Phase Relationship in System $3CaO \cdot P_2O_5$-MgO-SiO_2

By Toshiyuki SATA

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The author already presented in 1958 the result of a study on system $3CaO \cdot P_2O_5$–$MgO \cdot SiO_2$–SiO_2 in this Bulletin[1]. This is a partial system at high silica portion in the three-component system $3CaO \cdot P_2O_5$–MgO–SiO_2. The present report concerns a basic portion in the system $3CaO \cdot P_2O_5$–MgO–SiO_2, and its phase relationships are important for the study of a composition of fused phosphate fertilizer[2] and a corrosion problem of magnesia-containing basic refractories against the molten fertilizer. This report consists of four parts; system $3CaO \cdot P_2O_5$–MgO, system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$, system $3CaO \cdot P_2O_5$–MgO–$2MgO \cdot SiO_2$, and the synthesis of these to system $3CaO \cdot P_2O_5$–MgO–SiO_2. Phase equilibria studies in these systems have never been published in any paper.

Experimental

Tricalcium phosphate ($3CaO \cdot P_2O_5$), forsterite ($2MgO \cdot SiO_2$), and magnesia (MgO) were used as raw materials. The first was prepared by the reaction of calcium carbonate with phosphoric acid at 1350°C as mentioned in the previous paper[1]. The second was prepared by calcining the stoichiometric mixture of magnesia and silica constituents at 1300°C. The magnesia and silica fired from 1200 to 1300°C were used as raw materials respectively. After weighing, the batches were thoroughly mixed in an agate mortar with some methyl alcohol until they became dry. They were heated in a platinum crucible or in a platinum envelope above their melting points. Then they were rapidly cooled in air or water. For batches having the melting point above 1600°C, perfect glassification was impossible. These mixing, heating, and quenching processes were repeated once more.

The silicon carbide resister furnace with an inner diameter of 25 mm. was used for this study. The sample in a platinum envelope (8×8 mm.) was suspended by a platinum wire (0.5 mm. in diameter, 200 mm. in length) at the center of the furnace tube, and quenched together with the wire in water after holding for some minutes at constant temperature (±1°C). For measuring the temperature, two kinds of thermocouples (Pt-PtRh 10% and PtRh 5%-PtRh 20%) were used. These were calibrated with the melting point of silver, copper, diopside, and palladium.

The quenched samples were powdered and examined by a polarizing microscope and by an X-ray diffractometer. Pure silicon metal was used as a standard material in X-ray examination, its accuracy being ±0.003 Å

Results and Discussion

System $3CaO \cdot P_2O_5$–MgO. — In the first place, specimens slowly cooled from 1650°C were examined in their microstructure. The specimen containing 3.20% of MgO consisted of a primary crystal part of β-tricalcium phosphate and an eutectic part which is a turbid phase containing periclase spots surrounded by tricalcium phosphate matrix. The specimen containing 5.28% of MgO revealed the eutectic structure only. The specimen containing 7.98% of MgO consisted of the eutectic part and large periclase grains. The softening temperatures of small cones of these three compositions were measured on platinum plates in the usual way. It was found that their temperatures decreased in order of contents of MgO ranging from 1620 to 1530°C.

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[1] T. Sata, This Bulletin, 31, 408 (1958).

[2] T. Sata and R. Kiyoura, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 62, 63 (1959).

TABLE I. QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$–MgO

No.	Composition			Holding		Phases present
	C_3P wt. %	MgO wt. %	MgO mol. %	temp. °C	time min.	
193	99	1.0	7.2	1470	60	β-C_3P, α-C_3P
19	98.58	1.42	10.0	1450	60	β-C_3P
20	96.8	3.2	20.0	1568	15	β-C_3P, small α-C_3P, periclase, glass
				1450	60	β-C_3P, periclase
21	94.7	5.3	30.0	1568	15	β-C_3P, periclase
22	92.1	7.9	40.0	1568	15	β-C_3P, periclase
				1555	10	〃
				1524	10	〃

The subsequent quenching runs, as listed in Table I, indicated that the specimen containing 3.20% of MgO, quenched from 1568°C, consisted of tricalcium phosphate (β and small amount of α), periclase, and glass. It is estimated from these results that this $3CaO \cdot P_2O_5$–MgO system is a binary one and its eutectic occurred at a composition of 4~7% of MgO and at a temperature near 1570±20°C, as shown in Fig. 1.

It is noted from Fig. 2, in which some X-ray diffraction lines of β-tricalcium phosphate quenched from 1450°C are plotted, that 15±3 mol. % of MgO is apparently dissolved into β-tricalcium phosphate as a solid solution. Another fact is that the transition temperature of β-α modification is considerably elevated nearly to 1550°C with increasing magnesia contents. These facts concerning tricalcium phosphate are difficult to discuss further without direct examination by a high-temperature X-ray technique. There is a new presentation of super α-$3CaO \cdot P_2O_5$ phase by Nurse et al.[3]

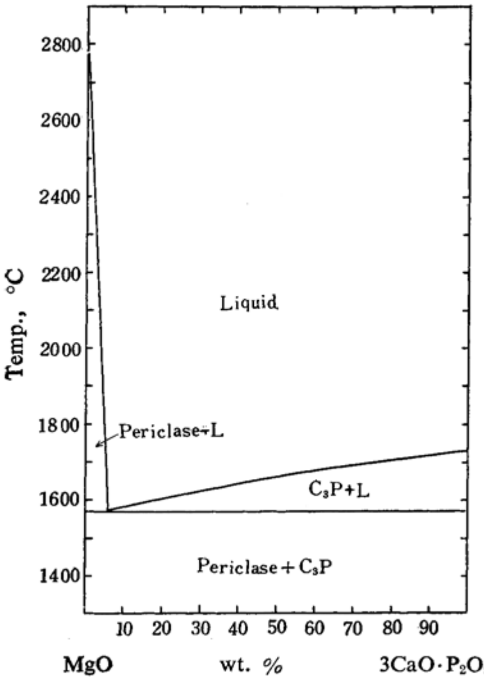

Fig. 1. The system $3CaO \cdot P_2O_5$–MgO.

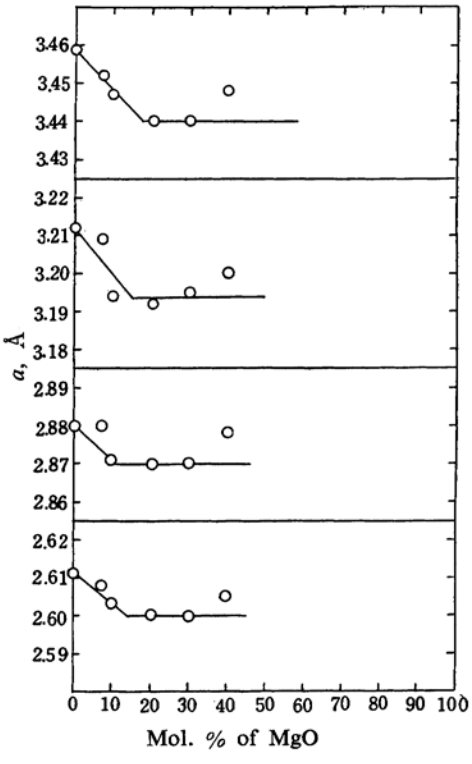

Fig. 2. The change in spacings of β-tricalcium phosphate at 1450°C in the system $3CaO \cdot P_2O_5$–MgO.

System $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$. — Fasting and Haroldsen[4] have made X-ray tests of specimens in this system fired at 1000~1500°C, and Bobrownicki and Swiecki[5] have measured

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[3] R. W. Nurse, J. H. Welch and W. Gutt, *J. Chem. Soc.*, 1959, 1077.

[4] J. P. Fasting and H. Haroldsen, *Tid. Kjemi., Bergvesen Met.*, 3, 48 (1943); *Chem. Abstr.*, 39, 13419 (1945).

[5] W. Bobrownicki and Z. Swiecki, *Bull. Acad. Polon. Sci., Classe* III, 3, 232 (1955); *Chem. Abstr.*, 49, 15419 (1955).

TABLE II. QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$

No.	Composition		Holding		Phases present
	C_3P wt. %	M_2S wt. %	temp. °C	time min.	
191	98	2	1342	60	β-C_3P only
75	95	5	1370	60	β-C_3P, gl.
			1340	40	β-C_3P
			1290	120	β-C_3P
			1242	180	β-C_3P, faint forst.
192	93	7	1342	60	β-C_3P only
71	90	10	1517	30	α-C_3P, β-C_3P, gl.
			1467	60	α-C_3P, β-C_3P, gl.
			1442	50	β-C_3P, α-C_3P, gl.
			1392	60	β-C_3P, gl.
			1372	540	β-C_3P, gl.
			1340	40	β-C_3P
			1312	40	β-C_3P
			1290	40	β-C_3P, forst.
70	80	20	1545	20	Ng., gl.
			1442	20	Ng., gl.
			1392	60	Ng., β-C_3P, gl.
			1372	60	β-C_3P, Ng., gl.
			1357	40	β-C_3P, gl.
			1352	300	β-C_3P, forst., small gl.
			1342	60	β-C_3P, forst.
72	75	25	1575	15	gl.
			1566	15	Ng., gl.
			1515	15	Ng., gl.
			1374	40	β-C_3P, Ng., gl.
			1352	40	β-C_3P, forst.
73	72.5	27.5	1548	15	Ng., gl.
			1528	15	Ng., gl.
			1442	60	Ng., gl.
			1382	40	β-C_3P, Ng., gl.
			1372	40	β-C_3P, Ng., forst., gl.
			1365	50	β-C_3P, forst., small gl.
			1352	40	β-C_3P, forst.
66	70	30	1398	40	gl.
			1392	40	β-C_3P, Ng., faint forst., gl.
			1372	40	β-C_3P, Ng., forst., gl.
			1347	40	β-C_3P, forst.
74	67.5	32.5	1432	60	gl.
			1407	50	β-C_3P, small forst., gl.
			1374	40	β-C_3P, forst.
67	60	40	1465	40	gl.
			1458	20	forst. gl.
			1452	40	Ng., forst., gl.
			1400	60	Ng., small forst.
			1382	50	Ng., forst.
			1342	60	β-C_3P, forst.
			1300	60	β-C_3P, forst.
68	50	50	1537	20	gl.
			1522	20	forst., gl.
			1507	20	forst., gl.
			1442	60	Ng., forst., gl.
69	40	60	1442	60	Ng., forst., gl.

Abbreviations: $C_3P = 3CaO \cdot P_2O_5$, $M_2S = 2MgO \cdot SiO_2$, Ng. = nagelschmidtite forst. = forsterite, gl. = glass.

the softening points of this system. But the phase relationships of this system have not been presented.

Results of the quenching runs of this two-component system are summarized in Table II, from which a preliminary phase diagram of this system was obtained as shown in Fig. 3. Nagelschmidtite[6] (which was identified by a hexagonal X-ray pattern similar to that in $3CaO \cdot P_2O_5$–$2CaO \cdot SiO_2$ system) appeared over a wide range of this system above a temperature of 1350°C, and was crystallized primarily in the composition range of $3CaO \cdot P_2O_5$ side.

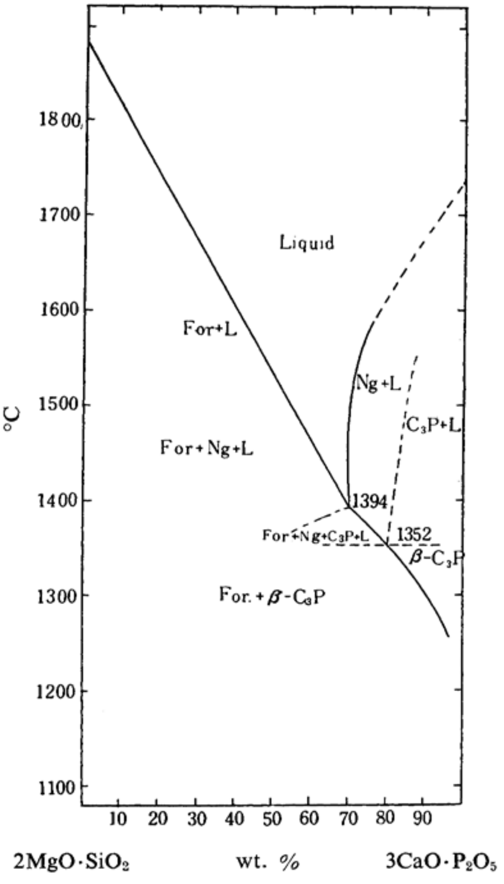

Fig. 3. The system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$.

The liquidus line falls very steeply to a temperature minimum at 1394°C and a composition of 70% $3CaO \cdot P_2O_5$ and 30% $2MgO \cdot SiO_2$. Below this temperature 1394°C, the secondary crystallization temperature of forsterite from nagelschmidtite and liquid decreases. Below 1352°C, nagelschmidtite and liquid disappeared, and forsterite and β-tricalcium phosphate phase only appeared. The meaning of this disappearance temperature 1352°C is not clear now. β-Tricalcium phosphate seems to contain magnesia component, judging from the fact that the crystallization temperature of forsterite from β-tricalcium phosphate phase descends with increasing contents of $3CaO \cdot P_2O_5$, and *d*-spacings of β-tricalcium phosphates in their X-ray patterns decrease till the content of 15 mol. % (7.4 weight %) of $2MgO \cdot SiO_2$ is attained, as shown in Fig. 4. Below about 1200°C, this two-component system is a binary one consisting of forsterite and β-tricalcium phosphate.

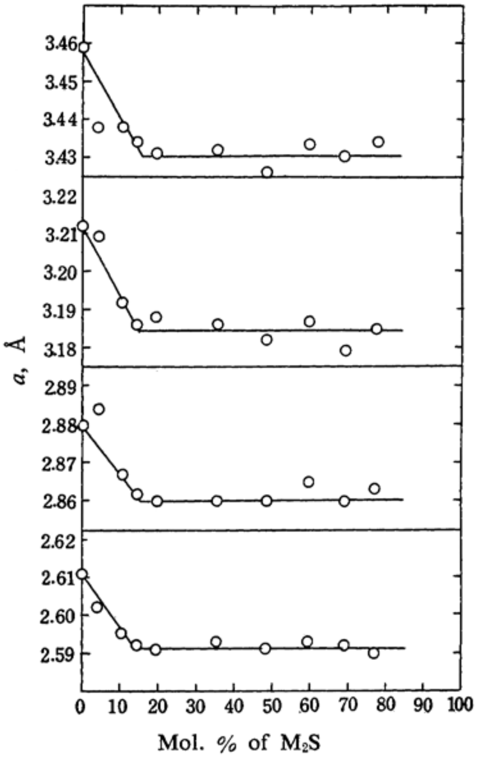

Fig. 4. The change in spacings of β-tricalcium phosphate in the system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$.

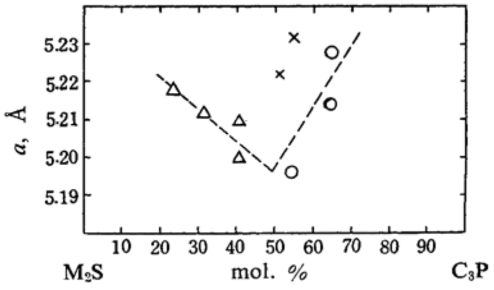

Fig. 5. The change in lattice constants of nagelschmidtite in the system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$ at 1370∼1490°C.
○ Ng.+L, △ Ng.+forst.+L,
× Ng.+β-C_3P+L

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[6] G. Nagelschmidt, *J. Chem. Soc.*, **1937**, 865.

When the lattice constants *a* of hexagonal negelschmidtite are calculated from their (110) peak and plotted against molar compositions, a valley-type change are obtained, whose bottom may occur at the composition of temperature minimum of liquidus as shown in Fig. 5.

From the results mentioned above, this system was found to be complex, owing to the formation of nagelschmidtite above 1350°C, below which it is considered to be binary.

System $3CaO \cdot P_2O_5$ – MgO – $2MgO \cdot SiO_2$. — Although all of the specimens of this system slow-cooled to room temperature consisted of β-tricalcium phosphate, periclase, and forsterite, the primary crystal in the area of high content of $3CaO \cdot P_2O_5$ was nagelschmidtite, being the same as that mentioned in the system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$. But it was found by the preliminary quenching test that a ternary eutectic among their three components seems to be present. This paragraph described results of quenching experiments made to decide the position of a three-component eutectic.

The twelve compositions, which are expected to locate near the eutectic, were taken on the two tie lines connecting No. 24 ($60C_3P$–40M) with No. 72 ($75C_3P$–$25M_2S$) and No. 74 ($67.5C_3P$–$32.5M_2S$) along the C_3P–M_2S join, as represented in Fig. 6. Results obtained are listed in Table III, from which a eutectic position was graphically decided to locate at the composition of 70% $3CaO \cdot P_2O_5$, 21% MgO and 9% SiO_2, and at 1362±5°C.

This eutectic temperature is close to the transition point between nagelschmidtite and β-tricalcium phosphate. It was, however, found that β-tricalcium phosphate was present at this eutectic temperature. The primary field of nagelschmidtite was approximately estimated as a dotted boundary from the previous results of the investigation in the systems C_3P–MS and C_3P–M_2S. The facts that a small amount of periclase was present even in the specimens quenched above liquidus temperatures of all compositions, and that nagelschmidtite was present even in the primary field of periclase or forsterite above eutectic

TABLE III. QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$–MgO–$2MgO \cdot SiO_2$

No.	Composition					Holding		Phases present (peri. = periclase)
	wt. %		C_3P	M wt. %	S	temp. °C	time min.	
	No. 74	No. 24						
78	95	5	67.1	19.7	13.2	1442	60	gl. (faint peri.)
						1407	40	small forst., peri., gl.
						1364	60	β-C_3P, forst., peri.
80	90	10	66.8	20.7	12.5	1442	60	small peri., gl.
						1412	50	small forst., gl.
						1392	50	β-C_3P, forst., gl.
81	85	15	66.4	21.8	11.8	1407	50	small peri., gl.
						1382	50	β-C_3P, small forst., gl.
82	80	20	66.0	22.9	11.1	1422	40	gl.
						1392	60	peri., gl.
						1382	50	β-C_3P, forst., gl.
83	75	25	65.6	24.0	10.4	1390	50	peri., gl.
						1382	50	β-C_3P, forst., peri., gl.
101	65	35	64.9	26.1	9.0	1382	40	peri., gl.
						1372	40	peri., β-C_3P, forst.
102	55	45	64.2	28.2	7.6	1365	20	peri., gl.
						1356	60	peri., β-C_3P, forst.
103	45	55	63.3	30.4	6.3	1375	40	peri., gl.
						1356	40	β-C_3P, forst., peri.
104	35	65	62.6	32.5	4.9	1356	50	β-C_3P, forst., peri.
	No. 72	No. 24						
151	90	10	73.5	16.9	9.6	1372	60	peri., gl.
152	80	20	72.0	19.5	8.5	1398	40	Ng., peri., gl.
						1372	50	Ng., peri., gl.
						1369	40	β-C_3P, peri., forst., gl.
						1364	25	no gl.
153	70	30	70.5	22.0	7.5	1372	60	peri., Ng., gl.
						1364	40	peri., β-C_3P, forst., gl.

temperature, were neglected in drawing this phase diagram at the step of this study, Detailed studies of the system containing nagelschmidtite will be made in future, because of the interesting scope of nagelschmidtite structure (super α-tricalcium phosphate by Nurse or its solid solution containing MgO and SiO_2).

System $3CaO \cdot P_2O_5$–MgO–SiO_2. — The preliminary phase diagram, as shown in Fig. 6, was obtained from the results of previous paragraphs and the separate report of the system $3CaO \cdot P_2O_5$–$MgO \cdot SiO_2$–SiO_2[1]. The probable boundary curve between the phosphate and the forsterite fields in the $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$–$MgO \cdot SiO_2$ triangle was drawn from the results without a cooling experiment.

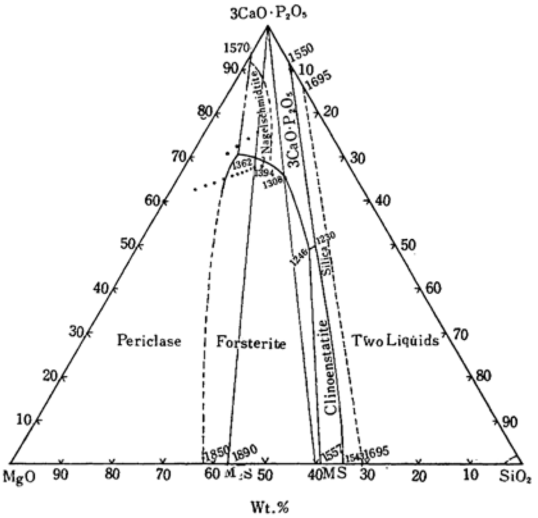

Fig. 6. The system $3CaO \cdot P_2O_5$–MgO–SiO_2.

Summary

The phase relationship in the system $3CaO \cdot P_2O_5$–MgO–SiO_2 was investigated by a cooling experiment in the usual manner. The system $3CaO \cdot P_2O_5$–MgO, a side of this triangle, is a simple binary one, its eutectic being located at the composition of 4∼7% by weight of magnesia and 1570±20°C. The system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$ is not binary over the temperature of about 1350°C, below which it is considered as binary. Above 1350°C, nagelschmidtite is formed over the whole composition range and crystallized primarily from liquid at a high $3CaO \cdot P_2O_5$ portion. The minimum liquidus temperature is 1394°C, which is located at the composition of 70% C_3P and 30% M_2S. The system $3CaO \cdot P_2O_5$–MgO–$2MgO \cdot SiO_2$ was considered to be complex owing to the presence of nagelschmidtite, but the eutectic among their three components is located at the composition of 70% $3CaO \cdot P_2O_5$, 21% MgO, and 9% SiO_2, and 1362±5°C.

From the results described above and from those of the author's previous reports, the preliminary phase diagram of the system $3CaO \cdot P_2O_5$–MgO–SiO_2 was constructed. In this diagram the problem that nagelschmidtite is formed in the composition range which is rich in $3CaO \cdot P_2O_5$ was not mentioned in detail. In addition to this, it was found by X-ray examination that β-tricalcium phosphate may be apparently stabilized at a higher temperature than β-α transition point, and has the appearance of dissolving magnesia component.

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Research Laboratory of Engineering Materials
Tokyo Institute of Technology
Meguro-ku, Tokyo