The mineralogical characteristics of calcium–iron olivines

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Summary. For the estimation of the properties of calcium–iron olivines in iron-ore sinters, synthetic mixtures of CaO, FeO, and SiO_2 were prepared and melted; the obtained olivines were then examined microscopically and by X-ray powder method. The investigations allowed to state, that with the increase of the basicity of sinters, the relation of Fe:Ca in olivines decreases, which causes the change of their physical, optical, and röntgenometric properties.

THE chemical composition and melting temperatures of calcium–iron olivines are presented in the diagrams (CaO–FeO–SiO_2 and Fe_2SiO_4–Ca_2SiO_4) of N. L. Bowen, J. F. Schairer, and E. Posnjak (1932, 1933). From these diagrams it is apparent that calcium–iron olivines form solid solutions with limited solubility. The extreme member fayalite Fe_2SiO_4 has a melting temperature 1205°, and the extreme member with the highest amount of calcium contains 42 % Fe_2SiO_4 and 59 % Ca_2SiO_4 by weight. Calcium–iron olivines are the chief component of the silicate phase in iron-ore sinters, strongly influencing the reducibility and strength of self-fluxing sinters.

Synthesis. The varying chemical composition of olivines in iron-ore sinters necessitated an investigation of the mineralogical characteristics of calcium–iron olivines. Therefore a number of syntheses of olivines were carried out at a temperature above the melting point, using pure components CaO, FeO, and SiO_2; FeO was obtained by the dissociation in vacuum of ferrous oxalate, $Fe(C_2O_4).2H_2O$. The samples were melted in pots made of armco-iron in vacuum or in argon. The assumed and actually obtained analyses of synthetic olivines are presented in table I. From the figures in this table it is apparent that the passing of some FeO into Fe_3O_4 could not be avoided. The presence of Fe_3O_4 has been confirmed by microscopic examination; Bowen, Schairer, and Posnjak found 2·0 to 2·8 % Fe_2O_3 in their silicate melts.

Optical properties of synthetic calcium–iron olivines. These olivines are characterized by a dark colour, from dark green or brown for fayalite

to dark grey or grey for olivines containing more than 20 % CaO; in thin sections, fayalite and olivines containing little CaO are bright brown and other olivines are colourless. The crystals are idiomorphic, and appear in the form of rods, rhomboid or square-shaped in cross-section. On several grains irregular cleavage is visible; it seldom agrees
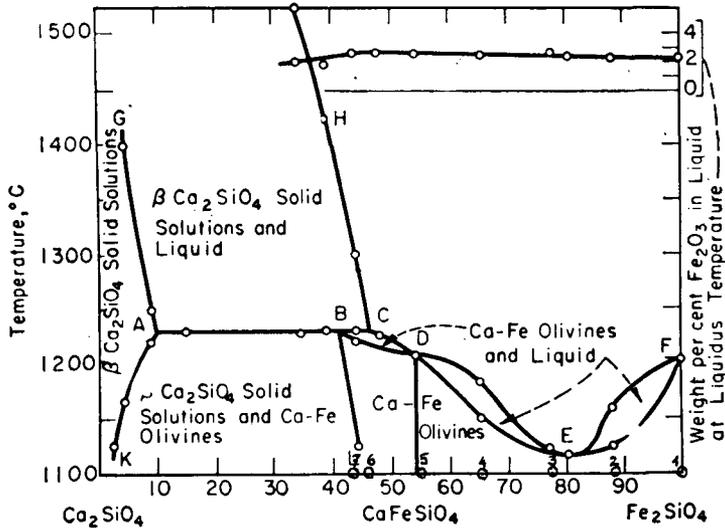
FIG. 1. Ca_2SiO_4–Fe_2SiO_4 phase diagram after Bowen, Schairer, and Posnjak. The numbered points 1 to 7 indicate the assumed compositions of the olivines examined.

with (001). The cleavage according to third pinacoid is particularly characteristic for synthetic fayalite, whereas for natural fayalite cleavage according to (010) is typical.

The indices of refraction were measured by the immersion method using mixtures of methylene iodide and sulphur (table I). It is apparent that the refractive index decreases as the ratio Fe:Ca decreases. Calcium–iron olivines have straight extinction and high birefringence (0·046–0·054), diminishing with increasing content of CaO. They are biaxial, $2V_\alpha$ 44–47° for fayalite and 48–50° for kirschsteinite.[1]

Physical properties. To confirm the influence of the content of CaO on the physical properties of calcium–iron olivines, their specific gravity

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[1] Kirschsteinite is the name accepted by the I.M.A. Commission on New Mineral Names for $CaFeSiO_4$; the name ferromonticellite is widely used in metallurgical literature.

and microhardness (pressure on the pyramid 200 g) were investigated. It is apparent that the specific gravity and hardness decrease as the content of CaO increases. Observation of the surface of samples after the hardness test shows fissures around the dent, caused by stress; the number of these increases with the brittleness of the mineral.

TABLE I. Chemical, physical, and X-ray data for calcium–iron olivines

Analyses of synthetic olivines wt %

	Assumed			Obtained				wt %	
No.	FeO	CaO	SiO$_2$	FeO	Fe$_2$O$_3$	CaO	SiO$_2$	Fe$_2$SiO$_4$	Ca$_2$SiO$_4$
1	70·60	0·00	29·40	69·66	1·14	0·00	29·04	100·00	—
2	63·00	7·00	30·00	58·91	3·63	7·25	30·12	88·75	11·25
3	55·10	14·00	30·90	51·51	4·03	14·64	29·72	77·24	22·76
4	46·90	21·85	31·25	43·53	4·03	22·47	29·98	64·98	35·02
5	38·30	29·79	31·91	37·29	1·28	30·60	30·84	54·53	45·47
6	34·30	33·00	32·60	30·47	3·21	34·50	31·76	45·66	54·34
7	30·50	37·00	32·50	28·00	1·61	38·00	32·34	41·82	58·18

No.	α	β	γ	sp. gr.	Micro-hardness kg/mm^2	a	b	c
1	1·830	1·868	1·880	4·29	625–700	4·822 Å	10·517 Å	6·056 Å
2	1·800	1·836	1·850	4·06	627–700	4·846	10·685	6·136
3	1·762	1·803	1·812	4·00	588–680	4·854	10·830	6·240
4	1·730	1·763	1·783	3·78	585–600	4·870	11·078	6·385
5	1·692	1·728	1·740	3·64	548–640	4·910	11·126	6·457
6	1·690	1·720	1·735	3·41	about 600	4·922	11·202	6·489
7	1·685	1·720	1·732	3·40	about 570	4·906	11·206	6·485

There are also scaly cracks, parallel to the surface of the sample; they appear in cases when the axis of the pyramid is perpendicular to the plane of cleavage (001). In this position olivines have smaller hardness, which indicates the dependence of the hardness on the crystallographic orientation of the surface investigated.

X-ray data. Olivines obtained by synthesis were examined by the X-ray powder method, using cameras of diameter 57·3 and 114·6 mm and Fe-$K\alpha$ and Co-$K\alpha$ radiation, monochromatized by Mn and Fe filters. Voltage 30 kV, intensity 12 mA, exposure 8 h. The film was put on asymmetrically. NaCl was used as an internal standard. In the calculations of interplanar spacings, corrections for the film shrinkage and for the absorption of radiation in the sample were taken into consideration. The intensity of reflections was estimated visually. The

TABLE II. X-ray diffraction data for investigated synthetic calcium–iron olivines

No. / hkl	I (1)	d (1)	I (2)	d (2)	I (3)	d (3)	I (4)	d (4)	I (5)	d (5)	I (6)	d (6)	I (7)	d (7)
020	4	5·192	—	—	5	5·380	8	5·471	7	5·588	6r	5·564	4r	5·576
?	2r	4·366	—	—	2r	4·403	—	—	—	—	—	—	—	—
021	5	3·967	5r	4·062	4	4·094	6	4·132	6	4·229	5	4·205	5r	4·229
101	1r	3·749	1r	3·804	1r	3·865	2	3·860	2r	3·868	2r	3·900	1r	3·885
111, 120, 030	9	3·518	7	3·572	8	3·596	9	3·631	8	3·653	7	3·659	7	3·656
?	1r	3·325	3r	3·326	2	3·347	—	—	—	—	—	—	—	—
002	4	3·033	3r	3·068	2	3·116	4	3·166	3	3·196	4r	3·235	3r	3·227
130	10	2·802	9	2·855	10	2·885	10	2·930	10	2·957	9	2·950	10	2·952
?	1r	2·725	—	—	—	—	—	—	—	—	—	—	—	—
040	4r	2·629	4r	2·671	1r	2·707	4	2·769	5	2·782	4	2·801	3	2·802
131	7	2·543	7r	2·591	5	2·622	8	2·673	9	2·690	8	2·695	9	2·707
112	10	2·468	10	2·503	10	2·529	10	2·584	10	2·615	9	2·612	10	2·612
041	5	2·392	3	2·420	—	—	4	2·513	1r	2·540	1r	2·540	2r	2·537
140, 122	7	2·290	7	2·334	5	2·356	6	2·392	8	2·411	7	2·421	8	2·426
211, 220	4	2·180	4	2·203	2	2·208	3	2·219	3	2·241	3r	2·241	3	2·248
?	2r	2·139	—	—	—	—	—	—	—	—	—	—	—	—
132, 221	5	2·061	4	2·081	3r	2·143	6	2·152	4r	2·174	2r	2·187	4	2·184
222, 240	3	1·984	1r	2·001	3r	2·093	2	2·081	—	—	4r	2·132	1r	2·095
150	2	1·915	1r	1·934	1r	1·970	4	2·014	4	2·027	4	2·025	4r	2·034
142, 151	6	1·835	4	1·853	3	1·980	4	1·944	4	1·931	3r	1·944	6	1·947
222, 240	10	1·766	10	1·785	10	1·801	10	1·823	10	1·842	9	1·841	10	1·851
241	4	1·698	5	1·713	4	1·731	2	1·760	3r	1·783	3r	1·789	4	1·790
061	4	1·673	—	—	—	—	—	—	—	—	—	—	—	—
133	5	1·645	5r	1·664	4r	1·688	5	1·721	5r	1·738	4r	1·746	3r	1·750
043	4	1·617	2r	1·624	4r	1·665	5	1·682	5r	1·707	4r	1·718	6r	1·716
310	3	1·594	1r	1·590	1r	1·604	—	—	—	—	—	—	—	—
301	2	1·584	4r	1·562	—	—	—	—	—	—	—	—	—	—
004	8	1·514	8	1·534	7	1·560	9	1·596	9	1·614	8	1·622	9	1·621
062	1	1·491	—	—	—	—	3	1·556	3	1·562	3r	1·567	3	1·570
024	4	1·455	4	1·475	4	1·474	4	1·506	5	1·519	6	1·519	6	1·519
233	6	1·427	3	1·441	—	—	4	1·478	2	1·485	1r	1·484	3	1·481
312	4	1·402	5	1·414	2r	1·421	3	1·431	2	1·443	2	1·445	4	1·450
322, 340	7	1·368	6	1·374	4r	1·389	5	1·400	4	1·417	—	—	6	1·424
134, 243	7	1·338	6	1·348	3r	1·372	—	—	4	1·340	5r	1·406	6	1·410
044	2	1·317	—	—	1r	1·357	1r	1·362	1	1·373	1r	1·374	2r	1·377
214, 262	4	1·280	4	1·293	3	1·313	4	1·335	4	1·347	4	1·349	5	1·349
303, 253	3	1·248	1r	1·254	2	1·274	4r	1·283	2r	1·280	—	—	—	—
400	4	1·205	3	1·211	3	1·213	5	1·217	4	1·227	5r	1·230	6r	1·226
333, 025	2	1·185	5	1·182	3	1·198	6	1·204	4	1·220	3r	1·221	4r	1·217
420, 125	5	1·175	3	1·163	4	1·179	4	1·174	3	1·191	2r	1·188	4	1·192
421	4	1·154	1r	1·144	1r	1·154	—	—	—	—	—	—	—	—
430	3	1·136	2r	1·127	2r	1·144	—	—	—	—	—	—	—	—
343, 412	4	1·117	2r	1·118	2	1·120	4	1·136	3	1·181	—	—	1	1·182
422, 440	7	1·095	6	1·105	3	1·106	5	1·124	5	1·145		1·146	4	1·147
353, 441	3r	1·084	1r	1·086	3	1·095	5	1·116	5r	1·134	4r	1·129	4r	1·131
432	1r	1·078	—	—	4	1·074	5	1·099	5r	1·126				
334	7	1·060	6	1·072	1r	1·057	3	1·053	5r	1·110	4r	1·112	4r	1·112
423	2	1·054	2r	1·061	—	—	—	—	1r	1·078	1r	1·080	1r	1·103
433	5	1·043	3r	1·050	—	—	—	—	6r	1·063	4	1·064	4r	1·066
354, 452	3	1·031	1r	1·036	2r	1·036	4	1·039	4r	1·050	2r	1·053	2r	1·051

r — diffuse line

position of the lines was determined using a comparator with the accuracy of ± 0.05 mm. Table II gives the indices, interplanar spacings d_{hkl}, and intensities I for the investigated olivines. The patterns of calcium–iron olivines have four very strong lines in the ranges 2·80–2·96 Å, 2·47–2·61 Å, 1·76–1·84 Å, and 1·51–1·62 Å and five with medium intensity in the ranges 3·52–3·69 Å, 2·55–2·71 Å, 2·28–2·42 Å, 1·36–1·42 Å, and 1·33–1·41 Å. The change in the chemical composition,

particularly the change in the content of CaO and FeO are distinctly reflected on powder patterns. As the content of CaO in olivine increases, the interplanar spacings also expand; for instance, the strongest line for fayalite has the value 2·802 Å and for ferromonticellite 2·957 Å. The increase of d_{hkl} progresses to the extreme content of CaO, 39 %, which corresponds to the olivine with 41·82 % Fe_2SiO_4 and 58·18 % Ca_2SiO_4 by weight; above this content of Ca_2SiO_4, d_{hkl} does not show further increase. A greater content of CaO in synthetic samples above the extreme value results in the formation of dicalcium silicate together with olivine of the extreme chemical composition. The increase of interplanar spacings in dependence on the relation $Fe^{2+}:Ca^{2+}$ is given in fig. 2. Ca^{2+} with radius 0·99 Å substituting Fe^{2+} with radius 0·80 Å enlarges all interplanar spacings, the parameters a, b, and c, and the volume of the unit cell. The median increase of the interplanar spacings is 6 %; it is particularly big for the olivines with Ca_2SiO_4 content from 0 to 45·47 %, whereas for the olivines with greater Ca_2SiO_4 content, the values of d_{hkl} show only a slow rise.

Table I and fig. 3 give calculated values of a, b, and c for all investigated olivines. The increase in c is 7·1 %, in b 6·5 %, whereas the increase in a is only 2·1 %. The figure shows the direct dependence between the amount of Ca^{2+} substituting Fe^{2+} and the dimensions of the unit cell along axes a, b, and c for the olivines with Ca_2SiO_4 content up to 45·47 wt % (50 mol %); with greater amounts of Ca_2SiO_4, a, b, and c remain almost constant.

The replacement of ions Fe^{2+} by ions Ca^{2+} on one of two possible positions in the olivine structure will influence the geometry of the unit cell. From table I it is apparent, that the greatest increase of parameters occurs normal to (010) and (001). One can therefore assume, that in these positions, ions Ca^{2+} replacing ions Fe^{2+} are located chiefly.

Calcium–iron olivines in iron-ore sinters, developed from the melt, are visible as idiomorphic crystals in the shape of a rhomb. In the case of incomplete crystallization, olivines form xenomorphic grains or lath-shaped aggregates; in quickly cooled sinters, olivines settle into skeletal dendritic grains, forming the background of magnetite. The examination of crystals of olivine in sinters in this study by means of an electron microprobe made it possible to establish their chemical composition (table III). It is evident that with the increase of the basicity of sinters the chemical composition of olivines changes up to the highest saturation with calcium, which occurs with sinters of basicity about 1·0. With further increase of sinter basicity, the chemical
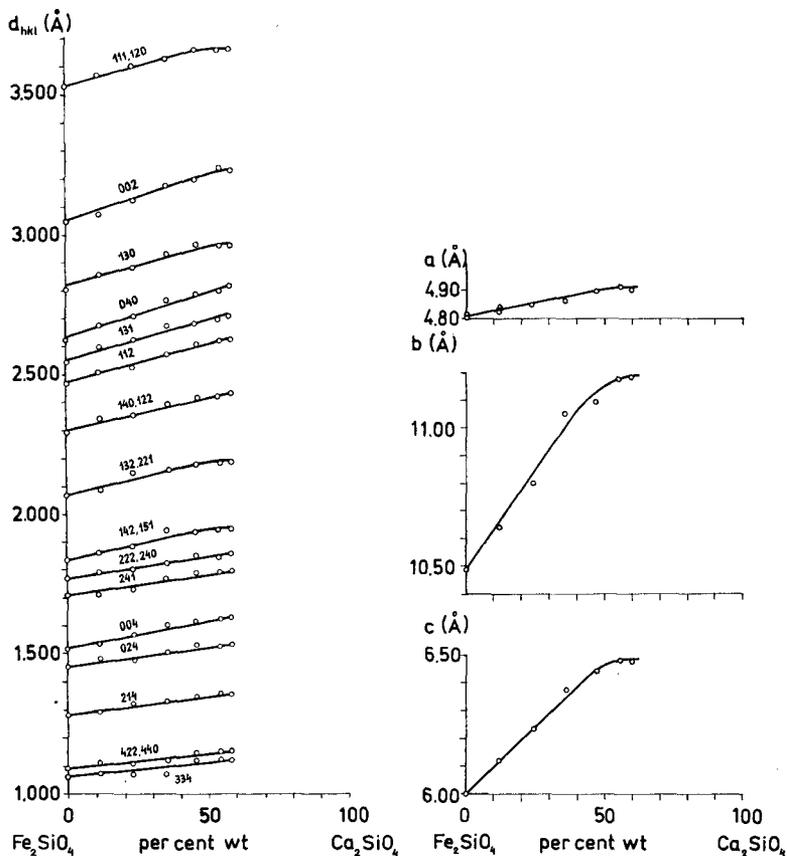
FIGS. 2 and 3: FIG. 2 (left). Correlation of the spacings of various planes *hkl* with the composition of calcium–iron olivines. FIG. 3 (right). Correlation of the cell-dimensions with the composition of calcium–iron olivines.

TABLE III. Chemical composition of calcium olivines examined by microprobe on polished surfaces of iron ore sinters

Sinter basicity $CaO:SiO_2$	FeO %	CaO %	SiO_2 %	Sinter basicity $CaO:SiO_2$	FeO %	CaO %	SiO_2 %
0·40	49·4	14·0	31·0	1·15	26·0	36·0	31·0
0·55	36·4	24·0	29·0	1·20	26·0	38·0	34·0
0·70	37·7	24·0	31·0	1·41	27·3	37·0	31·0
0·87	29·4	35·6	31·0	1·60	27·3	34·0	31·0
1·00	27·0	33·0	34·0				

composition of the olivines does not undergo any further change; by sinter basicity about 2·0 the amount of olivine in sinters declines.

Conclusions. The microscopic examination and investigation by X-ray diffraction made possible the identification of calcium olivines with different chemical composition, from fayalite through kirsch-steinite to a calcium–iron olivine with extreme saturation with CaO. The X-ray data (intensity, interplanar spacings, unit cell parameters, *a*, *b*, *c*, and volume of the unit cell) allowed the establishment of the highest content of CaO in silicate melt, i.e. of the extreme content of Ca_2SiO_4 at which only the olivine phase exists. The diagrams present all the discussed correlations.

References

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