The occurrence of iron-cordierite in blast-furnace linings.[1]

By H. M. RICHARDSON, B.Sc., and G. R. RIGBY, Ph.D.

British Ceramic Research Association, Stoke-on-Trent.

I. INTRODUCTION.

IN an earlier paper[2] the authors described the occurrence of arti-
ficial kalsilite in the hearth of no. 3 blast-furnace of the Kettering
Iron Company. That paper contained a detailed description of the
furnace campaign together with the peculiar conditions observed in the
excavated hearth which was found to exhibit zoning in a vertical direc-
tion. The third zone containing kalsilite was described in detail, but the
only reference to the second zone stated that it was 2 inches deep (fig. 2,
p. 77, this vol.) and consisted of a black glassy slag containing numerous
crystals of cordierite (p. 78). The detailed examination of this zone now
forms the basis of the present paper.

II. EXAMINATION OF THE BLACK SLAG COMPRISING ZONE 2.

Samples of this slag were examined by X-ray, petrological, and
chemical methods. The percentage chemical analysis was: SiO_2 38·20,
TiO_2 0·64, total iron as Fe_2O_3 27·07, Al_2O_3 32·89, CaO 0·59, MgO 0·68,
K_2O 0·74, Na_2O 0·50. When examined under the microscope, thin
sections of various samples from this zone were found to consist of
numerous colourless crystals in a small amount of glassy matrix (fig. 1).
The sizes of the crystals varied appreciably in different parts of the zone,
but they were all square in cross-section as shown in figs. 1 and 2. They
were biaxial negative, gave straight extinction, and polarized in first-
order colours. The refractive indices of the crystals as determined
by immersion of the powder were α 1·539 and γ 1·555. Certain
crystals exhibited complicated twinning, as can be observed in
fig. 2.

An X-ray powder photograph, using filtered cobalt radiation, gave a
strong pattern closely resembling that given by artificially prepared

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cordierite, $2MgO.2Al_2O_3.5SiO_2$. The main strong reflections appeared to be almost identical with those of cordierite, but there were differences in spacing and intensity in some of the weaker reflections, as can be seen by comparing the data given in table I. The X-ray and petrological examinations also revealed the presence of small amounts of mullite and hercynite in some of the samples from this zone. Reference to the
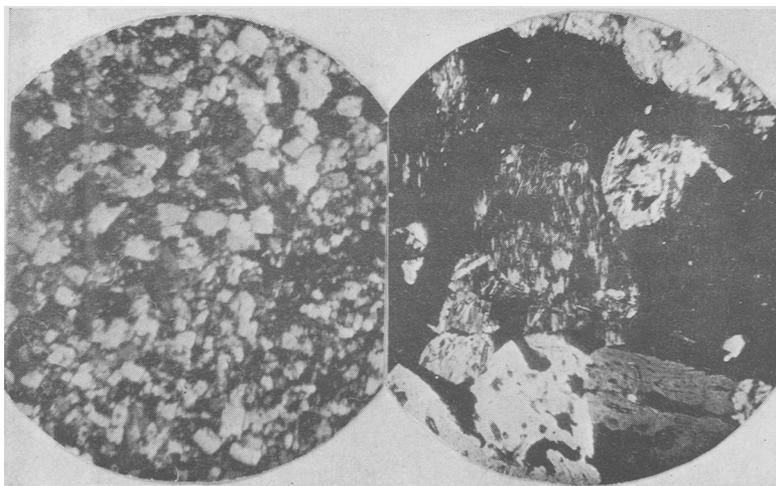
<div align="center">FIG. 1   FIG. 2</div>

FIG. 1. Thin section from the slagged material in zone 2, showing numerous colourless iron-cordierite crystals in a glass matrix. (Crossed nicols, × 100.)

FIG. 2. Larger iron-cordierite crystals from zone 2, exhibiting twinning. (Crossed nicols, × 100.)

chemical analysis clearly shows that these crystals, which formed the major phase in the samples from zone 2, could not be magnesium-cordierite as the magnesia content was very low (0·68%). On the other hand, the iron oxide content was quite high. The most probable assumption was that the crystals were those of a ferrous cordierite in which the magnesium ions in the structure of the mineral $2MgO.2Al_2O_3.5SiO_2$ were entirely replaced by ferrous irons.

Additional support was given to this hypothesis by the behaviour of the samples on oxidation. A sample of material was ground, magnetted to remove any metallic iron, and then heated in a stream of oxygen at 800° C. Under these conditions the sample gained 0·8% in weight, but X-ray powder photographs showed that an appreciable amount of iron-cordierite was still present. A second sample was then heated in oxygen

at 1200° C., when a gain in weight of 2·5% was finally obtained. X-ray examination showed that under these conditions the iron-cordierite had completely decomposed into ferric oxide, cristobalite, and mullite. A gain in weight of 2·5% is equivalent to the presence of 22·5% of ferrous iron in the original sample, so that the chemical analysis then approached very closely to that of $2FeO.2Al_2O_3.5SiO_2$. That the colourless crystals are composed of iron-cordierite is therefore placed beyond reasonable doubt, and table I lists the lattice reflections of this mineral together with those of the magnesium analogue to emphasize the close similarity between the powder photographs from the two minerals.

TABLE I. Lattice reflections of iron- and magnesium-cordierites.

Magnesium-cordierite		Iron-cordierite	
d (Å.)	Intensity.	d (Å.)	Intensity.
8·54	vs	8·54	vs
4·91	m	4·92	w
4·66	w	4·56	vw
4·09	s	4·06	s
3·37	s	3·43	s
3·13	s	3·13	fs
3·07	s	3·03	s
2·85	vw	2·85	vw
2·64	m	2·64	m
2·51	w	2·55	vw
2·42	m	2·45	m
2·34	m	2·31	m
2·28	vw		
2·23	w	2·23	vw
2·17	w	2·17	w
2·10	m	2·10	m
2·02	w	2·03	w
1·936	mw	1·954	mw
1·872	m	1·877	m
1·853	vw	1·858	vw
1·798	m	1·790	m
		1·718	w
1·685	fs	1·685	fs
1·650	w	1·658	vw
1·588	m	1·594	w
1·488	m	1·497	w
		1·473	w
1·457	w	1·451	w
1·444	w	1·415	vw
1·398	w	1·389	w
		1·368	w
1·348	m	1·353	m
		1·330	w
1·315	m	1·310	w
1·296	w	1·295	vw

III. EARLIER REFERENCES TO IRON-CORDIERITE.

In 1900 H. Bücking[1] investigated a few black fragments resembling obsidian in appearance associated with ejected blocks of andesite from the volcano Seputan in north Celebes. Under the microscope they consisted of minute crystals of fresh cordierite with a very little glass and associated with magnetite (about 4%) and either augite or sillimanite. The percentage analysis was as follows: SiO_2 49·15, Al_2O_3 31·84, Fe_2O_3 2·88, FeO 11·49, CaO 4·30, MgO 0·55, loss on ignition 0·06. He gave the name *Kalkeisencordierit* to this mineral; and that of *Eisencordierit* to similar (unanalysed) material in 'vitrified' Bunter sandstone in contact with basalt in central Germany. It is interesting to note that if Bücking's sillimanite mineral was in reality mullite, his natural product bears a close resemblance to the material found in the blast-furnace hearth.

L. L. Fermor[2] in 1923 applied the name *iron-cordierite* to a violet-coloured cordierite rich in ferrous oxide and almost devoid of magnesia occurring in shale that had been fused by burning coal-seams in India. Analyses of cordierite listed by Dana (System, 6th edit., 1892, p. 420) show various amounts of ferrous oxide up to a maximum of 9·24%. In 1936 H. Shibata[3] described iron-rich cordierites (FeO 15·31, MgO 1·48 and FeO 13·17, MgO 2·70%) from Japan, occurring in pegmatites intrusive into and contaminated by sandstone and amphibolite.

E. Dittler and A. Köhler[4] were unsuccessful in their attempts to prepare pure iron-cordierite by heating the oxides at 1000–1400° C., as the products of reaction contained magnetite, spinel, and sillimanite. They claimed, however, to have prepared small optically negative crystals of the general composition $2(Mg,Fe)O.2Al_2O_3.5SiO_2$. These mixed crystals contained 25, 50, and 75% of iron-cordierite in their composition.

The $FeO–Al_2O_3–SiO_2$, ternary phase-rule diagram as far as it has been determined, has no provision for any ternary compounds,[5] although the corresponding ternary diagram $MnO–Al_2O_3–SiO_2$ includes fields of stability of two ternary compounds, a spessartine garnet, $3MnO.Al_2O_3.3SiO_2$, and

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[1] H. Bücking, Ber. Senckenberg. Naturfor. Gesell. Frankfurt am Main, 1900, p. 3. [Min. Mag. 1903, vol. 13, pp. 367, 369.]

[2] L. L. Fermor, Abstr. Proc. Geol. Soc. London, 1923, for 1922–23, p. 96; Quart. Journ. Geol. Soc. London, 1924, vol. 80, p. 70. [Min. Mag., 1924–25, vol. 20, pp. 250, 456.]

[3] H. Shibata, Japanese Journ. Geol. Geogr., 1936, vol. 13, p. 205. [M.A. 6–479.]

[4] E. Dittler and A. Köhler, Zentralbl. Min., Abt. A, 1938, p. 149. [M.A. 7–283.]

[5] J. F. Schairer, Journ. Amer. Ceram. Soc., 1942, vol. 25, p. 245. [M.A. 9–16.]

a manganese-cordierite, $2MnO.2Al_2O_3.5SiO_2$.[1] The latter mineral has the following reported optical properties; uniaxial or biaxial negative with a small axial angle, refractive indices α 1·537, γ 1·558. In addition, a manganese analogue of anorthite has been stated by J. R. Rait and H. W. Pinder[2] to occur in inclusions in steel. The garnet almandine, $3FeO.Al_2O_3.3SiO_2$, has been reported from time to time as occuring in slags,[3] but confirmatory evidence is lacking, so that iron-cordierite must be considered as the only ternary compound of FeO, Al_2O_3, and SiO_2 to occur artificially.

IV. ATTEMPTS TO SYNTHESIZE IRON-CORDIERITE IN THE LABORATORY.

Since iron-cordierite has been detected in the blast-furnace it might be thought that synthesis of it in the laboratory would present no unusual difficulties. Contrary to expectations, however, it has been found most difficult to prepare and the best of the laboratory samples falls far short of those obtained in the furnace hearth.

Preliminary experiments have already been described in which it was shown that the hearth sample of iron-cordierite on oxidation was decomposed to ferric oxide, cristobalite, and mullite, accompanied by a gain in weight of 2·5%. At 800° C. the oxidation was very slow, and when heated in air over a Méker burner the gain in weight remained constant at 0·9%, but the material after this treatment still contained a high percentage of iron-cordierite together with some ferric oxide. The blast-furnace sample therefore appeared fairly resistant to oxidation, the crystals of iron-cordierite probably being protected by the glass matrix.

The refractoriness of a cone cut from the glassy layer was 1200° C. in an atmosphere of nitrogen. The deformed cone contained iron-cordierite along with a spinel solid solution, thereby indicating that the mineral was slowly decomposing at 1200° C. into hercynite, magnetite, and a siliceous glass. More extended experiments fixed the upper temperature limit of stability at below 1100° C., while at 1400° C. decomposition into hercynite, mullite, and magnetite was complete after 2 hours. The presence of metallic iron did not appreciably increase the stability range, as decomposition still occurred at 1200° C.

The glassy nature of the layer indicated that iron-cordierite had crystallized out from a glass. This suggested that at one period in the furnace campaign the hearth of zone 2 must have contained a considerable

[1] R. B. Snow, ibid., 1943, vol. 26, p. 15. [M.A. 10–461.]

[2] J. R. Rait and H. W. Pinder, Journ. Iron and Steel Inst., 1947, vol. 154 (no. 2 for 1946), p. 371P. [M.A. 10–462.]

[3] H. E. Simpson, Journ. Amer. Ceram. Soc., 1932, vol. 15, p. 520.

amount of liquid on account of the temperature of this zone being around or above 1200° C. At a later stage the temperature of zone 2 must have dropped below 1100° C. to allow the crystallization of iron-cordierite, the temperature possibly remaining at this lower level for a considerable period. The instability of iron-cordierite above 1100° C. provides a ready explanation of its absences from the ternary $FeO-Al_2O_3-SiO_2$ diagram. It has also been shown that when firebricks are attacked by ferrous oxide, hercynite and fayalite are generally found in the products of reaction.[1]

Attempts were next made to induce ferrous oxide to react with firebrick and china-clay at a low temperature. No reaction could be detected below 900° C., but even at this temperature the first product of the reaction was hercynite and not iron-cordierite, and the presence of various fluxes, metallic iron, or carbon did not alter the trend of the reaction, as in all cases hercynite and fayalite were formed and no iron-cordierite could be detected. It was next thought that iron-cordierite might be induced to form in the presence of magnesium-cordierite. Mixtures of ferrous oxide and magnesium-cordierite ranging from 5 to 50 % of FeO were heated together at temperatures varying between 800° and 1200° C. No reaction took place below 900° C., but at higher temperatures the cordierite was decomposed to hercynite and fayalite, and X-ray photographs gave no evidence of the formation of mixed crystals of magnesium- and iron-cordierite due to replacement of magnesium by ferrous ions. Further experiments in which mixtures of firebrick or china-clay with metallic iron or mixtures of metallic iron and ferrous oxide were heated in nitrogen and steam for prolonged periods at 1080° C. proved equally abortive, as the reaction products always included hercynite, fayalite, mullite, cristobalite, magnetite, or ferric oxide, with no trace of iron-cordierite. The application of external pressure to the mixture or the introduction of small amounts of magnesium-cordierite had no influence on the course of the reactions.

Partial success was at last achieved by one method alone. A mixture of ferrous oxide, alumina, and hydrated silica in the correct molecular proportions for iron-cordierite was prepared, and to this was added 5 % of potassium carbonate. The potash addition facilitated melting and the formation of a glass, for on heating in an iron tube to 1480° C. in nitrogen following by quenching, a glass was obtained which only contained a trace of undissolved corundum and hercynite.

[1] H. M. Richardson, F. Ball, and G. R. Rigby, Gas Research Board, 38th Report of the Refractory Materials Joint Committee, 1946–47, p. 38.

A sample of this glass was then held at various temperatures between 800° and 1100° C. in an atmosphere of nitrogen for periods of up to 200 hours. After being heated for 120 hours at 850° C. iron-cordierite had crystallized out, but the maximum amount was obtained after heating the glass at 900° C. for about 100 hours. This iron-cordierite was always accompanied by other crystalline phases such as hercynite, fayalite, and pyroxene, and, if the temperature of crystallization rose to 1000° C. or higher, the relative proportions of iron-cordierite decreased in favour of the hercynite phase.

These experiments, while not being as conclusive as one could wish, have clearly shown, however, that iron-cordierite can be formed by inducing certain glasses to crystallize over the temperature range 850–1000° C. It is considered that the mechanism by which iron-cordierite was synthesized in the blast-furnace hearth followed a similar procedure.

V. The Presence of Iron-Cordierite in Refractory Materials.

Since the detection of iron-cordierite in samples from the Kettering blast-furnace hearth, this mineral has been identified in vitrified bricks taken from the hearths of four other furnaces, although the amounts present were very much smaller than those in the Kettering samples.

It has also been found to occur in the black cores associated with certain fireclay casting-pit refractories. In a thin section, minute crystals of iron-cordierite can be readily detected in the fringes of pores present in the darkest areas of the black core. Traces of iron-cordierite have also been noticed associated with glassy iron spots in various types of firebricks. Indeed, it is possible that the mineral is found in a wide range of refractory products, though nearly always in very small amounts and then only in isolated areas within the refractory. The material has also been observed in various refractory materials by K. W. Andrews and J. Mackenzie of the United Steel Companies, Ltd., and their findings are given in the appendix to this paper.

VI. The Reversible Thermal Expansion of Iron-Cordierite.

Particular interest attaches to the thermal expansion of iron-cordierite since it is well known that the corresponding expansion of the magnesium analogue is very small, the coefficient being only about $2 \cdot 3 \times 10^{-6}$ between 100° and 1000° C.[1] With the samples available it was found impossible to free the iron-cordierite crystals from the glass, and accordingly a suitable specimen for a thermal expansion determination was cut from the

[1] G. R. Rigby and A. T. Green, Trans. Brit. Ceram. Soc., 1942, vol. 41, p. 123.

glassy material of zone 2. The reversible thermal expansion data are given in table II, where they are compared with similar data obtained earlier for magnesium-cordierite. It must be remembered, however, that unlike the magnesium-cordierite, the sample of iron-cordierite was contaminated with a little glass, mullite, hercynite, and metallic iron, all of which would tend to increase the reversible expansion, the figures reported in table II being too high. The results clearly show that iron-cordierite has a remarkably low coefficient of expansion, being well below that of mullite or the ferrous silicates generally. It has been found earlier that the substitution of magnesium ions for ferrous ions, in the case of the olivine minerals, results in a slight increase in the expansion coefficient.[1] It may well be, therefore, that if a pure specimen of iron-cordierite could be prepared, the thermal expansion would be as low or even lower than that of magnesium-cordierite.

TABLE II. The thermal expansion characteristics of magnesium- and iron-cordierite.

	Percentage thermal expansion and coefficient of expansion $\times 10^6$ between 100° C. and						
	200°	300°	400°	500°	600°	700°	800° C.
Magnesium-cordierite	0·006	0·020	0·034	0·057	0·081	0·110	0·139
	0·6	1·0	1·2	1·4	1·6	1·7	1·9
Iron-cordierite ...	0·02	0·048	0·075	0·103	0·130	0·158	0·185
	2·0	2·4	2·5	2·6	2·6	2·6	2·7

APPENDIX

By K. W. ANDREWS, D.Phil., and J. MACKENZIE, B.Sc.

The United Steel Companies, Ltd., Research and Development Dept., Stocksbridge, near Sheffield.

The presence of a cordierite-type mineral, similar to that described by H. M. Richardson and G. R. Rigby as iron-cordierite, has been confirmed in samples taken from the break-out area of a blast-furnace hearth and the black core of certain fireclay casting-pit refractories.

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[1] G. R. Rigby, G. H. B. Lovell, and A. T. Green, Trans. Brit. Ceram. Soc., 1946, vol. 45, p. 237.

The results of an examination of the break-out area of the fireclay hearth of no. 6 furnace, Appleby-Frodingham, have been reported elsewhere.[1]

The typical zoned deterioration of the brickwork was noted at the time, i.e. the almost unchanged metal-free brickwork on the casing side changing to the metal-bearing FeO reduction zone and slagged zones on the metal side. Samples of these individual zones were examined by the X-ray powder method, the mineralogical constitution together with chemical composition being shown in table III.

The cordierite-type compound has spacings near to those given by Richardson and Rigby, but the agreement is not exact and the presence of some MgO or even other oxides is suggested.

The existence of this iron-cordierite mineral therefore confirms constitutionally the presence of a ferrous iron compound in the blast-furnace hearth resulting from the slagging of the alumino-silicate refractory by the oxidized metal in the pores of the brick.

Certain fireclay casting-pit refractories, which contain a black core, were examined by X-rays with the following results:—

Guide tube I—

    (a) Clear portion: mullite, large amount; quartz, small to medium.

    (b) Black core: mullite, large amount; quartz, medium to small; iron-cordierite, very small to small.

Guide tube II—

    (b) Black core: mullite, large amount; quartz, small to very small; iron-cordierite, medium to small; cristobalite, possible, small.

TABLE III.

Sample.	Chemical analysis.					Mineralogical constitution and amount.
	SiO$_2$.	Al$_2$O$_3$. Fe$_2$O$_3$.	FeO.	MgO.	MnO.	
Outer zone (casing side), mauve-coloured brickwork	58·3	33·8 0·76	2·78	0·69	0·01	Mullite, medium to large. Cristobalite, medium.
White zone	58·4	33·5 0·84	2·85	0·78	—	Mullite, medium to large. Cristobalite, medium. Iron-cordierite, small.

[1] G. D. Elliot and collaborators, Iron and Steel Inst., 1944, Spec. Rep. no. 30, p. 262.

TABLE III (cont.)

| Sample. | Chemical analysis. | | | | | | Mineralogical constitution and amount. |
	SiO₂.	Al₂O₃.	Fe₂O₃.	FeO.	MgO.	MnO.	
FeO reduction zone, slagged	48·65	27·39	4·31	13·35	0·69	—	Mullite, small. Cristobalite, small. Iron-cordierite, large. Metallic iron.*
Inner zone (metal side), slagged.	56·35	31·96	0·28	2·93	0·69	3·89	Mullite, medium to large. Cristobalite, medium. Iron-cordierite, small. Metallic iron.*

*Metallic iron was removed by a magnet.

The cordierite compound had lattice spacings near to those given for iron-cordierite, but again a small amount of solid solution is possible.

The presence of a cordierite-type compound in the black core was also suggested by petrological examination, but in such small amounts this was difficult to identify with certainty. A magnetic separation was carried out and it was found that the very small amount of iron-cordierite tended to concentrate in the magnetic fraction. It is not suggested that iron-cordierite is itself magnetic, but it would appear to be associated with the magnetic iron material present in the fireclay brick.

The authors of the appendix wish to thank Mr. F. H. Saniter, Director of Research, United Steel Companies, Ltd., for permission to publish this information, and Dr. W. Davies for his assistance in petrological examinations.