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PHASE RELATIONS IN THE SYSTEM CaO-IRON OXIDE-TiO_2 IN AIR[1]

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ABSTRACT

Phase-equilibrium data are presented for the liquidus-solidus region of the system CaO-iron oxide-TiO_2 in air, as determined by quenching experiments in the temperature range of approximately 1200–1700°C.

The following crystalline phases occur in equilibrium with liquids in this system: Rutile, perovskite, $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid solutions, pseudobrookite, hematite, magnetite, dicalciumferrite, monocalciumferrite, monocalciumdiferrite, and lime. These phases are solid solutions rather than end-member compounds. Eight liquidus piercing points (=isobaric invariant points), each involving the equilibrium coexistence of three crystalline phases and a liquid, have been determined.

Particularly noteworthy among the phase relations of this system are the extensive solid-solution formation between perovskite and dicalciumferrite, the extension of a $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid-solution series of the system CaO-TiO_2 into the "ternary" system, and the solid solubility of TiO_2 in monocalciumferrite. The perovskite occurring in this system accommodates as much as 83% of iron in substitution for titanium, while in dicalciumferrite up to six % of titanium may substitute for iron. The series $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ allows up to 57% substitution of iron for titanium, and monocalciumferrite can incorporate up to ~ five weight % TiO_2.

INTRODUCTION

Titanium is the ninth most abundant element in the earth's crust. Most of the titanium occurs in relatively minor amounts in substitution for other ions in the structures of the common rock-forming minerals. However, there are also a number of minerals in which titanium is a main constituent. Among these are the members of the hematite-ilmenite solid-solution series (Fe_2O_3-$FeTiO_3$), the magnetite-ulvospinel solid-solution series (Fe_3O_4-Fe_2TiO_4), sphene ($CaTiSiO_5$), perovskite ($CaTiO_3$), and the various polymorphs of TiO_2. All of these minerals, with the exception of sphene, are present as phases in the system Ca-Fe-Ti-O, for which very few equilibrium data are available. A study of phase relations in this system is an essential step toward a better understanding of the behavior of titanium in igneous rocks. Furthermore, the recent discoveries of high Ti contents of lunar materials has stimulated new in-

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terest in the role of titanium in oxide phases. In addition to the geochemical and cosmochemical importance of this system, considerable crystal-chemical and technological interest is centered around the ternary and quaternary solid-solution phases in the system.

The quaternary system CaO-FeO-Fe_2O_3-TiO_2 is enormously complex, and the delineation of its phase relations must be approached in steps whereby some of the parameters are kept constant. In the present study, we have kept the oxygen pressure of the system constant as that of air ($P_{O_2} = 0.2$ atm). Under these conditions, essentially all the titanium is kept in the Ti^{4+} state, and loss of iron to the Pt foil used as containers is minimized. Data for the system obtained in air will improve our understanding of the role of titanium in oxide phases and form a basis for further studies of the same system under experimental conditions (reducing atmospheres) which are more difficult to control.

PREVIOUS WORK

A number of studies have been made of phase relations in the binary system CaO-TiO_2. However, there are still some questions regarding certain aspects of this system particularly in the calcium-rich part. DeVries, Roy, and Osborn (1954), and Coughanour, Roth, and DeProsse (1954) reported almost simultaneously but independently the results of their equilibrium studies of the system CaO-TiO_2. The data of the two groups of investigators are generally in good agreement, and it appeared that the phase diagram for this system was well established. Then in 1958 Roth proposed, on the basis of new experimental data, that another compound, $Ca_4Ti_3O_{10}$, in addition to those previously reported, is stable in this system. The phase diagrams established by DeVries *et al.* and by Coughanour *et al.* as later modified by Roth, are shown in Figure 1.

The first extensive study of the system CaO-iron oxide in air was made by Hilpert and Kohlmeyer (1909). A few years later Sosman and Merwin (1916) delineated the phase diagram and showed the existence of two binary compounds, dicalciumferrite ($Ca_2Fe_2O_5$) and monocalciumferrite ($CaFe_2O_4$). They also pointed out that appreciable amounts of iron were present in the divalent state in the liquid phase. Hence, the system in air is not really binary but rather an isobaric section ($P_{O_2} = 0.2$ atm) through the ternary system Ca-Fe-O.

Several more recent investigations of this system in air have been reported in the literature (*e.g.*, Burdese, 1952; Edström, 1956; Batti, 1956; Phillips and Muan, 1958). Until fairly recently, there had been considerable controversy regarding the stability of the phase monocalciumdiferrite ($CaFe_2O_7$). However, the diagram reported by Phillips and

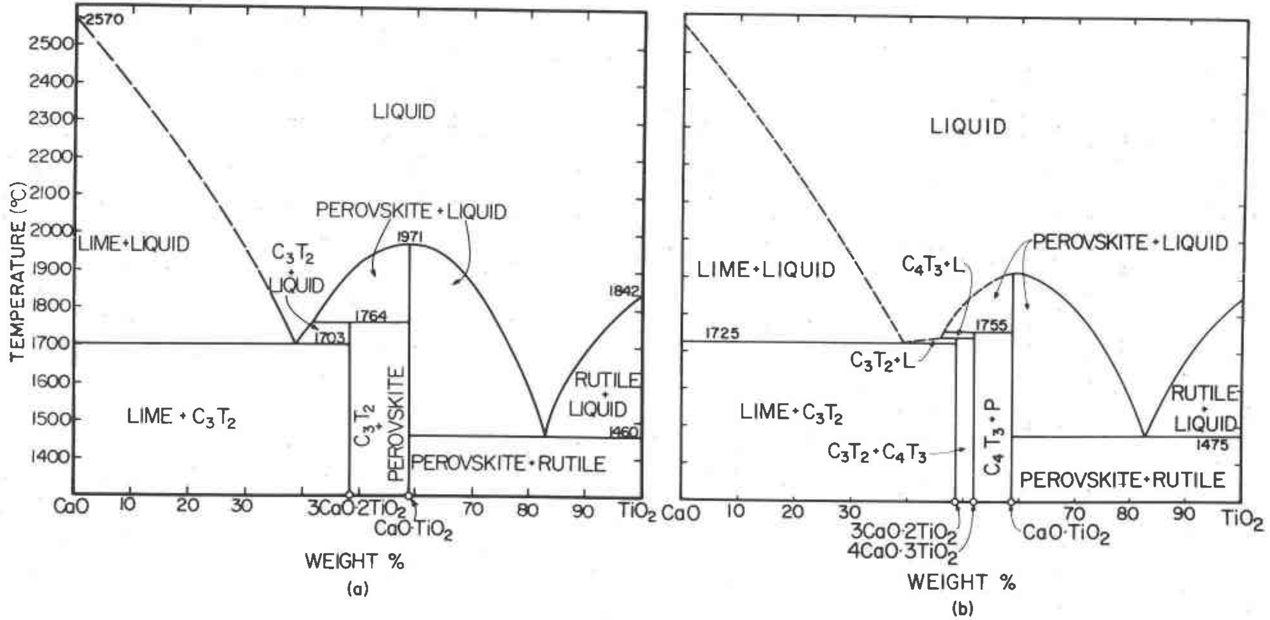

FIG. 1 Phase diagrams for the system CaO-TiO$_2$, as published in the literature. The diagram on the left is after DeVries, Roy, and Osborn (1954), and the diagram on the right after Coughanour, Roth and DeProsse (1954) as modified by Roth (1958). Abbreviations used have the following meanings: $C_3T_2 = Ca_3Ti_2O_7$; $C_4T_3 = Ca_4Ti_3O_{10}$.

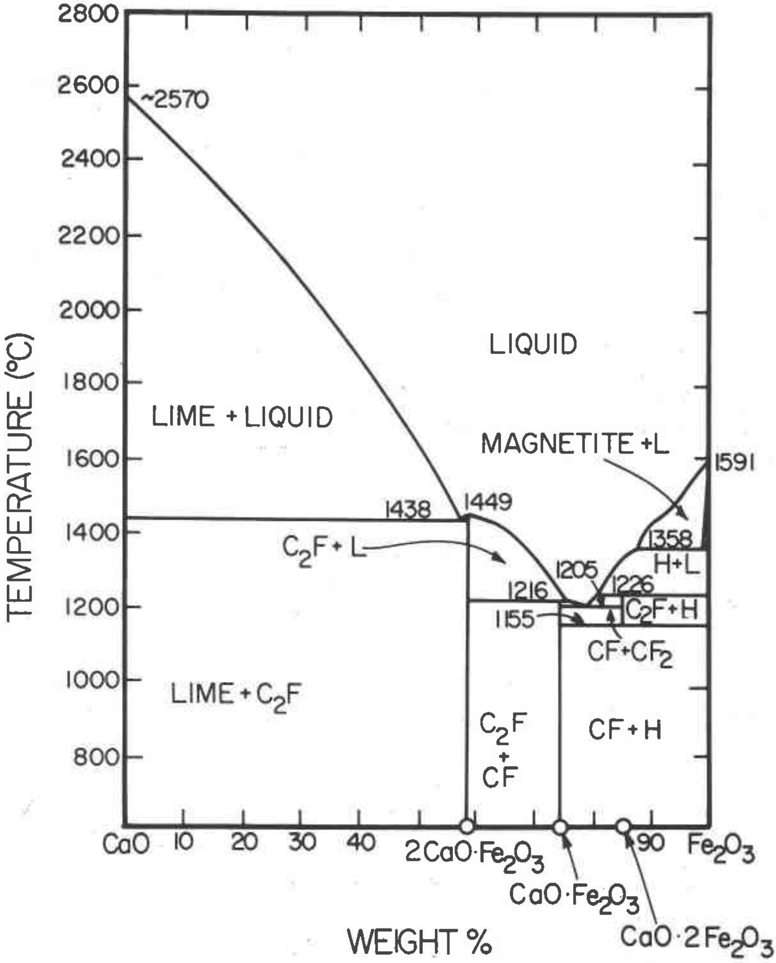

FIG. 2. Phase diagram for the system CaO-iron oxide in air, after Phillips and Muan (1958). Abbreviations used have the following meanings: C_2F = dicalciumferrite ($Ca_2Fe_2O_5$); CF = monocalciumferrite ($CaFe_2O_4$); CF_2 = monocalciumdiferrite ($CaFe_4O_7$); H = hematite; L = liquid.

Muan (1958), which incorporates this phase, now seems to be generally accepted. This diagram is shown in Figure 2.

A number of investigations of phase relations at liquidus temperatures in the system iron oxide-TiO_2 in air have been reported since Junker (1936) suggested a simple eutectic relation. Among the more recent studies of this system, those of Grieve and White (1939) and of Mac-

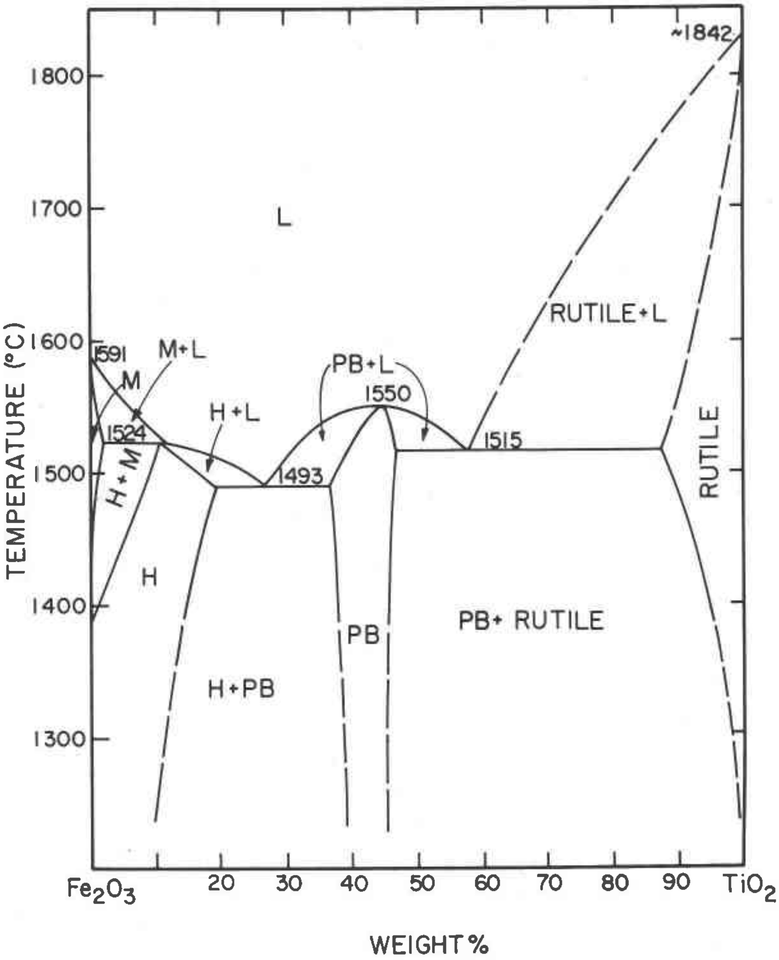

FIG. 3. Phase diagram for the system iron oxide-TiO_2 in air, after MacChesney and Muan (1959). Abbreviations used have the following meanings: M = magnetite; H = hematite; PB = pseudobrookite; L = liquid

Chesney and Muan (1959) are the most extensive. The diagram presented by MacChesney and Muan (1959) is shown in Figure 3.

No detailed phase-equilibrium study of the system CaO-iron oxide-TiO_2 in air has been reported. There is, however, some information available on compatibility relations and solid-solution formation among crystalline phases present in the system. Coates and MacMillan (1964) studied the substitution of trivalent iron for titanium in perovskite,

$CaTiO_3$, and found that this structure is kept intact up to a maximum of 50 percent substitution of iron for titanium. The addition of more iron was reported to lead to the formation of dicalciumferrite.

EXPERIMENTAL METHODS

Mixtures of known compositions were held at known temperatures in air until equilibrium was attained. The samples were then quenched to room temperature, and the phases present were determined by X-ray diffraction and observation of polished sections under a microscope.

Starting materials were reagent-grade $CaCO_3$, Fe_2O_3, and TiO_2. Mixtures of desired compositions were ground under acetone and intimately mixed in an agate mortar. Each mixture was then preheated in air in a globar furnace for $\sim$ 24 hours in order to decompose the carbonate and promote partial or complete reaction among the oxide components. The temperature of preheating varied with the composition of the mixture, and was usually slightly below the solidus temperature. In no case was the preheating in the globar furnace done at a temperature higher than 1400°C.

Mixtures on or close to the join CaO-TiO_2 were preheated again at approximately 1660°C in a molybdenum-wound furnace for 12 hours to promote formation of the stable crystalline phases of this system.

Equilibration runs at temperatures below 1500°C were made in a vertical quench furnace with platinum-rhodium (80:20) resistance wire, whereas equilibration runs above 1500°C were carried out in a molybdenum-wound vertical quench furnace. The temperature of the Pt-Rh furnace was kept constant to ±4°C with a Celectray controller activated by a Pt *vs.* 90% Pt 10% Rh thermocouple positioned at the hot spot of the furnace. The temperature of the molybdenum furnace was controlled by a controller working on the principle of Wheatstone-Bridge balancing.

Temperatures were measured immediately before and after each run. A Pt *vs.* 90%Pt 10%Rh thermocouple was used for measuring temperatures up to 1500°C, whereas a 95%Pt5%Rh *vs.* 80%Pt20%Rh thermocouple was used to measure higher temperatures. The thermocouples were calibrated at the melting points of gold (1063°C), diopside (1391.5°C), pseudowollastonite (1546°C), and the temperature of coexistence of cristobalite and two liquids in a mixture of 90 weight percent SiO_2, 10 weight percent CaO (1707°C).

Approximately 50–100 mg of powdered, preheated samples were placed in a small platinum envelope and suspended in the furnace. For the runs at temperatures above 1500°C, attainment of equilibrium was facilitated by first heating the samples at a higher temperature and then lowering it to the final equilibration value.

Considerable experimental difficulties were encountered in the study of the system CaO-TiO_2. One was the relatively rapid deterioration of the 95%Pt5%Rh-80%Pt20%Rh thermocouples at temperatures above 1650°C. This made it necessary to calibrate the thermocouple immediately after each equilibration in critical runs used for determination of the liquidus invariant points. It is thought that this approach ensured an accuracy in the measured temperatures of ±5°C or better. Another difficulty was the formation of traces of liquid at temperatures which were obviously below the solidus temperatures. For the measurement of invariant temperatures, this was not a serious problem because of the disappearance of one of the crystalline phases above the invariant temperatures. However, it was a problem in mixtures of compositions between $4CaO \cdot 3TiO_2$ and $3CaO \cdot 2TiO_2$ where the solidus temperatures vary with composition. The temperatures of formation of the first trace of liquid in these mixtures was not a reliable criterion for determining solidus

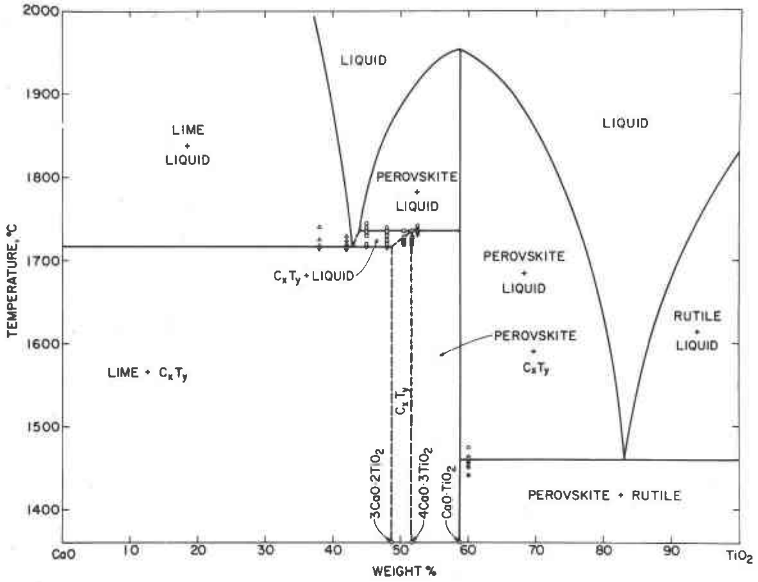

FIG. 4. Suggested revised phase diagram for the system CaO-TiO_2. Liquidus curves are mainly after DeVries, Roy and Osborn (1954), with tentative modifications of the diagram in the 4CaO·$3TiO_3$—3CaO·$2TiO_2$ composition range based on data obtained in the present investigation. The boundary curves in this region have been dashed because of the uncertainties still existing regarding each phase assemblage, as labelled on the diagram. Abbreviation used has the following meaning: $C_xT_y = Ca_4Ti_3O_{10}—Ca_3Ti_2O_7$ solid solutions.

temperatures. Instead, the relative amounts of liquid and solid, as determined under the microscope, were used as a main means of ascertaining the position of the solidus curve in this composition range.

RESULTS AND DISCUSSION

The System CaO-TiO_2. Results of equilibration runs are shown graphically in Figure 4.[1] The diagram is different from previous diagrams with respect to the stabilities of the compounds $Ca_4Ti_3O_{10}$ and $Ca_3Ti_2O_7$.

Microscopic examination of quenched samples in the composition range between these two compositions failed to reveal the presence of more than one phase. Hence, the microscopic examination lends support to the observation of a continuous change in solidus temperature in this composition range and the suggestion that the composition range be-

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[1] Tables 1 & 2 listing results of 359 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, payable to CCMIC-MAPS.

tween these two compositions is a complete solid-solution series. X-ray diffraction study of quenched samples from this composition range, however, indicated the coexistence of two phases, $Ca_4Ti_3O_{10}$ and $Ca_3Ti_2O_7$. This may be accounted for, however, by exsolution during quenching. If the crystal structure of $Ca_4Ti_3O_{10}$ is such that triple perovskite layers are interleaved with CaO layers, as Roth (1958) suggested, it does not seem unreasonable to assume that exsolution may occur in this series during quenching, although this could not be observed under the microscope.

In view of this uncertainty, the continuous solid-solution series between $Ca_4Ti_3O_{10}$ and $Ca_3Ti_2O_7$ must be considered tentative, but studies in ternary systems involving these two components (*e.g.*, the system CaO-iron oxide-TiO_2 to be described in a later section of the present paper, and the system CaO-MgO-TiO_2, Shultz and Muan, (private communication) lend support to the interpretation of melting relations as presented in Figure 4.

Imlach and Glasser (private communication) have done a considerable amount of X-ray diffraction work on phases in the $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ range as part of an investigation of phase relations in the ternary system CaO-Al_2O_3-TiO_2, and they conclude that they cannot prove that there is a distinct phase of composition $Ca_4Ti_3O_{10}$, nor can they conclusively disprove its existence.

The System CaO-Iron Oxide-TiO_2 in Air. Data obtained in the study of the system CaO-iron oxide-TiO_2 in air are shown graphically in Figures 5 and 6.[1] The first of these diagrams shows a projection of the liquidus surface, with liquidus isotherms drawn at 100°C intervals, and the second diagram (Fig. 6) shows a projection of the solidus surface, with solidus isotherms drawn at 100°C intervals.

Ten crystalline phases were found to have stable existence at liquidus temperatures in this system. These phases are rutile (TiO_2) solid solution, perovskite ($CaTiO_3$) solid solution, $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid solution, magnetite (Fe_3O_4) solid solution, hematite (Fe_2O_3) solid solution, pseudobrookite (Fe_2TiO_5) solid solution, dicalciumferrite ($Ca_2Fe_2O_5$) solid solution, monocalciumferrite ($CaFe_2O_3$) solid solution, monocalciumdiferrite ($CaFe_4O_7$), and lime (CaO).

There are seven liquidus piercing points (=isobaric invariant points)[2] in this system, with temperatures and phase assemblages as listed in Table 3.

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[1] See footnote p. 1336.

[2] These points represent intersections between quaternary univariant curves in the system Ca-Fe-Ti-O and the isobaric surface corresponding to the oxygen pressure of air.

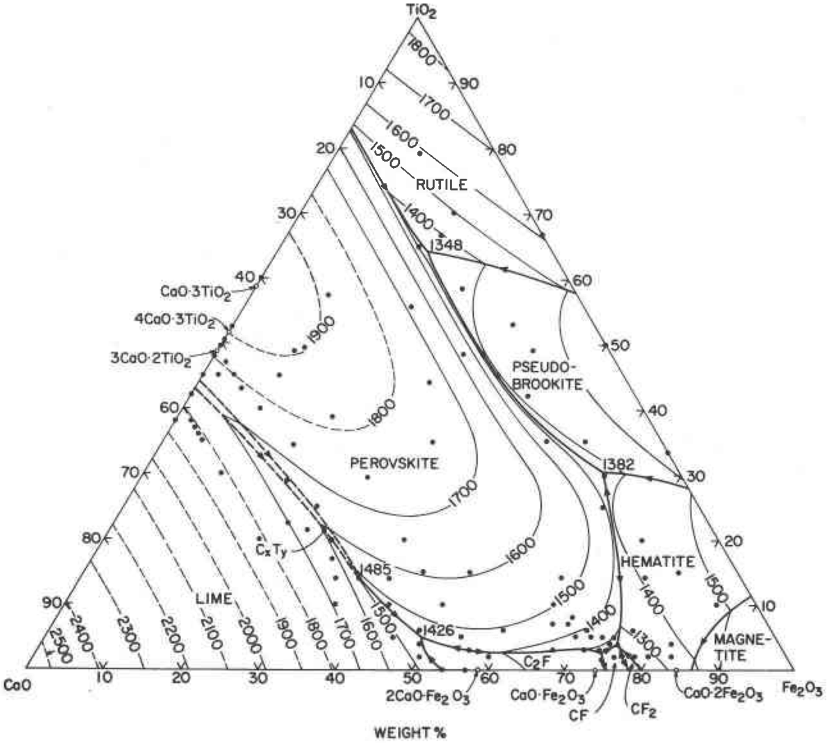

FIG. 5. Liquidus surface of the system CaO-iron oxide-TiO_2 in air. Solid dots represent compositions of mixtures studied. Liquidus isotherms are drawn at 100°C intervals. Boundary curves outlining the region of $Ca_4Ti_3O_{10}$–$Ca_3Ti_2O_7$ solid solutions are dashed because of the uncertainties still existing regarding the nature of this phase. Abbreviations used have the same meanings as explained in legends to Figs. 2 and 4.

Among the features of particular interest in the present system are the equilibria along the join $CaTiO_3$-$Ca_2Fe_2O_5$, the extension into the ternary[1] system of the $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid-solution series in the bounding binary system CaO-TiO_2, the monocalciumferrite solid solution, and the liquidus relations attending the appearance of the latter phase.

Phase relations along the join $CaTiO_3$-$Ca_2Fe_2O_5$ in air are shown in Figure 7. The crystalline phases coexisting at the eutectic temperature have the following compositions: perovskite, 17 weight percent $CaTiO_3$, 83 weight percent $Ca_2Fe_2O_5$; dicalciumferrite, 94 weight percent $Ca_2Fe_2O_5$,

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[1] The system CaO-iron oxide-TiO_2 in air is not a truly ternary system because iron occurs in different oxidation states in varying proportions. However, when the oxygen pressure of the atmosphere is fixed, one degree of freedom is expended, and the system can be treated like a ternary system.

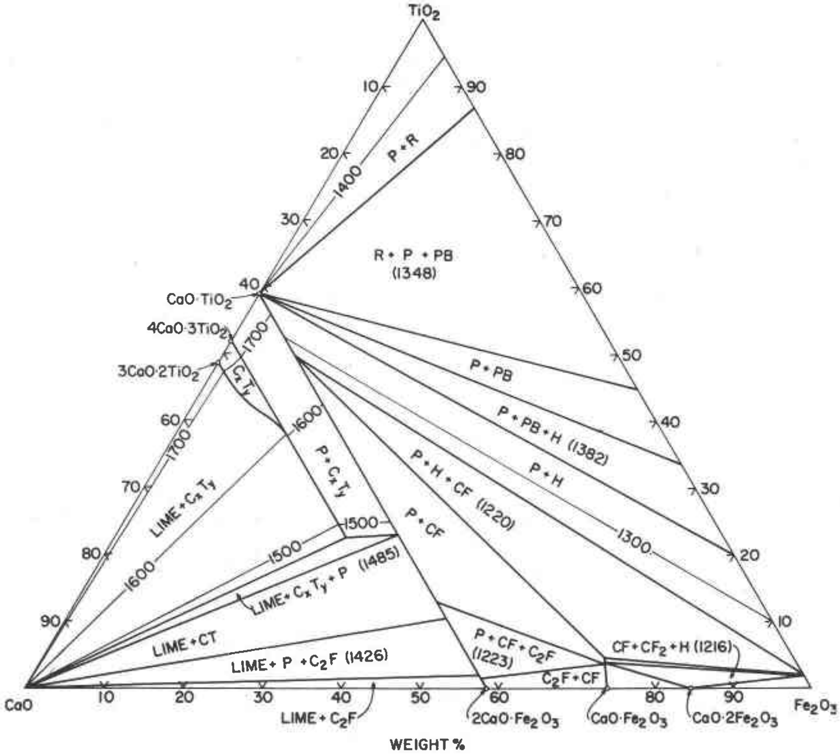

FIG. 6. Solidus surface of the system CaO-iron oxide-TiO_2 in air. Light lines are solidus isotherms drawn at 100°C intervals. Numbers in parentheses are solidus temperatures within composition triangles where three crystalline phases coexist with liquid. Boundary curves outlining the region of $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid solutions are dashed because of the uncertainties still existing regarding the nature of this phase. Abbreviation used in addition to those explained previously has the following meaning: P=perovskite.

6 weight percent $CaTiO_3$. Coates and McMillan (1964) reported a maximum solubility of approximately 50 weight percent[1] of $Ca_2Fe_2O_5$ in perovskite at 1350°C. Although their experiments were carried out at a temperature of about 90°C below the eutectic temperature established in Figure 7, their solubility limit seems low in comparison with the present data. It is suspected that the lower solubility observed by Coates and McMillan may be explained by a tendency for the solid-solution crystals to exsolve during cooling. In the present study, perthite-like

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[1] Fifty weight percent $Ca_2Fe_2O_5$ in perovskite means that x is approximately 0.5 in the formula $CaFe_xTi_{1-x}O_{3-1/2x}$, because $Ca_2Fe_2O_5$ and $Ca_2Ti_2O_6$ have approximately the same formula weights, 271.86 and 271.96, respectively.

TABLE 3

Temperatures and Phase Assemblages of Liquidus "Invariant"* Points in the System CaO-Iron Oxide-TiO_2

Temperature, °C**	Phases Present***
1348	Rutile, perovskite, pseudobrookite, liquid (16 wt.% CaO, 64 wt.% TiO_2, 20 wt.% iron oxide)****.
1382	Perovskite, pseudobrookite, hematite, liquid (10 wt.% CaO, 30 wt.% TiO_2, 60 wt.% iron oxide).
1220	Perovskite, hematite, monocalciumferrite, liquid (21 wt.% CaO, 4 wt.% TiO_2, 75 wt.% iron oxide).
1216	Hematite, monocalciumferrite, monocalciumdiferrite, liquid (21 wt.% CaO, 3 wt.% TiO_2, 76 wt.% iron oxide).
1223	Perovskite, monocalciumferrite, dicalcium ferrite, liquid (24 wt.% CaO, 3 wt.% TiO_2, 73 wt.% iron oxide).
1426	Perovskite, dicalciumferrite, lime, liquid (46 wt.% CaO, 5 wt.% TiO_2, 49 wt.% iron oxide).
1485	Perovskite, $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid solutions, lime, liquid (50 wt.% CaO, 13 wt.% TiO_2, 37 wt.% iron oxide).

* These are not truly invariant points but rather piercing points or isobaric invariant points representing intersections between quaternary univariant curves in the system Ca-Fe-Ti-O and the isobaric section corresponding to a total pressure of 1 atm. and an oxygen pressure of 0.2 atm.

** The temperatures given are estimated to be accurate to ± 5°C.

*** The crystalline phases listed are solid solutions rather than pure end-member compounds. (Compare Fig.6)

****Total iron oxide calculated as Fe_2O_3.

lamellae were observed in perovskite crystals containing more than 50 weight percent dicalciumferrite and quenched to room temperature.

Gallagher, MacChesney, and Buchanan (1964, 1965) studied Mössbauer spectra of mixtures in the systems $Sr_2Fe_2O_{5.0-6.0}$ and $Ba_2Fe_2O_{5.0-6.0}$,

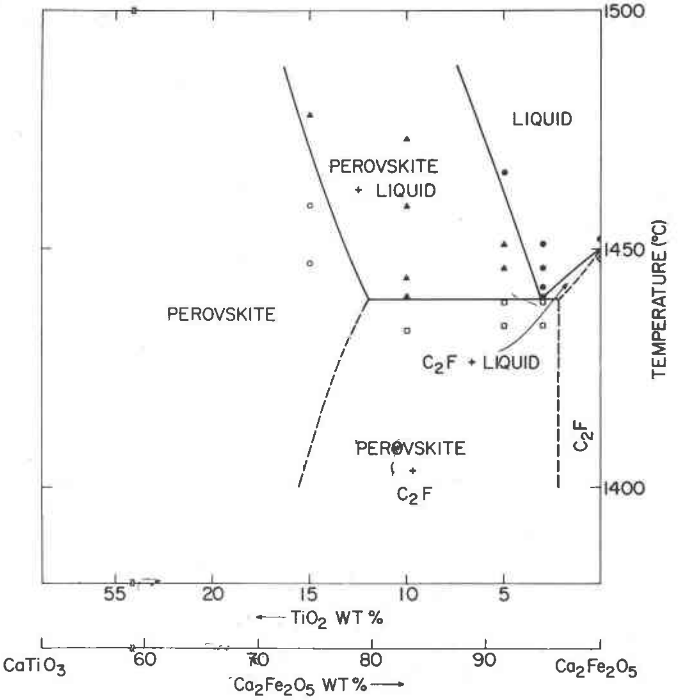

FIG. 7. Phase relations along the join $CaTiO_3$-$Ca_2Fe_2O_5$ of the system CaO-iron oxide-TiO_2 in air. Dashed curves are inferred only. A different point symbol is used for each phase assemblage, as labelled on the diagram.

and found stable perovskite-type phases represented by the formulae $Sr_2Fe_2O_{5.5-6.0}$ and $Ba_2Fe_2O_{5.68-6.0}$ in which some of the iron is in the tetravalent state. The question arises as to whether or not a similar situation may exist in the case of the perovskite-dicalciumferrite solid solution in the present system. The perovskite solid solution could conceivably extend toward a hypothetical compound $Ca_2Fe_2O_6$ where all the iron would be in the tetravalent state, or at least toward a hypothetical phase represented by $Ca_2Fe_2O_{6-2x}$ where some of the iron is in the tetravalent state. In order to test this possibility, a mixture containing 50 weight percent $Ca_2Fe_2O_5$ and 50 weight percent $CaTiO_3$ was run in a reducing atmosphere ($CO_2/CO = 18/82$) and subsequently analyzed as follows: One part of the sample was subjected to a chemical analysis to determine the ferrous oxide content. The other part of the sample was heated in air at 1150°C, and the weight increase during the heating was determined. The two results were compared. The chemical analysis showed the ferrous oxide content in the reduced specimen to be 5.2 ± 0.5 weight percent, while the weight increase by heating in air was determined to be 0.47 ± 0.05 percent, corresponding to 4.7 ± 0.5 weight percent of ferrous oxide in the specimen before heating, if it is assumed that the heating in air yields all the iron in the trivalent state. The two results agree within the experimental error. It is therefore concluded that there is no appreciable amount of tetravalent iron present in the mixture of 50 weight percent $Ca_2Fe_2O_5$ and 50 weight percent $CaTiO_3$ after heating in air at 1150°C. This is in good agreement with the observation of Coates and McMillan (1964), who found that a mixture of this composition has an oxygen-deficient perovskite structure.

As shown in Figure 6, the ternary solid solution originating in the $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ region of the binary system CaO-TiO_2 extends into the system CaO-iron oxide-TiO_2 roughly parallel to the perovskite solid solution just discussed. The Ca/(Fe+Ti) ratio in this series is close to 4/3, except in the region near the CaO-TiO_2 join where the solid solution gradually widens into the range of Ca/(Fe+Ti) ratios from 4/3 to 3/2 as the iron content decreases. The highest iron/titanium ratio in this series at solidus temperatures is represented by a formula

$$Ca_4(Ti_{0.43}Fe_{0.57})_3O_{9.15}.$$

The data on the $Ca_4Ti_3O_{10}$-$Ca_3Ti_2O_7$ solid-solution in the "ternary" system lend support to the tentative conclusion made from the study of the binary system CaO-TiO_2 that there is a complete solid-solution series between $Ca_4Ti_3O_{10}$ and $Ca_3Ti_2O_7$. If these two compounds appeared as separate and distinct phases, there should be an invariant point in the "ternary" system, characterized by the coexistence of $Ca_4Ti_3O_{10}$, $Ca_3Ti_2O_7$, lime, and liquid. No such invariant point was observed.

Monocalciumferrite, $CaFe_2O_4$, was found to have a solid-solution extension terminating at the point 24.0 weight percent CaO, 4.5 weight percent TiO_2, and 71.5 weight percent Fe_2O_3. Powder X-ray diffraction study indicated a slight change in the positions of the peaks as titanium is added. Some increase in the a-edge[1] and some decrease in the b-edge of the unit cell were observed, whereas the change in the c-edge is unknown because of overlapping of peaks.

The crystallization paths of mixtures in the vicinity of the monocalciumferrite composition are complicated because of the existence of this solid solution. The phase assemblage of mixtures with compositions in this vicinity change in a complicated manner within a 10–20°C temperature range during equilibrium cooling. For sake of clarification, a distorted diagram of the field of monocalciumferrite is shown together

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[1] The method of choosing a, b, c-axes is after Bertaut, Blum, and Magnano. (1955).

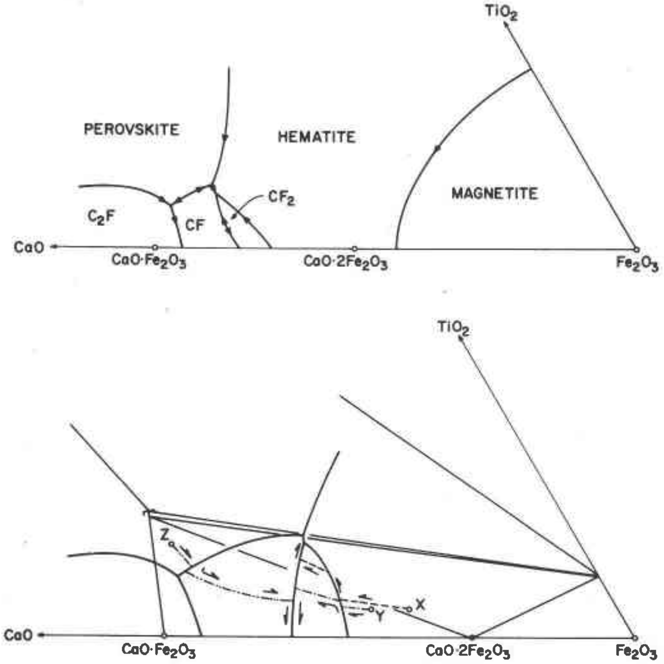

FIG. 8. Phase relations in the vicinity of the calcium ferrite areas of the liquidus surface of the system CaO-iron oxide-TiO_2 in air. An undistorted diagram is shown at the top, and a distorted diagram is presented below in order to better illustrate crystallization sequences of selected mixtures. In the latter diagram, the changes in liquid compositions of mixtures *X*, *Y*, and *Z* during equilibrium cooling are illustrated with arrows indicating directions of composition changes with decreasing temperatures.

with an undistorted one in Figure 8. Three mixtures, X, Y, and Z, are chosen to demonstrate what may happen in this part of the system. The sequence of phase changes[1] in each of these mixtures during equilibrium cooling is as follows:

$$\begin{aligned}\text{Mixture X: liquid} &\rightarrow \text{liquid} + \text{H} \rightarrow \text{liquid} + \text{H} + \text{CF}_2\\ &\rightarrow \text{liquid} + \text{CF}_2 \rightarrow \text{liquid} + \text{CF}_2 + \text{CF}\\ &\rightarrow \text{CF}_2 + \text{CF} + \text{H}\end{aligned}$$

$$\begin{aligned}\text{Mixture Y: liquid} &\rightarrow \text{liquid} + \text{H} \rightarrow \text{liquid} + \text{H} + \text{CF}_2\\ &\rightarrow \text{liquid} + \text{CF}_2 \rightarrow \text{liquid} + \text{CF}_2 + \text{CF}\\ &\rightarrow \text{CF}_2 + \text{CF}\end{aligned}$$

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[1] Abbreviations used are as follows: H = hematite; CF_2 = monocalciumdiferrite ($CaFe_4O_7$): CF = monocalciumferrite ($CaFe_2O_4$); CT = perovskite ($CaTiO_3$).

$$\begin{aligned}\text{Mixture Z: liquid} &\rightarrow \text{liquid} + \text{CT} \rightarrow \text{liquid} + \text{CT} + \text{CF}\\ &\rightarrow \text{liquid} + \text{CF} \rightarrow \text{liquid} + \text{CF} + \text{CF}_2\\ &\rightarrow \text{CF} + \text{CF}_2\end{aligned}$$

The complexity of the relations is demonstrated, for instance, by the fact that four changes in phase assemblage take place in mixture X within the 8°C temperature interval between 1222°C and 1214°C.

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