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THE SYSTEM, Ca_2SiO_4–Fe_2SiO_4.

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INTRODUCTION.

The compound, Fe_2SiO_4, is found in nature as the mineral fayalite, known from a number of localities but not of common occurrence. The compound, Ca_2SiO_4, has been found in only one locality as a natural mineral, viz., near Larne, County Antrim, Ireland, and has been named larnite.[1] Both minerals are formed only under rather special conditions and are not of great importance as rock-forming minerals, but a knowledge of their stability relations may well throw light on factors involved in the formation of more important minerals with which they are associated.

The system, Ca_2SiO_4-Fe_2SiO_4, represents a join, specifically the orthosilicate join, in the more general system, CaO-FeO-SiO_2, upon the investigation of which we are now engaged. The results of a study of one of the fundamental systems of this general system, viz., the system FeO-SiO_2, have recently been published.[2]

To metallurgists the join now under discussion is of considerable importance because slags having such compositions are frequently used and are termed by them, monosilicate or singulo-silicate slags, following a system of naming silicates that has fallen into disuse in mineralogy.

METHOD OF INVESTIGATION.

The method which we have found satisfactory for the investigation of silicates containing ferrous oxide is described in full detail in the paper referred to above. In brief it may be said that mixtures were made up by taking silica, ferrous oxalate (or Fe_2O_3) and calcium carbonate in the proportions calculated to give the desired product and melting them

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[1] Tilley, C. E., Min. Mag., 22, 77-86, 1929.

[2] Bowen and Schairer, this Journal, 24, 177-213, 1932.

together three times in a platinum crucible in a gas furnace. Thus was obtained a product deviating somewhat from the desired composition by reason of a slight deficiency in iron (taken up by the platinum crucible) and the existence of some of the iron in the ferric state. Small samples of the mixture were then heated at measured temperatures in crucibles of pure electrolytic iron in a stream of nitrogen and the temperatures of beginning of melting, completion of melting, and of any other changes of phase were determined by the method of quenching, combined with microscopic determination of the phases in the quenched product. Upon heating in the iron crucible, a small change in the composition of the charge occurs which is principally due to reduction of ferric oxide by the iron crucible and consequent increase of the total iron content of the charge. This increase may partly balance or more than balance the deficiency produced by melting in platinum but the extent of balance cannot be predicted. A sample of each mixture was, therefore, subjected to chemical analysis after heating in an iron crucible at the temperature at which a change of phase was found to occur. Ordinarily, the temperature of heating was that at which completion of melting occurs and the analysis thus gave the composition of the liquid at the liquidus point for that composition. By repeating this procedure for a series of mixtures and plotting the determined liquidus and solidus temperatures and analyzed compositions (with microscopic determination of the crystalline phases) the equilibrium diagram was constructed.

Chemical Analysis of Charges.

Ferrous iron was determined by the Pratt[3] method modified somewhat. The exact procedure was as follows: Weigh 0.2 to 0.3 gram sample into a 150 cc. transparent silica glass[4] Erlenmeyer flask, add about 60 cc. distilled water. Displace the air in the flask by a stream of CO_2 (free from air) entering by a silica glass tube through a two-hole rubber stopper. Heat to boiling, remove flame and add 15 cc. (1:1 by volume) H_2SO_4 and 5 cc. of 40% hydrofluoric acid from a platinum

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[3] This Journal, **48**, 149, 1894.

[4] Silica glass was used to secure the advantage of observing the progress of solution of the sample. Other glasses would meet this requirement but were found to affect the FeO determination seriously. Blanks run on the silica glass used showed that no material which affected the FeO determination was dissolved from the glass by the acids.

dish by just lifting the stopper while CO_2 is still running. Replace stopper and boil gently until sample is completely dissolved (3 to 8 minutes). Cool in ice bath for 15 minutes, with CO_2 stream still running. Stop CO_2, remove from ice bath and add a large excess of solid boric acid (about 5 or 6 grams), titrate at once with standard $KMnO_4$ solution.

Total iron was determined by dissolving 0.2 to 0.3 gram sample in 15 cc. (1:1 by volume) H_2SO_4 and 8 cc. of 40% hydrofluoric acid in a large platinum dish and heating on a hot plate until all H_2F_2 had disappeared. The dish was cooled, contents diluted, and 5 cc. of concentrated HNO_3 added and the liquid transferred to a 250 cc. beaker. The iron was separated from CaO by triple precipitation using a large excess of NH_4OH and washing the precipitates well with hot water. The precipitate was ignited and weighed as Fe_2O_3. The difference between total iron and FeO gave Fe_2O_3. To check the separation of iron from CaO by the method of triple precipitation, on one sample the total iron was determined by reduction with H_2S and titration with $KMnO_4$. The results were practically identical.

EXPERIMENTAL RESULTS.

The results of the determination by these methods of the temperatures at which changes of phase occur, together with the analyzed composition of the charges, are given in Table I.

TABLE I.

Melting temperatures of mixtures.

at liquidus temperature Composition of liquid				Temp. of beginning of melting	Temp. of completion of melting	Solid phases in equilibrium with liquid at liquidus temperature
CaO	FeO	Fe_2O_3	SiO_2			
....	68.36	2.25	29.39	1205 ± 2°	1205 ± 2°	Fayalite and Fe
7.48	59.99	2.36	30.17	1125 ± 5°	1160 ± 2°	Ca-Fe olivine and Fe
12.95	53.80	2.43	30.82	1117 ± 3°	1117 ± 3°	Ca-Fe olivine and Fe
14.97	51.57	2.61	30.85	1120 ± 3°	1122 ± 3°	Ca-Fe olivine and Fe
22.47	43.53	2.54	31.46	1150 ± 5°	1182 ± 2°	Ca-Fe olivine and Fe
29.75	35.80	2.55	31.90	1208 ± 2°	1208 ± 2°	$CaFeSiO_4$ and Fe
33.80	31.17	2.80	32.23	1215 ± 3°	1226 ± 2°	Ca-Fe olivine and Fe
36.21	28.83	2.71	32.25	1220 ± 3°	1300 ± 5°	Ca_2SiO_4 and Fe
39.34	26.35	1.84	32.47	1230 ± 2°	1425 ± 5°	Ca_2SiO_4 and Fe
43.02	21.82	2.15	33.01	1228 ± 2°	1525° (appr'x.)	Ca_2SiO_4 and Fe

The table shows that even after holding the mixtures in a molten condition in an iron crucible in nitrogen some of the iron of the liquid is in the ferric state. In our former publication it was shown that even when the mixtures are melted in iron in an evacuated, sealed, silica-glass tube there is still failure of complete reduction of the iron of the mixtures to the ferrous state and reasons were there given for the belief that the small amount of ferric iron persisting in our runs made in an iron crucible in nitrogen represents a true equilibrium relation with metallic iron. Iron is incapable of further reducing the ferric iron content of the liquid; indeed, an attempt at further reduction by a powerful reducing agent would result only in the separation of metallic iron from the liquid without decrease in its Fe_2O_3 content. We have not regarded it as necessary in the case of the present mixtures to resort to any of the special procedures that were adopted in the earlier work to prove this fact since it had already been proved for one mixture that is common to both systems, viz., a mixture of the composition of fayalite.

The manner in which the content of Fe_2O_3 varies with the total iron content of liquids of the present series in equilibrium with metallic iron is of considerable interest. In the work on the system, FeO-SiO_2, it was found that the Fe_2O_3 content always decreased with content of total iron, though not at a uniform rate, the decrease being more rapid at high than at low iron concentrations. When the iron content is decreased by adding, not silica alone as formerly, but both silica and lime as in the present series, no simple decrease of Fe_2O_3 content is obtained. Indeed, as one passes from fayalite towards Ca_2SiO_4, the amount of Fe_2O_3 in the liquid in equilibrium with metallic iron does not at first decrease but actually increases slightly. The amount of increase is within the limit of error of analysis of an individual mixture, but the trend of the series, representing a decrease of total iron content (expressed as FeO) from about 70 per cent to less than 35 per cent, is distinctly upward, being 2.25 per cent Fe_2O_3 at fayalite and about 2.8 per cent at a point more than half-way over to Ca_2SiO_4. The maximum appears to come at the point where the solid phase in equilibrium with liquid (in addition to solid Fe) changes from Ca-Fe olivines to Ca_2SiO_4. Beyond that point the Fe_2O_3 content of the liquid decreases, but we are unable to follow the decrease far on account of the fact that the mixtures melt at too high a temperature to obtain complete melting in an iron crucible. The Fe_2O_3 content must, of course, become zero when the total iron content becomes zero at Ca_2SiO_4.

Ternary Diagram of Equilibrium.

On account of the fact that the Fe_2O_3 content of the liquids cannot be reduced to zero, a ternary diagram is necessary for the accurate presentation of the results. Such a diagram is given in Fig. 1. It shows that all the mixtures on the orthosilicate join lie in the field of metallic iron and that all the orthosilicate mixtures, if perfectly pure, would melt incongruently with separation of metallic iron. Not only is this true but even if some Fe_2O_3 is present in the crystalline orthosilicates its amount must exceed a certain minimum value in order to carry the composition outside the field of metallic Fe and eliminate the formation of metallic Fe upon melting. The minimum value for each orthosilicate composition is, of course, that given in Table I and shown by the position of the boundary curves limiting the field of iron in Fig. 1.

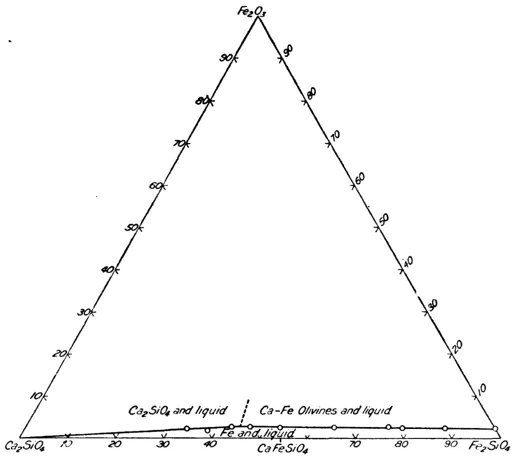

Fig. 1. Ternary diagram showing the composition of the liquids in equilibrium with metallic iron and crystalline orthosilicates of Ca and Fe.

Incongruent Melting of Fayalite.

In our former paper we demonstrated that fayalite melts incongruently with separation of iron. For this purpose we used natural fayalite from Rockport, Massachusetts, and from Mourne Mountains, Ireland. Since then we have determined the chemical composition of the Rockport fayalite, the precise material that was used for our thermal investigation.

In the analysis of Rockport fayalite FeO was determined by the Pratt[5] method modified. Iron and manganese were separated by a double basic acetate precipitation. Careful tests showed the absence of Al_2O_3, CaO, and MgO. Total iron was also determined by direct titration with $KMnO_4$ after reduction with H_2S and gave an almost identical value with that from weighing Fe_2O_3 after the basic acetate separation and reprecipitation with NH_4OH. Water was determined by the Penfield tube method.

The results are given in Table II. The material proves to have a considerably higher manganese content than that in fayalite from the same locality analyzed by Penfield.

TABLE II.

Composition of fayalite from Rockport, Massachusetts.

SiO_2	29.75
Al_2O_3	none
Fe_2O_3	0.83
FeO	66.10
MnO	3.20
MgO	none
H_2O	0.19
	100.07

The fact that there is as much as 0.83 per cent Fe_2O_3 in this fayalite and that it still shows separation of iron on melting is of particular interest, for it furnishes indisputable evidence that a content of Fe_2O_3 at least somewhat greater than 0.83 per cent is necessary to carry fayalite out of the field of iron. The amount determined by analysis of the liquid, in synthetic material, is 2.25 per cent, as Table I shows.

We have also attempted to prepare pure fayalite synthetically and to demonstrate the separation of iron when it melts. To obtain most crystalline silicate compounds it is only necessary to prepare a liquid by melting together the ingredients in the proper proportion and then to bring about crystallization under appropriate conditions. With fayalite this method cannot be adopted because a liquid of the composition of fayalite does not exist, at least up to temperatures as high as the melting point of iron. The preparation of fayalite was, therefore, carried out by another method that is sometimes used for silicates, namely, by baking together its solid ingredients at a temperature below the melting point. In the case of fayalite,

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[5] Op. cit.

iron powder, Fe_2O_3, and SiO_2 were mixed in the proper proportions, sealed in an evacuated silica-glass tube, and heated at 1100° for 4 days. In this manner a satisfactory product consisting of small, equant grains of fayalite, free from uncombined iron, was obtained. This material, after the microscopic examination which determined its character as just described, was again sealed in an evacuated silica tube and suspended in a furnace whose temperature was already fixed at 1255°, some 50° above the melting point of fayalite. Unfortunately it was found that the fayalite could not be held long under these conditions, for the liquid rapidly attacks the silica tube. In only 2½ minutes some liquid had penetrated to the outside of the tube, so that runs of even moderate length, such as one might expect to be necessary to obtain the full separation of the equilibrium quantity of iron, were not practicable. Nevertheless, in one run in which the charge was left in the furnace only one minute and in which it had happened to be placed unsymmetrically in the furnace, it was found that the one side of the charge had melted and the other had not. The unmelted part remained in the same equant grains as the original material, the melted part recrystallized as bladed crystals. In the bladed portion rare minute points of metallic iron were found; in the granular portion none was found. The contrast between the two portions furnishes very satisfactory evidence of the fact of incongruent melting of synthetic fayalite. In their quantitative relations, however, the experiments are frankly disappointing, presumably because it is impossible to hold the fayalite in the liquid state an adequate length of time. We have postponed further investigation of this question until we find a container more nearly inert to molten fayalite than is silica glass.

Results Represented as a Binary System.

On account of the necessary presence of some Fe_2O_3 in the liquid phase our results require a diagram of more than two components for their accurate presentation. However, if the small amount of Fe_2O_3 is calculated as FeO, i.e., if all the iron of the mixtures is stated as FeO, all of our mixtures lie very close to the orthosilicate join, Ca_2SiO_4-Fe_2SiO_4, and there is much gain in convenience if the results are so presented. In Table III we give the composition of our mixtures so calculated and the temperature of phase changes, and in Fig. 2 we give a "binary" diagram based upon this table.

TABLE III.

The data of Table I recalculated to a binary basis by expressing all iron oxide as FeO.

Composition		Temp. of beginning of melting	Temp. of completion of melting	Solid phases in equilibrium with liquid at liquidus temperature
Fe_2SiO_4	Ca_2SiO_4			
100	..	1205 ± 2°	1205 ± 2°	Fayalite
88	12	1125 ± 5°	1160 ± 2°	Ca-Fe olivine
81	19	1117 ± 3°	1117 ± 3°	Ca-Fe olivine
77	23	1120 ± 3°	1122 ± 3°	Ca-Fe olivine
66	34	1150 ± 5°	1182 ± 2°	Ca-Fe olivine
54.5	45.5	1208 ± 2°	1208 ± 2°	$CaFeSiO_4$
48	52	1215 ± 3°	1226 ± 2°	Ca-Fe olivine
44[a]	56	1220 ± 3°	1300 ± 5°	β-Ca_2SiO_4
39	61	1230 ± 2°	1425 ± 5°	β-Ca_2SiO_4
34	66	1228 ± 2°	1525° (approx.)	Ca_2SiO_4[b]
15[c]	85	1230 ± 2°	......	......
0	100	2130 ± 20°[d]	2130 ± 20°	α-Ca_2SiO_4

"Invariant points."

Composition of liquid	Composition of solids		Temperature
% Fe_2SiO_4	% Fe_2SiO_4	% Fe_2SiO_4	
46	10	41	1230 ± 2°
54.5	54.5		1208 ± 2°
81	81		1117 ± 3°
100	100		1205 ± 2°

[a] Additional determination on this mixture: Temperature of disappearance of Ca-Fe olivine and appearance of β-Ca_2SiO_4 = 1230 ± 2°.

[b] Probably α-form.

[c] This mixture not made by complete fusion as were all others, but merely by mixing powders of Ca_2SiO_4 and mixture E (Fig. 2) and heating at various temperatures until temperature of beginning of melting was found.

[d] Rankin and Wright, this Journal, 39, 7, 1915.

Discussion of Figure 2.

As shown in Fig. 2, Ca_2SiO_4 and Fe_2SiO_4 form the 1:1 compound, $CaFeSiO_4$ (54.5 per cent Fe_2SiO_4), analogous in composition to monticellite, $CaMgSiO_4$. $CaFeSiO_4$ has a congruent melting point at 1208 ± 2°. Crystals of the compound, $CaFeSiO_4$, have frequently been found in slags but have not been recognized in nature. Between $CaFeSiO_4$ and fayalite there is a complete series of solid solutions of the type with a minimum melting point (Type III, Roozeboom).[6] The minimum is at the composition 81 per cent Fe_2SiO_4, and the

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[6] Z. phys. Chem., **30**, 385-412, 1899.

temperature 1117 ± 3°. The series of solid solutions also continues through the composition of the compound, $CaFeSiO_4$, with the result that there is solid solution of the compound with the other end member, Ca_2SiO_4, but in this case only a partial series of the type without a eutectic (Type IV, Roozeboom). The limit of solid solution in this series is at 41 per cent Fe_2SiO_4 (B, Fig. 2) at the point where solid solution is in equilibrium with liquid of composition 46 per cent Fe_2SiO_4 (C, Fig. 2) and Ca_2SiO_4 solid solution of composition 10 per cent Fe_2SiO_4 (A, Fig. 2) and the temperature is 1230°.

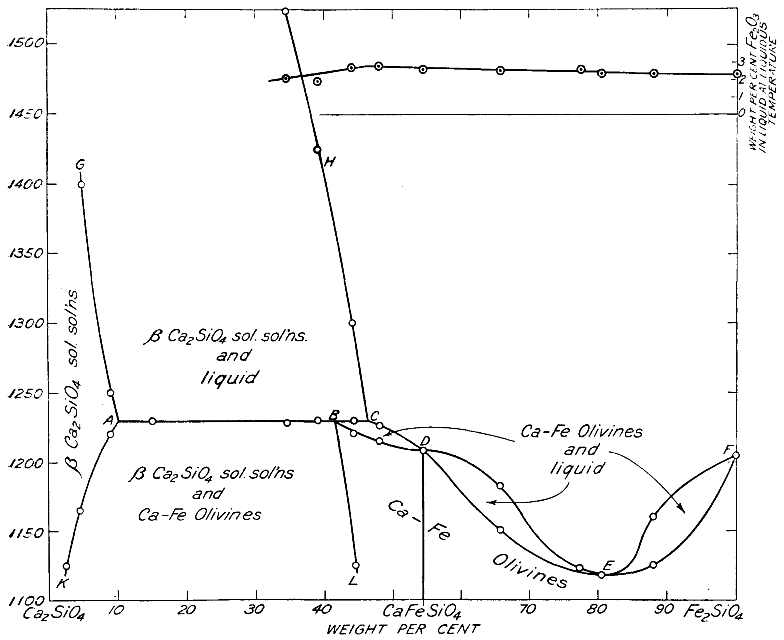

Fig. 2. Experimental results expressed in the form of a binary diagram by calculating all iron oxide as FeO. Upper right—Actual amounts of Fe_2O_3 in each liquid at liquidus temperature.

Calcium Orthosilicate and its Solid Solutions.

In earlier work of this Laboratory the compound, Ca_2SiO_4, has been shown to occur in three forms termed α, β, and γ. The α-form is stable at temperatures from 1420° to its melting point at 2130°, the β-form is stable between 675° and 1420° and the γ-form below 675°. The α- and β-forms have closely similar properties and their differentiation is not very satisfactory, but the α-form always shows a complicated twinning and the β-form only occasionally shows twinning.[7] We have found the same contrast in charges containing Ca_2SiO_4 when quenched from above or below 1420°, but are unable to add anything to the information regarding the distinction between the forms. The indices of these forms are given as follows[8]:

	γ	β	α
α-form	1.737	1.720	1.715
β-form	1.735	....	1.717

The α- and β-forms are obtainable only with difficulty on account of their strong tendency to invert to the γ-form on cooling, but with very rapid cooling and especially when they occur as small crystals embedded in another phase, the higher-temperature forms may sometimes be obtained at room temperature and examined microscopically. Only occasionally did we obtain grains of the α- or β-forms in our iron-bearing mixtures. In these cases it was not possible to measure the properties of the crystals with great accuracy but there was no obvious change in the properties of these forms when they grew in liquids containing some 45 per cent Fe_2SiO_4 except perhaps that the birefringence of the β-form seemed to be somewhat lowered. On the other hand, the γ-form produced by inversion of such grains of β-Ca_2SiO_4 has refractive indices notably higher than those of pure γ-Ca_2SiO_4. From this fact we concluded that the β-form must have contained iron in solid solution before its inversion, even though its properties were not obvously changed,[9] and we, therefore, investigated the limit of the solid solutions. To do this we mixed pure Ca_2SiO_4 as a very fine powder with varying amounts of material of the composition of the minimum E (Fig. 2) and held the mixture in iron foil at 1220°, i.e., about 10° below the horizontal ABC. At this temperature the material of composition E forms a liquid which soaks into the Ca_2SiO_4 and forms a solid solution with it. It was found that all mixtures up to a concentration corresponding with the point A

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[7] Day and Shepherd, this Journal, **22**, 280-284, 1906.

[8] Rankin and Wright, this Journal, **39**, 7-8, 1915.

[9] That β-Ca_2SiO_4 should suffer no great change of mean refractive index through solid solution of $CaFeSiO_4$ is not surprising since their mean refractive indices are not far apart, but a very different condition prevails in the case of γ-Ca_2SiO_4.

(10 per cent Fe_2SiO_4) were thus converted into homogeneous solid solutions. Beyond the point A (more than 10 per cent Fe_2SiO_4) an excess phase appeared and this corresponded in properties with the saturated Ca-Fe olivine (point B). In this manner the limit of solid solution of $CaFeSiO_4$ β-Ca_2SiO_4 was determined as 10 per cent Fe_2SiO_4(A).

It should be pointed out that, although the method described gave the limit of β-Ca_2SiO_4 solid solutions, the material examined under the microscope had in all cases inverted partially and in some cases completely to the γ-form. There is a progressive change in the readiness of inversion depending upon the composition. Thus pure β-Ca_2SiO_4 can be cooled rapidly enough so that a fair proportion remains in that form. With 5 per cent Fe_2SiO_4 in solid solution the cooling must be very rapid to retain even a small proportion in the β-form, and with 10 per cent Fe_2SiO_4 in solid solution we were unable to prevent complete inversion to the γ-form. It was upon such γ-Ca_2SiO_4 solid solutions of known composition that the change of refractive indices of this form with composition was determined.

Slopes of the Curves AK and BL.

Obviously, the method used to determine the point A can be used to determine other points on the curve AK and likewise points on the curve BL. The lower limit of temperature to which the method may be extended is, however, that of the point E (1117°), for to attain equilibrium there must be melting of the mixture E to a liquid in order that this liquid may soak into the Ca_2SiO_4 and give the appropriate solid solution. At a temperature at which no liquid forms, equilibrium proceeds too slowly to permit its determination. By determining the composition at which Ca-Fe olivine appears as an excess phase at 1165° and at 1125° the curve AK was fixed. It will be noted that at lower temperatures there is a very marked decrease in the amount of the iron compound taken into solid solution. At 1125° the saturated solid solution contains only about 2 per cent Fe_2SiO_4. By working in a similar manner with compositions in the neighborhood of the curve BL and determining the composition in which a small amount of Ca_2SiO_4 appears together with the Ca-Fe olivine, the limit of concentration of the Ca-Fe olivine at various temperatures was determined and thus the curve BL located. It will be noted that the curve BL slopes to the right downward.

Calcium Orthosilicate Solid Solutions in the γ-form.

It has been stated above that the β-Ca_2SiO_4 solid solutions inverted either completely or partially to the γ-form on cooling to room temperature. The result was that the material examined under the microscope appeared in the γ-form with not more than an occasional remnant of β-form. The γ-solid solutions thus formed by inversion have indices notably higher than pure γ-Ca_2SiO_4. It would, of course, be possible for β-solid solutions to invert to the γ-form with separation of Ca-Fe olivine in so fine a form that the microscope could not detect it, in which case the raised refractive indices would be merely aggregate refractive indices. That this is not true and that there is real solid solution in the γ-form is shown by the fact that the X-ray powder pattern shows a change of spacing of the lines (see Fig. 6). We have not found it possible to determine the limit of the series of solid solutions in the γ-form. When one prepares them by inversion from the β-form one cannot, of course, go beyond the limit of solution in the β-form, viz., 10 per cent Fe_2SiO_4. There is no reason for believing that solution in the γ-form stops at this point, but attempts to prepare γ-solid solutions richer in iron by baking together solid ingredients at temperatures from 650-750° gave only nondescript products even with the aid of a flux.[10] The attempts were made particularly because a recent investigation by Greer suggests that γ-Ca_2SiO_4 forms a complete series of solid solutions with Mn_2SiO_4[11] and it might be expected that similar relations would hold with Fe_2SiO_4. It must be admitted that the change of refractive indices of the γ-form with composition is such that the extrapolated curves might be connected up with the extrapolated curves for the Ca-Fe olivines though this would necessitate strong curvature of the missing portion of the curves and the determined portions seem to be nearly, if not quite, straight (see Fig. 5). On the other hand, some of the thermal results indicate that there cannot be complete solid solution with the γ-form, and these are the results which fixed the curve BL (Fig. 2). The determined slope of the curve BL necessitates that the completed diagram showing the relations at lower temperatures should have the general form shown in Fig. 3. There is no means of predicting the actual length of ST, representing the

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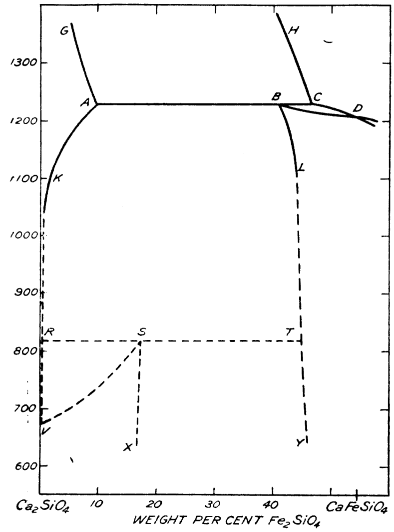
[10] It was necessary, of course, to carry on this work in evacuated, sealed tubes to prevent oxidation of iron to the ferric state.

[11] Greer, W. L. C., Am. Mineral, 17, 135-142, 1932.

magnitude of the break in the solid solution series, but complete solid solution could occur only if S and T coincide, when the curves BLT and SV become a single curve as shown in Fig. 4 (VR and RA likewise become a single curve).



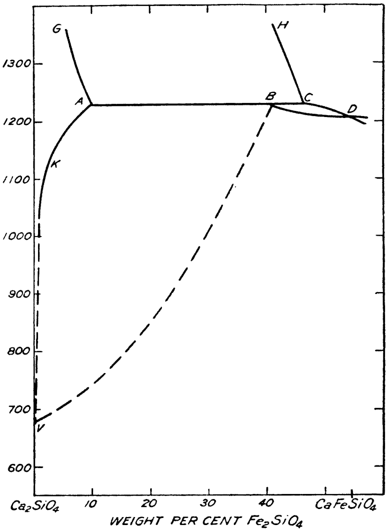


Fig. 3. Hypothetical completion of the equilibrium diagram at lower temperatures in the general form necessitated by the determined slope of BL.

Area RABT = β-Ca_2SiO_4 solid solutions and Ca-Fe olivines.
Area VSR = β-Ca_2SiO_4 and γ-Ca_2SiO_4 solid solutions.
Area VSX = γ-Ca_2SiO_4 solid solutions.
Area XSTY = γ-Ca_2SiO_4 solid solutions and Ca-Fe olivines.

Fig. 4. Hypothetical completion of the equilibrium diagram in the general form necessary if γ-Ca_2SiO_4 formed a complete series of solid solutions with $CaFeSiO_4$.

Area VAB = β-Ca_2SiO_4 solid solutions and γ-Ca_2SiO_4 solid solutions.
Area bounded upward and to the left by
VBD = γ-Ca_2SiO_4 solid solutions or Ca-Fe olivines, which become synonymous terms.

Obviously, this type of diagram can obtain only when the curve BV slopes downward to the left throughout its length, whereas our determined portion BL has the opposite slope. These considerations have led us to conclude that the diagram as completed at lower temperatures must have the general form of Fig. 3, presenting a break in the solid solution series.

It should, perhaps, be emphasized that the difficulty of determining the equilibrium conditions at these lower temperatures is due to the fact that one cannot cool any of these mixtures from the high temperatures at which they are completely molten without obtaining crystallization of β-Ca_2SiO_4 solid solutions on passing through the region GACH (Fig. 3) and without crystallization of Ca-Fe olivine in the region RABT, giving complete consolidation. Even several days' heating of this two-phase solid material at low temperatures fails to give any change of the composition of the phases by interdiffusion, the only change obtained being inversion of β-Ca_2SiO_4 solid solution as such to γ-Ca_2SiO_4 solid solution of the same composition, the Ca-Fe olivine remaining unchanged. It is difficult to see how conditions can be greatly different in the corresponding Mn system. The temperatures must rise to the same high values at the Ca_2SiO_4 end of the diagram. Cooling through the region where β-Ca_2SiO_4 is stable must likewise result in the separation of that phase so that Greer's results indicating complete solid solution in the γ-phase, obtained by the simple method of cooling a liquid, would seem to necessitate the conclusion that in the Mn system there is complete solid solution in the β-phase as well and that β-solid solutions formed at high temperatures inverted to the γ-form without change of composition.

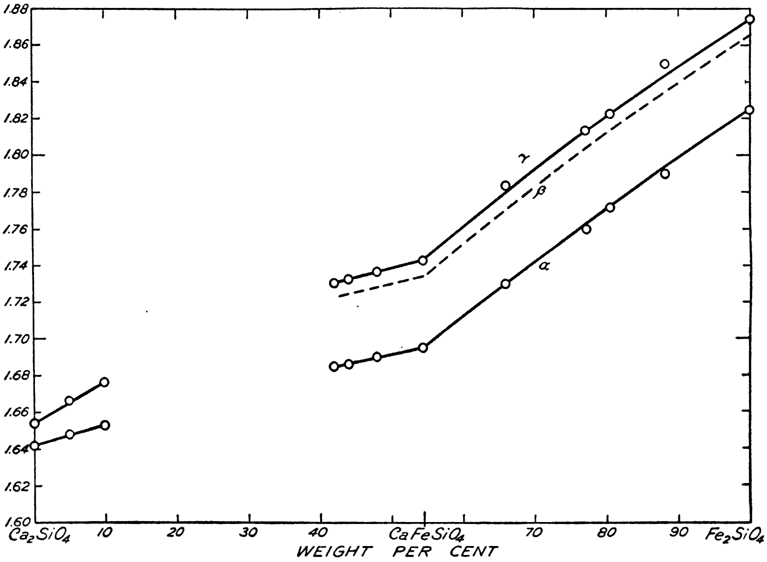


Fig. 5. Refractive indices of crystalline phases. To the right—Ca-Fe olivines. To the left—γ-Ca_2SiO_4 solid solutions.

OPTICAL PROPERTIES OF THE SOLID SOLUTIONS.

The Ca-Fe Olivines.

The refractive indices of the crystalline phases were measured in immersion liquids in sodium light. For the Ca-Fe olivines and for γ-Ca_2SiO_4 solid solutions the results are given in Table IV and plotted in Fig. 5, only γ and α being determined for each composition. The exact character of the material used requires some discussion. The crystalline material, in the case of the Ca-Fe olivines, was made merely by permitting a liquid to crystallize upon cooling. These liquids always contained some Fe_2O_3, but upon crystallization with moderately slow cooling, this Fe_2O_3 is not uniformly distributed in the crystals for it can be observed that the core of the crystals is nearly colorless, whereas the rims are notably colored. There is thus a concentration of Fe_2O_3 in the portions of later crystallization. In powder under the microscope more highly colored grains are found to have higher refractive indices than the colorless grains, a condition that is to be expected from their content of Fe_2O_3. In measuring the refractive indices these colored grains were avoided and we thus believe that our results refer to the almost purely ferrous composition.

TABLE IV.

Refractive indices of crystalline phases.

Ca-Fe Olivines

Composition			
Fe_2SiO_4	Ca_2SiO_4	γ	α
100	..	1.874 ± .003	1.824 ± .003
88	12	1.850	1.790*
81	19	1.823	1.772
77	23	1.814	1.760*
66	34	1.785	1.730*
54.5	45.5	1.743	1.696
48	52	1.737	1.690
44	56	1.733	1.686
41	59	1.730	1.684
	γ-Ca_2SiO_4 solid solutions		
10	90	1.677 ± .002	1.653 ± .002
5	95	1.667	1.647
..	100	1.654	1.642

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* Slight zoning of crystals present in these compositions.

In some of the mixtures there is zoning of another kind, namely, of the ordinary type that could be predicted from inspection of the equilibrium diagram (Fig. 2). Indeed, it was found impossible to crystallize those mixtures for which the solidus and liquidus temperatures are far apart (as for example the mixture with 88 per cent Fe_2SiO_4) without obtaining some effect of that kind unless the cooling was made so rapid that only feathery crystals, not well adapted to index measurements, were obtained. It was necessary in dealing with such mixtures to strike a compromise between a slow rate of cooling which gave the former effect and a rapid rate giving the latter. Fortunately, there are three compositions in which zoning of that kind is impossible, namely, that of the compound, $CaFeSiO_4$, that of the compound, Fe_2SiO_4, and that of the minimum melting temperature (E, Fig. 2). These can be cooled as slowly as one may wish and thus crystalline material obtained that is entirely suitable for accurate measurement of indices. In drawing the curves of variation of refractive indices with composition (Fig. 5) greatest weight has been given to these three compositions, in fact the curves were drawn through the points determined for them. It will be noted that for other mixtures there is a tendency for the points representing γ to lie somewhat above the curve and for those representing α to lie somewhat below the curve. The nature of the deviation is thus always of the kind that is to be expected in material that is slightly zoned and in which maximum and minimum refractive indices have been measured statistically. The magnitude of the deviation is always small and does not destroy the plain evidence of continuous variation with composition.

The birefringence of the Ca-Fe olivines changes only a small amount from end to end of the series, γ-α being 0.050 at fayalite, 0.47 at $CaFeSiO_4$ and 0.045 at the lime-rich extreme which has 41 per cent Fe_2SiO_4. All are optically negative and 2V is sensibly constant throughout at $50 \pm 2°$. An interesting feature of the series is the very marked change of slope of the curves of refractive indices at the composition of the compound, $CaFeSiO_4$.

The values we have obtained for fayalite, $\gamma = 1.874$, $\alpha = 1.824$, are practically the same as those found by Penfield for fayalite from Rockport, Massachusetts. The material measured by Penfield analyzed nearly pure fayalite. Considerably higher values than these ($\gamma = 1.886$, $\alpha = 1.835$) based upon measurements by Busz[12] are sometimes given for fayalite. The crystals came from a slag and in the light of our measurements there is reason to believe that they must have contained some material in solid solution which raised their indices above those for pure fayalite.

The γ-Ca_2SiO_4 Solid Solutions.

Solid solution of Fe_2SiO_4 in γ-Ca_2SiO_4 up to 10 per cent Fe_2SiO_4, which limits the series as prepared by us, induces a rapid rise of refractive indices, the measured values being given in Table IV and plotted in Fig. 5. For reasons already stated in the discussion of the equilibrium studies the series is to be regarded as extending at least somewhat farther. On account of intricate twinning we were unable to measure any of the optical properties except γ and α with any degree of satisfaction. This twinning shows on the sections giving maximum birefringence as three sets of lamellae cutting each other at approximately 60°. Occasionally the number of lamellae is reduced so that the grain is divided into six sextants with only an extra lamella or two, giving trillings analogous to those seen in aragonite, and in such sections the extinction is symmetrical. The more familiar orthosilicates, the rock-forming Mg-Fe olivines, occasionally show twinning on the dome (011) which gives trillings. Possibly we have in the present γ-Ca_2SiO_4 solid solutions a twinning after a similar law and the apparently complex twinning is not necessarily to be taken as indicating monoclinic symmetry. The γ-Ca_2SiO_4 series is possibly orthorhombic.

It should be noted that in the Ca-Fe olivines of our preparations no twinning of any kind was observed.

THE X-RAY POWDER PATTERNS OF THE CRYSTALLINE PHASES.

Together with the thermal and optical investigation of the system, Ca_2SiO_4-Fe_2SiO_4, an X-ray study by the "powder method" was also made. The diffraction patterns obtained from a number of compositions in this system are reproduced in Fig. 6. They were made with a General Electric diffraction apparatus using molybdenum K_α radiation. Their examination will readily show that starting from pure Fe_2SiO_4 (fayalite), and increasing by equal steps the Ca_2SiO_4 content to over

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[12] Busz, K., and Rüsberg, F. W., Central. Min., p. 625, 1913.

60 per cent by weight, a continuous displacement of the diffraction lines takes place without, however, changing the general characteristics of the diffraction pattern. The interpretation of this as existence of a series of solid solutions in this portion of the system is obvious, and the observed displacement of lines in the spectrograms results from the expansion of the crystal lattice which would be expected from substitution of the Ca^{2+} for the smaller Fe^{2+} (the ionic radii are 1.06 and 0.83 respectively). It should be noticed at the same time that the displacements are quite large up to the composition with 45.5 per cent Ca_2SiO_4 ($CaFeSiO_4$), and that with a further increase in the calcium content a relatively

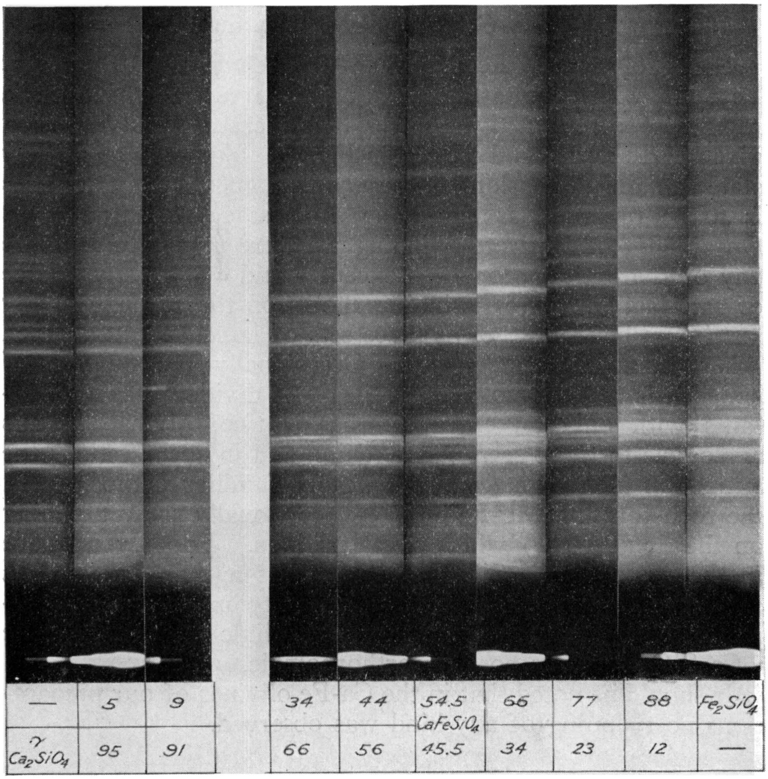

Fig. 6. X-ray diffraction patterns of γ-Ca_2SiO_4 solid solutions and of Ca-Fe olivines.

much smaller additional displacement takes place. It will be recalled also that the rate of change of refractive indices becomes much less at the composition of the compound (see Fig. 5). The preparation containing 66 per cent Ca_2SiO_4 lies beyond the limit of the Ca-Fe olivines and is found, when examined optically, to contain some γ-Ca_2SiO_4. The amount of the second phase is, however, not great enough to show in the powder spectrogram on account of the large number of diffraction lines from the principal constituent. Beyond the statement of the existence of a series of solid solutions to over 60 per cent content of Ca_2SiO_4 the X-ray data do not permit further direct conclusions. They support, however, the conclusion drawn from the thermal study which gave proof of the existence of the compound, $CaFeSiO_4$, in that they show that a different amount of displacement of the diffraction lines takes place on each side approaching the composition corresponding to this compound. The combined evidence proves complete miscibility from Fe_2SiO_4 to $CaFeSiO_4$ as well as some further miscibility of Ca_2SiO_4 and $CaFeSiO_4$; also that no unmixing of these solid solutions has taken place on cooling to room temperature.

It was mentioned above that the preparation containing 66 per cent of Ca_2SiO_4 was found to contain two phases when examined microscopically. Beyond this composition no homogeneous products were obtained until the Ca_2SiO_4 content was increased to about 90 per cent. The X-ray diffraction patterns obtained from melts containing 91, 95, and 100 per cent Ca_2SiO_4 were identical except for a small offset of the lines (see Fig. 6). The displacement, which represents a contraction of the lattice relative to pure Ca_2SiO_4, and is due to substitution of the larger Ca^{2+} by Fe^{2+}, proves that solid solutions exist also in this portion of the system.

It has already been shown in another part of the paper that β-Ca_2SiO_4 takes up a maximum of 10 per cent Fe_2SiO_4 in solid solution and that, since the γ-Ca_2SiO_4 was obtained only by inversion from the β-form, the limit of concentration of Fe_2SiO_4 in the γ-solid solutions obtained by us was necessarily 10 per cent. It was further shown that solid solution of Fe_2SiO_4 in γ-Ca_2SiO_4 must extend at least a little farther, but complete miscibility extending over to the Ca-Fe olivine series was excluded by the thermal results. The X-ray diffraction evidence taken by itself tends to confirm the existence of an hiatus. The diffraction patterns of the two series exhibit differences which suggest a distinct difference in their symmetries.

In this connection it is of interest to recall that in the study of the system, Ca_2SiO_4-Mn_2SiO_4, Greer[13] stated that in this case there is an unbroken series of solid solutions. He mentions some difficulties in preparing members of this series containing 50, 60, and 70 per cent Ca_2SiO_4, which are apparently overcome by annealing at 1100°. What this heat treatment does is not clear, and his presentation does not permit independent judgment.

Two other studies of interest here are the crystal structure determinations of forsterite[14] and monticellite.[15] These minerals were found to have identical structures. This is possible because the eight magnesium atoms in the unit cell of forsterite do not occupy equivalent positions, but are divided into two groups of four each, and it is possible to replace one group of magnesium atoms by calcium without a change in symmetry. The close similarity of forsterite and monticellite on one hand, with that of fayalite and $CaFeSiO_4$ on the other, would suggest that a similar structural relation exists in the latter case. This would furnish a plausible explanation for the existence of the unbroken series of solid solutions which has actually been found between Fe_2SiO_4 and $CaFeSiO_4$. The explanation, however, becomes less convincing in view of the fact that there is much doubt regarding the existence of continuous solid solutions between forsterite and monticellite; firstly, because the available analyses of the respective minerals fail to show any members of intermediate composition, and secondly, because the investigation of the system, CaO-MgO, SiO_2, by Ferguson and Merwin[16] indicated a miscibility of about ten per cent (their experiments, however, give only the lower limit). The elucidation of these interesting questions requires further investigation.

PETROLOGIC APPLICATIONS.

It is rather surprising that Ca-Fe olivines of the series we have prepared are not found in nature. The most likely manner of occurrence would be in contact metamorphic deposits involving metasomatism. Perhaps the oxides concerned more

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[13] Greer, W. L. C., Am. Mineral., **17**, 135, 1932.
[14] Bragg, W. L., and Brown, G. B., Z. Krist, **63**, 538, 1926.
[15] Brown, G. B., and West, J., Z. Krist, **66**, 154, 1927.
[16] Ferguson, J. B., and Merwin, H. E., this Journal, **48**, 81, 1919.

readily form garnet under such conditions especially if much ferric iron is present. Nevertheless, it does seem probable that these olivines should occur. The optical properties are not strikingly different from those of the more familiar Mg-Fe olivines and mere observation of relief and interference colors in thin section might not serve to distinguish them. With careful study and especially with measurement of refractive indices the distinction is readily made, for in the Ca-Fe series the birefringence is much greater for a given mean index of refraction than in the Mg-Fe series.

The finding that $CaFeSiO_4$ forms a complete series of solid solutions with fayalite, which in turn almost certainly forms a complete series with forsterite, renders it rather surprising that the ordinary rock-forming Mg-Fe olivines do not contain more CaO. The content of CaO in these olivines is ordinarily very low, such an amount as 2 per cent being apparently exceptional, though as much as 5 per cent has been noted in the olivine of a rock type of alkaline affinities from Cape Verde Islands. The significance of the low lime content of most rock-forming olivines may become apparent after a thermal study of the system involving all three of these orthosilicates.

The occurrence of the natural mineral larnite is very remarkable. Although the distinction between α- and β-Ca_2SiO_4 is not as clear as could be desired, the properties of larnite agree best with those of the α-form as Tilley has pointed out.[17] This form, in its pure state, is stable only above 1420° and the other forms are quite unknown as natural minerals. We have here a very unusual state of affairs. Ordinarily, it is the low-temperature forms of silicate compounds that are found in nature. Thus, of the two forms of the metasilicate of lime, wollastonite and pseudowollastonite, only wollastonite is known in nature and of the two forms nephelite and carnegieite only nephelite is found. Or, if more than one form occurs naturally, the low-temperature form is the common one, the others relatively rare, as for example in quartz, tridymite, and cristobalite.

Another remarkable feature of larnite is its survival. The α-form of Ca_2SiO_4 and the β-form as well are extremely difficult to prepare in any quantity on account of their marked tendency to change to the γ-form. Yet in larnite we have one

[17] Op. cit., p. 81.

of these forms, probably α, made in quantity in nature and persisting through the period of very slow cooling that must have prevailed after its formation. In our study of Ca_2SiO_4 containing Fe_2SiO_4 in solid solution we found that the tendency to invert increases with the content of Fe_2SiO_4. It is probable that natural larnite contains some material in solid solution that has the opposite effect. Tilley's analysis shows 1.12 per cent Al_2O_3 and 0.69 per cent MgO which he says "are probably represented in finely divided spinel,"[18] but the spinel, separately analyzed, shows much Fe_2O_3, whereas the larnite analysis gives only a trace. It seems doubtful, therefore, that the content of extraneous oxides is entirely accounted for by inclusions. There is probably some solid solution and possibly the material in solid solution decreases the inversion tendency of the larnite. It is certain, at least, that the natural larnite, which we have heated under varying conditions, has a distinctly smaller tendency to invert than pure Ca_2SiO_4. Nevertheless, inversion can be induced, though with varying ease in different specimens, and there is still the problem of the survival of the larnite in nature. Perhaps the pressure to which larnite was subjected during cooling was sufficient to prevent the change to the γ-form, which is accompanied by a 10 per cent increase of volume. This change of volume is particularly large and of the opposite sign to that usually observed with silicates, the density of the low-temperature form being ordinarily greater than that of the high-temperature form. High pressure should, therefore, induce a marked lowering of the inversion temperature of larnite and it is possible that during its formation the pressure may have been such that no excessively high temperature was necessary in order that the larnite should have formed within its stability range. The temperature may not have approached the value 1420°, which is the minimum temperature of stable existence of pure α-Ca_2SiO_4 at ordinary pressure.

APPLICATIONS TO SLAGS.

The slags of widest use in non-ferrous metallurgy are those made up principally of CaO, FeO, and SiO_2 and the monosilicates (orthosilicates) are not uncommonly employed. Since fayalite contains about 30 per cent SiO_2, and Ca_2SiO_4 about 35 per cent, all intermediate compositions contain intermediate amounts of SiO_2 so that all lime-iron slags with a little more

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[18] Op. cit., p. 81.

than 30 per cent SiO_2 lie close to the orthosilicate join. More siliceous slags, approaching the metasilicates, are usually preferred in the copper blast furnace because the loss of copper in the slag is less than with the orthosilicates. In the copper converter, however, orthosilicate slags are used, a composition with a very high iron content approaching fayalite being common. It is to be noted that fayalite forms a liquid at 1205°, a temperature considerably lower than the value commonly stated in metallurgical literature (1250-1270°).

In lead smelting a wide range of orthosilicate slags have been used. Our results do not, of course, enable us to predict anything about metal losses and other factors of great importance in the practical working of slags. We can say only that the orthosilicate slag of lowest melting temperature is that with 81 per cent Fe_2SiO_4. Though it was not part of our work to measure fluidity, nevertheless, impressions were gained during the handling of the mixtures and it appeared that at any given temperature the fluidity increased with the iron content so that this minimum-melting mixture is also a very fluid slag.

Other investigators have made measurements of the melting temperatures of mixtures corresponding with the orthosilicate series here studied. Among these we shall mention only Loo and Kern, who made cones of several orthosilicate mixtures and observed their deformation temperatures.[19] Fig. 7 permits comparison of their results with ours, and shows that there is good general agreement. We may note, however, that their mixture No. 31 (see Fig. 7) corresponding with 29 per cent Fe_2SiO_4 71 per cent Ca_2SiO_4, for which they give a "fusion temperature" of 1250°, could have been no more than about 55 per cent liquid at that temperature and a rise of temperature of 400° is necessary before complete fusion occurs. This is a striking example of the inadequacy of observations of softening and flowage as a means of determining fusion temperatures of mixtures. Our results show that in orthosilicate slags the steeply rising fusion surface of Ca_2SiO_4 is encountered at a point corresponding with about 35 per cent CaO. With a greater proportion of CaO melting may appear to take place at 1230°, but it is only partial melting and if one attempted to use an orthosilicate slag with more than 35 per cent CaO at a temperature in the neighborhood of 1230° difficulties would certainly be encountered as a result

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[19] Trans. Am. Inst. Mining and Metallurg. Eng., **76**, 503-505, 1928.

of segregation of crystals of Ca_2SiO_4. Among the 25 mixtures that Loo and Kern used in actual tests of their efficacy as practical slags this one was not tried. Of the four mixtures selected by them as "the best slags to produce in the smelting of roasted cassiterite concentrates" two were the orthosilicate mixtures, Nos. 14 and 15 (Fig. 7). It will be noted that these, and especially the latter, are not far from the composition of the minimum-melting mixture.

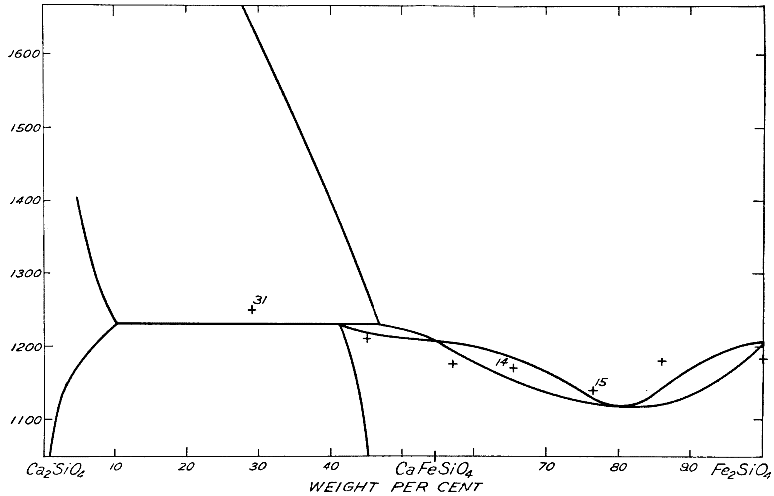

Fig. 7. Comparison diagram showing in full curves the results of the present investigation and by crosses "Fusion Points" determined by Loo and Kern (op. cit., p. 504), whose "Mixture No." is given for three of these points.

In the basic open-hearth process for steel the slag as first melted may be not far from orthosilicate composition so that our determinations have some application to that process in its early stages. At later stages the slag ordinarily acquires large amounts of phosphorus, the elimination of which is an important feature of the process, and the slag then departs notably in composition, and, therefore, in its thermal relations, from any purely siliceous slag.

SUMMARY.

The system, Ca_2SiO_4-Fe_2SiO_4, has been studied thermally by using iron crucibles as containers and an atmosphere of nitrogen to prevent oxidation. Even in the presence of metallic iron not all of the iron oxide of these mixtures is reduced to the ferrous state, but an equilibrium is established when there is still a small amount of Fe_2O_3. Accurate presentation of the results requires a ternary diagram in order to show the presence of this small amount of Fe_2O_3. This is done in Fig. 1. A great gain in the utility of the results is made if the small amount of Fe_2O_3 is calculated as FeO and thus all the iron oxide expressed as FeO. We thus obtain a "binary" diagram from which temperatures and compositions are easily read. Such a diagram is shown in Fig. 2. The diagram shows that there is one intermediate compound, viz., $CaFeSiO_4$, which melts at 1208 ± 2° and forms a complete series of solid solutions with fayalite which melts at 1205 ±2°. The solid solution series is of the type with a minimum (Type III, Roozeboom) and the minimum is at 1117 ± 3° with a composition 81 per cent Fe_2SiO_4.

In addition $CaFeSiO_4$ and β-Ca_2SiO_4 form a series of solid solutions of the type with an hiatus and with all melting temperatures intermediate between those of the end members (Type IV, Roozeboom).

The existence of these solid solutions is confirmed by optical evidence, which is presented in Fig. 5, and by X-ray evidence, presented in Fig. 6.

The results are discussed in connection with certain problems of the petrologist and of the metallurgist.

ACKNOWLEDGMENTS.

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