Phase Relation in the System $\text{Ca}_3(\text{PO}_4)_2\text{-MgSiO}_3$

Toshiyuki SATA†

Department of Industrial Chemistry, Kumamoto Institute of Technology, 4-22-1, Ikeda, Kumamoto-shi 860

 $\text{Ca}_3(\text{PO}_4)_2\text{-MgSiO}_3$ 系の相関係

佐多敏之†

熊本工業大学工業化学科, 860 熊本市池田 4-22-1

Phase relations in the system tricalcium phosphate ($3\text{CaO}\cdot\text{P}_2\text{O}_5=\text{C}_3\text{P}$)-enstatite ($\text{MgO}\cdot\text{SiO}_2=\text{MS}$) have been investigated in the temperature range 1100 to 1600°C by means of the quenching method. C_3P takes β -type (whitrockite) in a wide region by dissolution of MgO , and diopside (d) appeared in the composition range more than 40 mass% C_3P by a reach in between MgSiO_3 and liberated CaO . The enstatite transfers to iron-free pigeonite (pi) by taking CaO in an MS-rich region, where pi coexists with protoenstatite, MgSiO_3 (pr). Primary crystals which appeared in a wide region are $\beta\text{-C}_3\text{P}$ and pi, and primary diopside appears in a narrow region at a minimum temperature (1265–1305°C). In the sub-solidus region below 1245°C, $\beta\text{-C}_3\text{P}$ coexists with d, pi or pi-pr mixture. The system is not binary and it should be discussed from the ternary system $\text{C}_3\text{P-M-S}$ and the quaternary system $\text{C}_3\text{P-CMS}_2\text{-MS-S}$.

[Received November 17, 1995; Accepted February 9, 1996]

Key-words : Phase diagram, The system $\text{Ca}_3(\text{PO}_4)_2\text{-MgSiO}_3$, Tricalcium phosphate, Magnesium silicate, Diopside, Pigeonite

1. Introduction

In the system $\text{CaO-P}_2\text{O}_5$,¹⁾⁻⁵⁾ 6 kinds of phosphates with $\text{CaO/P}_2\text{O}_5$ molar ratios of 4, 3, 2, 1, 2/3 and 1/2 have been reported (Figs. 245, 246, 247, 248 and 250 in "Phase Diagrams for Ceramists"⁶⁾). Among these Ca-phosphates, 3 : 1 compound $\text{Ca}_3(\text{PO}_4)_2=3\text{CaO}\cdot\text{P}_2\text{O}_5=\text{C}_3\text{P}$ is a major component of phosphate rock (apatite= $\text{Ca}_5(\text{PO}_4)_3\text{F}$), which has been used to manufacture phosphate fertilizers (superphosphate, water soluble 1 : 1 compound produced by reaction with H_2SO_4). Another phosphate fertilizer is calcium magnesium phosphate which is fabricated by fusion and quenching processes of the phosphate rock with serpentine rock ($3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$). This author investigated on the system $3\text{CaO}\cdot\text{P}_2\text{O}_5\text{-MgO}\cdot\text{SiO}_2 (= \text{C}_3\text{P-MS})$ in order to find the minimum fusion temperature region for the above fertilizer, and the results were already published in 1958.⁷⁾ During about 30 years after this publication, phase diagrams in the system diopside-enstatite had been improved.⁸⁾⁻¹²⁾ Referring to these results, phases present in the system $\text{C}_3\text{P-MS}$ were re-examined in this study. Compositions relating to this region are important for compositions of the above-mentioned fused phosphate fertilizer¹³⁾⁻¹⁹⁾ and P_2O_5 -containing metallurgical slags, and for understanding corrosion mechanism of refractories against P_2O_5 -containing melts of the above fertilizer and slags. It may be also important for the recently advanced glass ceramics and bioceramics with related compositions. The $\text{C}_3\text{P-MS}$ sys-

tem is one of the most important joins in the 4-component tetrahedron $\text{C}_3\text{P-CMS}_2\text{-MS-S}$ which will be reported later. Any report on this 2-component system has not appeared yet on literature, except for the author's.

2. Experimental

A starting materials, tricalcium phosphate C_3P , was synthesized by a reaction of CaCO_3 with phosphoric acid at 1200°C, as described in the previous paper.⁷⁾ Another C_3P specimen was synthesized from CaCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ too. For determination of transition temperature of C_3P , 3 levels of calcination temperatures were used, as described later (Section 3.1). Enstatite (MS) was also synthesized by firings of MgCO_3 and SiO_2 at 1200°C. After weighing above materials for the nominal compositions, these were thoroughly mixed in an agate mortar using alcohol or acetone. The powdered mixture was pressed to pellets and fired 1 or 2 times at 1350–1400°C for 3–5h on a platinum plate accompanied by intermediate grindings. Chemical compositions of these fired starting materials were confirmed by chemical analyses.

The powders of the fired specimen was enclosed in the Pt-envelope and then suspended with Pt wire (0.5 mm) at a homogeneous temperature region in a mullite tube (40 mm in outer diameter) of a furnace with an SiC spiral heater and was held at a constant temperature controlled within $\pm 1^\circ\text{C}$ by a thyristor unit. A thermocouple of Pt-Pt13%Rh alloy was positioned near by the specimen. In the quenching of the specimen into water, the suspending Pt wire was dropped with the sample envelope. The quenched

† Current address: 1-28-16, D7-504, Unomori, Sagami-hara-shi 228

現在連絡先 : 228 相模原市鶴野森 1-28-16 D7-504

specimen was examined mainly by X-ray diffraction analysis (XRD) and 2θ angles were calibrated using pure silicon powders. Optical microscopy was also applied to confirm a presence of liquid.

The thermocouple used was calibrated by observation of melting points of gold and paradium wires and by quenching method using diopside and walstonite powders. Generally, 4 or 5°C should be added to the read values. MoSi₂ furnace and Pt6Rh–Pt30Rh or Pt20Rh–Pt40Rh thermocouple were used for measurement at temperatures more than 1450°C.

3. Results and discussion

3.1 Transition temperature of C₃P

Three kinds of C₃P specimens synthesized at 900, 1000 or 1300°C for 3h were used, as described in the experimental method. These specimens were quenched from 1005–1405°C after 1–15h holdings. Thus, the transition temperature was compared with the preceding results in the literatures. To know rough contents of α -type and β -type, peak intensities at 24.1° (261) of 2θ for α -type and 27.7° (214) for β -type were used and the transition temperature was determined as a temperature at which α -type began to appear from β -type. The X-ray patterns were referred to 29–359 for α -C₃P and 9–169 for β -C₃P described in JCPDS data.²⁰⁾

The results of the quenching are listed in Table 1. The quenched temperature in the table shows the maximum temperature in waving temperature controlling of ± 5 or $\pm 1^\circ\text{C}$. Contents of β -C₃P in α - β mixtures are plotted against temperatures as shown in Fig. 1. From the figure, the transition temperature between α and β is estimated to be between 1100 and 1120°C. Coexistence of both type C₃P is observed up to 1260°C and it was noted that α -type heated at 1300°C was difficult to transform to β -type even in holding at 1100°C. The transition temperatures of β - α and of α - α' had been reported using the high temperature XRD method as follows:

β - α	α - α'	mp	
1125°C	1430°C	1756°C	by Nurse et al. ²¹⁾
1120°C	1470°C	1800°C	by Fix et al. ²²⁾

Author's values for the β to α transition are consistent with these above values. The α to α' transition was difficult to observe by XRD at room-temperature and microscopy in the quenching experiments.

3.2 The system diopside–enstatite

Many studies^{8)–12)} on the solid solutions between diopside (CMS₂) and enstatite (MS) had been carried out since a publication by Bowen²³⁾ relating to cooled products of magma, but there are many facts remained obscured even in present.²⁴⁾ In particular, the field for the iron-free pigeonite solid solution was reported in 1972 to 1975^{9)–12)} on the phase diagram of the system diopside–enstatite. Natural pigeonite was iron-contained metasilicate (Ca_{0.04}Mg_{0.45}Fe_{0.48}SiO₃),^{25),26)} and iron-free pigeonite with a composition Ca_{0.09}Mg_{0.91}SiO₃^{9),10)} newly formed at Mg-rich

Table 1. Quenching Experiments for Ca₃(PO₄)₂(=C₃P). Specimen 434 was Synthesized from CaCO₃ and H₃PO₄ and 404 from CaCO₃ and (NH₄)₂HPO₄. Temperature Controls were Generally in $\pm 5^\circ\text{C}$ and * Indicates Those in $\pm 1^\circ\text{C}$

No. Preheat. Holding					C ₃ P								
temp.		temp.	time	α	β	temp.		temp.	time	α	β		
°C		°C	h	%	%	°C		°C	h	%	%		
434	1000	1355	1	92	8	404	1300	1405	1	94	6		
		1265	1	92	8			1305	1.5	93	7		
		1205	1	93	7			1205	1	94	6		
		1155	1	74	26			1105	3.5	96	4		
		1105	1	4	96			1105*	20	74	26		
434	900	1185	1	95	5	404	900	1250	1	93	7		
		1165	1	85	15			1215	1	91	9		
		1155*	15	83	17			1185	1	92	8		
		1145*	1	50	50			1155	1	84	16		
		1135*	1	27	73			1150*	5	83	17		
		1125*	1	13	87			1145*	4	82	18		
										1105	1	26	74
										1005	1	0	100

Fig. 1. Contents of β -C₃P in mixtures with α -C₃P against quenched temperatures. α to β transition was estimated from appearance temperature of α -C₃P.
(a) for specimen 434 and (b) for 404, shown in Table 1.

region in the phase diagram. To simplify, this iron-free pigeonite is abbreviated as pigeonite (pi) in this report. In the system diopside-enstatite, the pigeonite field is located only in the temperature range 1230 to 1430°C and at compositions 10–25 mol% of diopside.^{8)–11)} And a larger area for the presence of pigeonite was reported at SiO_2 -rich side in the system diopside-enstatite. In the phase diagram published in 1975,¹²⁾ the lowest temperature of presence of pigeonite decreased below 1000 or even to 700°C from the high-temperature XRD study. In this system, forsterite is widely present up to 75 mol% in diopside content just under the liquidus curve below which diopside solid solution, 2-phase region, above mentioned pigeonite solid solution and enstatite solid solution occupy. The diopside has no crystal transition up to its melting point, while the enstatite has 2 or 3 type of transition as below.¹²⁾

Enstatite (Low clinoenstatite, E or LCE)

→High clinoenstatite (HCE)

→Protoenstatite (PE)

→Forsterite + liquid.

The transition temperatures are 1000–1080°C, 1230 and 1560°C,⁷⁾ respectively. The author's publication⁷⁾ on the system C_3P -MS in 1958 was re-examined in this study, because the both phases of diopside and pigeonite widely formed in the system C_3P -MS.

Starting materials CMS_2 and MS were prepared from CaCO_3 , MgO and amorphous silica at 1300°C for 4h after preliminary firings at the same temperature and regrindings. Specimen compositions were

from 80–20 to 1–99 mol% for CMS_2 -MS and were quenched using the same technique in the temperature range 1100 to 1400°C. Holding time was 1–2h at 1350–1400°C, 8–12h at 1200°C and 7–50h at 1100°C. For the X-ray examinations, JCPDS data²⁰⁾ were referred. Especially, data from 11–654 for diopside and 11–273 for protoenstatite were used. The X-ray data for iron-free pigeonite was cited from the literature.⁹⁾ Compositions of the mixture, temperatures and holding time in the heat treatments, and phases present examined by XRD are listed in Table 2.

Figure 2(a) shows the results of the phases present. This result in the temperature range 1105 to 1405°C agrees well with the results of Kushiro¹⁰⁾ by quenching method rather than those of Schwab and Schwerin¹²⁾ by XRD at high-temperature. This is natural because this study used the quenching method. In the wide intermediate region, a mixture of diopside and pigeonite appeared (Fig. 2(b)). Decrease in the X-ray peak intensity for diopside begins from 50 mol% of MgSiO_3 with increases of pigeonite, and diopside peaks disappear at 90–95 mol% of MgSiO_3 . Protoenstatite appears as a mixture with pigeonite in the region over 95 mol% of MgSiO_3 (Fig. 2(c)) and no clinoenstatite appeared between 1105 and 1405°C. Formation of the diopside solid solution at the diopside side and the pigeonite solid solution were confirmed by the smooth change of d -value for (220) at 27.6–28.0°, (310) at 30.3–31.0° and (002) at 35.5–36.3° of 2θ . These d -values slightly decrease with increasing mol% of MgSiO_3 (Fig. 2(d)). These changes are not understood in the present step. These results near the MS side are not perfectly consistent with those by Kushiro,¹⁰⁾ because pure pr solid solution phase does not appear. The results for d -spacing in Fig. 2(d) were employed to decide phase compositions in the system CMS_2 -MS as described later.

3.3 The system C_3P -MS

A phase diagram on this system has been already reported in 1958 by the author.⁷⁾ As mentioned above, diopside and iron-free pigeonite were found widely in this re-examination. Thus, the diagram should be corrected to a new one. Quenching results are shown in Table 3. The phase diagram obtained is shown in Fig. 3. Primary crystals are C_3P (α or β) in a C_3P side, pigeonite (pi) and forsterite (f) in an MS-side, and diopside (d) at the lowest fusion temperature region (1265–1305°C) of a narrow center part. Under the solidus line, pi coexists with protoenstatite (pr) in a wide region of the MS-side. In this MS-side, β - C_3P solid appears only below 1245°C as mixtures with diopside, pigeonite and protoenstatite in composition above 20% MS and clinoenstatite was not found in the temperature range 1105 to 1405°C.

$\text{C}_{2.7}\text{M}_{0.3}\text{P}$ formed from C_3P by dissolving MgO from MS in a temperature range 1105 to 1405°C.

Table 2. Quenching Experiments for the System CMS_2 -MS. d=diopside (CMS_2), pi=pigeonite ($\text{C}_{0.09}\text{M}_{0.91}\text{S}$), pr=protoenstatite (MS), cr=cristobalite and f=forsterite. Order in Phases Present is According to Amounts of Them

No.	CMS_2 -MS wt. % (mol%)	Holding temp. °C time h	Phases present	No.	CMS_2 -MS wt. % (mol%)	Holding temp. °C time h	Phases present
453	89.6–10.4 (80–20)	1355 1 1205 10.5 1205 8 1105 15	d, cr d, cr, f d d	422	10.2–89.8 (5–95)	1355 1 1205 8 1105 15	pi pi pi
454	80–20 (65–35)	1355 1 1205 13.5 1105 7	d, cr, f d, cr, f d	488	8.2–91.8 (4–96)	1405 1.5 1305 1.5 1205 5 1105 22	pi, pr pi, cr pi, pr, cr pi, cr
417	68.3–31.7 (50–50)	1355 1 1205 8 1105 15	d d, pi d, pi	489	6.3–93.7 (3–97)	1405 2 1305 1.7 1205 3.5 1105 23	pi, pr, cr pi, cr pi, cr pi
418	59–41 (40–60)	1355 1 1205 18 1105 16	d, pi d, pi d	486	4.2–95.8 (2–98)	1405 1 1355 1 1205 3 1205 4 1155 52	pi, pr, cr, f pi, pr, cr, f pi, pr, cr, f pi, pr, cr pi, pr, cr, f
419	48–52 (30–70)	1355 1 1205 8.5 1105 15	pi, d pi, d pi, d	487	2.1–97.9 (1–99)	1405 3.5 1305 1 1205 2.5 1105 40	pi, pr, cr, f pi, pr, cr, f pi, pr, cr, f pi, pr, cr, f
420	35–65 (20–80)	1355 1 1205 9 1105 17	pi, d pi, d pi, d	550	0–100	1585 0.33L 1555 0.5 1505 0.66pr 1455 1	 pi, pr, f, cr, L pr, f, cr pr, f, cr
421	19.3–80.7 (10–90)	1355 1 1205 8 1105 21.5	pi, cr pi pi

Fig. 2. (a) Phase distribution obtained from quenching results in the system CMS₂-MS.

(b) amounts of d and pi in the system CMS₂-MS at 1355°C. Relative amounts were obtained from peak intensity ratios $d_{(002)}/pi_{(002)}$.

(c) amounts of pi and pr in an MS-rich region more than 95 mol% of MS. The amounts were obtained from peak intensity ratios (left) $pi_{(002)}/pr_{(221)}$ and (right) $pi_{(021)}/pr_{(211)}$ in a temperature range 1105–1400°C.

(d) change in d -spacings for d and pi with compositions in the system CMS₂-MS, obtained from mean values at 1105–1355°C.

Table 3. Quenching Experiments for the System C₃P-MS. $\alpha = \alpha\text{-C}_3\text{P}$, $\beta = \beta\text{-C}_3\text{P}$, d=diopside (CMS₂), pi=pigeonite (C_{0.09}M_{0.91}S), pr=protoenstatite (MS), cr=cristobalite, tr=tridymite, f=forsterite, L=liquid. Order in Phases Present is According to Amounts of Them

No. C ₃ P-MS wt. % (mol %)	Holding temp. time °C h	Phases present	No. C ₃ P-MS wt. % (mol %)	Holding temp. time °C h	Phases present
490 98.3-1.7	1555 0.66	α, L	476 45 - 55	1325 1	L
	1505 0.33	α, d, L		1295 1	L
(95-5)	1405 1	α, β, d	(20.9-79.1)	1285 3	L
	1305 1	β, α, d		1275 1	d, L
	1205 3	β, d		1255 1	d, L
	1105 14	β, d		1245 1	d
491 96.5-3.5	1555 0.66	α, d, L		1225 2	β, pi
	1505 0.66	α, d, L		1205 2	β, pi, pr
(90-10)	1405 1	α, β, d, L		1175 17	β, pi, d
	1305 1	β, d	496 42.5-57.5	1305 2	L
	1205 2.5	β, d		1295 2	d, pi, L
	1105 12.5	β, d	(19.3-80.7)	1275 2	d, pi, L
492 94.6-5.4	1555 0.66	α, L		1255 2	β, d, pr, L
	1505 0.83	α, d, L		1255 16	pi, β, d, L
(85-15)	1405 2	β, α, d, L		1245 3	β, d
	1305 1	β, d		1235 3	β, d, pi
	1205 3	β, d		1175 24	β, d, pi
	1105 9	β, d	468 40 - 60	1315 2	L
493 92.5-7.5	1600 0.5	α, β, L		1305 1.2	pi, L
	1555 0.66	α, L	(17.5-82.5)	1295 1	pi, d, L
(80-20)	1505 0.83	α, d, L		1275 1	d, pi, L
	1405 1	β, d, L		1245 1	d, pi
	1305 1	β, d		1205 2.5	β, pi
	1205 3	β, d		1155 15	β, pi
	1105 15	β, d		1105 15	pi, β
494 87.8-12.2	21550 0.5	α, L	455 35.3-64.7	1345 1	L
	1505 0.83	α, L		1335 1	pi, pr, L
(70-30)	1405 1	β, L	(15-85)	1325 1	pi, pr, L
	1305 1	β, L		1295 1	pi, pr, L
	1205 3	β, d		1275 3	pi, pr, L
	1105 16	β, d		1255 1	pi, d, L
483 80 - 20	1465 0.83	L		1235 1	pi, β, cr
(56.4-43.6)	1425 0.5	β, d, L		1205 7.5	pi, β, cr
	1355 2	β, d, L		1205 15	pi, β, cr
	1305 1	β, d, L		1155 21	pi, β, cr
	1295 2	β, d, L	456 25.6-74.4	1405 1	L
	1295 2	β, d, L		1385 1	pi, L
	1245 2	β, d, L	(10-90)	1355 1	pi, pr, L
	1205 2.5	β		1305 1	pi, pr, L
	1155 8	β, d		1265 1	pi, pr, cr, L
482 70 - 30	1365 1.2	L		1265 1	pi, pr, cr, L
	1325 1.5	β, L		1245 2	pi, pr, d
(43-57)	1305 0.8	β, L		1225 4	pi, β, pr, Cr
	1285 1	β, d, L		1205 21	pi, β, pr
	1245 2	β, d, L		1155 45	cr, pi, β, pr
	1205 13	β, d	457 14 - 86	1450 1	L
	1155 8	β, d		1425 0.6	pi, L
	1155 15	β, d	(5-95)	1405 1	pi, pr, L
478 60 - 40	1325 1	L		1355 1	pi, pr, L
(32.7-67.3)	1315 1	L		1305 1	pi, pr, L
	1295 1	β, L		1265 2	pi, pr, cr
	1295 1	β, L		1255 1	pi, pr, cr
	1265 1	β, d, L		1245 15	pi, pr, cr
	1205 2	β, d		1225 4	pi, β, pr, cr
	1185 15	β, d		1205 19	pi, pr, β
	1155 15	β, d, pi		1155 54	pi, β, pr
495 55 - 45	1305 1.5	L	467 6 - 94	1500 1	pi, pr, L
	1280 2	β, d, L		1405 1	pi, pr
(28.3-71.7)	1265 2.5	d, β	(2-98)	1355 1.5	pi, pr, cr
	1245 3	β, d		1275 1.5	pi, pr, L
	1235 6	β, d		1245 2	pi, pr, cr
	1215 41	β, d		1205 2	pi, pr
	1195 23	β, d		1155 3	pi, pr
562 52 - 48	1255 1.5	d, β, L		1105 15	pi, pr
	1235 1.5	β, d	481 2 - 98	1575 0.33	L
(26-74)	1225 1.5	β, d		1555 0.83	pi, pr, L
477 50 - 50	1285 1	L	(0.7-99.3)	1405 1	pi, pr, cr
	1275 1	L		1305 2	pi, pr, cr
(24.5-75.5)	1265 1	d, β, L		1205 1.2	pr, pi
	1255 2	d, β, L		1205 2	pi, pr
	1245 1	d, β		1155 3	pi, pr, cr
	1155 16	β, d, pi		1105 15	pi, pr, cr
485 47.5-52.5	1275 1	L	484 1 - 99	1575 0.33	L
	1265 1	d, L		1555 0.33	pi, pr, L
(22.6-77.4)	1255 1	d, L	(0.3-99.7)	1505 0.33	pi, pr, L
	1245 1	β, d, L		1455 1	pr, f, cr
	1245 1.5	d		1305 1	pi, pr, cr
	1235 1.5	β, d		1205 4	pi, pr, cr
	1235 1	β, d, pi		1105 15	pi, pr, cr
	1205 1	β, d, pi	550 0-100	1585 0.33	L
				1555 0.5	pi, pr, f
				1505 0.66	pr, pi, f
				1455 1	pr, f, cr

Fig. 3. Phase diagram in the system $\text{C}_3\text{P-MS}$. All the dotted lines are those estimated.

This phosphate is whitrockite with same type as pure $\beta\text{-C}_3\text{P}$. From peak intensity ratios of (034) at 30.7° of 2θ for $\alpha\text{-C}_3\text{P}$ against (0210) at 31.1° of 2θ for $\beta\text{-C}_3\text{P}$, contents of both types were roughly determined as shown in Fig. 4(a). Alpha- C_3P disappears above 8 mol% of MS at 1300°C and above 17 mol% at 1400°C . All the d -values for $\beta\text{-C}_3\text{P}$ decrease with

Fig. 4. (a) Amount of $\alpha\text{-C}_3\text{P}$ at 1305 and 1405°C in the C_3P side.

(b) change in mean d -values for $\beta\text{-C}_3\text{P}$ widely formed in the system $\text{C}_3\text{P-MS}$ in the temperature range $1155\text{--}1425^\circ\text{C}$.

(c)–(e) change in mean d -values for d, pi and pr in the MS side of the system $\text{C}_3\text{P-MS}$ in the temperature range $1155\text{--}1425^\circ\text{C}$.

additions of MS to 42 mol% (20 mass%) accompanying a small break at 10–15 mol% till which $\alpha\text{-C}_3\text{P}$ coexists with $\beta\text{-C}_3\text{P}$. And then smaller variation (increase or decrease) is seen up to about 90 mol% of MS, as shown in Fig. 4(b). The decrease in d -value for $\beta\text{-C}_3\text{P}$ up to 42 mol% is due to the formation of solid solution with increasing MgO. These decreases occur by substitution of Mg-ion to Ca-ion site in $\beta\text{-C}_3\text{P}$. Smaller variations up to about 85 mol% MS are seen in the composition range of coexistence with pigeonite.

A reason of the coexistence of diopside in the system $\text{C}_3\text{P-MS}$ is discussed here. As mentioned above, $\beta\text{-C}_3\text{P}$ dissolves MgO component of about 10–15 mol% in maximum to form whitrockite. Thus it is thought that removed CaO reacts with MS component to form diopside. Assuming maximum solubilities of 10, 15 and 20 mol% of MgO against CaO in C_3P (x in $\text{C}_{3-x}\text{M}_x\text{P}$ = 0.3, 0.45 and 0.6, respectively), moles of formed CMS_2 and solid solution of $\text{CMS}_2\text{-MS}$ were calculated as listed in Table 4.

In $\text{C}_3\text{P-MS}$ compositions of 9–1, 8–2 and 7–3 mol, $\text{C}_{3-x}\text{M}_x\text{P}$ ($x=0\text{--}0.3$) first forms by dissolving MgO from MS, and then liberated CaO reacted with MS to form diopside. In 6–4–3–7 compositions, saturated whitrockite $\text{C}_{2.7}\text{M}_{0.3}\text{P}$ first forms and then phases in the system $\text{CMS}_2\text{-MS}$ forms. In 2–8–0.2–9.8 compositions pigeonite forms with saturated whitrockite. These above calculations for $x=0.3$ agree well with

Table 4. Calculations for Formations of Mg-Containing Tricalcium Phosphate $\text{Ca}_{3-x}\text{Mg}_x(\text{PO}_4)_2 = \text{C}_{3-x}\text{M}_x\text{P}$ and Diopside-Enstatite (d-e, mol %) Solid Solution.

(A) Constant d -Spacing for CMS_2 , (B) Formation of d-e Solid Solution, (C) Pigeonite Formation

C ₃ P-MS mol	Composition of solid solutions			
	x=0.3	x=0.45	x=0.6	
9-1	C _{2.94} M _{0.06} P 9 d 0.5	same as the left	same as the left	(A)
8-2	C _{2.87} M _{0.13} P 8 d 1	same as the left	same as the left	
7-3	C _{2.79} M _{0.21} P 7 d 1.5	same as the left	same as the left	
6-4	C _{2.7} M _{0.3} P 6 d-e (82-18) 2.2 or d 2.0	C _{2.67} M _{0.33} P 6 d 2	same as the left	(B)
5-5	C _{2.7} M _{0.3} P 5 d-e (43-57) 3.5	C _{2.55} M _{0.45} P 5 d-e (82-18) 2.75	C _{2.5} M _{0.5} P 5 d 2.5	
4-6	C _{2.7} M _{0.3} P 4 d-e (25-75) 4.8	C _{2.55} M _{0.45} P 4 d-e (43-57) 4.2	C _{2.4} M _{0.6} P 4 d-e (67-33) 3.6	
3-7	C _{2.7} M _{0.3} P 3 d-e (15-81) 6.1	C _{2.55} M _{0.45} P 3 d-e (24-76) 5.	C _{2.4} M _{0.6} P 3 d-e (35-65) 5.2	(C)
2-8	C _{2.7} M _{0.3} P 2 d-e (8-92) 7.4	C _{2.55} M _{0.45} P 2 d-e (13-87) 7.1	C _{2.4} M _{0.6} P 2 d-e (18-82) 6.8	
1-9	C _{2.7} M _{0.3} P 1 d-e (3.6-96.4) 8.7	C _{2.55} M _{0.45} P 1 d-e (5.3-94.7) 8.6	C _{2.4} M _{0.6} P 1 d-e (7-93) 8.4	
0.5-9.5	C _{2.7} M _{0.3} P 0.5 d-e (1.6-98.4) 9.35	C _{2.55} M _{0.45} P 0.5 d-e (2.4-97.6) 9.27	C _{2.4} M _{0.6} P 0.25 d-e (3.3-96.7) 9.2	(C)
0.2-9.8	C _{2.7} M _{0.3} P 0.25 d-e (0.8-99.2) 9.68	C _{2.55} M _{0.45} P 0.25 d-e (1.2-98.8) 9.64	C _{2.4} M _{0.6} P 0.25 d-e (1.6-98.4) 9.60	

the results of the phase diagram as shown in Fig. 3. The calculations as $x=0.45$ and 0.6 did not agree to the experimental results.

The decrease in d -spacing of β -C₃P up to 40 mol% MS (Fig. 4(b)) is due to a dissolution of MgO in β -C₃P up to the 7-3 or 6-4 composition. Over 40 mol% MS, β -C₃P has a constant content of MgO, and CMS_2 content in the CMS_2 -MS solid solution decreases accompanying decrease in d -value (Fig. 4(c)). Above 80 mol% MS, CMS_2 content becomes less than 10 mol% in the CMS_2 -MS system and pi begins to form as a major phase. The d -value of pi decreases with increasing MS contents and increasing MgO content in pi (Fig. 4(d)). The d -value for pr shows only a little increase to the MS-side (Fig. 4(e)).

In these results, there remains obscure facts. First is that α' -C₃P phase was not determined by this quenching experiment. The highest temperature form α' -C₃P had been detected only by the high-temperature XRD.¹²⁾ Accordingly the phase relation for the C₃P side at the highest temperature region was only assumed. Secondly is the easy appearance of diopside (d) even up to 1420°C, and wide coexistence with β -C₃P plus liquid. It might be due to an impossible quenching of the liquid. Thirdly is a problem in the MS side. Cristobalite appeared at 65 mass% MS below 1235°C, 94% below 1355°C, 98% below 1405°C, 99% below 1455°C and 100% below 1455°C.

Pigeonite also appeared even in the heated pure MS. These results are thought from a non-equilibrium reason for the MS-rich side. Forsterite formed by the decomposition of pure MS above 1550°C. Whereas, in 99 mass% MS composition and even in pure MS, pi already appears in coexistence with pr. pi appears in a wide composition range more than 40 mass% MS above 1100°C.

4. Conclusion

The transition temperature from β - to α -type of $3\text{CaO} \cdot \text{P}_2\text{O}_5$ (C₃P) and phase relation in the system $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ - $\text{MgO} \cdot \text{SiO}_2$ (CMS_2 -MS) were re-examined in the temperature range 1100 to 1600°C and a consistence with published results was mostly confirmed. In the system C₃P-MS, both pyroxene compounds of diopside and pigeonite widely occurred as respective solid solution. C₃P takes β -type whitlockite due to dissolution of MgO, and its transition temperature of β to α rises with MgO contents. MS appears as pigeonite taking CaO. Major primary crystals are β -C₃P in the C₃P side and pigeonite in the MS-side. Minimum liquidus temperature is 1265°C where primary crystals are β -C₃P and diopside, and the diopside primary crystal appears in a narrow composition range (43-49 mass% MS). Under the liquidus curve, β -C₃P coexist with diopside as a non-equilibrium phase in the C₃P-side. Above 1245°C where no β -C₃P appears, diopside-pigeonite mixture and pigeonite-protoenstatite mixture exist with liquid. Below the solidus at 1245°C, the liquid disappears and β -C₃P remains accompanying with pigeonite and protoenstatite in a wide region up to 90% MS. As seen from the phase diagram, this C₃P-MS system is not perfect binary, having complex distribution of the phases, and accompanying both transitions of C₃P and MS and both solid solution formations of C₃P-M and CMS_2 -MS. This system should be understood from view points of the ternary system C₃P-M-S and the quaternary system C₃P- CMS_2 -MS-S.

References

- 1) J. H. Welch and W. Gutt, *J. Chem. Soc.*, **874**, 4442-44 (1961).
- 2) G. Tromel, *Stahl und Eisen*, **63**, 21-30 (1943).
- 3) G. Tromel, H. J. Harkort and W. Hotop, *Z. Anorg. Chem.*, **256**, 253-72 (1948).
- 4) W. L. Hill, G. T. Faust and D. S. Reynolds, *Am. J. Sci.*, **242**, 470-72 (1944).
- 5) W. L. Hill, G. T. Faust and D. S. Reynolds, *Am. J. Sci.*, **242**, 473-77 (1944).
- 6) Nat. Bur. Standards, "Phase Diagrams for Ceramists", Ed. by Am. Ceram. Soc. (1964).
- 7) T. Sata, *Bull. Chem. Soc., Japan*, **31**, 408-12 (1958).
- 8) F. R. Boyd and J. P. Schairer, *J. Petrol.*, **5**, 275-309 (1964).
- 9) H.-Y. Yang and W. R. Foster, *Am. Mineral.*, **57**, 1232-41 (1972).
- 10) I. Kushiro, *Am. Mineral.*, **57**, 1260-71 (1972).
- 11) H.-Y. Yang, *Am. J. Sci.*, **273**, 488-97 (1973).
- 12) R. G. Schwab and M. Schwerin, *Neues Jahrb. Mineral Abh.*, **124** [3] 223-45 (1975).

- 13) R. Kiyoura and T. Sata, *Kogyo-Kagaku-Zasshi*, **54**, 756–58 (1951).
- 14) R. Kiyoura and T. Sata, *Kogyo-Kagaku-Zasshi*, **56**, 666–69 (1953).
- 15) R. Kiyoura and T. Sata, *Kogyo-Kagaku-Zasshi*, **56**, 748–50 (1953).
- 16) T. Sata and R. Kiyoura, *Kogyo-Kagaku-Zasshi*, **62**, 63–64 (1959).
- 17) T. Sata and R. Kiyoura, *Kogyo-Kagaku-Zasshi*, **62**, 65–67 (1959).
- 18) R. Kiyoura and T. Sata, *Yogyo-Kyokai-Shi*, **59**, 530–32 (1951).
- 19) R. Kiyoura and T. Sata, *Yogyo-Kyokai-Shi*, **62**, 121–22 (1954).
- 20) JCPDS-International Centre for Diffraction Data, Powder Diffraction File, Set 1–36, 1974–90.
- 21) R. W. Nurse, J. H. Welch and W. Gutt, *J. Chem. Soc.*, **1959**, 1077–83 (1959).
- 22) W. Fix, H. Heymann and R. Heinke, *J. Am. Ceram. Soc.*, **52**, 346–47 (1969).
- 23) N. L. Bowen, *Am. J. Sci.*, 4th Ser., **38**, 207–64 (1914).
- 24) L. Atlas, *J. Geol.*, **60**, 140–47 (1952).
- 25) H. Kuno and H. H. Hess, *Am. J. Sci.*, **251**, 741–52 (1953).
- 26) H. H. Hess, *Am. Mineral.*, **34**, 621–66 (1949).