PHASE RELATIONS IN THE SYSTEM CaO-IRON OXIDE-TITANIUM OXIDE UNDER STRONGLY REDUCING CONDITIONS[1]

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Abstract

The quenching method has been used to determine phase relations in the system CaO-iron oxide-titanium oxide in the temperature range of approximately 1100 to 1350°C and at oxygen pressures close to those prevailing when the oxide phases are in equilibrium with metallic iron. Nine crystalline phases are stable at liquidus temperatures under these conditions, namely perovskite, dicalciumferrite, $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid solution, wüstite, lime, rutile, ulvöspinel, ilmenite, and ferropseudobrookite. These phases are solid solutions rather than pure end-member compounds. Three piercing points and five invariant points, each involving the equilibrium coexistence of three crystalline oxide phases and a liquid, were located. Particularly noteworthy among the phase relations observed are the predominance of the perovskite field and the appearance of dicalciumferrite solid solution on the liquidus surface of the system in equilibrium with metallic iron.

Introduction

In a recent paper (Kimura and Muan, 1971), we have presented phase-equilibrium data for the system CaO-iron oxide-TiO_2 in air as part of an effort to improve our understanding of the role of titanium in oxide systems. In the present paper we report on an extension of this work to lower oxygen pressures. This condition is more important geologically and technologically, but the experimental difficulties involved in the study of the system under strongly reducing conditions are larger than when the system is studied in air.

In the present study, we aim at maintaining oxygen pressures on the system such that the iron is kept in the divalent state and the titanium in the tetravalent state. However, it is well known (see for instance Bowen and Schairer, 1932) that iron oxide-containing phases under the most reducing conditions under which they are stable still contain some Fe^{3+}. Furthermore, MacChesney and Muan (1961) have shown that when TiO_2 is added to iron oxide in equilibrium with metallic iron, some of the titanium of the liquid phase will be reduced to oxidation states below 4+ when the TiO_2 content of the mixtures increases beyond a certain value. Similarly, Johnson, Woermann, and Muan (private com-

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munication) in a study of solid-solution phases in the system MgO-"FeO"-TiO$_2$ under strongly reducing conditions have shown that crystalline phases with titanium present in appreciable amounts in oxidation states lower than $4+$ are formed in mixtures high in TiO$_2$. In order to avoid this reduction to lower oxidation states of titanium inasfar as is practically possible, it is necessary that the oxygen pressure be maintained somewhat higher than that corresponding to equilibrium between the oxide phases and metallic iron when the TiO$_2$ content rises above a
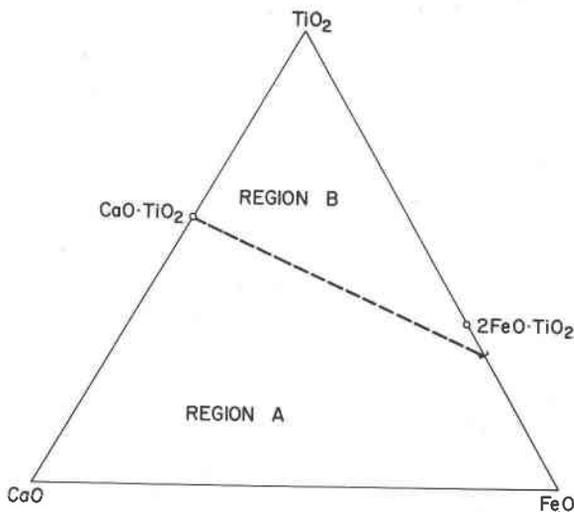
FIG. 1. Sketch showing subdivision of the composition triangle CaO-FeO-TiO$_2$ into two regions A and B, as discussed in the text. Mixtures in region A were studied in equilibrium with metallic iron, those in region B at oxygen pressures corresponding to the equilibrium between wüstite and metallic iron.

certain value. We have, therefore, divided the composition triangle CaO-FeO-TiO$_2$ (see Fig. 1) into two regions, labelled A and B. Region A comprises compositions of mixtures in which the titanium is maintained predominantly in the tetravalent state when the oxide phases are in equilibrium with metallic iron. The equilibria in this region were determined in contact with metallic iron, as will be described in detail in a subsequent section of the paper. Region B comprises compositions of mixtures in which a significant part of the titanium would be present in oxidation states below $4+$ when the oxide phases are in equilibrium with metallic iron. The phase relations in this region were determined at oxygen pressures corresponding to equilibrium between metallic iron and wüstite by the use of CO$_2$/CO mixtures, as described in detail in a subsequent section.
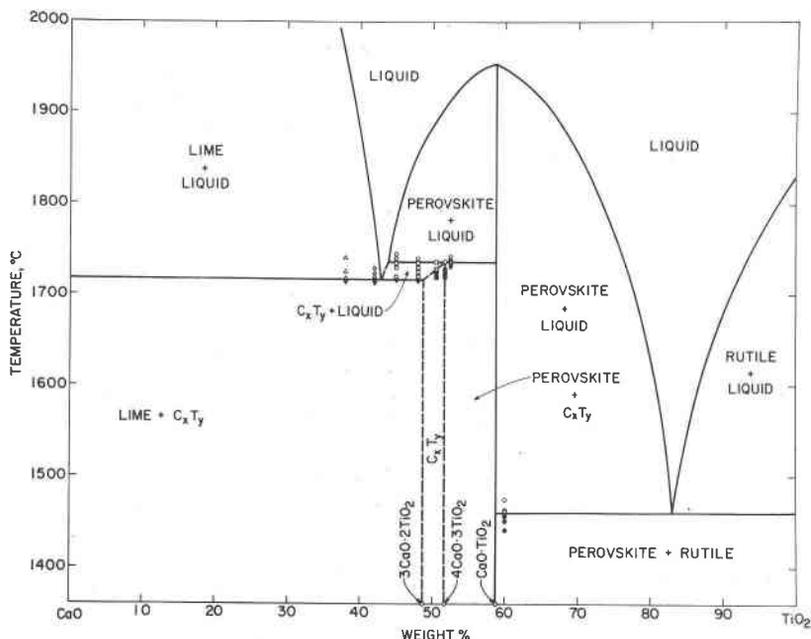
FIG. 2. Phase relations in the system CaO-TiO$_2$, mainly after DeVries, Roy, and Osborn (1954), with tentative modifications after Kimura and Muan (1971). Abbreviation used has the following meaning: $C_xT_y = Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid solutions.

PREVIOUS WORK

No detailed phase-equilibrium study of the "ternary"[1] system CaO-"FeO"-TiO$_2$ has been reported in the literature. However, the bounding "binary"[1] systems have been the subjects of several investigations. Previous work on the system CaO-TiO$_2$ was reviewed in considerable detail in our recent publication on the system CaO-iron oxide-TiO$_2$ in air (Kimura and Muan, 1971), and will not be repeated here. Also, in that paper some new data were presented for the composition range $4CaO \cdot 3TiO_2$-$3CaO \cdot 2TiO_2$. A diagram thought to represent the most consistent picture of phase relation in the system CaO-TiO$_2$ is shown in Figure 2.

The system CaO-iron oxide in contact with metallic iron has been studied by several investigators. Particular interest has centered around the problem of the stability of dicalciumferrite, $Ca_2Fe_2O_5$. Cirilli and Burdese (1954) showed that this phase in contact with metallic iron is stable relative to the lime-wüstite assemblage below 1070°, with the relation reversed above this temperature. Trömel, Jäger, and Schürmann (1955), on the other hand, claimed that dicalciumferrite was stable up to its incongruent melting point, where it forms

[1] The system CaO-iron oxide-TiO$_2$ under strongly reducing conditions as studied in the present investigation is not truly ternary because iron (and to a lesser extent titanium) occurs in different states of oxidation in varying proportions. However, the system is close to ternary, and is referred to as such for sake of convenience. Similarly the bounding systems CaO-iron oxide and iron oxide-TiO$_2$ under strongly reducing conditions are referred to as "binary" systems with the same limitations.

liquid and lime. Allen and Snow (1955) then reported that dicalciumferrite decomposes somewhat below the solidus temperature to form lime and wüstite, as previously indicated by Cirilli and Burdese. Aukrust and Muan (1965) later obtained data for this system in good agreement with those of Allen and Snow. The phase diagram of the system CaO-iron oxide in contact with metallic iron after Allen and Snow (1955), slightly modified by Aukrust and Muan (1965), is shown in Figure 3.

Phase relations in the system iron oxide-TiO₂ under strongly reducing conditions have been studied by MacChesney and Muan (1961) and by Taylor (1964). The former authors used a wüstite/metellic iron buffer in order to keep the compositions of the condensed phases as close to the FeO-TiO₂ join as practically possible (compare discussion of this problem in an earlier section of the present paper). The phase diagram for the system "FeO"-TiO₂ obtained in this way is shown in Figure 4.

Sporadic references to compatibility relations in the system CaO-iron oxide-TiO₂ have appeared in the literature. For instance, Reznichenko and Solovev (1959) investigated the effect of CaO as a flux for the smelting of ilmenite concentrate, and tentatively concluded that the reaction products from lime and ilmenite under reducing conditions are either ulvöspinel and perovskite, or metallic iron and perovskite.

In a study on the sinter produced from a mixture of perovskite and titanomagnetite concentrates, Rundneva (1962) found an assemblage of magnetite, hematite, and "com-
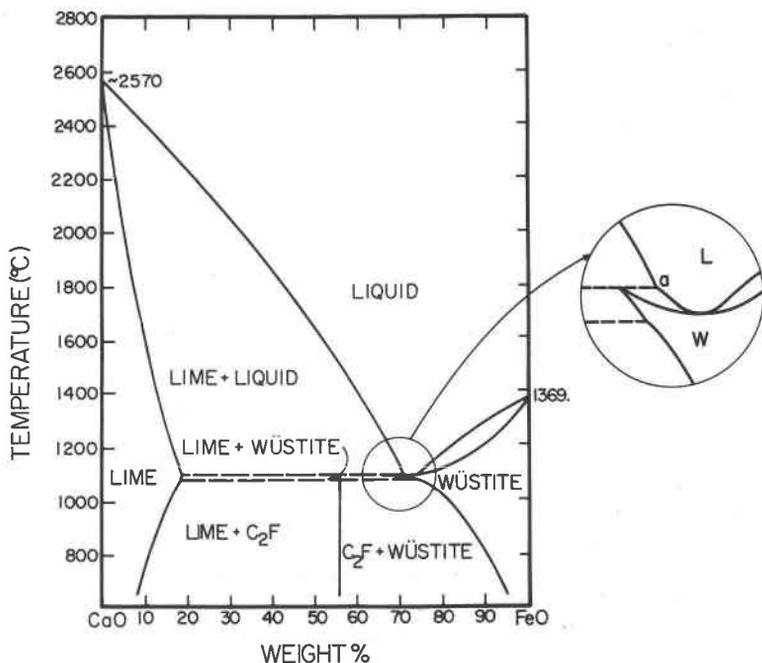
Fig. 3. Phase diagram for the system CaO-iron oxide in contact with metallic iron, mainly after Allen and Snow (1955), as modified by Aukrust and Muan (1965). Abbreviations used have the following meanings: C₂F = dicalciumferrite (Ca₂Fe₂O₅); W = wüstite (with CaO in solid solution); L = liquid.
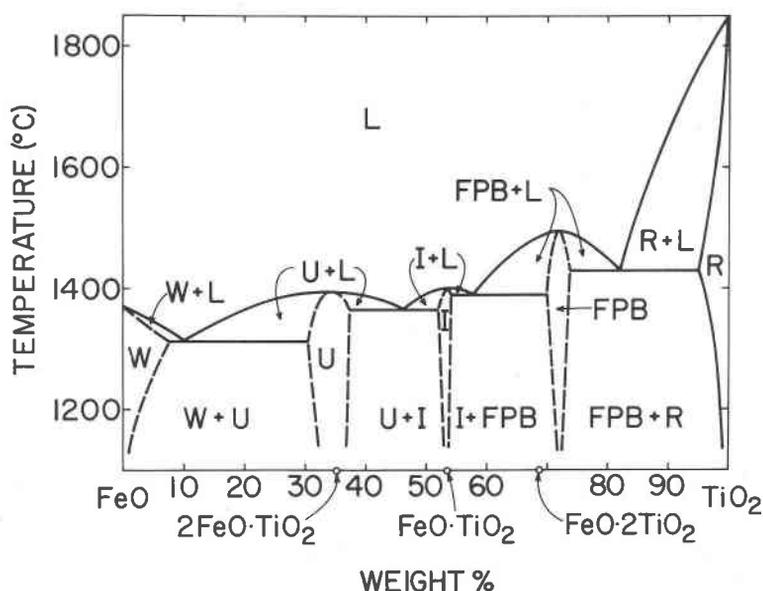
Fɪɢ. 4. Phase diagram for the system iron oxide-TiO₂ at oxygen pressures defined by the wüstite-metallic iron equilibrium, after MacChesney and Muan (1961). Abbreviations used have the following meanings: W=wüstite; U=ulvöspinel; I=ilmenite; FPB= ferropseudobrookite; R=rutile; L=liquid

plex titanium-containing oxides of perovskite constitution." Her study also suggests the coexistence of metallic iron, "complex titanium-containing oxides," and one of the calcium ferrites. Thus perovskite seems to be compatible not only with iron-titanium oxide phases, but with calcium ferrites as well.

Associations of perovskite and iron-titanium oxides in nature have been reported by various authors. The occurrence of perovskite-ilmenite-magnetite rocks in Iron Hill, Colorado, for example, as reported by Larsen (1942), strongly suggests the compatibility of perovskite with members of the hematite-ilmenite, magnetite-ulvöspinel, and pseudo-brookite solid-solution series.

EXPERIMENTAL METHODS

Phase relations were determined by the quenching technique (Shepherd, Rankin, and Wright, 1909). The general methods used in selecting starting materials, in mixture preparation, temperature control and measurements, and examination of quenched samples were identical to those described in a recent paper on the system CaO-iron oxide-TiO₂ in air (Kimura and Muan, 1971), and will not be repeated here. Special precautions taken to control the oxidation state of iron and titanium in the present work were as follows:

Approximately 50 mg of powdered samples from region A (see Fig. 1) were well mixed with approximately 20 mg metallic iron powder and placed in an iron crucible (1/4 in. O.D., 3/16 in. I.D., and 1/2 in. high). The iron crucibles were machined from an iron rod (Armco iron, purity≧99.9%). A disc made from the same iron rod was used as a lid. The sample-containing crucible was placed in a silica tube and sealed in vacuum. The silica
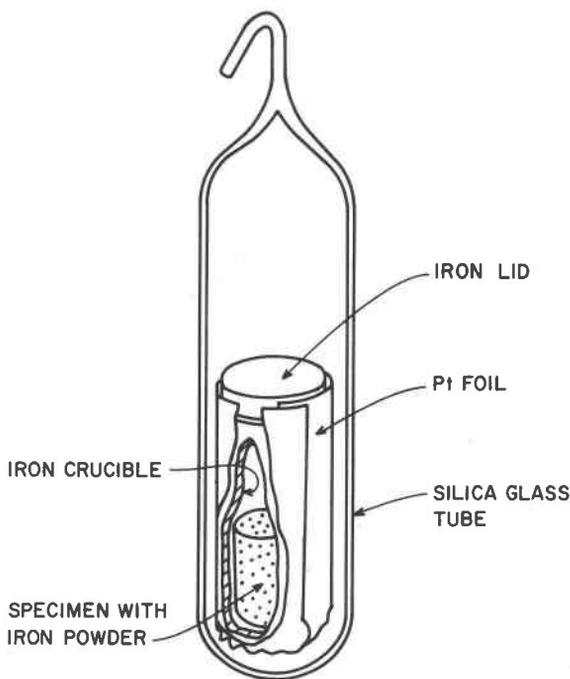
Fɪɢ. 5. Schematic illustration of the assembly used for
runs in sealed silica tubes in the present study.

tube was then suspended in the quench furnance for equilibration at desired temperature,
and subsequently quenched in water. For runs at temperatures above 1177°C (lowest
eutectic temperature in the system "FeO"-SiO$_2$, Bowen and Schairer, 1932), the iron
crucible was wrapped with platinum foil in order to prevent reaction between silica and
iron. The assembly used for runs at temperatures above 1177°C is illustrated in Figure 5.
The gas-tightness of the silica tubes was checked by equilibrating a mixture containing iron
powder at 1200°C for 24 hours and weighing the whole assemblage before and after the run.
No change in weight was detected.

Lumps of approximately 0.1 g of samples from region B (see Fig. 1) were suspended
with thin platinum wire (0.004 in.diameter) in the furnance and quenched to room tem-
perature. The furnace atmosphere in these runs was a mixture of CO$_2$ and CO with ratios
corresponding to those of the iron-wüstite equilibrium. The ratio of CO$_2$ to CO for this
atmosphere was selected on the basis of the data of Darken and Gurry (1945) with a slight
adjustment based on data for the iron-wüstite equilibrium at 1300°C as obtained in the
present investigation. These runs were made only for determination at solidus and lower
temperatures, as the samples had a tendency to fall off the suspending wire in runs at
higher temperatures.

The quenched samples were analyzed for ferrous oxide content. The analytical method
was similar to those described previously (see for example Westwood and Meyer, 1951).
It consisted in dissolving the samples in HF-H$_2$SO$_4$ aqueous solutions, followed by KMnO$_4$
titration. The accuracy of the analysis is estimated to be ± 0.5 weight percent FeO or
better.
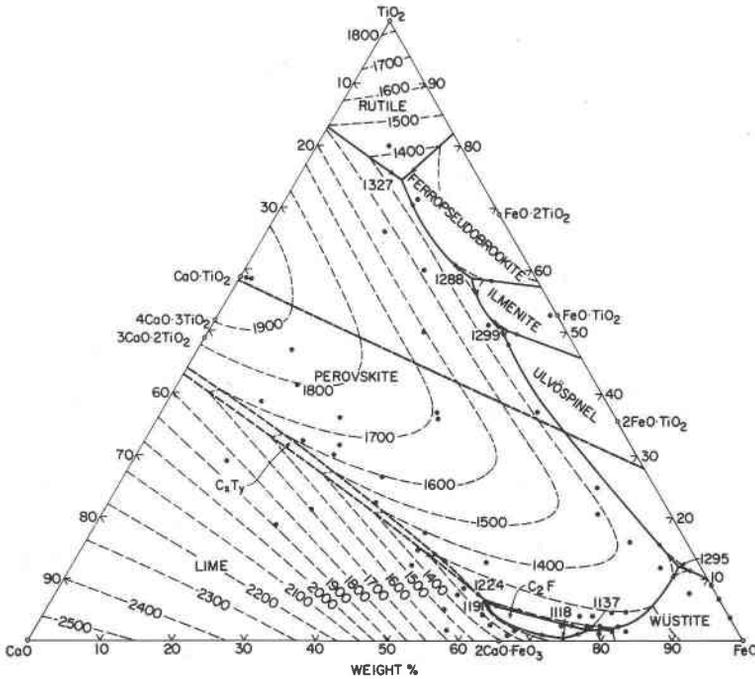
FIG. 6. Phase diagram for the system CaO-iron oxide-titanium oxide at liquidus temperatures under strongly reducing conditions. A heavy, dashed line divides the diagram into two parts. The lower part represents mixtures in contact with metallic iron, and the upper part mixtures equilibrated in an atmosphere corresponding to equilibrium between metallic iron and wüstite. Solid dots represent compositions of mixtures studied. The methods of projection used are explained in the text. Boundary curves outlining the region of $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid solutions are dashed because of the uncertainties still existing regarding the nature of this phase. Abbreviations used have been explained in legends to Figure 2 and 3.

RESULTS AND DISCUSSION

The results of equilibration runs are shown graphically in Figures 6 and 7.[1] The first of these diagrams shows a projection of the liquidus surface, and the second diagram (Fig. 7) shows a projection of the solidus surface. Although these surfaces are presented in terms of the triangle CaO-FeO-TiO₂, some of the phases, notably the liquid, contain small amounts of Fe^{3+} and/or Ti^{3+}. In areas of Figures 6 and 7 corresponding to region A of Figure 1, the projection onto the plane CaO-FeO-TiO₂

[1] Table 1 listing results of 109 individual quench runs may be ordered as NAPS Document 01479 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation 909 Third Avenue, New York, N.Y. 10022; remitting in advance $2.00 for microfiche or $5.00 for photocopies, in advance payable to CCMIC-NAPS.
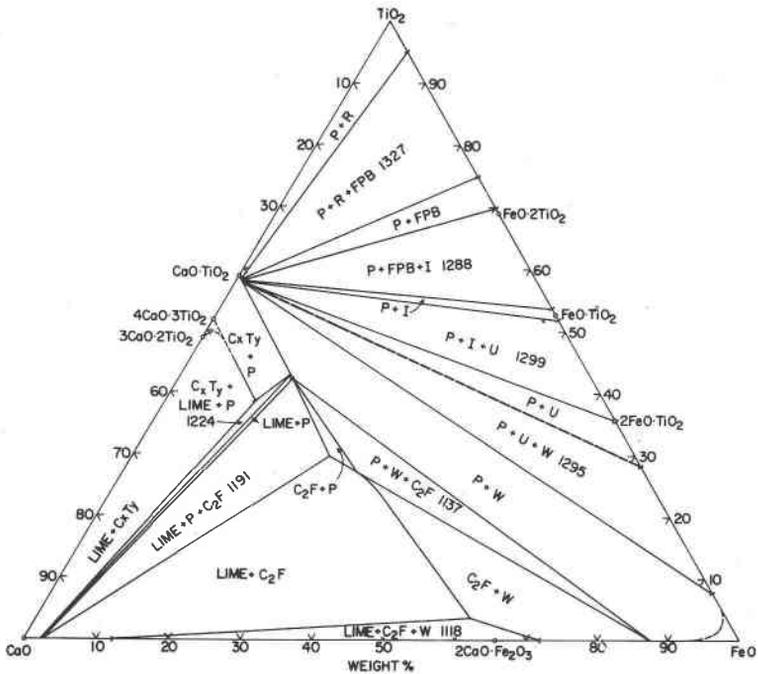
Fig. 7. Phase diagram for the system CaO-iron oxide-titanium oxide at solidus temperatures under reducing conditions. A heavy dashed line divides the diagram into two parts. The lower part represents mixtures in contact with metallic iron, and the upper part mixtures equilibrated in an atmosphere corresponding to equilibrium between metallic iron and wüstite. The methods of projection used are explained in the text. Abbreviations used have the same meanings as in Table 1. Solidus temperatures are listed for composition triangles within each of which three crystalline phases coexist with liquid. Boundary curves outlining the region of $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid solutions are dashed because of the uncertainties still existing regarding the nature of this phase. Abbreviation not explained previously has the following meaning: CT = perovskite ($CaTiO_3$).

was made along lines radiating from the Fe apex of the Ca-Ti-Fe-O tetrahedron, whereas in areas corresponding to region B the projection onto the plane CaO-FeO-TiO_2 was made along lines radiating from the O apex of the tetrahedron.

Nine crystalline phases are stable at liquidus temperatures. These are rutile (TiO_2 with some iron oxide in solid solution), perovskite ($CaTiO_3$ solid solution), ($Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$) solid solution, lime (CaO with iron oxide in solid solution), ferropseudobrookite ($FeTi_2O_5$ solid solution), ilmenite ($FeTiO_3$ solid solution), ulvöspinel (Fe_2TiO_4 solid solution), wüstite ($Fe_{1-x}O$ with calcium oxide and/or titanium oxide in solid solution), and dicalciumferrite ($Ca_2Fe_2O_5$ solid solution).

TABLE 2

Temperatures and Phase Assemblages of Liquidus Piercing Points
and Invariant Points in the System CaO-Iron Oxide-Titanium
Oxide under Strongly Reducing Conditions*

Temperature, °C**	Phases Present***
Piercing Points	
1327	Rutile,perovskite,ferropseudobrookite, liquid (11 wt.% CaO, 75 wt.% TiO$_2$, 14 wt.% FeO).
1288	Perovskite,ferropseudobrookite,ilmenite,liquid (8 wt.% CaO, 59 wt.% TiO$_2$, 33 wt.% FeO).
1299	Perovskite,ilmenite,ulvöspinel,liquid (8 wt.% CaO, 51 wt.% TiO$_2$, 41 wt.% FeO).
Invariant Points	
1295	Perovskite,ulvöspinel,wüstite,metallic iron, liquid (3 wt.% CaO, 12 wt.% TiO$_2$, 85 wt.% FeO).
1137	Perovskite, wüstite, dicalciumferrite,metallic iron, liquid (20 wt.% CaO, 2 wt.% TiO$_2$, 78 wt.% FeO).
1118	Wüstite, dicalciumferrite,lime,metallic iron, liquid (25.5 wt.% CaO, 0.5 wt.% TiO$_2$, 74 wt.% FeO).
1191	Perovskite, dicalciumferrite, lime, metallic iron, liquid (33 wt.% CaO, 7 wt.% TiO$_2$, 60 wt.% FeO).
1224	Perovskite, Ca$_4$Ti$_3$O$_{10}$-Ca$_3$Ti$_2$O$_7$ solid solutions, lime, metallic iron, liquid (34 wt.% CaO, 8 wt.% TiO$_2$, 58 wt.% FeO).

*   The piercing points were determined in CO$_2$/CO atmosphere corresponding to equilibrium between wüstite and metallic iron, and the invariant points were determined for oxide phase assemblages in equilibrium with metallic iron, as explained in the text.

** The temperatures given are estimated to be accurate to $\pm$ 5°C.

*** The crystalline phases are solid solutions rather than end-member compounds. (Compare Fig.7)

Three liquidus piercing points[1] and five liquidus invariant points have been determined in the system, with temperatures and phase assemblages as shown in Table 2.

Probably the most characteristic features of this system are the predominance of the perovskite primary-phase area and the stable existence of dicalciumferrite solid solution at liquidus temperature. (Note that

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[1] These piercing points are in region B where the oxide phases were not in contact with metallic iron. Each of these points involves three crystalline phases in equilibrium with liquid instead of four in the case of an invariant point. However, because the oxygen pressures used in region B are reasonably close to those of equilibrium of the oxide phases with metallic iron, the piercing points are located close to the CaO-FeO-TiO$_2$ plane and are very similar to true invariant points.

TABLE 3. RESULTS OF EQUILIBRATION RUNS ALONG THE JOIN $CaTiO_3$-$FeTiO_3$
AT 1280°C AND AN ATMOSPHERE OF $CO_2/CO = 0.291$

Mixture No.	$CaTiO_3$, wt. %	Phases Present
301	98.0	Perovskite, rutile, ferrospeudobrookite
302	96.0	Perovskite, ferropseudobrookite, ilmenite
311	2.0	Ilmenite, perovskite

dicalciumferrite is not stable in equilibrium with metallic iron at liquidus temperatures in the bounding binary system CaO-iron oxide; see Fig. 3.)

Special attention in the present study was directed toward determining the presence or absence of mutual solubilities between perovskite and ilmenite, toward delineating relations along the dicalciumferrite-perovskite join in contact with metallic iron, toward determining the "ternary" extension of the $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid-solution phase in the system CaO-TiO_2, and toward establishing the extent of the wüstite solid solution.

Three mixtures were prepared along the join $CaTiO_3$-$FeTiO_3$ in order to check the mutual solubilities of perovskite and ilmenite. The results of the equilibration runs are listed in Table 3. The mixture containing two weight percent of the ilmenite component (301) did not contain ilmenite as a phase after equilibration, but small amounts of ferropseudobrookite and rutile. However, the mixture containing four weight percent of the ilmenite component (302) does contain ilmenite as a phase, although ferropseudobrookite is also present. The data are best explained with reference to the sketch in Figure 8. It is concluded that nonexistence of ilmenite in mixture No. 301 is due to the width of the two-phase region rutile plus perovskite, and that there is no appreciable solid-solution formation along the join $CaTiO_3$-$FeTiO_3$. Furthermore, the observation of mixture No. 311 suggests that ilmenite does not incorporate as much as two weight percent of perovskite under the present experimental conditions.

Incomplete solid-solution series exist between perovskite and dicalciumferrite, as illustrated in the solidus diagram in Figure 7. One of these, the perovskite solid solution, originates at the $CaTiO_3$ composition and extends in a direction toward a hypothetical compound Ca_2FeTiO_5, although the series terminates about halfway toward the latter composition point. The termination point is represented approximately by the formula $Ca_2Fe_{0.6}Ti_{1.4}O_{5.4}$. The other solid solution, the dicalciumferrite phase, starts within the "ternary" system rather than at the composition point $Ca_2Fe_2O_5$, because this phase is unstable in contact with metallic iron at liquidus and solidus temperatures in the
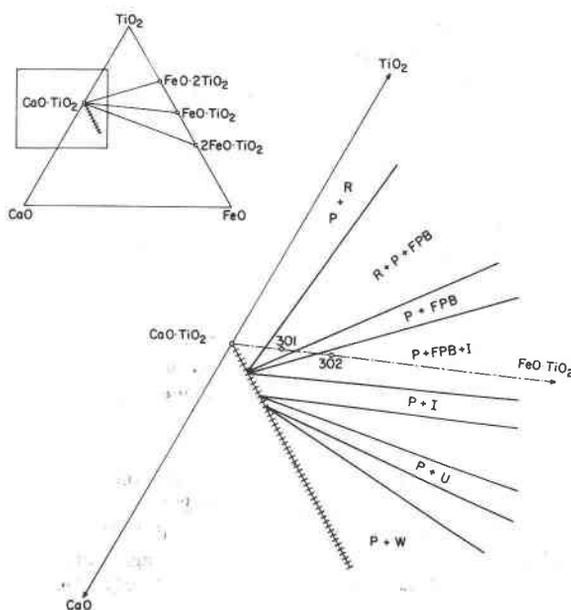
Fɪɢ. 8. Phase relations among crystalline phases in the vicinity of the CaO·TiO₂ composition in the system CaO-iron oxide-titanium oxide at 1280°C in an atmosphere defined by equilibrium between metallic iron and wüstite. Compositions of two mixtures (301 and 302) discussed in the text are shown.

"binary" system CaO-iron oxide (see Fig. 3). Hence, the dicalciumferrite solid solution in the system CaO-iron oxide-TiO₂ in contact with metallic iron has two termination points. One of these has a projected composition onto the CaO-FeO-TiO₂ plane at 36 weight percent CaO, 3.5 weight percent TiO₂, and 60.5 weight percent FeO, and the other end is close to the composition point of the hypothetical compound Ca_2FeTiO_5. The data obtained suggest that the dicalciumferrite solid solution is not represented by a join corresponding strictly to a replacement of one ferrous and one titanium ion for two ferric ions.

A ternary solid-solution series extends from the $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ region of the system CaO-TiO₂ into the "ternary" system, probably in a direction toward a hypothetical compound $Ca_4FeTi_2O_9$, although the solid-solution series does not extend that far. The termination point is represented approximately by the formula $Ca_4Fe_{0.8}Ti_{2.2}O_{9.2}$.

The reactions attending the formation of these solid solutions were so sluggish that crystals of sufficient perfection for more detailed study were not obtained.

MacChesney and Muan (1961) suggested that there may be some solubility of TiO₂ in wüstite, although they did not have data to confirm

this inference. Taylor (1964) claimed, however, that there was no formation of titaniferous wüstite in his study. In the present work, the formation of wüstite solid solution toward titanium oxide was confirmed both by the sealed-tube technique and by runs in an open system in atmospheres of mixed gases. The maximum solubility ot TiO_2 in wüstite in contact with metallic iron was found to be 8 ± 2 weight percent at 1290°C. X-ray diffraction studies showed no appreciable change in the unit-cell dimension of wüstite with the addition of titanium oxide $(a_0 = 4.305 \pm 0.002 \text{ Å})$.

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