X-ray data on some calcium–iron–oxygen compounds

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Summary. Synthetic mixtures of CaO and Fe_2O_3 fired in air at temperatures in the range 1180° C to 1240° C in some cases lost oxygen and formed ferrous-iron-bearing compounds. Samples after firing were examined by incident light microscopy and X-ray diffraction; new powder data are presented for the phases reported. In addition to α-Fe_2O_3, $CaFe_2O_4$, and $Ca_2Fe_2O_5$, four distinct phases have been identified. These are $CaFe_4'''O_7$, $Ca_{7\cdot2}Fe''_{0\cdot8}Fe'''_{30}O_{53}$, and two forms of $(Ca,Fe'',Mg)_4Fe'''_{14}O_{25}$, described previously by Braun and Kwestroo (1960). The likely compositions of these phases are given.

THE system CaO–FeO–Fe_2O_3 has long been recognized as important in connexion with iron-making and has been the subject of many investigations. The following compounds have been reported, the references given being selected with regard to their containing X-ray data:

2CaO.Fe_2O_3, Bertaut *et al.*, 1959; CaO.Fe_2O_3, Decker and Kasper, 1957; CaO.2Fe_2O_3, Edstrom, 1956, Phillips and Muan, 1958, and Chessin and Turkdogan, 1962; CaO.FeO.Fe_2O_3, Cirilli and Burdese, 1952; CaO.3FeO.Fe_2O_3, *ibid.*; 4CaO.FeO.4Fe_2O_3, Phillips and Muan, 1960, and Holmquist, 1960; 4CaO.FeO.8Fe_2O_3, Phillips and Muan, 1960; 4CaO.FeO.9Fe_2O_3, Burdese *et al.*, 1960; 3CaO.FeO.7Fe_2O_3, Holmquist, 1960; α- and β-4CaO.7Fe_2O_3, Braun and Kwestroo, 1960; and γ-4CaO.2FeO.9Fe_2O_3, *ibid.*

The elucidation of the constitution of iron ore agglomerates at the Research & Development Department of United Steel Cos. Ltd. has required the identification of the individual calcium–iron–oxygen compounds, but this has been difficult owing to the complexity of the subject and lack of detail in published data. A programme of work was, therefore, planned to synthesize as many of the compounds as possible and to collect detailed X-ray data. This paper describes the work done and the results obtained.

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Experimental work

Synthetic mixtures were prepared using Analar $CaCO_3$ and Spec-pure Fe_2O_3 and Fe_3O_4 as raw materials, the constituents being thoroughly mixed in a mechanical agate mortar prior to firing. Pellets were compressed in a small mould and fired in platinum crucibles in air in a furnace controlled to $\pm 3°$ C. The mixtures were $2CaO.Fe_2O_3$, $CaO.Fe_2O_3$, $CaO.2Fe_2O_3$, $4CaO.7Fe_2O_3$ (with and without 3 mol. % MgO) and $3CaO.FeO.7Fe_2O_3$. Various firing temperatures between 1180° C and 1240° C were used with times ranging up to 120 hr. The samples were quenched either in water or liquid nitrogen.

Powder photographs were obtained using a Nonius focusing camera and Co-$K\alpha$ radiation. Quartz was used as an internal standard where interplanar spacing measurements were made. In certain cases lattice parameters were determined using a least squares method. The samples were examined microscopically in reflected light and some chemical analyses for ferrous and total iron were carried out. In addition, a small amount of thermogravimetric work was undertaken on heating the mixture $CaO.2Fe_2O_3$ in air.

X-ray diffraction data

Mixture $2CaO.Fe_2O_3$. This mixture was fired for 6 hr at 1195° C and was identified as virtually pure $2CaO.Fe_2O_3$. The unit cell is given in table I with spacings and indices of all planes with d values greater than 1·35 Å. Whilst the previous data available was relatively good, a further seventeen weak lines have been detected and indexed.

Mixture $CaO.Fe_2O_3$. Reaction was substantially complete in the mixture fired for 19 hr at 1195° C and the compound gave a good diffraction pattern. Table II details the unit cell and gives a fully indexed list of interplanar spacings. As with dicalcium-ferrite, a large number of lines not previously reported were detected.

Mixture $CaO.2Fe_2O_3$. This mixture was examined in more detail and the phases identified are listed in table III. Below about 1200° C reaction was incomplete, even after 119 hours, and some α-Fe_2O_3 and $CaO.Fe_2O_3$ were present. In samples fired above this temperature α-Fe_2O_3 was virtually absent but $CaO.Fe_2O_3$ persisted in variable amounts. The phases $CaFe'''_4O_7$, $Ca_{7\cdot2}Fe''_{0\cdot8}Fe'''_{30}O_{53}$ and β-$(Ca, Fe'')_4Fe'''_{14}O_{25}$ were identified. X-ray data for these are detailed in tables IV and V and the diffraction patterns are shown in fig. 1.

Mixture $4CaO.7Fe_2O_3$. Two mixtures of this kind were prepared with and without 3 mol. % MgO, to relate the X-ray patterns obtained by Braun and Kwestroo (1960) to other patterns reported. The phases detected are also listed in table III. $\text{CaO.Fe}_2\text{O}_3$ appeared in substantial amounts even in mixtures fired at 1240° C. Table V lists the diffraction data for several examples of $\beta\text{-(Ca,Fe}'',\text{Mg)}_4\text{Fe}'''_{14}\text{O}_{25}$. Although not readily apparent in the table, there are significant differences between some of the patterns due to solid-solution effects. Table VI lists extra lines detected in the mixture with 3 mol. % MgO after 70 hr at 1195° C. These are consistent with the phase described as 'γ-$4\text{CaO}.2\text{FeO}.9\text{Fe}_2\text{O}_3$' by Braun and Kwestroo (1960) but a full diffraction pattern was not obtained in the present work owing to interference by $\beta\text{-(Ca,Fe}'',\text{Mg)}_4\text{Fe}'''_{14}\text{O}_{25}$.

TABLE I. X-ray diffraction data for $2\text{CaO.Fe}_2\text{O}_3$. Unit cell: *a* 5·598, *b* 14·754, *c* 5·427 Å, space group *Pcmn*.

I	*hkl*	$d_{\text{obs.}}$	$d_{\text{calc.}}$
m	020	7·368	7·377
w	110	5·228	5·234
w	101	3·893	3·897
vw	111	3·764	3·768
wm	130 040	3·691	3·695 3·689
vw	121	3·445	3·446
wm	131	3·058	3·054
ms	200	2·803	2·799
ms	002	2·717	2·714
s	141	2·685	2·679
wm	150 220	2·613	2·610 2·617
vw	022	2·543	2·547
w	201	2·488	2·488
vw	211	2·453	2·453
wm	221 151	2·352	2·357 2·352
w	240	2·226	2·230
wm	132 042	2·186	2·187 2·186
m	161	2·080	2·080
m	241	2·062	2·063
ms	202	1·950	1·948
vw	212	1·936	1·932
w	251	1·902	1·902
wm	152 222	1·883	1·881 1·884
m	260 080	1·846	1·847 1·844
w	062	1·821	1·822
wm	330	1·743	1·745
vw	162	1·730	1·733
vw	113	1·713	1·710
w	181 072	1·665	1·667 1·665
wm	133	1·623	1·625
w	271	1·607	1·608
m	341	1·593	1·592
w	350	1·576	1·577
m	143	1·559	1·560
wm	280	1·540	1·540
wm	082	1·525	1·525
vw	203	1·518	1·519
wm	223 153	1·486	1·488 1·487
wm	332	1·471	1·468
wm	361 272	1·434	1·434 1·431
wm	163	1·409	1·410
w	370 400	1·398	1·397 1·400
w	1.10.1	1·380	1·380
w	420	1·373	1·375
w	352	1·362	1·364
w	004	1·356	1·357
w	014 253	1·349	1·351 1·351

Mixture $3CaO.FeO.7Fe_2O_3$. This was prepared using Fe_3O_4 which contained some Fe (metal) and 'FeO'. The phases identified are included in table III.

Microscopic examination

This supported the X-ray findings with regard to the occurrence of α-Fe_2O_3 and $CaO.Fe_2O_3$ and, in addition, a more precise estimate of the amounts of these constituents present was made by means of point counts. Results are included in table III. From these it is possible to calculate the ratio Ca/(Ca+Fe) for the various types of phases present. This is of value in ascertaining their possible composition. The general optical characteristics of the phases $CaFe_4'''O_7$, $Ca_{7\cdot2}Fe_{0\cdot8}''Fe_{30}'''O_{53}$, and β- and γ-$(Ca,Fe'',Mg)_4Fe_{14}'''O_{25}$ are: Grey, without detectable birefectance. Under white light in air, magnetite is lighter than these phases, with a brownish tinge, but calcium-rich magnetite is slightly darker; in comparison, calcium monoferrite is slightly darker when in orientations giving its lowest reflectivity. Under white light in oil, calcium monoferrite is distinctly darker than these four phases, and is distinctly anisotropic with strong blood-red internal reflections, whereas they show only very slight anisotropy. The habit of all four phases varies with the

TABLE II. X-ray diffraction data for $CaO.Fe_2O_3$. Unit cell: *a* 9·159, *b* 10·709, *c* 3·015 Å, space group *Pnam.*

I	*hkl*	$d_{obs.}$	$d_{calc.}$	*I*	*hkl*	$d_{obs.}$	$d_{calc.}$
< 3	020	5·338	5·355	< 3	321	1·998	1·991
25	200	4·605	4·580	10	141	1·957	1·956
10	220	3·488	3·480	< 3	250	1·944	1·940
< 3	130	3·326	3·326	10	331	1·844	1·839
< 3	310	2·956	2·936	75	241	1·836	1·834
5	011	2·908	2·902	< 3	401	1·819	1·824
< 3	230	2·821	2·816	15	510	1·806	1·806
5	111	2·767	2·766	10	051	1·744	1·746
90	040	2·674	2·677	5	520	1·733	1·733
90	320	2·664	2·652	10	260	1·663	1·663
< 3	140	2·559	2·570	5	251	1·630	1·632
100	121	2·526	2·525	15	511	1·542	1·549
5	330	2·328	2·320	10	360	1·537	1·541
5	240	2·305	2·311	85	610	1·510	1·511
5	400	2·284	2·290		540		1·512
< 3	410	2·255	2·239	5	261	1·455	1·456
35	131	2·236	2·234	< 3	460	1·410	1·408
10	420	2·118	2·105	< 3	222	1·385	1·383
25	311	2·111	2·103	< 3	132	1·375	1·373
< 3	150	2·085	2·086		361		1·372
< 3	231	2·062	2·058	15	621	1·321	1·320

TABLE III. Phases identified in mixtures: tr, trace; s, small; m, medium; l, large amounts present. Figures refer to point-count analyses in volume %; 1000 points were counted in each case and the estimated accuracy is about ±2% for 10% recorded. The ratio Ca/(Ca+Fe) was calculated from the batch composition and the point-count data, assuming a ratio of $\frac{1}{3}$ for CaO.Fe$_2$O$_3$

Mixture	Treatment		Phases present						Observed	Total	Ferrous
	hrs	°C	CaFe$_4'''$O$_7$	Ca$_{7\cdot2}$Fe$''_{0\cdot8}$Fe$'''_{30}$O$_{53}$	β-(Ca,Fe$''$,Mg)$_4$Fe$'''_{14}$O$_{25}$	γ-(Ca,Fe$''$Mg)$_4$Fe$'''_{14}$O$_{25}$	CaO.Fe$_2$O$_3$	α-Fe$_2$O$_3$	$\frac{\text{Ca}}{(\text{Ca+Fe})}$ atoms %*	Fe wt. %	Fe wt. %
CaO.2Fe$_2$O$_3$	2	1195	s	—	—	—	s/m	m	—	—	—
„	5·5	1195	s/m	—	—	—	s/m	s/m	—	—	—
„	19	1195	m	—	—	—	s	s/m	—	—	—
„	22	1195	m	—	—	—	s	s/m	—	—	—
„	72	1195	85·1	—	—	—	8·7	6·2	19·98	59·95	0·16
„	119	1190	m/l	—	—	—	s	s	—	—	—
	20·5	1210	m/l	s	—	—	tr	—	—	—	—
	18·5	1215	m/l	s	—	—	tr	—	—	59·85	1·10
	15	1225	m	(95·5) m	—	—	4·2	0·3	19·43	—	—
	2	1240	—	93·3	—	—	6·7	—	19·02	—	—
„	18	1240	—	—	86·5	—	13·5	—	17·90	59·50	0·96
4CaO.7Fe$_2$O$_3$	19	1195	s/m	—	—	—	s/m	s/m	—	58·30	0·13
„	18	1230	s	(81·7) m	—	—	18·3	—	19·76	58·80	0·71
„	2	1240	—	—	74·6	—	25·4	tr	18·33	—	—
4CaO.7Fe$_2$O$_3$ with 3 mol. % MgO	71	1180	—	—	m/l	—	s/m	—	—	57·85	0·20
„	70	1195	—	—	m	s	s/m	—	—	—	—
„	17	1210	—	—	m/l	—	s/m	—	—	—	—
„	24	1210	—	—	m	(82·8) s/m	17·2	—	19·37	58·05	0·35
„	24	1240	—	—	68·9	—	31·1	—	16·68	—	—
3CaO.FeO.7Fe$_2$O$_3$	21	1195	s/m	s/m	—	—	tr	s/m	—	61·35	0·12
„	22	1210	s	m	—	—	—	s/m	—	—	—

* Ca/(Ca+Mg+Fe) for the mix with 3 mol. % MgO.

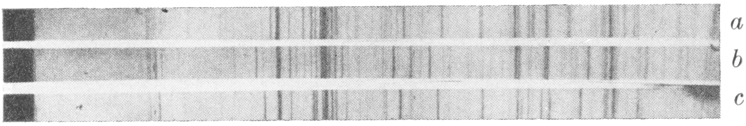

FIG. 1. X-ray diffraction patterns of some Ca-Fe-O compounds: (*a*), $\mathrm{CaFe_4'''O_7}$ with traces of $\mathrm{CaFe_2O_4}$ and α-$\mathrm{Fe_2O_3}$. (*b*), $\mathrm{Ca_{7\cdot 2}Fe''_{0\cdot 8}Fe'''_{30}O_{53}}$ with trace of $\mathrm{CaFe_2O_4}$. (*c*), β-$\mathrm{(Ca,Fe'',Mg)_4Fe'''_{14}O_{25}}$ with trace of $\mathrm{CaFe_2O_4}$.

TABLE IV. X-ray diffraction data for $\mathrm{CaFe_4'''O_7}$—mix $\mathrm{CaO.2Fe_2O_3}$ fired for 119 hr at 1195° C (A), and $\mathrm{Ca_{7\cdot 2}Fe''_{0\cdot 8}Fe'''_{30}O_{53}}$—mix $\mathrm{CaO.2Fe_2O_3}$ fired for 2 hr at 1240° C (B)

A		B		A		B		A		B	
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*
		w	15·80	w	2·569	m	2·571	w	1·743		
w	5·246	w	5·240	m	2·554	vw	2·553	s	1·733	s	1·729
w	5·186	w	5·180	vw	2·540	m	2·536	m	1·721	s	1·721
w	5·078					m	2·484			w	1·696
vw	5·004	w	5·014	w	2·448	vw	2·448	m	1·692	w	1·690
w	4·843	w	4·848	w	2·399			m	1·680		
vw	4·755	vw	4·763	w	2·388	vw	2·386			m	1·649
		vw	4·449	vw	2·355			m	1·646	m	1·643
w	4·234			w	2·304			vw	1·636		
vw	3·934	vw	3·938			vw	2·290			vw	1·609
vw	3·794					vw	2·276			vw	1·602
w	3·593			w	2·252	w	2·248	m	1·591	vw	1·588
w	3·495	w	3·494	w	2·224			w	1·586	vw	1·583
vw	3·313					m	2·194	vw	1·578	vw	1·574
		m	3·219	w	2·173	w	2·171			vw	1·555
w	3·148	w	3·148	m	2·143					m	1·547
m	3·060	vw	3·053	w	2·113	m	2·111	w	1·531		
s	3·004	s	3·002	w	2·072	vw	2·071	w	1·519	w	1·517
s	2·990	s	2·986	w	2·061			w	1·513	m	1·509
vw	2·955					m	2·024	s	1·501	s	1·498
m	2·884	m	2·886	m	1·974	vw	1·975	w	1·495	w	1·490
vw	2·830	w	2·829	vw	1·950	vw	1·950	w	1·487		
vw	2·806			vw	1·886	w	1·883	w	1·472	vw	1·473
m	2·763	w	2·759	vw	1·876	vw	1·875	w	1·447	w	1·443
w	2·710	w	2·708	vw	1·811	vw	1·806			w	1·431
s	2·628	s	2·627			vw	1·772	vw	1·418		
vs	2·605	vs	2·604	vw	1·752	vw	1·748	vw	1·403	vw	1·400

temperature of formation, but is typically prismatic (fig. 2). The four phases cannot be differentiated optically.

Etching with cold dilute or 50 % HCl for 1 to 2 min has very little effect, merely showing grain boundaries. With 50 % HCl at 60° C for 1 to 2 min or cold concentrated HCl fumes for ½ to 1 min, all four phases are distinctly darkened. Of the four, β- and γ-$\mathrm{(Ca,Fe'',Mg)_4Fe'''_{14}O_{25}}$ are

TABLE V. X-ray diffraction data for β-(Ca,Fe″,Mg)$_4$Fe$'''_{14}$O$_{25}$. (*a*) Mixture CaO.2Fe$_2$O$_3$ fired for 18 hr at 1240° C; (*b*) Mixture 4CaO.7Fe$_2$O$_3$+MgO fired for 71 hr at 1180° C; (*c*) Mixture 4CaO.7Fe$_2$O$_3$+MgO fired for 70 hr at 1195° C;* (*d*) Mixture 4CaO.7Fe$_2$O$_3$+MgO fired for 24 hr at 1240° C

	d					*d*			
I	(*a*)	(*b*)	(*c*)	(*d*)	*I*	(*a*)	(*b*)	(*c*)	(*d*)
m	15·80	15·80	15·80	15·80	s	2·001	1·998	2·000	1·994
vw	5·255	5·245	5·248	5·241	w	1·971	1·969	1·970	1·968
w	5·185	5·165	5·180	5·170	w	1·754	1·749	1·751	1·747
m	4·916	4·910	4·916	4·908	m	1·727	1·723	1·727	1·718
w	4·330	4·320	4·327	4·320	m	1·715	1·712	1·717	1·707
vw	3·935	3·925	3·932	3·931	m	1·696	1·694	1·696	1·695
w	3·695	3·670	3·678	3·676	w	1·685	1·684	1·685	1·679
m	3·130	3·135	3·130	3·140	m	1·662	1·662	1·662	1·657
m	—	3·120	3·119	3·117	m	—	—	—	1·642
s	2·991	2·985	2·984	2·980	m	1·640	1·637	1·638	1·633
s	2·694	2·684	2·688	2·688	vw	1·580	1·578	1·581	1·574
m	2·625	2·623	2·625	2·626	m	1·565	1·562	1·565	1·565
vs	2·603	2·594	2·596	2·591	s	1·495	1·492	1·494	1·488
s	2·552	2·559	2·555	2·545	w	1·488	1·485	1·487	1·482
m	2·464	2·457	2·458	2·452	w	1·468	1·465	1·468	1·462
w	2·384	2·377	2·382	2·375	m	1·447	1·445	1·446	1·447
w	2·340	2·337	2·334	2·342	w	1·439	1·437	1·440	1·437
w	2·323	2·318	2·317	2·316	vw	1·395	1·397	1·391	1·391
w	2·251	2·246	2·246	2·258	w	1·388	1·391	1·385	1·386
w	—	—	—	2·166	w	1·379	1·377	1·379	1·376
s	2·165	2·161	2·160	2·158	w	1·370	1·368	1·370	1·366
w	2·067	2·067	2·064	2·062	w	1·354	1·348	1·352	1·350

* Also contained γ-(Ca,Fe″,Mg)$_4$Fe$'''_{14}$O$_{25}$. This gave rise to some extra lines, which are omitted from this table (see table VI).

TABLE VI. X-ray diffraction data for γ-(Ca.Fe″,Mg)$_4$Fe$'''_{14}$O$_{25}$, present in the 4CaO.7Fe$_2$O+MgO mixture after 70 hr at 1195° C, together with β-(Ca,Fe″,Mg)$_4$Fe$'''_{14}$O$_{25}$ and CaO.Fe$_2$O$_3$; these lines are in addition to others superimposed on β-(Ca,Fe″,Mg)$_4$Fe$'''_{14}$O$_{25}$

I	*d*	*I*	*d*	*I*	*d*	*I*	*d*
w	4·835	s	2·780	vw	2·278	m	1·651
vw	3·840	vs	2·610	s	2·128	m	1·619
vw	3·385	w	2·507	w	1·881	w	1·610
s	3·012	m	2·490	vw	1·873	w	1·600
w	2·948	w	2·440	m	1·736	m	1·592
w	2·885	w	2·375	w	1·692	s	1·499

somewhat less etched than the other two, but this is not diagnostic. In comparison, calcium monoferrite is little affected but assumes a bluish appearance.

Textures of the fired samples are shown in fig. 2. Up to about 1200° C

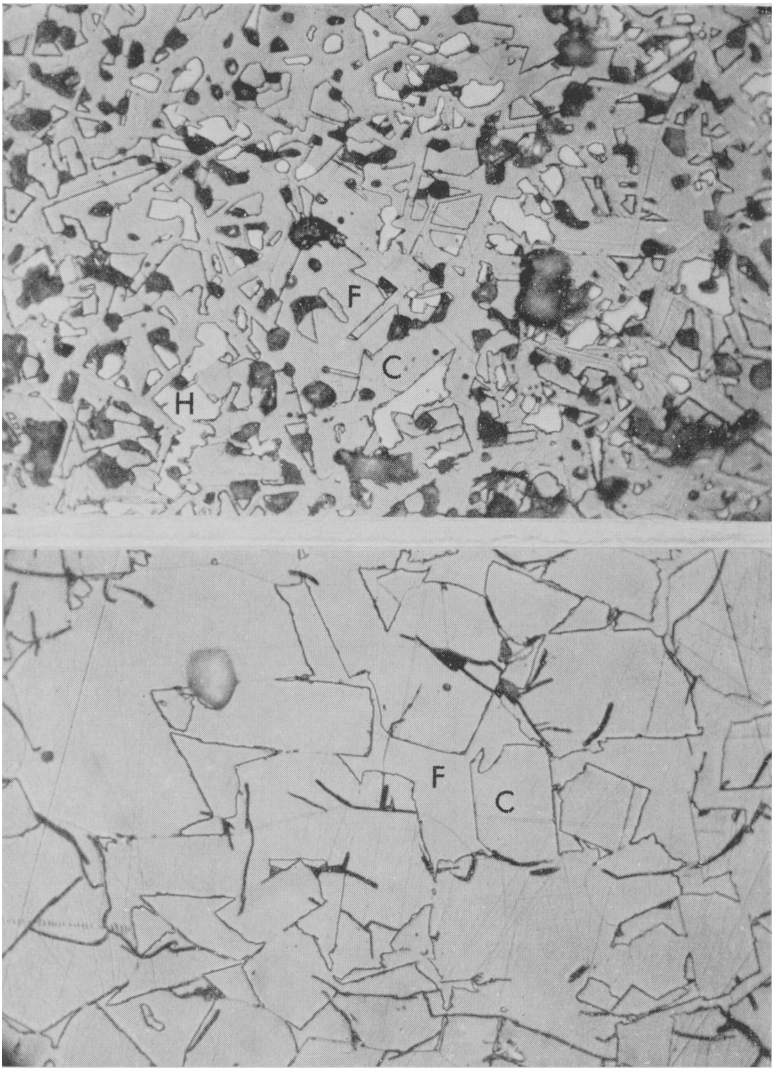

FIG. 2. Textures of fired samples, ×330, etched. (*a*) (top), mix $CaO.2Fe_2O_3$, fired for 72 hr at 1195° C. (*b*) (bottom), mix $4CaO.7Fe_2O_3$ fired for 18 hr at 1230° C. H, hematite; F, $CaFe_2O_4$; C, $CaFe_4'''O_7$; and $Ca_{7.2}Fe_{0.8}''Fe_{30}'''O_{53}$. Pores dark.

there was little indication of crystal habit, the $CaO.Fe_2O_3$ being interstitial and the α-Fe_2O_3 residual (fig. 2*a*). With increased temperature the $Ca_{7\cdot2}Fe''_{0\cdot8}Fe'''_{30}O_{53}$ and β-$(Ca,Fe'',Mg)_4Fe'''_{14}O_{25}$ increased in grain size and showed distinct crystal outlines, resulting from the melt environment (fig. 2*b*). The sample of mixture $CaO.2Fe_2O_3$ fired for 18 hr at 1240° C was particularly coarse-grained and the mixture $4CaO.7Fe_2O_3$ fired for 2 hr at 1240° C contained a trace of α-Fe_2O_3, forming small globules and probably arising from the incongruent melting (Phillips and Muan, 1958). The samples of the mix $4CaO.7Fe_2O_3$ with 3 mol. % MgO in which γ-$(Ca,Fe'',Mg)_4Fe'''_{14}O_{25}$ was identified by X-ray diffraction showed two distinct phases; the β-$(Ca,Fe'',Mg)_4Fe'''_{14}O_{25}$ showed better crystal outlines and etched more readily compared to the γ-form, which was anhedral.

Thermogravimetric results

Preliminary thermogravimetric work on the firing of the mixture $CaO.2Fe_2O_3$ in air has shown small but significant weight losses at temperatures in the range 1190° C to 1300° C consistent with loss of oxygen from the sample and the formation of a ferrous-iron-containing melt and compounds in equilibrium with it. An initial weight loss in the temperature range 1190° C to 1210° C of approximately 1 mg/gm $CaO.2Fe_2O_3$ mixture does not appear to be associated with the formation of Fe″ ions, since $CaFe'''_4O_7$ is formed in this temperature range in large amounts. This weight loss is not easily reversed on cooling. Further weight losses at higher temperatures amounting to about 1 mg/gm $CaO.2Fe_2O_3$ mixture per 20° C temperature rise are quickly regained on cooling. In the temperature range 1215° C to 1235° C the loss is associated with the formation of $Ca_{7\cdot2}Fe''_{0\cdot8}Fe'''_{30}O_{53}$ in substantial amounts. Above this temperature range the relation between phase composition of the quenched melt and weight loss requires further elucidation, but one sample quenched from about 1240° C and having lost about 2 mg/gm $CaO.2Fe_2O_3$ up to this temperature contained β-$(Ca,Fe'')_4Fe'''_{14}O_{25}$ in subsidiary amounts to α-Fe_2O_3 (resulting from incongruent melting) and $CaO.Fe_2O_3$.

Discussion

$2CaO.Fe_2O_3$ and $CaO.Fe_2O_3$. The present work has added considerably to previous data, approximately 20 weak lines being detected in each pattern that had not been reported before. These lines were in most cases predicted from calculations when the structures were determined.

$CaFe'''_4O_7$. The data for this phase (table IV) agrees with regard to the stronger lines with that of Phillips and Muan (1958) for $CaO.2Fe_2O_3$. Chemical analysis shows a little ferrous iron to be present, although one anomalous value of 1·1 % was obtained for the mixture fired for 18·5 hr at 1215° C. The observed values of Ca/(Ca+Fe) atoms derived from the quantitative petrographic analyses are in good agreement with the calculated value of 20 %. The composition is therefore believed to be very close to $CaFe'''_4O_7$. The weight loss shown by the thermogravimetric work is not easy to explain; there is the possibility of some oxygen loss without structural changes detectable by X-ray diffraction analysis.

$Ca_{7{\cdot}2}Fe''_{0{\cdot}8}Fe'''_{30}O_{53}$. The diffraction pattern for this phase may be directly compared with that of $CaFe'''_4O_7$ in table IV. There are striking similarities but significant differences in detail. With regard to possible composition, three points are significant: First, that the phase forms in the solid state when ferrous ions are present (i.e. from the $3CaO.FeO.7Fe_2O_3$ mixture); secondly, that there is oxygen loss associated with its formation from the mixture $CaO.2Fe_2O_3$; thirdly, that the observed values of Ca/(Ca+Fe) atoms % are distinctly lower than for pure $CaO.2Fe_2O_3$. Hence, it is considered that the phase is ternary; the possible composition determined from the present work is shown in fig. 3. Reference to the work of Burdese *et al.* (1960) suggests they may have synthesized the same phase: they conclude that a sample whose composition was said to be $4CaO.FeO.9Fe_2O_3$ has a similar pattern to that of $CaO.2Fe_2O_3$ of Phillips and Muan (1958); comparison with table IV, however, suggests that their diffraction pattern may be a mixture of $CaFe'''_4O_7$ and $Ca_{7{\cdot}2}Fe''_{0{\cdot}8}Fe'''_{30}O_{53}$. Similarly, the data for $CaO.2Fe_2O_3$ given by Chessin and Turkdogan (1962) in the authors' opinion represents a mixture of $Ca_{7{\cdot}2}Fe''_{0{\cdot}8}Fe'''_{30}O_{53}$ and $\beta\text{-}(Ca,Fe'')_4Fe'''_{14}O_{25}$. The view of Chessin and Turkdogan that their data and that of Holmquist (1960) for $3CaO.FeO.7Fe_2O_3$, of Phillips and Muan (1960) for $CaO.2Fe_2O_3$, and of Braun and Kwestroo (1960) for $\beta\text{-}4CaO.7Fe_2O_3$ all represent one phase cannot be substantiated. Fig. 1 clearly shows the differences between the phases as described in the present work. It is concluded that the $Ca_{7{\cdot}2}Fe''_{0{\cdot}8}Fe'''_{30}O_{53}$ phase contains essential ferrous ions but is very closely related structurally to $CaFe'''_4O_7$.

$\beta\text{-}(Ca,Fe'',Mg)_4Fe'''_{14}O_{25}$. Comparison of the data for the three phases $\beta\text{-}4CaO.7Fe_2O_3$ (Braun and Kwestroo, 1960), $3CaO.FeO.7Fe_2O_3$ (Holmquist, 1960), and $4CaO.FeO.8Fe_2O_3$ (Phillips and Muan, 1960) suggests that they are the same. Braun and Kwestroo stabilized the phase by the addition of 1 to 5 mol. % MgO but also reported that ferrous iron was present. The phase was synthesized in a similar mixture in the present work but also occurred without MgO in both the $CaO.2Fe_2O_3$ and $4CaO.7Fe_2O_3$ mixtures after suitable firing. There are again

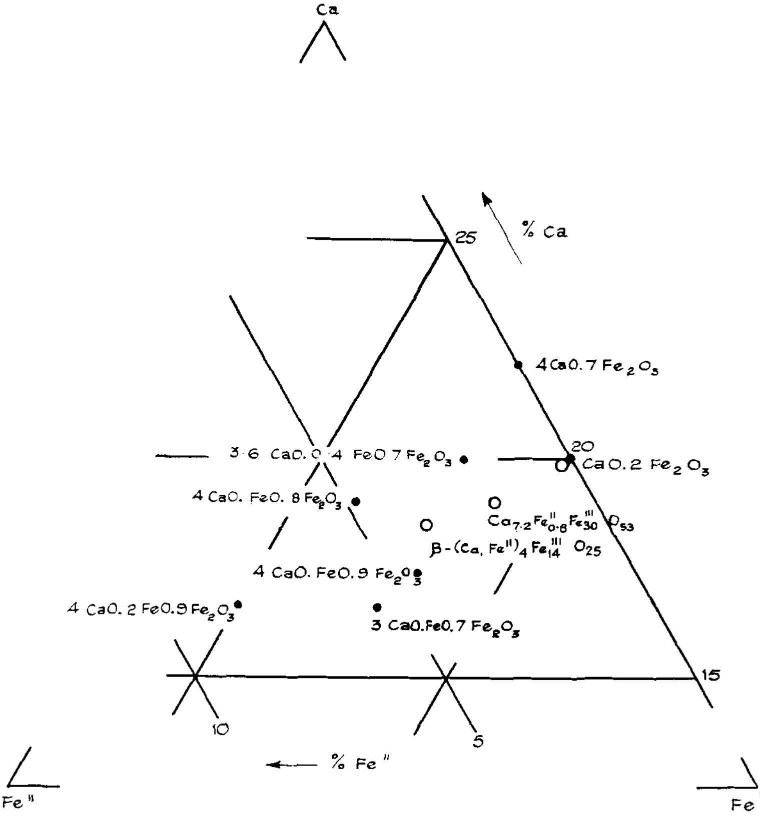

FIG. 3. Partial diagram of the Ca-Fe-O system, in atoms % of Ca, Fe″, and Fe‴, showing the relative compositions of some compounds cited. Possible compositions of compounds identified in this paper as shown as open circles.

similarities between the pattern for this phase and $Ca_{7\cdot 2}Fe''_{0\cdot 8}Fe'''_{30}O_{53}$, especially the line at 15·8 Å, and the two structures must be closely related. The unit cell suggested by Braun and Kwestroo is hexagonal with *a* 6 Å and *c* 31·6 Å.

Values of Ca/(Ca+Fe) atoms % fall between those of $CaO.2Fe_2O_3$ and $3CaO.FeO.7Fe_2O_3$. The thermogravimetric results are inconclusive but it is clear that the phase forms with ferrous iron present and the composition of $\mathrm{3{\cdot}3\,CaO.0{\cdot}7FeO.7Fe_2O_3}$ suggested by the present work is on the join $\mathrm{3CaO.FeO.7Fe_2O_3}$—$\mathrm{3{\cdot}6\,CaO.0{\cdot}4FeO.7Fe_2O_3}$.

'γ-$(Ca,Fe''Mg)_4Fe'''_{14}O_{25}$.' Two examples of this phase were identified in the present work, both from the mixture $\mathrm{4CaO.7Fe_2O_3}$ with 3 mol. % MgO. The lines indicated in table VI are in addition to other lines that coincide with those of β-$\mathrm{(Ca,Fe'',Mg)_4Fe'''_{14}O_{25}}$. Braun and Kwestroo (1960) give the unit cell as double that of the β-form, that is, hexagonal with a 6·0 Å and c 62·3 Å. There is little evidence to add to that of Braun and Kwestroo's regarding composition, except that the samples in which this phase was present contained comparatively little $\mathrm{CaO.Fe_2O_3}$ and much of the β-form. In view of the value of Ca/(Ca+Fe) determined from point counts for β-$\mathrm{(Ca,Fe'',Mg)_4Fe'''_{14}O_{25}}$ of 17 to 18 atoms %, this must place the composition of the γ-form close to $\mathrm{4(Ca,Mg)O.7Fe_2O_3}$, little ferrous iron being present (table III). It seems likely that the stabilizing component (e.g. Mg, Co, or Yt) is essential and it is possible that the phase, like the 'α-$\mathrm{4CaO.7Fe_2O_3}$' (Braun and Kwestroo, 1960) does not occur in the Ca–Fe–O system *per se*.

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