PHASE RELATIONS IN THE SYSTEM CALCIUM ORTHOSILICATE-ORTHOPHOSPHATE

M. A. BREDIG.*

Abstract

Two different crystal structures, isotypic with hexagonal $\alpha$ and orthorhombic $\beta$-potassium sulphate, occur in calcium orthosilicate containing small amounts of various additions. This, and the fact that $\gamma$-Ca$_3$SiO$_4$ is isotypic with $\beta$-Na$_2$BeF$_4$, whose high-temperature, $\alpha$, form is also isotypic with $\alpha$-K$_2$SO$_4$, 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$_3$SiO$_4$-Ca$_3$(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 "Ca$_4$Na$_6$(PO$_4$)$_4$CO$_3$" (3) is a solid solution of Na$_2$CO$_3$ in the high-temperature form of CaNaPO$_4$, that glaserite "K$_3$Na(SO$_4$)$_3$" actually is just a member of the uninterrupted solid solution series (K,Na)$_2$SO$_4$, between $\alpha$-K$_2$SO$_4$ and $\alpha$-Na$_2$SO$_4$, and that the "compound Na$_8$Ca$_3$O$_{25}$" (4) is nothing but a solid solution of CaSO$_4$ in the high-temperature modification of Na$_2$SO$_4$ (1).

In the system CaO-SiO$_2$-P$_2$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 CaO-P$_2$O$_5$, not to speak of SiO$_2$-P$_2$O$_5$. These are: "5CaO·P$_2$O$_5$·SiO$_2$" (silicocarnotite) (5, 6), "4CaO·P$_2$O$_5$·SiO$_2$" (compound "X" (5) or "B" (7)), and "7CaO·P$_2$O$_5$·2SiO$_2$" (6, 8). They all were described as ternary compounds of the system CaO-P$_2$O$_5$-SiO$_2$, until the substance "7CaO·P$_2$O$_5$·2SiO$_2$" was shown by the writer (1, 2) to possess the simple crystal lattice of a group of simple compounds of the type A$_2$XO$_4$, such as Na$_2$SO$_4$, K$_2$SO$_4$, CaNaPO$_4$, CaKPO$_4$, the high-temperature, $\alpha$, modifications of which form solid solutions with other compounds to an extensive degree. It was therefore concluded that the substance "7CaO·P$_2$O$_5$·2SiO$_2$" very likely is not a ternary compound but a solid solution of Ca$_3$(PO$_4$)$_2$ in Ca$_2$SiO$_4$, and that the individual com-

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<table>
<thead>
<tr>
<th>Brutto Formula</th>
<th>Designation</th>
<th>Lattice Constants</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>proposed</td>
<td>previous</td>
<td>(a)</td>
</tr>
<tr>
<td>(\alpha)-K(_2)SO(_4)</td>
<td>(\alpha), hexagonal high-temp. form</td>
<td></td>
<td>5.71(\pm)5</td>
</tr>
<tr>
<td>(\text{Ca}<em>1.26\text{Si}<em>6\text{O}</em>{18}\text{P}</em>{0.6}\text{O}_4)</td>
<td>solid sol. of (\text{Ca}_3(\text{PO}_4)_2) in hexagonal (\alpha)-(\text{Ca}_2\text{SiO}_4)</td>
<td>ternary compound “7(\text{CaO} \cdot \text{P}_2\text{O}_5\text{Si}_2\text{O}_7)” nagelschmidtite ref. (6), (8), (15)</td>
<td>5.38</td>
</tr>
<tr>
<td>(\text{Ca}_2\text{SiO}_4 \cdot 0.135\text{Na}_2\text{O} \cdot 0.068\text{Fe}_2\text{O}_3)</td>
<td>solid sol. in hexagonal (\alpha)-(\text{Ca}_2\text{SiO}_4)</td>
<td>—</td>
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<tr>
<td>(\beta)-K(_2)SO(_4)</td>
<td>(\beta), orthorhombic low-temp. form</td>
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<td>5.76</td>
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<td>(\text{Ca}_2\text{SiO}_4 \cdot 0.09\text{Ca}_2\text{SiO}_4)</td>
<td>solid sol. of (\text{Ca}_2\text{SiO}_4) in orthorhombic (\alpha')-(\text{Ca}_2\text{SiO}_4)</td>
<td>ternary compound “23 (\text{CaO} \cdot \text{K}_2\text{O} \cdot 12\text{SiO}_2)” ref. (10)</td>
<td>5.18</td>
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<tr>
<td>(\text{Ca}<em>1.98\text{Si}<em>6\text{O}</em>{18}\text{P}</em>{1.1}\text{O}_4)</td>
<td>solid sol. of (\text{Ca}_3(\text{PO}_4)_2) in orthorhombic (\alpha')-(\text{Ca}_2\text{SiO}_4)</td>
<td>“(\text{Ca}_3(\text{PO}_4)_2 \cdot 12\text{Ca}_2\text{SiO}_4)” ref. (9)</td>
<td>not reported</td>
</tr>
</tbody>
</table>

\(\pi^+\) Number of molecules \(\text{A}_2\text{XO}_4\) per unit cell.

\(\pm\) Measured at 800° C.
pound calcium orthosilicate itself possesses the simple hexagonal crystal structure of the high-temperature, \( \alpha \), 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 \( \beta \)-potassium sulphate, was found in yet another ternary combination of a highly complex composition such as \( \text{Ca}_{27} \left( \text{SiO}_4 \right)_{12} \left( \text{PO}_4 \right)_2 \) (9), and also in a substance of the composition \( \text{Ca}_{23} \text{K}_2 \left( \text{SiO}_4 \right)_{12} \), 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 \( \text{Ca}_8 \left( \text{PO}_4 \right)_2 \) and of \( \text{CaK}_2 \text{SiO}_4 \), respectively, in a large excess of calcium orthosilicate. Pure calcium orthosilicate also is assumed to possess this structure (henceforth designated \( \alpha' - \text{Ca}_2 \text{SiO}_4 \)), in addition to the forms \( \alpha \) (hexagonal), \( \beta \), and \( \gamma \) (olivine type). Most probably, \( \alpha' \) is stable immediately above the transition point at 1420°C. Accordingly, the hexagonal, \( \alpha \), structure, isotypic with \( \alpha \)-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, \( \alpha \) and \( \alpha' \), are believed to be similar to those given for the solid solutions \( \text{Ca}_1.75 \left( \text{PO}_4 \right)_2 \left( \text{SiO}_4 \right)_5 \) ("\( \text{Ca}_7 \left( \text{PO}_4 \right)_2 \left( \text{SiO}_4 \right)_2 \)"), and \( \text{Ca}1.91 \text{K}1.16 \text{SiO}_4 \) ("\( \text{Ca}_{23} \text{K}_2 \left( \text{SiO}_4 \right)_{12} \)"), respectively, in Table 1, in which the isotypy with \( \alpha \) and \( \beta \) potassium sulphate is demonstrated.

Spacings, calculated from the constants given for "\( \text{Ca}_{23} \text{K}_2 \left( \text{SiO}_4 \right)_{12} \)" 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 "\( \text{Ca}_{23} \text{K}_2 \left( \text{SiO}_4 \right)_{12} \)" 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, \( \alpha \), structure to the orthorhombic, \( \alpha' \), 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 \( \text{Na}_2 \text{O} \) and \( \text{Fe}_2 \text{O}_3 \) (or \( \text{Al}_2 \text{O}_3 \)) in calcium orthosilicate also showed the existence of the hexagonal lattice with \( a_0 = 5.40 \) and \( c_0 = 6.996 \, \text{Å} \), \( c/a \approx 1.296 \).
The specific gravity, calculated from the lattice constants with the assumption of \( \text{Ca}_2\text{K}_2(\text{SiO}_4)_3 \) actually representing the mass content of 6 unit cells, is 3.43, which compares with 3.24 as measured experimentally. 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. Uffelmann (11), of the hexagonal high-temperature modifications of \( \text{CaNaPO}_4 \), \( \text{CaKPO}_4 \) and of other analogous substances of the type \( A_2XO_4 \) with which \( \alpha \)-potassium sulphate (1, 2) and \( \alpha \)-calcium orthosilicate were shown to be isotypic, have as little physical reality as those of the low-temperature, \( \beta \), form of \( \text{CaNaPO}_4 \) (isomorphous with \( \beta \)-K\(_2\)SO\(_4\) and \( \alpha' \)-Ca\(_2\)SiO\(_4\)), 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 \( \alpha \)-Na\(_2\)SO\(_4\) (\( a_0 = 5.38 \), \( c_0 = 7.26 \) Å, \( c/a = 1.35 \)), and by O’Daniel and Tscheischwili (14) on \( \alpha \)-Na\(_2\)BeF\(_4\) (\( a_0 = 5.31 \), \( c_0 = 7.08 \) 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-

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**Table 2. X-ray Pattern of \( \alpha' \)-Calcium Orthosilicate**

<table>
<thead>
<tr>
<th>hkl</th>
<th>( d_{\text{calc.}} )</th>
<th>( d_{\text{exp.}} )</th>
<th>Intensity</th>
</tr>
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<tr>
<td>022</td>
<td>2.765</td>
<td>2.75</td>
<td>v.s.br.</td>
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<tr>
<td>130</td>
<td>2.71</td>
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<td></td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>2.63?</td>
<td>2.63</td>
<td>w.</td>
</tr>
<tr>
<td>220</td>
<td>2.28</td>
<td>2.29</td>
<td>w.</td>
</tr>
<tr>
<td>041</td>
<td>2.24</td>
<td>2.24</td>
<td>w.</td>
</tr>
<tr>
<td>013</td>
<td>2.195</td>
<td>2.185</td>
<td>m.</td>
</tr>
<tr>
<td>113</td>
<td>2.025</td>
<td>2.034</td>
<td>m.</td>
</tr>
<tr>
<td>042</td>
<td>1.950</td>
<td>1.959</td>
<td>s.</td>
</tr>
</tbody>
</table>

etc.
phates. Na₂BeF₄ was shown by them to be isotypic with γ-Ca₂SiO₄. In Table 2, Na₂BeF₄ is demonstrated to be also isotypic, at elevated temperatures, below its melting point, with the solid solution of calcium phosphate in calcium orthosilicate, Ca₁.₇₆(PO₄)₃(SiO₄)₅.

**Table 3. Isotypy of α- and β-Na₂BeF₄ with α- and γ-Ca₃SiO₄**

<table>
<thead>
<tr>
<th>Brutto Formula</th>
<th>Designation</th>
<th>a₀</th>
<th>b₀</th>
<th>c₀</th>
<th>a:b:c</th>
</tr>
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<tbody>
<tr>
<td>Na₂BeF₄</td>
<td>β</td>
<td>4</td>
<td>4.892</td>
<td>10.90</td>
<td>6.560</td>
</tr>
<tr>
<td>Ca₃SiO₄</td>
<td>γ</td>
<td>4</td>
<td>5.06</td>
<td>11.28</td>
<td>6.78</td>
</tr>
</tbody>
</table>

| Na₂BeF₄       | α (solid)  | 2  | 5.31 | —    | 7.08  | c/a=1.335 |
| Ca₁.₇₆Si₃P₅O₁₄ | α (solution) | 2  | 5.38 | —    | 7.10  | c/a=1.320 |

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

O'Daniel and Tscheischwili consider the isotypy of Ca₃SiO₄ and Na₂BeF₄ as limited to the low-temperature modifications, the isotypy of α-Na₂BeF₄ and Ca₁.₇₆Si₃P₅O₁₄ 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 Na₂BeF₄ (α). However, as mentioned above, the validity of our previous knowledge of α-Ca₃SiO₄ is now very doubtful (1). It has also been shown that, although each of the compounds Na₃SO₄, K₂SO₄, CaKPO₄, 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 CaNaPO₄ and K₂SO₄. It is therefore believed that the isotypy of β-Na₂BeF₄ with γ-Ca₃SiO₄ together with the isotypy of α-Na₂BeF₄ with Ca₁.₇₆Si₃P₅O₁₄ represents strong additional evidence for the assumption that α-Ca₃SiO₄ is isotypic with hexagonal α-Na₃SO₄, α-K₂SO₄, α-CaNaPO₄, α-Na₂BeF₄, and the other members of this group of compounds of the type A₃BX₄. 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-K₃SO₄, while the low-temperature form of
Na₂BeF₄(β) 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 sta-
bility of solid calcium orthosilicate, which is due to the higher electric
charge of the ions involved.

Observations on the system CaO-P₂O₅-SiO₂ 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 com-
pounds such as "5CaO·SiO₂·P₂O₅" or "7CaO·2SiO₂·P₂O₅," 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 Steckeneriter (4) claim to have obtained a high-
temperature phase of the composition of "5CaO·SiO₂·P₂O₅," of a crystal
structure different from that of silicocarnotite but analogous to that of
"7CaO·2SiO₂·P₂O₅" which was shown now to be that of α-Ca₃SiO₄.

Although the lack of sufficient data at the very high temperatures of
the liquidus curves makes considerable caution imperative, an equi-
librium diagram of the system Ca₅SiO₇-Ca₃(PO₄)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 inter-
mediary compounds in equilibrium with the liquid melt are assumed here.
Silicocarnotite—according to the experimental result of Klement and
Steckeneriter—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 silicocarno-
tite 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 eute-
toids 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-K₃SO₄) is identical with the phase α', while his phase
"R" (for rhenanite, refs. 1 and 3) is identical with hexagonal, $\alpha$, 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 $\beta$ potassium sulphate. In connection with the observation, by N. A. Toropov and P. F. Konovalov
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(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 Ca₃(PO₄)₂, but of P₂O₅, on the transitions in calcium orthosilicate. Their low value for the solid solubility of P₂O₅ therefore must not be considered to be in disagreement with the relations postulated in the present paper.

ACKNOWLEDGMENT

The cooperation of Dr. W. C. Taylor, Research Associate, Portland Cement Association Fellowship at the National Bureau of Standards, Washington, D. C., and of Professor Lars Thomassen of the University of Michigan, Ann Arbor, Mich., in supplying a sample of Ca₂₃K₂(SiO₄)₁₂, and in preparing an x-ray picture thereof, respectively, is gratefully acknowledged.

REFERENCES