THE SYSTEM CaO-SiO$_2$-P$_2$O$_5$

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Abstract

The system contains, in addition to the binary phases previously described in the literature, two ternary phases, nagelschmidtite and silicocarnotite, which have been known as constituents of certain slags. The equilibrium diagram presents some features of special interest. The field of cristobalite is very large. There is an extensive region of liquid immiscibility in which two liquids in equilibrium with cristobalite are formed. Very extensive solid solution prevails in the four phases, calcium orthosilicate, nagelschmidtite, silicocarnotite, and tricalcium phosphate, which form a binary system with the first and last named as end members. Calcium orthosilicate may contain up to 10% P$_2$O$_5$ in solid solution, and nagelschmidtite, the formula for which may be expressed as Ca$_7$Si$_2$P$_2$O$_{16}$, can have a P$_2$O$_5$ content varying between 12% and 24%. The solid solution seems to be of the substitution sort with PO$_4$ replacing SiO$_4$ groups. In both phases refractive indices decrease as P$_2$O$_5$ content increases.

Introduction

The system CaO-SiO$_2$-P$_2$O$_5$ is of greater interest to the mineral technologist than to the student of igneous rocks for reasons which will be considered later in this paper. The system has been the subject of study by chemists and metallurgists for more than fifty years, at first in connection with the "Thomas" or basic Bessemer process of steel making and, more recently, through attempts to develop new methods for producing high grade phosphatic fertilizers. Although many investigators have worked in this field, the fundamental equilibrium relationships have never been worked out, and not even a tentative equilibrium diagram has ever been presented. It is the purpose of this paper to supply this omission in some degree, with the hope that a better understanding of this system may further our knowledge of basic steel making reactions and perhaps contribute something of value to ceramics, glassmaking, or other related industries.

Historical

The pioneer work in the study of this system was done in the 1880's by Hilgenstock (13) (14), Carnot and Richards (6), and Stead and Risdale (31). These investigators, working independently, studied carefully selected crystals from slowly cooled "Thomas" slags and published chemical analyses and crystallographic data. In addition to some iron-bearing phases, they established the presence of tetracalcium phosphate, an apa-

tite-like phase, and a calcium silico-phosphate, the generally accepted formula for which is $5\,CaO\cdot SiO_2\cdot P_2O_5$. Kroll in 1911 (18) summarized the work of the aforementioned investigators and named the three phases after their discoverers, respectively, hilgenstockite, steadite, and silicocarnotite. The latter name seems highly unfortunate in view of the fact that the name carnotite has been given to an entirely different mineral. However, the word silicocarnotite has now been used by so many different writers, that it seems firmly entrenched in the literature and must perforce be accepted.

H. Blome (3) and O. Nielson (24) in 1910 and 1913 investigated synthetic preparations in this system by chemical means. Their data are of some interest, but they lacked a suitable means of phase identification and consequently came to conclusions not in accord with more recent investigations.

In more recent times a number of workers have studied "Thomas" and open hearth slags by means of the petrographic microscope. Scott and McArthur (30) published the results of their investigation in 1922. In addition to an oxide phase which does not concern us here, they found three silico-phosphate phases. Their descriptions do not include complete optical data and they attempted to arrive at the composition of the phases by inference from the analyses of the slags themselves. The compositions they give do not correspond exactly to those recognized in this paper, but the phases described appear to be silicocarnotite, an apatite, and the phase later described by Nagelschmidt (23) from an English slag.

Schneiderhöhn (28) (29) has in recent years made an extensive petrographic study of various basic slags, mainly by the examination of polished sections, but also in part by the use of thin sections and fine powders. In normal "Thomas" slags he found three phases which he identified as tetracalcium phosphate, silicocarnotite, and a dark phase consisting of mixed oxides. In a slag to which sand had been added, only the last two phases were found. Reheating and slow cooling produced no change in constitution, indicating that equilibrium conditions prevailed in the slags studied. The citrate solubility content varied with the amount of silicocarnotite. Schneiderhöhn examined various other ‚'Thomas" slags of varying composition with results similar to those indicated acove. He found, however, that slags to which $1\frac{1}{2}$ per cent CaF_2 had been added in the converter, contained no silicocarnotite, having in its place apatite and beta dicalcium silicate. Open hearth slags of various compositions ranging from 8 per cent to 26 per cent P_2O_5 were also examined. Schneiderhöhn found silicocarnotite in most of these slags and in addition three phases whose compositions were unknown.

He states that two of these phases contain phosphorus and the third he believes to be a silicate. Open hearth slags to which fluorspar had been added contained apatite but dicalcium silicate was not observed. Plates showing polished sections of various slags were included in this paper.

Nagelschmidt (23) in 1937 reported a phase having the composition $7CaO \cdot 2SiO_2 \cdot P_2O_5$ which he recovered by specific gravity separation from an English basic open hearth slag. He gives the optical properties of this phase and shows that it is distinct from silicocarnotite by a comparison of x-ray diffraction patterns. Apparently it did not occur to him to distinguish this phase from dicalcium silicate, or a solid solution of it, but a comparison of diffraction patterns shows distinct differences.
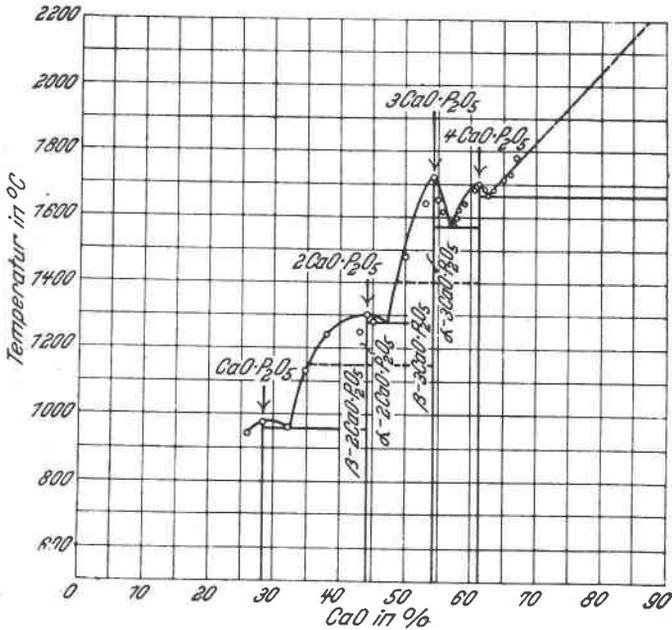

FIG. 1. System CaO-P_2O_5 from Körber and Trömel, *Arch. Eisenhüttenwesen* 1, 7 (1933).

The equilibrium diagram for the two-component system CaO-SiO_2 was published by Rankin and Wright (25) in 1915 and revised by Ferguson and Merwin (8) (9) in 1919. This work is well known in American literature and need not be summarized here.

Bredig, Franck, and Füldner (4) (5) and Körber and Trömel (16) (17) (32) in 1932 and 1933 published phase diagrams for part of the two-component system CaO-P_2O_5. These writers find the following phases: $4CaO \cdot P_2O_5$, two crystal modifications of $3CaO \cdot P_2O_5$, and two crystal

modifications of $2CaO \cdot P_2O_5$, and $CaO \cdot P_2O_5$. The final papers of the two groups of writers are in essential agreement and Fig. 1, taken from Körber and Trömel's paper, shows the equilibrium relationships found. They also give x-ray diffraction patterns for the phases and in a paper by Trömel (32) there is a description of the optical properties as determined by Hans Schneiderhöhn.

In their first efforts, Bredig, Franck, and Füldner failed to exclude water vapor and they were obliged to retract and revise the first equilibrium diagram they published. It was found that an apatite phase was formed at temperatures as high as 900° C. in even slightly moist air, but if water vapor was rigidly excluded no apatite phase occurred. In this connection it is worth noting that the apatite structure readily permits the substitution of various ions, and apatites occur with a wide range of compositions, as has been shown by Gruner and McConnell (11), McConnell (19) (20) (21), Hendricks, Jefferson, and Mosley (12), and others. There is every indication that the apatite configuration is a very stable one and that other phosphates of not too different compositions are readily converted into apatites where conditions permit. This "reversion" to the apatite structure has been a difficult problem in the production of high grade phosphatic fertilizers. It is particularly noteworthy that Gruner and McConnell found that the SiO_4 group could substitute for the PO_4 group in the apatite structure as it will be shown in this paper that extensive solid solutions involving this type of substitution prevails in the CaO-SiO_2-P_2O_5 system. Trömel (33) has given cogent reasons for the non-existence of a pure "oxyapatite" and no such phase is found in either the two-component system, CaO-P_2O_5 or the three-component system, CaO-SiO_2-P_2O_5, when water is carefully excluded. Hydroxyl apatite, however, is readily formed and apparently may exist with less than the theoretical amount of water.

Behrendt and Wentrup (2) studied a portion of the three-component system between the CaO-P_2O_5 join and silicocarnotite by means of cooling curves. Their determinations of transition temperatures are of interest but were not supplemented by any identification of phases.

Hill, Hendricks, Jefferson and Reynolds (15) have studied a small part of the three-component system in connection with the defluorination of rock phosphates in fertilizer manufacture. This subject has been much investigated by these writers and others of the Bureau of Soils of the U. S. Department of Agriculture. Their preparations were held at 1400° C. (below the liquidus). The phases they found were tricalcium phosphate, an apatite phase, and an unidentified phase having a composition probably intermediate between silicocarnotite and tricalcium phosphate. The unidentified phase which these writers call phase "B"

they believe to be identical with the phase described by Bredig, Franck, and Füldner as being formed in place of silicocarnotite where the time of heating was too short or the temperature was below 1400° C., and designated by them as phase "X." The writers have not encountered this phase in their own work which was mainly carried to the temperature of the liquidus.

Körber and Trömel (17) state that in 1930 the Kaiser-Wilhelm-Institut für Eisenforschung began a "planmässige" thermal and microscopic
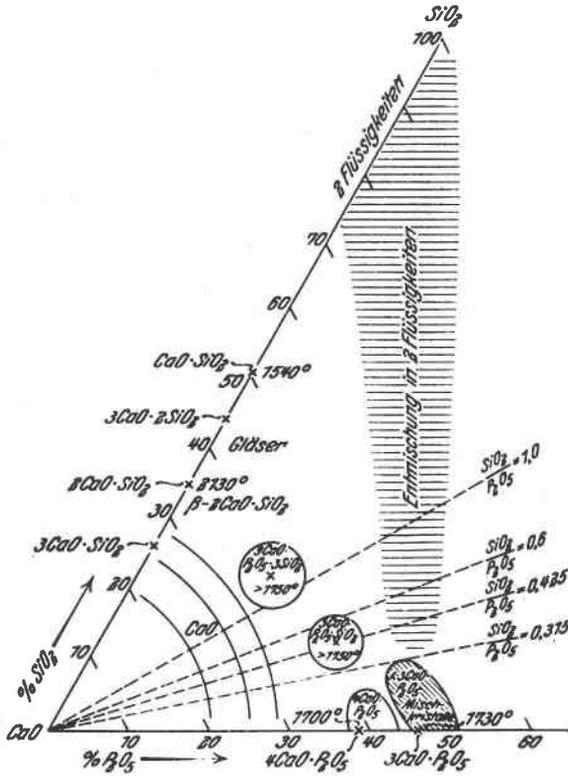
FIG. 2. Sketch for system CaO-P$_2$O$_5$-SiO$_2$ from Körber and Trömel, *Arch. Eisenhüttenwesen*, 1, 7 (1933).

study of the system CaO-P$_2$O$_5$-SiO$_2$. By 1933 they had published the diagram for the CaO-P$_2$O$_5$ system already mentioned as Fig. 1 and in one paper (17) they gave the preliminary sketch of the three-component system reproduced here as Fig. 2. Since 1933 they have published nothing further in this field.

Many other papers dealing with phosphates of lime, structure of teeth and bones, phosphatic fertilizers, etc., have been published. These are

well summarized by Eisenberger, Lehrman and Turner (7) and are not mentioned here because, for the most part, they are only of indirect interest in connection with the purposes of our investigation.

Experimental Procedure

The investigations were begun with a general survey of the system to determine what phases are present, and to define the approximate field boundaries of the various phases.

Compositions varying, for the most part, at 5 per cent intervals for each of the three components were prepared, although in a number of cases intermediate compositions were also studied. Raw materials were thoroughly calcined, silicic acid for the SiO_2, calcined $CaHPO_4$ for $Ca_2P_2O_7$, and precipitated $CaCO_3$ for CaO, all reagents being "Bakers Analyzed."*

After weighing, the batches were given a preliminary mixing by shaking in a glass jar and then were ground in a porcelain mortar for about half an hour. They were then molded with water into cylinders about $\frac{1}{2} \times 1$ inch. At first a little dextrine was used to bind the ingredients, but this proved to be unnecessary and was eliminated.

The cylinders were then calcined, reground and remolded wet to further promote intimate contact of the ingredients. Best results were obtained when this preliminary calcining was carried on at about 1000° C., rather than at higher temperatures. This procedure evidently drives off the CO_2 from the $CaCO_3$ without inducing much combination between the lime and silica. The calcined material evolves considerable heat as it hydrates, and the hydrated lime thus produced seems to come into intimate contact with the grains of the other materials and thus promotes more complete combination during the subsequent procedures.

As is well known, calcium phosphates are readily reduced at high temperatures in the presence of carbon. Nielson (24) found that CO did not reduce phosphates at the temperatures he studied. However, we experimented with an Ajax-Northrup induction furnace using a graphite crucible, and also tried a "Norbide" crucible in an effort to obtain controlled high temperatures. Although the samples were not permitted to touch the crucibles, and the crucibles were left partly uncovered to permit ready access of air, the evolution of a dense white smoke indicated reduction of the phosphates. Accordingly, we have been particular to maintain oxidizing conditions in all heating operations.

* In some of our earlier experiments $Ca_3(PO_4)_2$ purchased from chemical supply houses was used. This material proved to contain more lime than the formula composition, and when fused yielded an apatite. It appears to be a finely divided form of hydroxyl-apatite. The calcined $CaHPO_4$, on the other hand, proved to be a reliable source of P_2O_5.

The furnace used for most of our work was a "Globar" resistance furnace which was capable of a temperature of 1550° C. and controlled by a "Micromax" controller. The samples, in the form of small cylinders, rested on a magnesite slab and, after heating, the portion which had been in contact with the slab was discarded. Where any apparent tendency to react with the magnesite was found, the sample was placed on a piece of platinum foil.

In the part of the system which was of most interest to us, liquidus temperatures were too high to be attained in this furnace. Accordingly, other samples were fused in an oxy-acetylene flame. One of the small cylinders was placed on a magnesite slab and the flame from an oxy-acetylene torch was played on its top. Care was taken to avoid contact with the reducing portion of the flame and only the top of the cylinder was fused, making a small pool of melt resting on the unfused portion of the cylinder. As soon as the flame was removed, the samples cooled very rapidly and on microscopic examination the melted portion usually proved to consist of one phase, or of one phase plus a glass.

All of the samples were examined under the petrographic microscope by the immersion method and the refractive indices and other optical properties of all phases observed were determined. Although some of the phases are rather similar in their optical properties and some show considerable variation due to solid solution, phase identification could be made with considerable assurance, once the range of variation had been determined.

X-ray diffraction patterns were made for each phase and, wherever it seemed desirable, phase identification was checked by a comparison of diffraction patterns. The x-ray studies were made by the powder method on a General Electric apparatus employing molybdenum radiation and a camera radius of 20 cm. The films were measured and interplanar spacings for each of the lines were calculated.

Through the kindness of Prof. A. S. Coffinberry of the Department of Metallurgy of Notre Dame University, x-ray films for calcium orthosilicate, nagelschmidtite, silicocarnotite, tricalcium phosphate, and tetracalcium phosphate were made using copper radiation and a camera radius of 57.2 mm. For purposes of visual comparison these films are reproduced in Fig. 6.

EQUILIBRIUM DIAGRAMS

The high melting temperatures prevailing in that portion of the system of most interest to us precluded the use of the platinum quenching furnace commonly employed in work of this sort. The somewhat crude expedient of melting in the oxy-acetylene flame permits the approximate mapping of field boundaries, although temperature measurements with

the optical pyrometer under these conditions are only rough approxima-
tions. The accompanying diagram, Fig. 3, shows the field boundaries of
the various phases as mapped by this means.

Because the high liquidus temperatures precluded accurate measure-
ment by the usual means, this diagram is presented without isotherms.
However, we believe it represents the essential equilibrium relationships
between the various phases and it embodies the principal contribution of

Phase	Temp
SiO_2	1710
CaO	2570
C_2S	2130
C_3S_2	1475
CS	1540
C_4P	1700
C_3P	1700
C_2P	1300
CP	980
nag	indef.
sc	1850

Point	Temp
1	2065
2	1475
3	1455
4	1436
5	1700
6	1670
7	1570
8	1280
9	1450
10	1350
11	1400
12	1600
13	1600
14	1250
15	1400
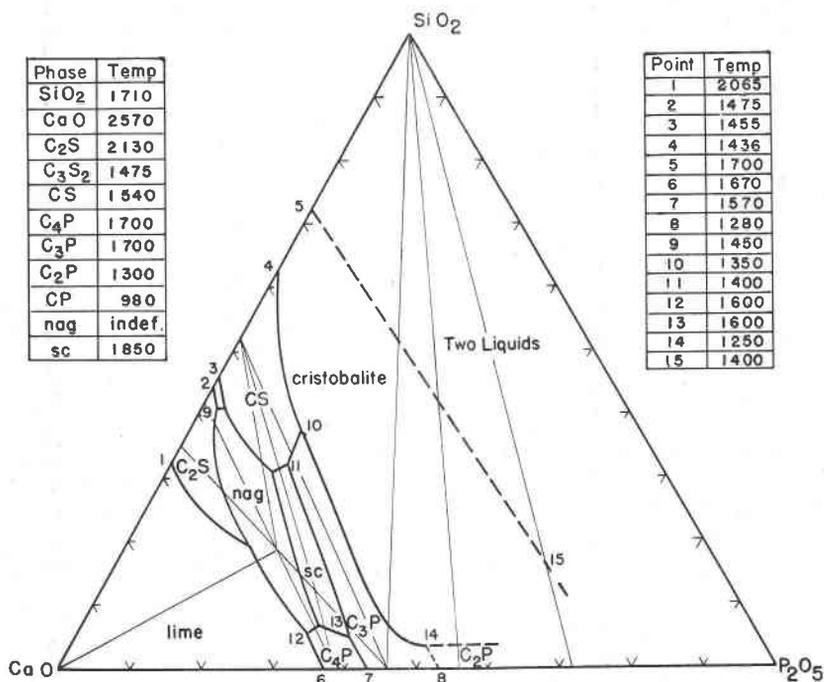
FIG. 3. Equilibrium diagram for the system CaO-SiO₂-P₂O₅.
Temperatures are approximate.

the present paper. The directions of falling temperature and the character
of crystallization can always be inferred from such an equilibrium dia-
gram without the aid of isothermal lines, or any table of temperatures.
However, for the convenience of the reader in visualizing the form of the
liquidus surfaces, a table is appended to the diagram giving the approxi-
mate temperatures for the various points. The presence of additional
components may be expected to affect the equilibrium relationships.
However, examination of a number of steel-making slags indicates that
the essential relationships are not altered by the presence of iron and
manganese oxides as long as CaF_2 is not present. Consequently, it may

be anticipated that this equilibrium diagram will be useful in furthering our understanding of the steel-making process.

Several years ago, in the course of some microscopic examinations of open hearth steel slags, the writers noticed that the dicalcium silicate phase in the slag had lower refractive indices and lower birefringence than the pure compound. Further investigation suggested that the change in indices was due to the presence of P_2O_5 in solid solution. This probability was confirmed by the fact that in the course of the present investigation it was found that dicalcium silicate occurring in preparations containing P_2O_5 always has lowered indices and birefringence. Since
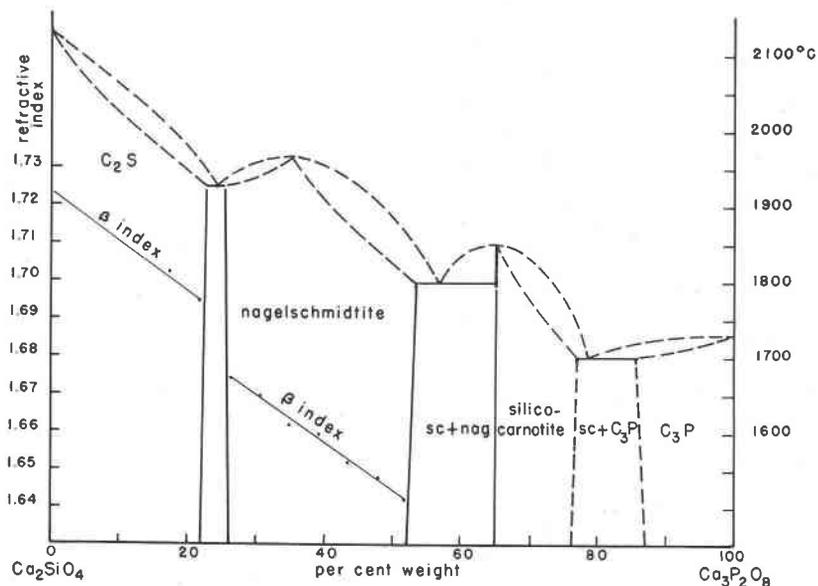
Fig. 4. Diagram showing probable equilibrium relationships in the system Ca_2SiO_4-$Ca_3P_2O_8$. Liquidus temperatures not definitely known. Extent of solid solution and variation in refractive index shown for calcium orthosilicate and nagelschmidtite.

a similar but even greater variation in optical properties was found in the ternary compound we have called nagelschmidtite, a series of compositions intermediate between dicalcium silicate and tricalcium phosphate was prepared and brought as nearly as possible to equilibrium at 1550° C. Microscopic examination of these preparations showed that over a considerable range of compositions only one phase is present and that there is a considerable variation in properties of this phase. The results of this investigation are shown in Fig. 4 in the form of a tentative equilibrium diagram for the binary system dicalcium silicate-tricalcium phosphate. Because of the very high temperatures involved

and the consequent difficulty of making accurate temperature measurements the liquidus lines are diagrammatic. However, the diagram probably shows the essential equilibrium relationships. The limits of solid solution for dicalcium silicate and nagelschmidtite are shown and the relationship between refractive index and composition for the β ray for those two phases is plotted. It will be noted that the homogeneity ranges for these two phases very nearly meet, and that the refractive index curves for the two phases are practically parallel straight lines. These facts are suggestive of the probable structural relationship between these two phases which is discussed later. The phenomenon of solid solution in silicocarnotite and tricalcium phosphate was not studied in detail and the homogeneity ranges shown for these phases are taken from the work of Hill, Hendricks, Jefferson and Reynolds (15).

Discussion of the Phases

Blome (3), Scott and McArthur (30), Schneiderhöhn (28) (29), and Körber and Trömel (17), have all suggested the existence of a silicophosphate having a higher SiO_2/P_2O_5 ratio than silicocarnotite. However, the first investigator to isolate such a phase and describe its physical properties was Nagelschmidt, in 1937 (23). He reported separating this phase from an English basic open hearth slag by using specific gravity methods. Accordingly, we have given this phase the name nagelschmidtite, since this name, cumbersome as it is, is easier to handle than the chemical formula. This phase is described by Nagelschmidt as being biaxial $(+)$, $\alpha = 1.652$, $\gamma = 1.661$, parallel extinction, $G. = 3.035$. The chemical analysis corresponds closely to the formula $7CaO \cdot 2SiO_2 \cdot P_2O_5$. The phase as prepared by us has an optic angle of about 20° and a birefringence of about 0.004. The higher birefringence reported by Nagelschmidt may perhaps be due to solid solution. The present investigation shows that in the three-component system this phase has a rather large field and a considerable homogeneity range, refractive indices varying between a maximum of 1.675 and a minimum of 1.642 for the β ray, the optic angle varying between 20° and practically zero.

Because of its lowered indices and birefringence dicalcium silicate containing P_2O_5 is rather difficult to distinguish from nagelschmidtite by microscopic means alone. However, with the aid of the x-ray diffraction pattern the distinction can be made with certainty.

Silicocarnotite, $5CaO \cdot SiO_2 \cdot P_2O_5$, is given by numerous investigators as the principal constituent of "Thomas" slags and as the cause of its solubility in citric acid, which is used as a test of the availability of the phosphorus for a fertilizer. It is the blue pleochroic phase described by Stead and Risdale (31). The process for the defluorination of phosphate

rock by heating in the presence of silica, aims at its conversion as completely as possible to silicocarnotite. Since upon slow cooling, in a moist atmosphere, there is a tendency to "revert" to the apatite structure, the range of compositions between silicocarnotite and tricalcium phosphate has been the subject of considerable study by the U. S. Bureau of Soils. Hill, Hendricks, Jefferson, and Reynolds (15) state their findings resulting from these studies, and they and others at the Bureau of Soils have published a number of papers on various phases of the fertilizer problem. The portion of Fig. 4 showing the homogeneity ranges of silicocarnotite and tricalcium phosphate is adapted from their paper.

It is difficult to prepare well crystallized silicocarnotite from the pure constituents, but the growth of crystals is facilitated in a slag. We held
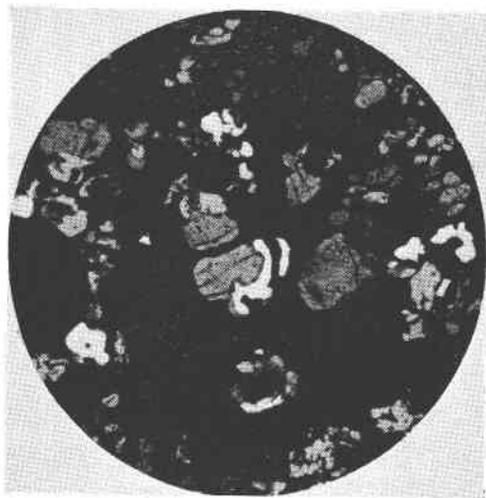

Fig. 5. Photomicrograph of thin section of remelted open hearth slag from Ensley Alabama. Magnification about 75 times. Crossed nicols. Gray grains are nagelschmidtite white grains are silicocarnotite. Background is dark colored interstitial phase.

a sample of the high phosphorus open hearth slag from Ensley, Alabama, at 1525° C. for 40 minutes and then slowly cooled it to 1400° C. Upon examination it proved to consist mainly of well crystallized silicocarnotite. Another sample of slag from the same mills and given the same treatment contained both silicocarnotite and nagelschmidtite. Figure 5 is a photomicrograph of a thin section of this slag. The two phases may be readily distinguished between crossed nicols by the pronounced difference in birefringence.

Silicocarnotite is readily recognized by its optical properties and diffraction pattern. It is biaxial with $2V$ nearly 90°. Because of the large

optic angle the sign is often indeterminate, but in most samples appears to be (+). The refractive indices are: $\alpha = 1.632$, $\beta = 1.636$, $\gamma = 1.640$. Hill and his co-workers (15) found it to have a homogeneity range in the direction of tricalcium phosphate as shown in Fig. 4.

Tricalcium phosphate (hereafter abbreviated C_3P) has a rather surprisingly large field in the three component system. The α form is biaxial (+), $2V$ about 70°, $\alpha = 1.588$, $\gamma = 1.591$. It inverts to the β form at about 1400° C., according to Körber and Trömel (15). Hill and his co-workers found that the inversion became very slow when silica was present in the lattice, the homogeneity range being as shown in Fig. 4. The presence of silica in solid solution can increase the refractive index to a maximum of about 1.615. The β form of tricalcium phosphate seems to be identical with the mineral whitlockite, described recently by Frondel (10).

Tetracalcium phosphate (hereafter abbreviated C_4P) was found by Hilgenstock (13) (14), Stead and Risdale (31), and others in "Thomas" slags nearly 60 years ago. It is readily synthesized by fusing the appropriate composition. It is biaxial (+), $2V$ about 30°, and is characterized by polysynthetic twinning, similar in appearance to that of the plagioclase feldspars. The refractive indices are: $\alpha = 1.650$, $\beta = 1.651$, $\gamma = 1.656$. The field of the phase is small. Solid solution, if it exists, is of very limited extent.

Calcium pyrophosphate (hereafter abbreviated C_2P) is readily prepared by calcining dicalcium hydrogen phopshate. Like C_3P it has an α and β modification with an inversion temperature of about 1150° C., as determined by Körber and Trömel in their study of the $CaO-P_2O_5$ system. The α form is biaxial (−) with small to moderate optic angle, $\alpha = 1.585$, $\gamma = 1.605$.

Pseudowollastonite (hereafter abbreviated CS) has an extensive field in the system. It is easily distinguished from neighboring phases by its higher birefringence. It apparently does not take P_2O_5 into solid solution at all, since no apparent variation in its optical properties occurs in the system.

CaP_2O_6 can be readily prepared by heating $CaH_4(PO_4)_2 \cdot H_2O$. It is biaxial (−) with $2V$ about 60°. The refractive indices are: $\alpha = 1.578$, $\beta = 1.588$, $\gamma = 1.593$. Except for somewhat larger optic angle and lower indices it appears under the microscope quite similar to C_2P.

LIQUID IMMISCIBILITY

The most striking fact about Fig. 3 is the very large size of the field of cristobalite. A melt of composition CaO 50 per cent, P_2O_5 45 per cent, SiO_2 5 per cent crystallized to α-C_3P but contained many small radiating

inclusions of cristobalite which were clearly the first crystals to form. These inclusions are usually spherulitic in character and being nearly isotropic they suggest the globular, glassy inclusions formed by the freezing of immiscible liquids. As a matter of fact, Körber and Trömel in their diagram, which we are reproducing as Fig. 2, indicate that the region of liquid immiscibility extends down into this area. However, in the case of immiscible liquids both liquids must be in equilibrium with the same crystal phase. If those spherulites were formed from the devitrification of globules of highly siliceous liquid, the host liquid would also have to be in equilibrium with silica. When we examine melts somewhat closer to the $CaO-SiO_2$ join, we frequently find skeleton crystals of cristobalite with an octahedral development imbedded in a glass. These are clearly primary cristobalite.

The actual region of liquid immiscibility is approximately shown by the dashed line on Fig. 3. We have not attempted to map this region accurately or to determine the compositions of the liquids formed. However, the more siliceous glass has a refractive index close to 1.46 in all the melts examined which suggests that its composition is close to pure silica. The temperature at which the two liquids separate is about 1700° C. on the $CaO-SiO_2$ join according to Grieg, and we found that two liquids formed in a melt of composition CaO 23 per cent, SiO_2 20 per cent, P_2O_5 57 per cent, at about 1400° C. The less siliceous of the two glasses formed in this latter melt has a refractive index of about 1.535.

Because of the volatility of P_2O_5, compositions lying within the composition triangle $CaP_2O_6-SiO_2-P_2O_5$ require a special technique for study and we have made no attempt to investigate them. However, it is interesting to note that Nielsen (24) reported preparing phases having compositions corresponding to $3SiO_2 \cdot P_2O_5$ and $2SiO_2 \cdot P_2O_5$. He considered these to be definite compounds, but his description of them suggests that they were glasses.

Solid Solutions

The most striking result of our investigation is the very extensive solid solution existing in the system calcium orthosilicate-tricalcium phosphate. Not only do the end members have considerable homogeneity ranges, but the two intermediate ternary compounds, nagelschmidtite and silicocarnotite, display the same phenomenon: nagelschmidtite particularly being found with P_2O_5 content varying between 12 per cent and 24 per cent. Unfortunately, the crystal structure of all four of these compounds is unknown and it is not our intent to go into this phase of the problem. However, a few relevant facts may be worth mentioning. As Fig. 6 shows there is a striking general similarity between the diffraction

patterns for the four phases which may be indicative of a similarity in crystal structure. The compositions are seen to be analogous if we write them thus:

C_2S	$Ca_{24}Si_{12}O_{48}$
Nagelschmidtite	$Ca_{21}Si_6P_6O_{48}$
Silicocarnotite	$Ca_{20}Si_4P_8O_{48}$
C_3P	$Ca_{18}P_{12}O_{48}$
Type formula	$Ca_{(2\ Si+3/2P)}\ (P,\ Si)_{12}O_{48}$

The PO_4 group is known to be a tetrahedral arrangement with dimensions similar to those of the SiO_4 group, and McConnell (19) has shown that SiO_4 can substitute for PO_4, in apatite, at least to some extent. It seems highly probable then that the solid solution encountered here is of
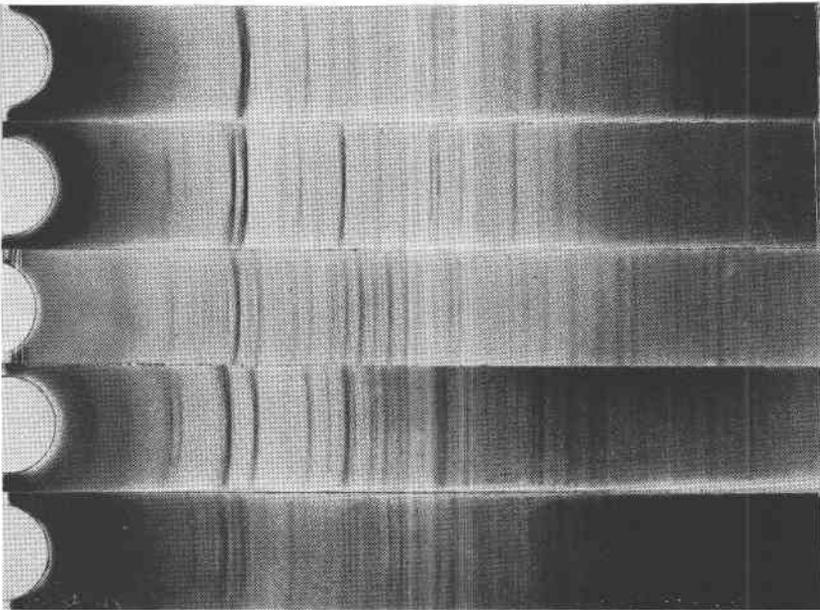

FIG. 6. *X*-ray powder diffraction patterns made with Cu radiation. Reading from top to bottom the phases are: β-calcium orthosilicate, nagelschmidtite, silicocarnotite, α-tricalcium phosphate, and tetracalcium phosphate.

the substitution type with PO_4 substituting for SiO_4 groups. Because of the difference in valence between the two groups, this substitution involves leaving some of the Ca positions in the lattice vacant. One might speculate that if it were not for this fact complete solid solution between the end members would exist, but that the emptying of some of the Ca positions in the lattice brings about structural changes which introduce the two ternary phases into the system.

It is notable that neither CS nor C_2P show appreciable homogeneity ranges. It appears that solid solution between the calcium silicates and calcium phosphates is limited to the orthosilicate ratio. According to the well established rules of silicate structure, the orthosilicate should be characterized by independent SiO_4 groups while the metasilicate would probably have a chain or ring structure of linked SiO_4 groups. It would seem then, that in this system PO_4 groups substitute freely for SiO_4 groups when they are independent, but that the substitution does not occur in the more complex silicate groupings. Certainly isomorphism between silicates and phosphates is not a common phenomenon.

The results of this investigation do not have a very direct bearing on the problem of the igneous rocks because magmas always contain fluorine and hydroxyl ions. There is excellent evidence that the presence of either of these profoundly changes the equilibrium relationships in this system. The formation of hydroxyapatite in the presence of moist air has already been mentioned as have been Schneiderhöhn's observations on slags to which fluorspar had been added.

In the field of mineral technology, however, the importance of this system has long been recognized as shown by the large volume of literature centering around the study of slags and phosphate fertilizers. The results of this investigation should contribute to a better understanding of the part played by basic slags in the elimination of phosphorus from steel in the refining process.

Summary

The equilibrium relationships in the system $CaO\text{-}SiO_2\text{-}P_2O_5$ were investigated and an equilibrium diagram prepared. The solid phases were identified by their optical properties as determined by the use of the petrographic microscope, and by their x-ray diffraction patterns.

In addition to the binary compounds previously described in the literature, two ternary phases, nagelschmidtite and silicocarnotite which have been previously known as constituents of certain slags, were found to exist in the system.

The equilibrium diagram presents two special features of particular interest. There is an extensive region of liquid immiscibility in which two liquids in equilibrium with cristobalite are formed. Very extensive solid solution prevails in the four phases, calcium orthosilicate, nagelschmidtite, silicocarnotite, and tricalcium phosphate, which form a binary system with the first and last mentioned as end members. A binary diagram portraying the homogeneity ranges and the variation in refractive indices resulting from solid solution is presented.

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