

## A silica-deficient pyroxene in iron ore sinters

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**SUMMARY.** A minor phase in iron-ore sinters has been synthesized and identified as a clinopyroxene with the approximate formula  $\text{Ca}_{1.0}(\text{Ca}_{0.14}\text{Fe}_{0.86}^{3+})(\text{Fe}_{0.32}\text{Al}_{0.60}\text{Si}_{1.08})\text{O}_6$ . This composition shows that it consists largely of the hypothetical Tschermak's molecule,  $M^{2+}R_2^{3+}\text{SiO}_6$ . The small size and sparse distribution of this phase in most iron-ore sinters has previously hindered analysis.

THE major constituents of iron-ore sinter are magnetite, hematite, and wüstite<sup>1</sup> together with silicate glass and the broad group of minerals related to the calcium ferrites but often containing other oxides, mainly alumina and silica.<sup>2</sup> A wide range of crystalline silicates may form as minor phases.

During an investigation of iron-ore sinters used in British ironworks, a commonly occurring minor phase of characteristic appearance was observed. This phase has also been noted by other workers both in Britain and Australia (Mr. D. G. Wasse, B.I.S.R.A. Middlesbrough, personal communication) although its identity had not been established.

The main obstacle to identification was the small size of the crystals and their sparse distribution. Consequently an attempt was made to synthesize crystals large enough for electron-probe microanalysis and abundant enough for X-ray diffraction examination.

*Synthesis.* Although electron microprobe analyses gave unreliable results because the crystals were usually smaller than the volume analysed, synthetic mixes of analytical grade  $\text{CaCO}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  were made up to the indicated compositions. These mixes were fired at approximately 1300 °C in alumina or platinum crucibles and the melt was air-quenched or cooled at 40 °C/minute.

The pyroxene crystallized from almost all the melts. Air-quenched specimens generally produced only small amounts of the pyroxene, set in glass, while those cooled more slowly often precipitated additional phases such as pseudowollastonite and gehlenite. The alumina content was found to be the most critical factor. With too little alumina the pyroxene did not form, while with about 15 % or more  $\text{Al}_2\text{O}_3$  present gehlenite and the silicoferrite of calcium and aluminium (abbreviated to SFCA; Coheur, *loc. cit.*) began to form at the expense of the pyroxene. Trial and error led to a composition of 37 %  $\text{CaCO}_3$ , 23 %  $\text{SiO}_2$ , 29 %  $\text{Fe}_2\text{O}_3$ , and 11 %  $\text{Al}_2\text{O}_3$  by

<sup>1</sup> E. M. McBriar, W. Johnson, K. W. Andrews, and W. Davies, *Journ. Iron Steel Inst.* **177**, 316-23 (1954).

<sup>2</sup> P. Coheur, *Journ. Iron Steel Inst.* **207**, 1291-7 (1969).

weight, which yielded up to 50 % of the pyroxene in crystals often large enough for accurate electron-probe microanalysis. The product also contained sufficient of the pyroxene to give a clear X-ray diffraction pattern when crushed without any physical separation.

Most of these syntheses were carried out using alumina crucibles as these could be split longitudinally so that a polished section of one half could be prepared. Although these sections showed that slight assimilation of the crucible walls had occurred, no components would have been introduced that were not already present.

*Petrography.* In iron-ore sinters the pyroxene usually forms delicate skeletal crystals (fig. 1) although in alumina-rich sinters it may form as more compact crystals or as



FIG. 1.

FIG. 2.

FIG. 3.

FIG. 1. Skeletal pyroxene crystals set in glass in an iron-ore sinter. The white phase is hematite. Reflected light,  $\times 330$ . FIG. 2. Skeletal pyroxene crystals set in glass near the centre of a synthetic specimen. The white phase is hematite. Reflected light,  $\times 330$ . FIG. 3. Blocky pyroxene crystals near the crucible wall in the same specimen as in fig. 2. There is a little pseudowollastonite in the glassy matrix. Reflected light,  $\times 330$ .

fringes around magnetite and SFCA. The synthetic pyroxenes also demonstrated this change in habit with increasing alumina content. This was particularly noticeable where the melt had been enriched by assimilation of alumina at the crucible walls. Fig. 2 shows a skeletal pyroxene crystal formed near the centre of the crucible while fig. 3 shows the short prisms, often hollow, formed in the same specimen at the crucible wall.

There is a marked pleochroism from yellow-green to orange. The interference colours, though partly masked by the strong absorption, are up to second-order green, suggesting a birefringence of 0.025–0.030. The crystals were too small to give an interference figure. The refractive indices were determined by measuring the reflectance of polished sections, both in air and oil to allow for the effects of

absorption. The indices were found to vary in the range 1.89–1.97, the higher values being for the more iron-rich specimens.

*Electron-probe microanalysis.* Selected particles from a wide variety of both commercial and synthetic samples were examined and the apparent elemental concentration of each obtained. Corrections for absorption, fluorescence, and atomic number were made using standard correction curves.<sup>1</sup> Table I shows the results of these examinations.

TABLE I. *Analyses of silica-deficient pyroxenes*

*Electron probe microanalyses*

	1*	2*	3†	4†	5†	6†
SiO <sub>2</sub>	27.5	26.1	26.0	22.0	25.0	27.0
Al <sub>2</sub> O <sub>3</sub>	9.5	9.5	15.0	12.0	15.5	12.0
Fe <sub>2</sub> O <sub>3</sub>	35.6	41.8	33.7	40.0	34.5	36.0
CaO	27.5	24.8	24.5	27.0	24.0	25.0
Totals	100.1	102.2	99.2	101.0	99.0	100.0

*Number of ions on the basis of 6 oxygens*

Si	1.17	1.10	1.10	0.95	1.06	1.14
Al	0.47	0.47	0.74	0.61	0.77	0.59
Fe <sup>3+</sup>	0.36	0.43	0.16	0.44	0.17	0.27
Fe <sup>3+</sup>	0.78	0.89	0.91	0.86	0.93	0.87
Ca	1.25	1.11	1.10	1.25	1.09	1.13
	2.00	2.00	2.00	2.00	2.00	2.00
	2.03	2.00	2.01	2.11	2.02	2.00

\* In iron ore sinters.

† Synthetic preparations.

Initial analyses of the commercial samples suggested that the phase was essentially formed of four oxides and that any other oxides present made up less than 1%. A high silica content was recorded for the smaller crystals, suggesting that the analysed volume extended into the surrounding glassy matrix. The compositions of larger crystals, mainly synthetic, show that the most variable components are the Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> although their ionic sum is relatively constant. Crystals with a relatively high alumina content seemed in general to be larger and more blocky than more iron-rich ones.

*X-ray investigation.* The diffraction data from the synthetic specimens were recorded using a Nonius focusing camera and Co-K $\alpha$  radiation. Three crystalline phases were observed: a calcium silicate, hematite, and an unidentified phase. The calcium silicate

<sup>1</sup> W. J. M. Salter, *A Manual of quantitative electron probe microanalysis*. Structural Publications Ltd. (London), 1970.

was wollastonite in some samples and pseudowollastonite in others. Leaching with concentrated cold HCl removed most of the calcium silicate and glass without obviously affecting the pyroxene, and these samples were used to obtain the X-ray data. The  $d$ -spacings, corrected using quartz as an internal standard, are given in

TABLE II. Comparison of observed and calculated interplanar spacings of the synthetic pyroxene

$d_{\text{meas}}$	$d_{\text{calc}}$	$I$	$hkl$	$d_{\text{meas}}$	$d_{\text{calc}}$	$I$	$hkl$
6.4657 Å	6.4575 Å	12	110	*1.942 Å	1.9421 Å	< 2	24 $\bar{1}$
4.7425	4.7373	9	200	*1.911	1.9120	< 2	51 $\bar{1}$
4.4680	4.4707	5	11 $\bar{1}$	*1.871	1.8708	3	33 $\bar{1}$
4.4145	4.4123	10	020	*1.865	1.8640	3	222
*3.365	3.3638	2	021	1.8535	{1.8570 1.8527}	6	{42 $\bar{2}$ 510}
3.2296	3.2287	18	220	1.8362	1.8359	5	132
2.9997	3.0013	100	22 $\bar{1}$	*1.798	1.7948	2	421
2.9740	2.9735	58	310	*1.750	1.7490	< 2	312
2.9202	2.9206	28	31 $\bar{1}$	1.7352	1.7351	13	150
*2.810	2.8092	2	130	1.6954	1.6962	9	31 $\bar{3}$
2.5960	{2.5990 2.5927}	64	{002 20 $\bar{2}$ }	1.6815	{1.6819 1.6803}	9	{042 24 $\bar{2}$ }
2.5567	2.5585	46	13 $\bar{1}$	*1.671	1.6708	2	15 $\bar{1}$
2.5412	2.5412	74	221	1.6589	1.6592	22	22 $\bar{3}$
*2.370	2.3686	2	400	1.6307	1.6302	16	53 $\bar{1}$
2.3385	2.3377	11	311	1.6153	1.6155	9	511
					1.6144		440
2.2692	2.2707	17	112	*1.595	1.5930	2	530
2.2371	{2.2394 2.2353}	8	{022 22 $\bar{2}$ }	*1.580	1.5791	3	600
2.1531	2.1525	10	330	1.5546	1.5543	9	402
2.1330	2.1322	21	33 $\bar{1}$	1.5469	1.5475	9	60 $\bar{2}$
2.1191	2.1191	18	42 $\bar{1}$	1.5405	1.5407	11	350
2.0870	2.0869	5	420	1.5306	1.5305	20	13 $\bar{3}$
2.0558	2.0566	12	202	*1.522	{1.5229 1.5205}	6	{42 $\bar{3}$ 53 $\bar{2}$ }
2.0453	2.0472	20	40 $\bar{2}$	*1.471	1.4708	4	060
2.0309	2.0308	18	04 $\bar{1}$	1.4350	1.4346	13	531
1.9870	1.9887	10	13 $\bar{2}$	1.4219	1.4217	8	223
				1.4090	1.4092	16	35 $\bar{2}$

\* Weak lines which cannot be measured more accurately.

table II. An X-ray examination of the less-magnetic fraction of a high-alumina iron-ore sinter showed the same pyroxene to be present.

*Discussion.* The X-ray powder diffraction pattern of the unidentified phase closely resembled that of diopside and the observed  $d$ -spacings were indexed, with the aid of computer programmes, on a monoclinic cell with:  $a$  9.840,  $b$  8.825,  $c$  5.398 Å,  $\beta$  105° 40',  $V$  451.34 Å<sup>3</sup>. The cell dimensions of all the synthetic preparations were similar. The 51 lines recorded in table II have indices compatible with the space group  $C2/c$ , the common pyroxene space group. The  $c$  parameter is significantly larger than

that of any other reported pyroxene while  $a$ ,  $b$ , and  $\beta$  are within the known ranges. Changes relative to the cell parameters of  $\text{CaMgSi}_2\text{O}_6$  (A.S.T.M. Card No. 19-239) are:  $a + 0.94\%$ ,  $b - 1.13\%$ ,  $c + 2.75\%$ ,  $\beta - 12'$ ,  $V + 2.68\%$ . The cell parameters of the synthetic pyroxenes reported by Coleman (1962) and Huckenholz *et al.* (1969) showed similar trends.

Pyroxenes with low silica contents suggest the existence of hypothetical silica-poor end-members of the solid-solution series (Tschermak, 1871) and in the absence of monovalent ions they could be considered mixtures of  $M^{2+}\text{SiO}_3$  and Tschermak's molecule  $M^{2+}R_2^{3+}\text{SiO}_6$  (Morozewicz, 1898). Although the proportion of Tschermak's molecule is generally low, Morozewicz synthesized a pyroxene containing 73 wt. % compared with more than 90 wt. % in the specimens described here. Aluminous pyroxenes have been reported containing approximately 40 wt. % of  $\text{CaAl}_2\text{SiO}_6$  in diopside, although different investigations give different solubility limits (Tsvetkov, 1945; Segnit, 1953; Sakata, 1957). Huckenholz *et al.* (1969) suggest that the solubility limit of diopside in  $\text{CaFe}_2\text{SiO}_6$  is between 31.1 and 35.0 wt. %. From an extrapolation of cell dimensions they deduce that the pure end-member could not be stable even at high pressures.  $\text{CaFe}^{3+}\text{AlSiO}_6$  crystallizes as a stable clinopyroxene and Hijikata and Onuma (1969) suggest that only Al ions replace Si ions in the 4-fold co-ordination sites.

The problems of allocating ions to the different sites has been discussed by Smith *et al.* (1969), who dealt with the closely related orthopyroxene structure. In the present case, the task is simplified by the smaller variety of cations present and also by the fact that the observed balance between the  $\text{Ca}^{2+}$  and  $\text{Si}^{4+}$  ions implies that all the iron should be  $\text{Fe}^{3+}$ . Any iron calculated as  $\text{Fe}^{2+}$  would lead to unbalanced valencies, apart from the fact that the syntheses were carried out in air, when any  $\text{Fe}^{2+}$  present would probably have been oxidized. Allocation of ions is further simplified by the assumption that  $\text{Al}^{3+}$  preferentially replaces  $\text{Si}^{4+}$  ions.

Table I presents both the microanalysis results and the distribution of the cations in the formula  $W_{1-p}(X,Y)_{1+p}Z_2\text{O}_6$  (Deer *et al.*, 1963). The  $W$  and  $Y$  cations are normally found in the  $M_2$  and  $M_1$  sites respectively while the  $X$  cations enter either site. Significant amounts of  $\text{Ca}^{2+}$  can thus enter the  $M_1$  sites and  $\text{Fe}^{3+}$  must replace Si ions. The magnitude of the  $c$  parameter is a measure of the silicate chain dimension. The chain length and breadth will expand when  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  substitutes for  $\text{Si}^{4+}$  ions—as in spodumene and augite. The  $a$  and  $b$  parameters will also be affected. Substitution of Ca and  $\text{Fe}^{3+}$  for Mg ions in  $M_1$  sites will alter the distance between the chains and will also cause changes in  $a$  and  $b$ . The replacement of Si and Mg ions must be equal in order to maintain the stoichiometry and the structural changes resulting from the substitutions cannot be separated. The difference between the cell dimensions of the unknown pyroxene and diopside suggest that the within-chain effect dominates the changes in  $a$  and  $c$  while the  $b$  dimension is dominated by the between-chain effect. Huckenholz *et al.* have suggested that the substitution of certain trivalent ions in the structure will expand the tetrahedra considerably and shrink the octahedra only slightly. Such variations in the atomic structure would reflect the observed cell parameter changes.

Whittaker (1960) suggested that the smaller the  $W$  ion the larger is  $\beta$  although the sizes of the  $X$  and  $Y$  ions may mask this tendency. However, the  $\beta$  angle determined is approximately the same as that for diopside and the  $W$  ions are wholly Ca in both structures.

Studies of the  $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$  system have apparently not recorded this phase. This is probably because the investigations have been based largely on an examination of the faces of the composition tetrahedron and the region of the CaO apex. The stability field of the pyroxene under examination must lie close to the  $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2$  face but does not appear to reach it and could thus be overlooked.

The illustration of a minor phase in iron ore sinter, identified as 'iron-gehlenite' (Coheur, *loc. cit.*) shows it to be very similar to the pyroxene described and it might well be the same phase.

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