We wish to express our thanks to Dr J.R.Plimmer for supplying the crystals and to Mr P.J.Jutsum for obtaining most of the intensity data.

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The Crystal Structure of an Iron Silicate, Iscorite

By J. Smuts and J. G. D. Steyn*

Research Laboratories, South African Iron and Steel Industrial Corporation, Limited, P.O. Box 450, Pretoria, South Africa

and J. C. A. Boeyens

Chemical Physics Group of the National Physical and Chemical Research Laboratories, CSIR, Pretoria, South Africa

The crystal structure of an iron silicate (Fe_7SiO_{10}), which has been found in material from the floor of a reheating furnace of a steel plant, has been determined by X-ray diffraction methods. The structure is based on a cubic close-packed arrangement of oxygen atoms with ferrous ions in octahedral interstices. Si^{4+} occurs in a tetrahedral environment while Fe^{3+} ions are distributed evenly between octahedral and tetrahedral sites. This structure represents a variety not encountered before.

Introduction

The mineral Fe_7SiO_{10}, for which we propose the name Iscorite, occurs in material from the floor of a reheating furnace of the Pretoria Works of the South African Iron and Steel Industrial Corporation (ISCOR). This furnace is normally kept at a temperature of $\sim 1300\,°C$. Although the refractories used in this type of furnace are supposed to be silica-free (magnesite and chrome-magnesite), the material in which iscorite occurs is rich in silica. It consists mainly of magnetite, wustite and fayalite ($2FeO.SiO_2$). Preliminary crystallographic investigations showed that iscorite was not isomorphous with any of the known silicates (Wyckoff, 1960). Existing phase diagrams of the system Fe–Si–O (Levin, Robbins & McMurdie, 1964; Muan & Osborn, 1964) do not indicate the existence of any phase with which iscorite can be identified. This is probably due to iscorite being formed only under exotic conditions. It has not been synthesized directly as yet. A detailed study of the crystal structure of this mineral was thus undertaken.

Mineralogical properties

The mineral is associated mainly with fayalite, magnetite and wustite. It occurs most commonly in irreg-

ularly shaped units (Fig. 1) as well as in narrow zones between crystals of fayalite and magnetite (Fig. 2), and occasionally as lath-shaped crystals. The mineral is opaque to transmitted light. In incident light it is slightly pleochroic and strongly anisotropic. The reflectance pleochroism is from bluish to grey with a brownish tinge and the polarization colours are dark-blue and reddish-brown. Its reflectivity is lower than that of magnetic and wustite, but higher than that of fayalite.

The mineral was extracted magnetically. Although the magnetic susceptibility of iscorite is considerably lower than those of wustite and magnetite, it is only slightly less than that of fayalite. The best recovery was obtained from powders of particle size 15–38 micron which were separated by air elutriation.

The composition was established, by chemical analysis of a material of 98% estimated purity, to be as given in Table 1.

Table 1. *The chemical analysis and calculated composition of an iscorite sample of 98% estimated purity*

	Experimental	Theoretical
SiO_2	10·1%	10·3%
Fe^{2+}	47·2	48·3
Fe^{3+}	19·4	19·3
MgO	0·2	–
Cr_2O_3	0·2	–
Al_2O_3	1·3	–

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* Mineralogical properties, separation and density measurement.

The theoretical values are based on a composition $5FeO.Fe_2O_3.SiO_2$. For identification purposes the complete X-ray powder pattern (114 mm Debye–Scherrer camera with Co $K\alpha$, Fe-filtered radiation) is given in Table 2. Indices are given only for those reflexions for which comparison with single–crystal intensities was possible, i.e. $h0l$ and $h1l$. Relative intensities have been estimated by use of a Zeiss–Schnell photometer. The shape of the crystals makes elimination of preferred orientation in samples prepared for diffractometry difficult. The preferred orientation is with [010] parallel to the sample surface.

This basic diffraction pattern remains constant after heating for 30 minutes at temperatures of up to 1100 °C. Differential thermal analysis work confirmed that no phase changes occurred in this temperature range.

Experimental and crystal data

Needle-shaped crystals as obtained from the original material which had cooled down over a period of days were examined by standard oscillation, Weissenberg and precession methods. They were found to be monoclinic, with $a = 21\cdot4$ Å, $b = 3\cdot06$ Å (needle axis), $c = 5\cdot88$ Å, $\beta = 98°$.

The density was measured pycnometrically as $5\cdot02$ g.cm^{-3} with the use of toluene as an immersion liquid. This corresponds to 2 formula units per unit cell. The only systematic absences observed were $0k0$ for $k \neq 2n$, but another pseudo-condition limiting possible reflexions (which included $0k0$) was also observed, viz. hkl: when $l = 2n$ for $k + h = 2n$. The centrosymmetric space groups $P2/m$ and $P2_1/m$ were considered the most probable and the choice of the latter was vindicated by the successful structure analysis based on $P2_1/m$

(No. 11 in *International Tables for X-ray Crystallography*, 1952).
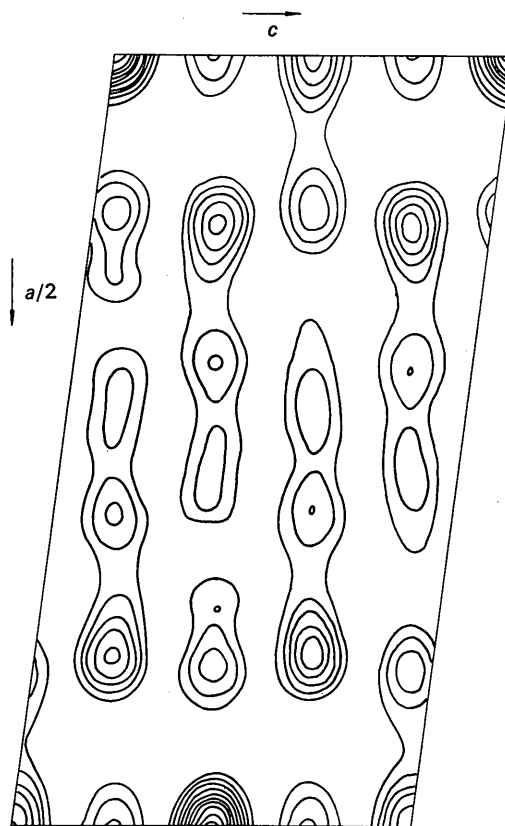

Fig. 3. (010) projection of the Patterson function. Contours are drawn at arbitrary but regular intervals.

Table 2. *Powder X-ray diffraction pattern of iscorite* (Co $K\alpha$ radiation)

d	I/I_1*	hkl	d	I/I_1	hkl
10·6	40	200	1·589	10	213
4·82	2	30$\bar{1}$	1·554	5	61$\bar{3}$
3·55	10	600	1·538	25	703
3·22	4	501	1·517	5	13·01
3·03	4	110	1·498	70	912, 11·1$\bar{2}$
2·90	15	002, 20$\bar{2}$	1·471	25	11·0$\bar{3}$, 20$\bar{4}$
2·85	10	601	1·442	20	13·10
2·81	20	310	1·426	15	12·02, 14·0$\bar{2}$
2·71	50	202, 40$\bar{2}$	1·334	7	
2·65	60	800, 21$\bar{1}$	1·326	10	16·00, 11$\bar{4}$
2·58	15	211, 31$\bar{1}$	1·292	5	12·12, 14·1$\bar{2}$
2·55	5	701	1·284	10	604, 10·0$\bar{4}$, 11·03
2·48	25	510, 311, 41$\bar{1}$	1·241	10	
2·41	15	402, 60$\bar{2}$	1·207	10	804, 12·0$\bar{4}$
2·35	10	411	1·178	5	18·00, 13·03
2·20	5	90$\bar{1}$	1·154	5	
2·15	5	710			
2·12	100	10·00, 11$\bar{2}$	1·059	20	20·00
2·08	40	112, 31$\bar{2}$	1·041	10	
1·867	5	910	1·028	25	11·14, 15·1$\bar{4}$, 17·12, 19·12
1·836	5	802, 811	0·984	15	12·1$\bar{5}$
1·767	3	12·00	0·958	5	80$\bar{6}$, 206, 21·10
1·654	10	712, 91$\bar{2}$	0·947	15	19·12 21·1$\bar{2}$
1·620	5	10·11			
1·612	5	10·02, 12·0$\bar{2}$, 41$\bar{3}$			

Heating of the crystals to 1100°C for 30 minutes led to the appearance of extra symmetry, probably due to the introduction of disorder, and an orthorhombic unit cell with $a=42\cdot4$ Å, $b=3\cdot06$ Å, $c=5\cdot86$ Å was found.

A similar but centred cell can, of course, be selected for the monoclinic variety. The transition from monoclinic to orthorhombic appears to be continuous, since heating to 1000°C leads to the formation of a phase giving X-ray intensities which are intermediate between those of the monoclinic and the orthorhombic phases. It is thus conceivable that some residual disorder persists even in the structure of the monoclinic phase which showed diffuse streaks along Weissenberg lines corresponding to zones with l odd. No attempt was made to eliminate this disorder but it is intended to investigate this effect in the future.

Determination and refinement of the structure

Suitable equi-inclination Weissenberg photographs showed that all the even layer lines had identical intensity distributions. The same is true for the odd layer lines. This shows that all the atoms in the structure
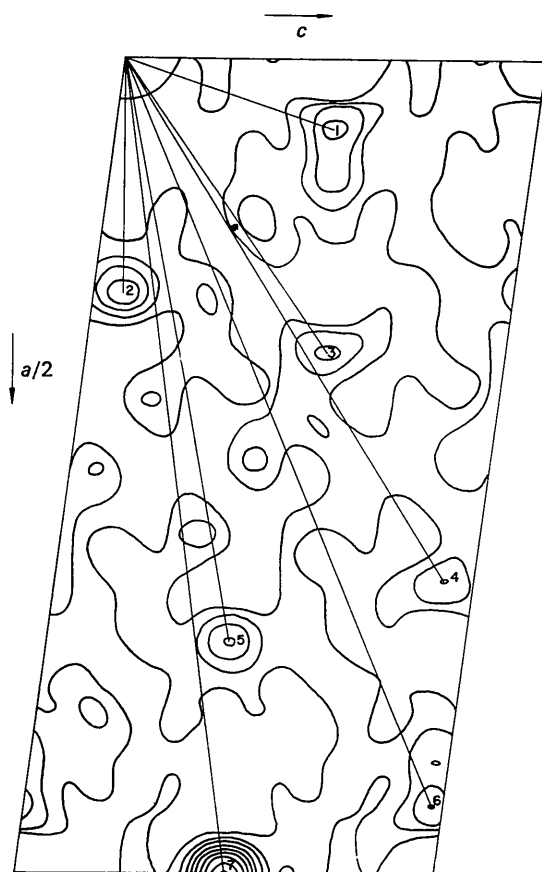
Fig.4. (010) projection of the 'difference' Patterson function calculated using all $h0l$ reflexions with l odd. Contours are drawn at arbitrary but regular intervals. The numbered peaks are identified in the text.

lie in the mirror planes. This is consistent with the expected cubic close-packed arrangement of oxygen ions as indicated by the cell dimensions and the calculated packing density of 19·0 Å³ per oxygen atom.

The intensities of 233 $h0l$ and 207 $h1l$ reflexions (including 140 unobserved) were measured from equi-inclination multiple-film Weissenberg photographs with a Zeiss–Schnell photometer. Co $K\alpha$ (Fe filter) radiation was used. Although absorption is slightly less for Mo $K\alpha$ radiation and there is an increase in the number of reflexions, the overall loss in intensity is so large that the use of this shorter wavelength has no advantages. A value of $\frac{1}{2}I_{min}$ was given to all unobserved reflexions (Hamilton, 1955) and all the usual corrections were applied by means of a suitable computer program. For absorption corrections the crystal was considered to be cylindrical and of average diameter 0·01 cm ($\mu R=1\cdot33$).

The corrected $h0l$ intensities were used to calculate a Patterson projection (Fig.3). The Patterson synthesis confirmed the existence of the expected oxygen framework and in addition indicated the positions of four of the ferrous ions. The sum of the contributions of all these atoms, in the positions as derived from the Patterson, to the structure factors of all reflexions with l odd was found to be zero. The positions of all the other atoms in the structure can thus be found by calculating a 'difference' Patterson with only the intensities of the reflexions with l odd. This 'difference' Patterson is shown in Fig.4. The peaks numbered from 1 to 7 in Fig.4 can be interpreted as follows:

Between atoms in the same asymmetric unit:

(1) Fe^{2+} — Fe^{3+}(tetrahedral)
    Si^{4+} — Fe^{3+}(octahedral)
(2) Fe^{2+} — Si^{4+}
    Fe^{3+}(oct.) — Fe^{3+}(tetraheeral)
(3) Fe^{2+} — Fe^{3+}(octahedral)

Between atoms in neighbouring asymmetric units:

(4) Fe^{3+}(oct.) — Fe^{3+}(octahedral)
(5) Fe^{2+}(oct.) — Si^{4+}
    Fe^{2+} — Fe^{3+}(tetrahedral)
(6) Fe^{3+}(oct.) — Fe^{3+}(tetrahedral)
(7) Fe^{2+} — Fe^{3+}(octahedral)
    Fe^{3+}(tetr.) — Si^{4+}

The final allocation of Si^{4+} and Fe^{3+} to tetrahedral sites was decided in terms of short range electrostatic neutrality. One Fourier synthesis (Fig.5) confirmed the conclusions reached from the Patterson syntheses. All Fourier summations were carried out on an IBM 360/40 computer, with the use of the centrosymmetric Fourier program of Gantzel & Hope as modified by Miss J.Hewitt.

The structure was refined three-dimensionally by the method of least squares with the use of the full-

matrix program, *ORFLS* of Busing, Martin & Levy (1962) adapted for use on the 360/40 by H.Messerschmidt. The scattering factors given in *International Tables for X-ray Crystallography* (1962) for Si^{4+}, Fe^{3+} and Fe^{2+} with corrections for anomalous dispersion according to Cooper (1963) applied to the iron scattering factors, and those given by Brill, Herman & Peters (1948) for O^{2-} were used. These were found to give a better refinement than the scattering factors for free atoms.

The refinement was considered complete when all parameter shifts were less than 0·1 of their estimated standard deviations. The final discrepancy $R = \Sigma \Delta F / \Sigma F_0$ was 0·165 for all reflexions. The final fractional coordinates and individual isotropic temperature factors with their estimated standard deviations are given in Table 3. Observed and calculated structure factors on an absolute scale are compared in Table 4.

Table 3. *Fractional atomic coordinates and individual temperature factors of the atoms in the asymmetric unit*

Estimated standard deviations are given below each value.

	x	y	x	B (Å^2)
O(1)	0·0497	¼	0·4091	0·64
	0·0012		0·0044	0·59
O(2)	0·0390	¼	0·8827	0·86
	0·0013		0·0047	0·63
O(3)	0·1469	¾	0·2025	1·32
	0·0013		0·0046	0·63
O(4)	0·1469	¾	0·6951	2·91
	0·0015		0·0056	0·81
O(5)	0·2342	¼	0·0126	5·54
	0·0023		0·0081	1·33
O(6)	0·2625	¼	0·5074	0·06
	0·0012		0·0041	0·55
O(7)	0·3498	¾	0·2918	2·49
	0·0015		0·0054	0·77
O(8)	0·3431	¾	0·8088	1·82
	0·0014		0·0049	0·68
O(9)	0·4542	¼	0·1058	1·32
	0·0014		0·0050	0·69
O(10)	0·4562	¼	0·6002	1·78
	0·0015		0·0054	0·75
Fe^{2+}(1)	0·0553	¾	0·1416	0·75
	0·0004		0·0013	0·19
Fe^{2+}(2)	0·0532	¾	0·6621	0·73
	0·0004		0·0013	0·19
Fe^{2+}(3)	0·1599	¼	0·4576	1·11
	0·0004		0·0014	0·20
Fe^{2+}(4)	0·4445	¾	0·3553	0·76
	0·0004		0·0013	0·19
Fe^{2+}(5)	0·4471	¾	0·8421	0·89
	0·0004		0·0013	0·19
Fe^{3+}(1)	0·1931	¾	0·9743	1·05
	0·0004		0·0014	0·20
Fe^{3+}(2)	0·3345	¼	0·0378	0·76
	0·0004		0·0013	0·19
Si	0·3018	¾	0·5251	0·07
	0·0005		0·0017	0·22

The relatively large R value and the scatter among the values of individual temperature factors was undoubtedly a result of disorder in the structure. An attempt was made to establish the nature of the disorder by calculating a three-dimensional difference synthesis but, apart from indicating considerable anisotropic thermal motion, it did not reveal any significant features. An attempt to refine anisotropic thermal parameters by least-squares was unsuccessful.

Description of the structure

The (010) projection of the structure is shown in Fig.6. The close packing of the oxygen ions in the (110) planes of the f.c.c. framework is immediately obvious. The determination of the structure was thus only a matter of allocating the cations to the available octahedral and tetrahedral interstices. Because of size considerations the Fe^{2+} are not expected to occupy any other than octahedral sites while Si^{4+} are not to be expected in these sites. However the Fe^{3+} ions can occupy both types of interstices as they do in the cases of magnetite and equilibrium wustite (*e.g.* Smuts, 1966). The structure can also be described in terms of alternating layers of FeO and Fe_3O_4 perpendicular to [100] with chains of SiO_2 running along [010] in the Fe_3O_4 layers.
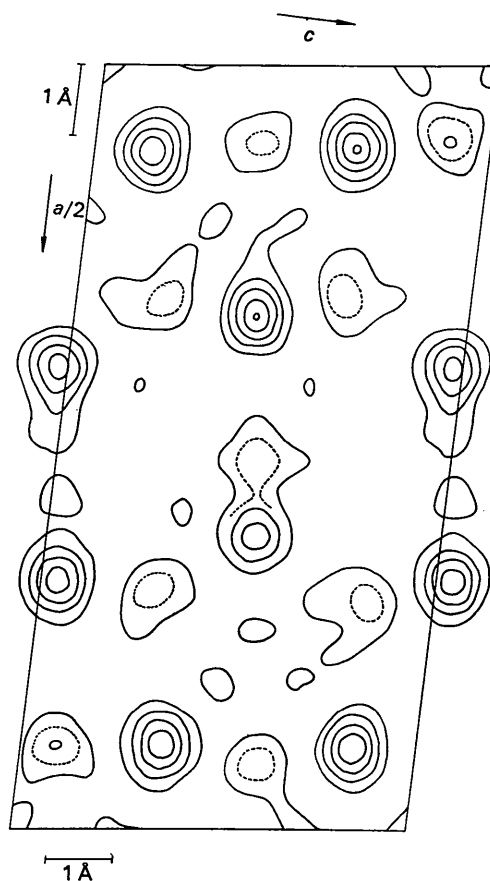

Fig. 5. Observed (010) electron density map phased on the atomic positions derived from the Patterson syntheses.

Table 4. *Observed and calculated structure factors on an absolute scale* ($F_{000} = 503$)
Unobserved reflexions are indicated by asterisks.

H	F_o	F_c	H	F_o	F_c	H	F_o	F_c	H	F_o	F_c	H	F_o	F_c	H	F_o	F_c	H	F_o	F_c	H	F_o	F_c	H	F_o	F_c	H	F_o	F_c	H	F_o	F_c	H	F_o	F_c
K=0, L=0			-3	28	27	-11*	2	6	-18	8	-2	19	33	39	15*	2	6	-7*	2	4	-18	14	11	19	9	-9	13*	4	-3	9	16	5	10*	4	-6
6	16	11	-2	7	-15	-10	35	33	-17	37	-41	K=0, L=4			16	38	-41	-6	47	-45	-17*	4	-10	20	16	15	14*	4	9	10	34	-29	11	75	80
7	1	2	-1	6	-7	-9*	2	-6	-16	13	13	-20	31	-37	K=0, L=5			-5*	2	1	-16*	4	-5	K=1, L=2			15	14	-9	11*	4	-1	12*	3	-1
8	165	-180	1	20	-19	-8	10	-11	-15	37	38	-19*	2	4	-17	37	-49	-4	31	25	-15*	4	2	-21	43	39	16*	4	-18	12*	4	5	13	31	39
9*	2	-3	2	10	-11	-7*	2	-3	-14	14	-11	-18	20	-22	-16	13	6	-3*	2	1	-14	20	18	-20*	3	13	17	90	100	13*	4	1	K=1, L=5		
10	176	-192	3	19	16	-6	81	90	-13	39	-43	-17*	2	-4	-15	25	28	-2	36	-31	-13*	4	1	-19	94	97	18*	3	13	14	11	-9	-13	10	-6
11*	2	1	4	7	2	-5*	2	11	-12	7	-8	-16*	2	3	-14*	2	-3	-1*	2	1	-12	19	-17	-18*	4	-18	19	40	37	15	8	-8	-12	42	-41
12	55	-54	5	66	59	-4	132	132	-11	54	-56	-15*	2	5	-13	9	9	0	53	54	-11	18	4	-17	14	-12	K=1, L=3			16	14	14	-11	13	6
13*	2	-5	6	37	25	-3*	2	-12	-10	21	16	-14	32	31	-12	8	-3	1*	2	-4	-10	75	73	-16*	4	9	-20	10	-11	17*	2	2	-10	11	8
14	6	-6	7	92	-87	-2	65	-57	-9	57	59	-13*	2	0	-11	21	-22	2	41	42	-9	15	2	-15*	4	2	-19	5	4	K=1, L=4			-9	12	-2
15*	2	10	8	26	-19	-1*	1	-1	-8	13	-14	-12	108	98	-10	16	11	3*	2	5	-8	29	-26	-14*	4	5	-18	27	24	-17	34	-40	-8	33	32
16	37	32	9	69	67	0	72	61	-7	34	-32	-11*	2	5	-9	64	60	4	9	-7	-7*	3	-2	-13*	4	-4	-17*	4	-2	-16*	3	4	-7	16	3
17*	2	-7	10	10	15	1*	2	11	-6	11	8	-10	109	104	-8	15	-3	K=1, L=0			-6	57	-45	-12*	4	-16	-16	9	8	-15	71	-73	-6	36	-31
18	71	63	11	28	29	2	149	-140	-5	18	18	-9*	2	-5	-7	6	1	3	83	87	-5	26	4	-11	179	-206	-15*	4	3	-14	4	6	-5	22	2
19*	2	-2	12	18	9	3	2	-12	-4	7	7	-8	24	-22	-6	9	11	4*	2	-15	-4	96	89	-10*	4	7	-14	17	16	-13	16	11	-4	61	53
20	90	91	13	61	-62	4	89	-88	-3	38	35	-7*	2	0	-5	8	-8	5	86	74	-3	36	5	-9	72	-62	-13	14	-5	-12*	4	-7	-3	7	5
K=0, L=1			14	21	-18	5*	2	3	-2	5	-5	-6	4	4	-4	4	0	6*	3	14	-2	82	-80	-8*	3	7	-12	45	-45	-11	47	-37	-2	20	14
-23	26	-32	15	49	47	6	10	10	-1	13	11	-5*	2	3	-3	6	-3	7	80	59	-1	9	-16	-7	14	-13	-11	19	3	-10*	4	1	-1	24	-7
-22	7	15	16	4	3	7*	2	5	0	13	2	-4	26	-26	-2*	2	-2	8*	3	-3	0	27	-25	-6*	3	-14	-10	26	25	-9	44	38	0	57	-47
-21	12	17	17*	2	-2	8	45	-40	1	22	-17	-3*	2	-3	-1	10	-7	9	62	-49	1	29	16	-5	25	-17	-9	7	-2	-8*	4	3	1	14	-4
-20	12	-11	18	4	3	9*	2	-4	2	9	-10	-2	217	-222	0*	2	-2	10*	3	-13	2	98	97	-4*	3	12	-8	23	-16	-7	64	56	2	37	31
-19	21	-22	19	51	-51	10	62	55	3	29	-29	-1*	2	-3	1	24	-19	11	15	9	3	35	4	-3	109	105	-7	13	-6	-6*	4	-8	3	12	-6
-18*	2	-3	20	11	-15	11*	2	3	4	13	-13	0	18	-18	2*	2	-2	12*	4	15	4	90	-73	-2*	3	-4	-6	78	-74	-5	51	42	4	28	-28
-17	12	-15	21	28	29	12	109	105	5	41	38	1*	2	4	3	39	-34	13	124	-123	5	22	-2	-1	205	221	-5	37	-6	-4*	4	4	5*	3	-1
-16	13	13	22	5	6	13*	2	-3	6	22	10	2	12	-8	4	24	-15	14*	4	-4	6	16	10	0*	3	-1	-4	79	77	-3	32	26	6	31	-30
-15	68	70	K=0, L=2			14	29	34	7	76	-69	3*	2	1	5	45	43	15	56	-60	7	12	6	1	114	103	-3	15	6	-2*	4	-3	7	14	-9
-14	18	-18	-22	20	22	15*	2	8	8	22	-17	4	25	-23	6	7	6	16*	4	-14	8	57	51	2*	3	10	-2	21	-17	-1	27	-23	8	26	27
-13	51	-52	-21*	2	4	16	16	13	9	23	18	5*	2	-5	7	23	-23	17	41	39	9	28	4	3	23	-13	-1	6	-8	0*	4	-3	K=1, L=6		
-12	8	-6	-20	21	22	17*	2	-4	10	15	8	6	126	110	8*	2	-3	18*	4	19	10	61	57	4*	3	-15	0	42	-39	1	57	-46	-8*	2	1
-11	29	-26	-19*	2	3	18	20	-19	11	47	44	7*	2	3	9	19	-5	19	29	-28	11*	4	8	5	12	-8	1	28	6	2*	4	7	-7	8	8
-10	20	20	-18	13	-10	19*	2	-3	12	14	19	8	111	93	10	9	-6	20*	3	-10	12	17	17	6*	3	9	2	101	92	3	68	-59	-6*	2	-3
-9	67	70	-17*	2	-6	20	24	-23	13	46	-43	9*	2	0	11	38	42	21	45	51	13*	4	-6	7	83	-67	3	28	5	4*	4	-6	-5	45	-44
-8	28	-22	-16	27	-32	K=0, L=3			14	13	-6	10	34	34	12	11	10	K=1, L=1			14*	4	-6	8*	4	6	4	36	-30	5	44	-35	-4*	2	1
-7	87	-91	-15*	2	5	-22	10	14	15	30	32	11*	2	0	K=0, L=6			-22	9	-14	15*	4	-6	9	184	-203	5	10	8	6*	4	2	-3	75	-69
-6	19	9	-14	100	-102	-21	48	52	16*	2	6	12	7	6	-10	10	8	-21	7	-4	16	14	10	10*	4	-15	6	22	-19	7	37	29	-2*	2	-1
-5	19	15	-13*	2	-4	-20	5	-5	17	20	22	13*	2	-6	-9*	2	-3	-20	32	-34	17*	4	2	11*	4	-3	7	10	0	8*	4	7	-1	40	-42
-4	5	5	-12	52	-51	-19*	2	6	18	12	14	14	21	-23	-8	41	-45	-19	6	5	18	20	-21	12*	4	8	8	47	43	9	15	-10	0*	2	-1
																																	1	5	4

c
a
1/4
3/4
Oxygen
Fe2+
Fe3+
Si4+

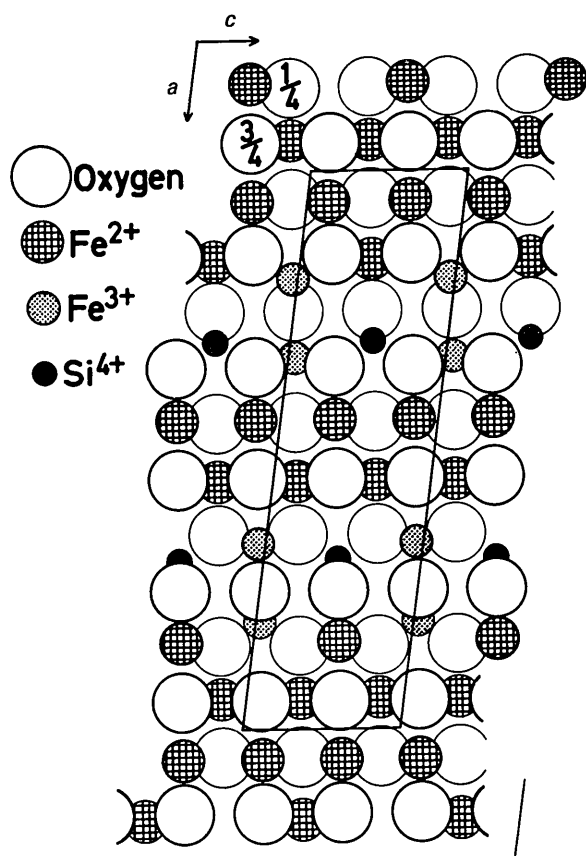

Fig. 6. The structure of iscorite shown in (010) projection. Partially obscured atoms all lie at $z=\frac{1}{4}$ and all others are at $z=\frac{3}{4}$. The size of the unit cell is indicated and the various atoms are identified in the legend.

The packing density of oxygen atoms (19·0 Å^3 per O) is very similar to that of fayalite (19·7 Å^3 per O) which is based on an h.c.p. lattice, and that of f.c.c. equailibrium wustite (19·9 Å^3 per O).

This paper is published with the permission of the South African Iron and Steel Industrial Corporation, Ltd., and the South African Council for Scientific and Industrial Research.

The authors are indebted to Dr J.N. van Niekerk and Dr G.Gafner for stimulating discussions and to Mr C.Janeke who supplied the original material.

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