a known amount of trivalent manganese, the excess of which was then determined by titration with standardized

hydroquinone solution. Silica was determined colorimetrically following alkaline fusion, and traces of zinc were estimated by a colorimetric dithizone method.

The analysis is given in table I, column I. The spinel is of interest in having a high Fe''' content, and two of the few other analyses that approach this composition, which lies chemically between the normal spinel series and the magnetite series, are also shown. In the analysis of the Scawt Hill spinel (col. A), the FeO figure was arrived at by calculation from Fe_2O_3, and another determination, thought to be low, yielded 10·40 % (Tilley, 1929).

TABLE I. Chemical analyses of spinel

	I	*II*	*A*	*B*
SiO_2	1·4	—	—	—
Al_2O_3	42·2	43·7	57·30	56·20
Fe_2O_3	29·0	30·2	11·71	17·06
TiO_2	0·20	0·21	—	0·50
FeO	4·0	4·2	12·41	tr.
MgO	20·2	21·0	18·50	26·40
CaO	2·5	—	—	—
MnO	0·60	0·62	—	—
NiO	—	0·061	—	—
ZnO	—	0·05	—	—
$H_2O > 105°$ C	n.d.	—	—	—
$H_2O < 105°$ C	0·03	—	—	—
Allow for minor constituents	0·15		—	—
	100·28		99·92	100·16

*Co	130 ppm
*Cr	80 ,,
*Cu	50 ,,
*Ga	15 ,,
*Ni	460 ,,
*Zr	20 ,,
*Zn	400 ,,

* Spectrographic determination
n.d. = not detected
tr. = trace

I. Ferrian chlorospinel. From larnite–spinel-rock, east face of plug, quarry beside laneway, Carneal, Co. Antrim. 1-in. geol. map. 29, 6-in. 46 N.E. Thin section N.I. 1608B. Lab. No. 2025. Anal. G. A. Sergeant; spect. work by C. Park.

II. Analysis I recalculated to remove SiO_2, Al_2O_3, and CaO in the proportions found in the larnite analysis, and to include Ni[O] and Zn[O].

A. Spinel from contact-rock, Scawt Hill, Co. Antrim (with Fe_2O_3 determination adjusted to FeO and Fe_2O_3: Tilley, 1929, p. 85).

B. Ferrian spinel, forsterite–spinel lens in marble at syenite contact, Aldan region, Yakutia, Siberia (Serdyuchenko and Moleva, 1958, p. 692).

The analysis yields the formula:

$$(Mg_{6\cdot82}Fe''_{0\cdot76}Mn_{0\cdot12}Ni_{0\cdot01}Zn_{0\cdot01})(Al_{11\cdot2}Fe'''_{4\cdot94}Ti_{0\cdot03})O_{32}$$

with the R''' group = 16·17, R'' group = 7·72, cations 23·89. If some of the R''' group is transferred to the R'' group, one formula is $R''_{7\cdot89}R'''_{16\cdot00}O_{32}$, more nearly approaching the ideal formula. It has been shown by Atlas and Sumida (1958) that at high temperatures Al can occur in both the octahedral and tetrahedral structural positions.

Two possible proximate mineral analyses are set out in table II.

TABLE II. Molar percentages of end-members from ferrian chlorospinel analysis

Spinel	54·88	47·39	Galaxite	1·52	1·52
Magnesioferrite	27·10	37·64	Ulvöspinel	0·58	0·58
Magnetite	12·20	—	Trevorite	0·19	0·19
Hercynite	—	19·16	γ-Al_2O_3	3·42	3·41
Gahnite	0·11	0·11			

The amounts of SiO_2 and CaO present are almost exactly in the proportions required for larnite. In the calculation of the mineral formulae, all of the CaO and SiO_2, and Al_2O_3 in the proportion in which it occurs in the larnite (which was also analysed), have been assigned to yield 4·06% larnite, but it is possible that small quantities of Ca and Si occur in the spinel lattice.

The X-ray powder data set out in table III were obtained from film X4670A, taken in an 11·46 cm diameter camera, using Co-$K\alpha$ radiation. The unit cell dimension $a = 8{\cdot}1905 \pm 0{\cdot}0003$ Å (at room temperature) was obtained by plotting the values obtained from the high angle lines against $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ and extrapolating to $\theta = 90°$. The intensities were obtained with a microdensitometer. The space group is *Fd3m*.

TABLE III. X-ray powder data of ferrian chlorospinel

d	I/I_0	hkl	d	I/I_0	hkl
4·73 Å	20	111	1·235 Å	<1	622
2·895	40	220	1·182	4	444
2·47	100	311	1·147	<1	711, 551
2·048	45	400	1·0945	4	642
1·672	10	422	1·0663	15	731, 553
1·576	40	333, 511	1·0238	5	800
1·448	60	440	0·9653	1	822, 660
1·384	1	531	0·9458	8	751, 555
1·295	3	620	0·9157	4	840
1·249	10	533			

In two comparable rocks (nos. N.I. 1606, 1609), from the same locality, the spinel has a slightly different composition, since the cell size, determined by Mr. Young, is 8·171 Å ± 0·001 Å.

Only negligible differences were found by Turnock and Eugster (1962) in the cell sizes, measured at room temperatures, of artificial spinels in the system magnetite–hercynite for crystals prepared at temperatures of 600 to 1400° C and pressures of 1 to 2000 bars. In related systems, cell size is therefore unlikely to be a guide to the temperature–pressure conditions.

Nomenclature. The mineral is a ferrian spinel but, partly as a result of the rarity of previously reported occurrences, no name is exactly appropriate: the difficulties of nomenclature that arise when a spinel contains Fe‴ were noted by Simpson (1920). Among the critical factors of the Carneal spinel are that the mineral is essentially a ferric iron, magnesium, aluminium spinel with minor ferrous iron, and negligible chromium and zinc; and the colour is brown. It lies in the magnesioferrite–magnetite–hercynite–spinel section of Hey's classification (1950), which is based on that of Simpson (1920), and especially in the chlorospinel–ferropicotite–ceylonite(pleonaste)–spinel area. Chlorospinel, originally named by Rose (1840), was shown by Bothwell and Hey (1958) to be a moderately ferrian spinel (Fe_2O_3 7·2 % equivalent to Fe‴ 1·1 in unit cell of 31·3 O) and is grass-green. Ferropicotite, picotite [chromian variety of hercynite] in which the Cr is replaced by Fe‴, is given by Hey (1950) as having both Mg:Fe″ and Al:Fe‴ from 3 to 1. In the Carneal mineral the ratios are 9:1 and 2·3:1 respectively. In ceylonite, or pleonaste (the name used in some classifications, including Deer *et al.*, 1962), Mg:Fe″ is from 3 to 1. The spinel from Scawt Hill (table I, col. A) was referred to by Tilley as a 'pleonaste with significant percentages of the magnetite molecule'; and that from Siberia (table I, col. B) was called ferrian spinel by Deer *et al.* (1962).

Several other ferriferous spinels containing Mg or Al, but in which Cr or Ti is not shown as being significant, have been recorded. A green spinel from Virginia in which Fe_2O_3 is 10·35 % and FeO 24·53 % was reported by Watson (1925) as 'more closely approaches hercynite' [than pleonaste]; and an unspecified one containing 38·30 % Fe_2O_3 was noted from Japan by Harada (1936). Opaque 'pléonaste ferrifère', containing 9·40 % Fe_2O_3, 15·35 % FeO, was reported by Babkine *et al.* (1965). They also gave an analysis, calculated from a total Fe determination made with an electron-probe microanalyser, in which Fe_2O_3 = 15·90 %; Fe = 11·60 %. They noted that a similar mineral had been referred to by Lacroix (1910) as 'ferropicotite', but they preferred to reserve 'picotite' for spinels containing Cr, and to avoid 'ferro' for ferriferous spinels, a view with which the present author agrees. The use of qualifying adjectives (e.g. ferrian) for varieties has been adopted by Hey (1963), following Schaller and Dana, in preference to prefixes, (e.g. ferri-), and it is accordingly suggested that the Carneal mineral should be termed a *ferrian chlorospinel.*

Conditions of formation of related artificial spinels. The result of studies of artificial mixtures has been to suggest that a spinel of the composition now described probably formed at high temperatures. In the magnetite–hercynite series, Turnock (1959) showed that complete solid solution only existed above 858° C, and spinels in the system Fe–Al–O studied by Atlas and Sumida (1958) were formed at higher temperatures. Continuous series between magnetite and alumina were found to 21·2 mol % Al_2O_3 by Hoffman and Fischer (1956) who reported the presence of Fe‴ in the lattice of crystals formed above 1650° C. A spinel having 11·6 mol % $FeO.Al_2O_3$, 69·9 mol % Al_2O_3 and 18·5 mol % Fe_3O_4, and a cell size of 8·115 Å, was formed at 1695° C. Artificial Fe_3O_4–$MgFe_2O_4$ (magnesioferrite) mixtures were shown by Richards and White (1954) to coexist in a single spinel phase over a range of high temperatures.

Although the temperatures of formation of spinels will be greatly influenced by such factors as the presence of other elements, occurrence of defects, deviation from stoichiometric relationships, etc., these studies of artificial materials suggest that high temperature of formation is probable. This accords with the geological relationships at Carneal, where the production of the larnite–spinel-rock resulted from the high temperature next to the dolerite plug, which was a feeder for the Antrim lavas.

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