

PHASE RELATIONS IN THE SYSTEM CALCIUM ORTHOSILICATE-ORTHOPHOSPHATE

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ABSTRACT

Two different crystal structures, isotypic with hexagonal α and orthorhombic β -potassium sulphate, occur in calcium orthosilicate containing small amounts of various additions. This, and the fact that γ - Ca_2SiO_4 is isotypic with β - Na_2BeF_4 whose high-temperature, α , form is also isotypic with α - K_2SO_4 , leads to the assumption that calcium orthosilicate, above 1420°C , is isomorphous with potassium sulphate. It is shown how these relations influence the shape of a schematic equilibrium diagram of the system Ca_2SiO_4 - $\text{Ca}_3(\text{PO}_4)_2$.

Many substances containing two or more components have simply been designated as binary, ternary, quaternary, or the like, compounds, no matter how complex molecular formulas had to be ascribed to them, if only they had been observed as individual solid phases, not known in any of the constituent one-component, binary, ternary, and so forth, systems. It has recently been shown by the writer (1, 2) that a number of such allegedly binary, ternary or quaternary compounds actually can be recognized as simple solid solutions, when the identity of their crystal structure with that of a hitherto unknown modification, usually the high-temperature form, of one of their components, is established. In this way, it was shown that for instance " $\text{Ca}_4\text{Na}_6(\text{PO}_4)_4\text{CO}_3$ " (3) is a solid solution of Na_2CO_3 in the high-temperature form of CaNaPO_4 , that glaserite " $\text{K}_3\text{Na}(\text{SO}_4)_2$ " actually is just a member of the uninterrupted solid solution series $(\text{K},\text{Na})_2\text{SO}_4$, between α - K_2SO_4 and α - Na_2SO_4 , and that the "compound $\text{Na}_8\text{CaS}_5\text{O}_{20}$ " (4) is nothing but a solid solution of CaSO_4 in the high-temperature modification of Na_2SO_4 (I).

In the system $\text{CaO-SiO}_2\text{-P}_2\text{O}_5$ at least three crystal phases thus far have been obtained, none of which has been known in the binary systems CaO-SiO_2 or $\text{CaO-P}_2\text{O}_5$, not to speak of $\text{SiO}_2\text{-P}_2\text{O}_5$. These are: " $5\text{CaO}\cdot\text{P}_2\text{O}_5\cdot\text{SiO}_2$ " (silicocarnotite) (5, 6), " $4\text{CaO}\cdot\text{P}_2\text{O}_5\cdot\text{SiO}_2$ " (compound "X" (5) or "B" (7)), and " $7\text{CaO}\cdot\text{P}_2\text{O}_5\cdot 2\text{SiO}_2$ " (6, 8). They all were described as ternary compounds of the system $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$, until the substance " $7\text{CaO}\cdot\text{P}_2\text{O}_5\cdot 2\text{SiO}_2$ " was shown by the writer (1, 2) to possess the simple crystal lattice of a group of simple compounds of the type A_2XO_4 , such as Na_2SO_4 , K_2SO_4 , CaNaPO_4 , CaKPO_4 , the high-temperature, α , modifications of which form solid solutions with other compounds to an extensive degree. It was therefore concluded that the substance " $7\text{CaO}\cdot\text{P}_2\text{O}_5\cdot 2\text{SiO}_2$ " very likely is not a ternary compound but a solid solution of $\text{Ca}_3(\text{PO}_4)_2$ in Ca_2SiO_4 , and that the individual com-

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TABLE 1. ISODIMORPHISM OF α AND α' CALCIUM ORTHOSILICATE WITH α AND β POTASSIUM SULPHATE

Brutto Formula	Designation		Lattice Constants			
	proposed	previous	a_0	c_0	c/a	z^+
α -K ₂ SO ₄		α , hexagonal high-temp. form	5.71 ⁺⁺	7.85 ⁺⁺	1.37 ⁺⁺	2
Ca _{1.75} Si _{1.5} P _{0.5} O ₄	solid sol. of Ca ₃ (PO ₄) ₂ in hexagonal α -Ca ₂ SiO ₄	ternary compound "7CaO·P ₂ O ₅ ·2SiO ₂ " nagelschmidite ref. (6), (8), (15)	5.38	7.10	1.32	2
Ca ₂ SiO ₄ , .135Na ₂ O, .068 Fe ₂ O ₃	solid sol. in hexagonal α -Ca ₂ SiO ₄	—	5.40 (cf. footnote 2)	6.996	1.296	2
β -K ₂ SO ₄		β , orthorhombic low-temp. form	a 5.76	b 10.05	c 7.46	4
Ca ₂ SiO ₄ , .09Ca ₃ K ₂ SiO ₄	solid sol. of Ca ₃ K ₂ SiO ₄ in orthorhombic α' -Ca ₂ SiO ₄	ternary compound "23 CaO·K ₂ O·12-SiO ₂ " ref. (10)	5.18	9.52	6.77	4
Ca _{1.88} Si _{.86} P _{.14} O ₄	solid sol. of Ca ₃ (PO ₄) ₂ in orthorhombic α' -Ca ₂ SiO ₄	"Ca ₃ (PO ₄) ₂ ·12Ca ₂ SiO ₄ " ref. (9)	not reported			4

+ Number of molecules A₂XO₄ per unit cell.

++ Measured at 800° C.

pound calcium orthosilicate itself possesses the simple hexagonal crystal structure of the high-temperature, α , forms of the alkali metal sulphates, in some temperature range above its upper transition point at 1420°C.¹

This view was further strengthened, when a second, well known crystal structure of the type A_2XO_4 , that of β -potassium sulphate, was found in yet another ternary combination of a highly complex composition such as $Ca_{27}(SiO_4)_{12}(PO_4)_2$ (9), and also in a substance of the composition $Ca_{23}K_2(SiO_4)_{12}$, which originally had been considered as ternary compound (10). On account of their simple, A_2XO_4 type, crystal structure (TABLE 1), both these substances are now considered as solid solutions, of $Ca_3(PO_4)_2$ and of CaK_2SiO_4 , respectively, in a large excess of calcium orthosilicate. Pure calcium orthosilicate also is assumed to possess this structure (henceforth designated α' - Ca_2SiO_4), in addition to the forms α (hexagonal), β , and γ (olivine type). Most probably, α' is stable immediately above the transition point at 1420°C. Accordingly, the hexagonal, α , structure, isotypic with α -potassium sulphate will have to be assigned to the range immediately below the melting point with a new transition point to be sought in the wide range between 1420° and 2200°C.

The crystal lattice dimensions of both the presumed highest-temperature modifications of calcium orthosilicate, α and α' , are believed to be similar to those given for the solid solutions $Ca_{1.75}(PO_4)_{.5}(SiO_4)_{.5}$ (= " $Ca_7(PO_4)_2(SiO_4)_2$ ") and $Ca_{1.917}K_{.167}SiO_4$ (= " $Ca_{23}K_2(SiO_4)_{12}$ "), respectively, in Table 1, in which the isotypy with α and β potassium sulphate is demonstrated.

Spacings, calculated from the constants given for " $Ca_{23}K_2(SiO_4)_{12}$ " in Table 1, are compared in Table 2 with those measured by H. F. McMurdie, as reported by W. C. Taylor (10). The agreement may be considered satisfactory.

In another x -ray diagram of a mixture of " $Ca_{23}K_2(SiO_4)_{12}$ " with NaCl, only the lines of the former were diffuse and also the relative intensities somewhat different from those reported by W. C. Taylor. Both facts are regarded as additional evidence that the crystals do not represent a ternary compound, but a solid solution which, in quenching, has suffered a transformation in the solid state from the hexagonal, α , structure to the orthorhombic, α' , structure. The complex polysynthetic twinning demonstrated by W. C. Taylor is considered as a further indication of this solid-phase transformation.

¹ The author is indebted to Dr. Kenneth T. Greene, Research Associate, Portland Cement Association Fellowship at the National Bureau of Standards for the personal communication that the x -ray data of a solid solution of small amounts of Na_2O and Fe_2O_3 (or Al_2O_3) in calcium orthosilicate also showed the existence of the hexagonal lattice with $a_0 = 5.40$ and $c_0 = 6.996$ Å, $c/a = 1.296$.

TABLE 2. X-RAY PATTERN OF α' -CALCIUM ORTHOSILICATE
 SOLID SOLUTION, $(\text{Ca}_{1.917}\text{K}_{.166}\text{SiO}_4)$
 $a_0 = 5.18\text{\AA}$, $b_0 = 9.52\text{\AA}$, $c_0 = 6.77\text{\AA}$, $a:b:c = 0.545:1:0.700$.

hkl orthorhombic	d_{hkl} calc.	$d_{hkl}(10)$ exp.	Intensity (10)
022	2.765	2.75	v.s.br.
130	2.71		
$\text{Ca}(\text{OH})_2?$	2.63?	2.63	w.
220	2.28	2.29	w.
041	2.24	2.24	w.
013	2.195	2.185	m.
113	2.025	2.034	m.
042	1.950	1.959	s.
	etc.		

The specific gravity, calculated from the lattice constants with the assumption of $\text{Ca}_{23}\text{K}_2(\text{SiO}_4)_{12}$ actually representing the mass content of 6 unit cells, is 3.43, which compares with 3.24 as measured experimentally.² The disagreement very likely results from the fact that in the calculation more than 4, namely 4.17, cations, Ca and K, were placed in the unit cell beside 2SiO_4 . If the mass content is reduced in the ratio 4:4.17, the specific gravity becomes 3.29 which is in better agreement with the experimental figure 3.24. It would however mean that 4% of the SiO_4 positions were unoccupied. Further efforts are therefore required to clarify this point.

The lattice constants, given by R. Klement and R. Uffelman (11), of the hexagonal high-temperature modifications of CaNaPO_4 , CaKPO_4 and of other analogous substances of the type A_2XO_4 with which α -potassium sulphate (1, 2) and α -calcium orthosilicate were shown to be isotypic, have as little physical reality as those of the low-temperature, β , form of CaNaPO_4 (isomorphous with β - K_2SO_4 and α' - Ca_2SiO_4), as calculated by Klement and Dihn (12), which were shown to be erroneous (2). The interpretation by M. A. Bredig of the x-ray patterns of the high-temperature forms of these substances is supported by the results, independently obtained by L. S. Ramsdell (13) on α - Na_2SO_4 ($a_0 = 5.38$, $c_0 = 7.26$ Å, $c/a = 1.35$), and by O'Daniel and Tscheischwili (14) on α - Na_2BeF_4 ($a_0 = 5.31$, $c_0 = 7.08$ Å, $c/a = 1.335$).

In the results of the latter authors additional confirmation is found in support of the assumption that in regard to crystal structure at high temperatures calcium orthosilicate is analogous to the alkali metal sul-

² Personal communication from Dr. W. C. Taylor, Portland Cement Association Fellowship, National Bureau of Standards, Washington, D. C.

phates. Na_2BeF_4 was shown by them to be isotypic with $\gamma\text{-Ca}_2\text{SiO}_4$. In Table 2, Na_2BeF_4 is demonstrated to be also isotypic, at elevated temperatures, below its melting point, with the solid solution of calcium phosphate in calcium orthosilicate, $\text{Ca}_{1.75}(\text{PO}_4)_{.5}(\text{SiO}_4)_{.5}$.

TABLE 3. ISOTYPY OF α - AND β - Na_2BeF_4 WITH
 α - AND γ - Ca_2SiO_4

Brutto Formula	Designation	z^*	a_0 Å	b_0 Å	c_0 Å	$a:b:c$
1. Low-Temperature Forms (orthorhombic):						
Na_2BeF_4	β	4	4.892	10.90	6.560	0.4488:1:0.6019
Ca_2SiO_4	γ	4	5.06	11.28	6.78	0.4485:1:0.6011
2. High-Temperature Forms (hexagonal):						
Na_2BeF_4	α	2	5.31	—	7.08	$c/a=1.335$
$\text{Ca}_{1.75}\text{Si}_{.5}\text{P}_{.5}\text{O}_4$	α (solid solution)	2	5.38	—	7.10	$c/a=1.320$

* z = number of molecules of Brutto formula per unit cell.

O'Daniel and Tscheischwili consider the isotypy of Ca_2SiO_4 and Na_2BeF_4 as limited to the low-temperature modifications, the isotypy of $\alpha\text{-Na}_2\text{BeF}_4$ and $\text{Ca}_{1.75}\text{Si}_{.5}\text{P}_{.5}\text{O}_4$ apparently not being known to them. They mention the lower symmetry of the high-temperature, α - and β -phases of calcium orthosilicate which, accordingly, could not be considered by them isotypic with the hexagonal high-temperature form of Na_2BeF_4 (α). However, as mentioned above, the validity of our previous knowledge of $\alpha\text{-Ca}_2\text{SiO}_4$ is now very doubtful (1). It has also been shown that, although each of the compounds Na_2SO_4 , K_2SO_4 , CaKPO_4 , and others, has its own individual orthorhombic crystal structure at room temperature, they are isotypic in their high-temperature modifications. This is in full agreement with expectation. Not only will substances of the type mentioned show at low temperatures the greater influence of the individual ions, but are also believed to be necessarily isotypic at high temperatures (where the influence of the individuality of the ions was shown to be diminished), if they are already isotypic at room temperature. An example is the isodimorphism of CaNaPO_4 and K_2SO_4 . It is therefore believed that the isotypy of $\beta\text{-Na}_2\text{BeF}_4$ with $\gamma\text{-Ca}_2\text{SiO}_4$ together with the isotypy of $\alpha\text{-Na}_2\text{BeF}_4$ with $\text{Ca}_{1.75}\text{Si}_{.5}\text{P}_{.5}\text{O}_4$ represents strong additional evidence for the assumption that $\alpha\text{-Ca}_2\text{SiO}_4$ is isotypic with hexagonal $\alpha\text{-Na}_2\text{SO}_4$, $\alpha\text{-K}_2\text{SO}_4$, $\alpha\text{-CaNaPO}_4$, $\alpha\text{-Na}_2\text{BeF}_4$, and the other members of this group of compounds of the type A_2BX_4 . Further attention may be given to the fact that the transformation of the low-

temperature, γ -form of calcium orthosilicate into the hexagonal highest-temperature α -modification is preceded by the transformation into the middle-temperature form β and, in addition, probably into the other form α' , isotypic with β - K_2SO_4 , while the low-temperature form of $\text{Na}_2\text{BeF}_4(\beta)$ transforms directly into the hexagonal high-temperature modification (α). This must naturally be connected with the much higher melting point, that is the much wider temperature range of stability of solid calcium orthosilicate, which is due to the higher electric charge of the ions involved.

Observations on the system $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$ were summarized by Barrett and McCaughey (15) in two equilibrium diagrams. Together with the considerations of the preceding paragraphs, the following points are bound to cause considerable changes in those diagrams:

1. No melting point maxima have been reported for any ternary compounds such as " $5\text{CaO} \cdot \text{SiO}_2 \cdot \text{P}_2\text{O}_5$ " or " $7\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{P}_2\text{O}_5$." Troemel and Koerber (8) who also considered both substances as ternary compounds state only that their melting points must lie somewhere above 1750°C .

2. Klement and Steckenreiter (4) claim to have obtained a high-temperature phase of the composition of " $5\text{CaO} \cdot \text{SiO}_2 \cdot \text{P}_2\text{O}_5$," of a crystal structure different from that of silicocarnotite but analogous to that of " $7\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{P}_2\text{O}_5$ " which was shown now to be that of α - Ca_2SiO_4 .

Although the lack of sufficient data at the very high temperatures of the liquidus curves makes considerable caution imperative, an equilibrium diagram of the system $\text{Ca}_2\text{SiO}_4-\text{Ca}_3(\text{PO}_4)_2$, which is thought to conform best with the information available at the present is given in the figure. It is obvious that, contrary to previous such diagrams, no intermediary compounds in equilibrium with the liquid melt are assumed here. Silicocarnotite—according to the experimental result of Klement and Steckenreiter—is assumed to transform into the hexagonal phase before melting. Whether this transformation is characterized by a peritectoid or a dystectoid temperature maximum of the stability of the silicocarnotite phase, cannot actually be stated. Also, the areas of the hexagonal highest-temperature, α , phase of calcium orthosilicate and of the second high-temperature, α' , phase were terminated in this diagram by eutectoids at relatively high temperatures, although these phases actually were observed at room temperature. It is considered likely that at low temperatures these solid solutions are metastable only.

The following recent publications became known to the writer while the paper was in the press:

G. Troemel (17) proposes a somewhat different diagram for the system calcium orthosilicate-orthophosphate. His phase "K" (so designated for its isotypy with β - K_2SO_4) is identical with the phase α' , while his phase

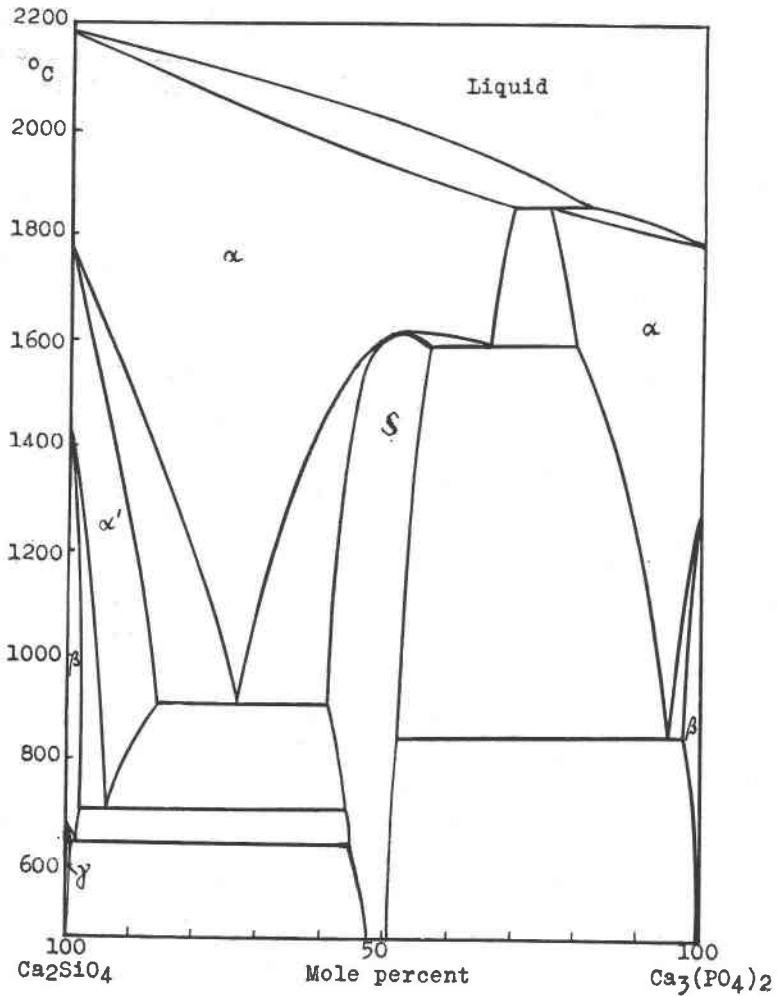


FIG. 1. Schematic Equilibrium Diagram of the System $\text{Ca}_2\text{SiO}_4\text{-Ca}_3(\text{PO}_4)_2$.

"R" (for rhenanite, refs. 1 and 3) is identical with hexagonal, α , calcium orthosilicate. Troemel's suggestion to consider "K" and "R" as intermediary phases between those of calcium orthosilicate and orthophosphate, if not as intermediary "compounds," must be rejected on the grounds discussed in the present paper.

H. O'Daniel and L. Tscheischwili (18) found both strontium and barium orthosilicates to be isotypic with β potassium sulphate. In connection with the observation, by N. A. Toropov and P. F. Kononov

(19), of solid solutions of calcium and barium orthosilicates, this may be considered another indication for the occurrence of the β potassium sulphate structure in the individual compound calcium orthosilicate (α').

S. Zerfoss and H. M. Davis (20) investigated the influence, not of $\text{Ca}_3(\text{PO}_4)_2$, but of P_2O_5 , on the transitions in calcium orthosilicate. Their low value for the solid solubility of P_2O_5 therefore must not be considered to be in disagreement with the relations postulated in the present paper.

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