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

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(Received November 11, 1957)

The ternary system $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$—SiO_2 is of great importance in considering the compositions of the calcium-magnesium phosphatic fertilizer (or fused phosphatic fertilizer), and of bone ash magnesia porcelain. The author studied this equilibrium as a partial system of the ternary system $3CaO\cdot P_2O_5$—MgO—SiO_2. The equilibrium phase diagrams in this system have never before been presented.

Kiyoura and Sata[1,2] presented in 1953 the softening and melting diagrams of the system phosphate rocks-dunite-quartzite, and showed the most suitable composition for the fused phosphatic fertilizer as the one with the lowest softening and melting temperature regions in these diagrams. This equilibrium study is an extension of these investigations.

Experimental Procedure

Batches of selected compositions in the system $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$—SiO_2 were held at constant temperatures and quenched in water. Thenceforth the equilibrium phases found therein were determined by microscopic and X-ray examination.

Tricalcium phosphate ($3CaO\cdot P_2O_5$), magnesium metasilicate ($MgO\cdot SiO_2$) and silica (SiO_2) were used as raw materials. The first was prepared by the reaction of calcium carbonate with phosphoric acid or dicalcium phosphate ($2CaO\cdot P_2O_5$) with calcium carbonate at 1350°C. The second was prepared by calcining the mixture of magnesia and silica at 1300°C. The silica gel fired at 1200°C was used as SiO_2 raw material. After weighing, the batches were thoroughly mixed in an agate mortar with some methyl alcohol until they were dried, and calcined in a platinum crucible at 1200°C. The sample was crushed and mixed again and then heated on a platinum plate at 1200—1500°C, followed by rapid cooling in air.

Two silicon carbide resistor furnaces were used for this equilibrium study, the one with an inner diameter of 40 mm. (up to 1450°C) and the other 25 mm. (up to 1550°C).

The samples in platinum envelopes (8×8 mm.) were suspended by platinum wire (0.5 mm., 200 mm. long) in the center of the furnace and quenched together with this wire in water after being held at a constant temperature (±1°C). A thermocouple of platinum-platinum rhodium (10%) was used, and calibrated against the melting point of silver, copper and diopside.

Quenched samples were powdered and examined by a polarization microscope in the usual way and by X-ray diffractometer. X-ray examinations were carried out adding silicon metal (99.9%) to the samples as the standard material with a scanning speed 2θ 1°/min. The accuracy in reading patterns was decided to be ±0.04° using pure magnesia, quartz and silicon.

Results

The System $3CaO\cdot P_2O_5$—SiO_2.—Three reports have been already published on this system, as listed in Table I.

TABLE I
PREVIOUS RESULTS ON THE SYSTEM $3CaO\cdot P_2O_5$—SiO_2

Investigater	Eutectic temp. °C	Eutectic composition SiO_2 %	Max. solid solubility of SiO_2 in C_3P* %
Trömel[3] (1948)	1540	10	5
Pierre[4] (1956)	1555	6—8	4
Wojciechowska[5] (1956)	1535	7.5	2.5

* Abbreviations used throughout this paper; $C_3P=3CaO\cdot P_2O_5$, $S=SiO_2$, $M=MgO$, $MS=MgO\cdot SiO_2$, $M_2S=2MgO\cdot SiO_2$.

The present experiments were intended to check the above observations, particularly the presence of the solid solution of SiO_2 in α or β modification of $3CaO\cdot P_2O_5$ by X-ray diffraction method. The results are shown in Table II.

These facts probably show the difficulty of the transition from α to β form of tricalcium phosphate in slow cooling and no variance of its transition temperature.

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1) R. Kiyoura and T. Sata, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **54**, 756 (1951).

2) R. Kiyoura and T. Sata, ibid., **56**, 666-8 (1953).

3) G. Trömel, H. J. Harkort and W. Hotop, *Z. anorg. allg. Chem.*, **256**, 253-72 (1948).

4) P. D. S. St Pierre, *J. Amer. Cer. Soc.*, **37**, (6) 243 (1954); **39**, (4) 147 (1956).

5) J. Wojciechowska, J. Berak and W. Trzebiatowskii, *Roczniki Chem.*, **30**, 743-56 (1956); *Chem. Abst.*, **51**, 2373a (1957).

TABLE II

QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$—SiO_2

No.	SiO_2 %	Temp. °C	Time hr.	Condition	Phases present by X-ray exam.		
					α-C_3P	β-C_3P	Cristbalite
185	2	1550	—	slow-cooled	very large	very small	—
		1530	1	quenched	α only	none	—
		1250	5	quenched	large	small	—
		1100	5	quenched	small	large	—
186	5	1550	—	slow-cooled	very large	very small	—
		1530	1	quenched	α only	none	—
		1250	5	quenched	large	small	—
		1200	5	quenched	small	large	—
194	10	1530	1	quenched	large	none	none
		1450	1	slow-cooled	large	none	small
23	40	1530	1	quenched	large	none	large
		1200	—	slow-cooled	large	small	large

TABLE III

QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$

No.	Composition		Holding		Phases present
	C_3P wt. %	MS	Temp. °C	Time min.	
6	75.5	24.5	1407	50	glass
			1317	30	β-C_3P, glass
			1282	60	β-C_3P, M_2S, glass
			1222	60	β-C_3P, M_2S, clinoenstatite
25	67.3	32.7	1337	60	glass
			1326	60	β-C_3P, glass
			1305	60	β-C_3P, M_2S, glass
26	64.0	36.0	1337	60	glass
			1323	60	M_2S, glass
			1260	80	β-C_3P, M_2S, glass
			1244	60	β-C_3P, M_2S, clinoenst.
15	60.7	39.3	1348	60	very small M_2S, glass
			1332	60	M_2S, glass
			1314	60	M_2S, (clinoenst.), glass
			1292	60	β-C_3P, M_2S, (clinoenst.) glass
			1267	60	β-C_3P, M_2S, (clinoenst.) small glass
			1240	50	all crystal
4	50.8	49.2	1407	80	small M_2S, glass
			1287	60	M_2S, glass
			1272	60	small C_3P, M_2S, glass
			1252	60	C_3P, M_2S, small glass
36	47.0	53.0	1274	60	M_2S, glass
			1258	60	C_3P, M_2S, glass
31	43.6	56.4	1289	60	M_2S, glass
			1262	60	β-C_3P, M_2S, glass
			1247	50	β-C_3P, M_2S, clinoenst.

The X-ray diffraction patterns of α and β tricalcium phosphate in fired specimens indicated no change from their original patterns, as given in Fig. 1. Therefore the solid solubility of silica in tricalcium phosphate $3CaO \cdot P_2O_5$ mentioned by preceding authors is thought to be doubtful by these X-ray examinations.

The System $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$.— The quenching runs for this binary system are listed in Table III. Fig. 2 shows the equilibrium diagram obtained from the quenching data. The eutectic of this pseudo-binary system is at 40% $3CaO \cdot P_2O_5$ and 60% $MgO \cdot SiO_2$, and 1246±3°C, these data being obtained in connection with

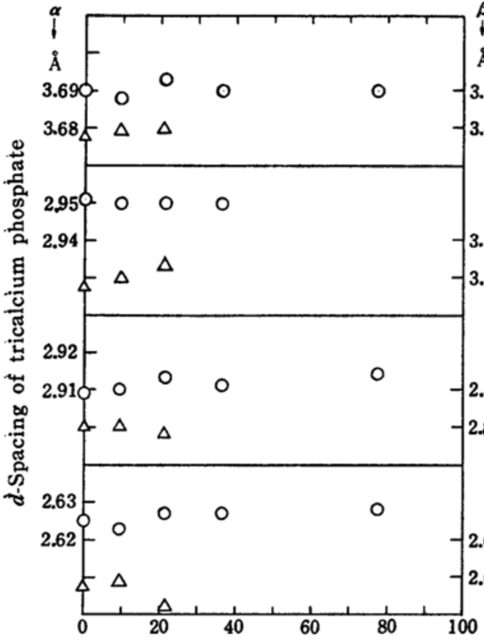

Fig. 1. The change of spacings of tricalcium phosphate.
○; α-$3CaO \cdot P_2O_5$, quenched from 1530°C.
△; β-$3CaO \cdot P_2O_5$, quenched from 1250°C.

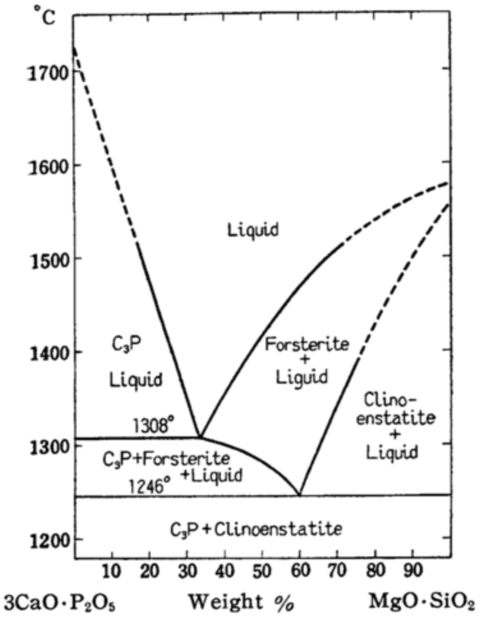

Fig. 2. The system tricalcium phosphate-magnesium metasilicate.

the result of the ternary system $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$—SiO_2. A minimum of the liquidus in the range from $3CaO \cdot P_2O_5$ to $2MgO \cdot SiO_2$ is at 33.5% $MgO \cdot SiO_2$ and at 1308°C.

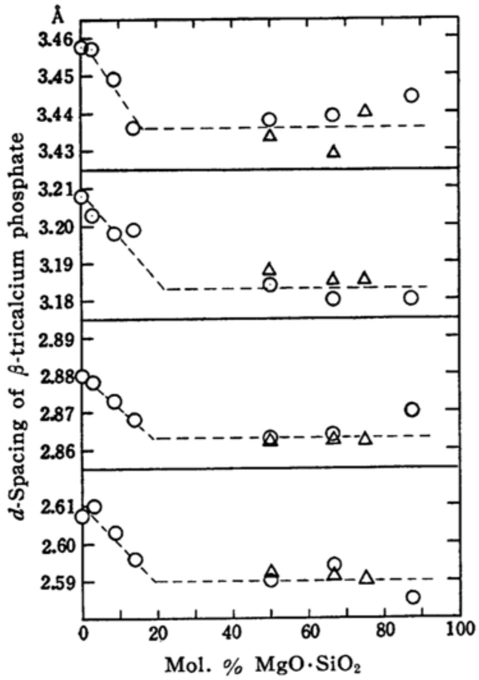

Fig. 3. The change of spacings of β-tricalcium phosphate.
○; quenched from 1250°C.
△; slow-cooled.

The presence of the pyroxene ($MgO \cdot SiO_2$) in quenched sample was chiefly determined by the microscopic examination of the powdered sample, however the X-ray diffraction patterns showed only β-tricalcium phosphate and forsterite, and no pyroxene line was found. It may owe to the difficulty of the equilibrium crystallization of magnesium metasilicate from this system. Only the β-modification, not α, of tricalcium phosphate appeared on X-ray diffraction patterns of all quenched samples at various temperatures, and there was no transition peak on the differential thermal analysis curves up to 1400°C. Thus it is to be concluded that β-tricalcium phosphate seemed to be stabilized at higher temperature over the transition point (1180°C) of pure tricalcium phosphate. The variation of the diffraction patterns of these β-form is indicated in Fig. 3, which shows the apparent solid solubility of 7 ± 2 wt.% (19 mol.%) magnesium metasilicate in β-tricalcium phosphate at 1250°C. Nevertheless it is not yet clear whether tricalcium phosphate just dissolves magnesium metasilicate.

The System $3CaO \cdot P_2O_5$–$MgO \cdot SiO_2$–SiO_2.—The quenching data for this system are listed in Table IV, and the compositions of the mixtures are plotted in Fig. 4.

TABLE IV
QUENCHING DATA IN THE SYSTEM $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$—SiO_2

No.			Composition			Holding		Phases present
			C_3P	MgO wt. %	SiO_2	Temp. °C	Time min.	
	No. 25	No. 23						
29	85	15	66.2	11.1	22.7	1332	60	C_3P, glass
						1232	45	C_3P, glass
						1208	60	C_3P, clinoenst., very small glass
37	80	20	65.8	10.5	23.7	1292	60	C_3P, glass
						1272	60	C_3P, small cristbl., glass
						1252	60	C_3P, cristbl., glass
27	70	30	65.1	9.2	25.7	1447	60	small cristbl., glass
						1352	60	cristbl., glass
						1324	60	cristbl., C_3P, glass
						1262	60	cristbl., C_3P, small glass
						1217	60	cristbl., C_3P, clinoenst.
	No. 15	No. 23						
48	90	10	60.6	14.2	25.2	1312	60	glass
						1282	50	small C_3P, glass
38	80	20	60.6	12.6	26.8	1312	60	glass
						1287	60	small C_3P, glass
32	70	30	60.5	11.0	28.5	1362	60	cristbl., glass
						1340	60	cristbl., tridymite, glass
						1290	60	cristbl., C_3P, glass
						1244	60	cristbl., C_3P, pyroxene*, glass
						1198	60	cristbl., C_3P, clinoenst.
	No. 4	No. 23						
44	80	20	52.6	15.8	31.6	1272	60	glass
						1264	60	M_2S, glass
						1255	50	C_3P, M_2S, glass
						1252	60	C_3P, M_2S, small glass
						1247	60	almost crystal
46	75	25	53.1	14.8	32.1	1252	60	small C_3P pyroxene* glass
45	70	30	53.5	13.8	32.7	1312	60	very small cristbl., glass
						1272	60	cristbl., glass
						1232	60	C_3P, cristbl., clinoenst.
	No. 31	No. 23						
42	90	10	45.3	20.3	34.4	1262	60	M_2S, small C_3P, glass
39	80	20	47.0	18.0	35.0	1282	60	very small M_2S, glass
						1262	60	M_2S, clinoenst., glass
						1254	60	almost crystal
47	75	25	47.7	17.0	35.3	1254	60	glass
						1247	60	clinoenst., glass
						1240	60	clinoenst., glass
						1232	60	clinoenst., C_3P, glass
						1224	60	all crystal
40	70	30	48.5	15.8	35.7	1272	60	glass
						1262	60	clinoenst., cristbl., glass
						1256	60	clinoenst., cristbl., glass
						1232	60	clinoenst., cristbl., C_3P
43	65	35	49.3	14.7	36.0	1447	60	glass
						1392	60	very small cristbl., glass
						1272	60	cristbl., glass
						1252	60	cristbl., clinoenst., glass
						1242	60	cristbl., clinoenst., C_3P, glass

41	60	40	50.2	13.6	36.2	1447	60	small cristbl., glass
						1332	60	cristbl., tridymite, glass
						1277	60	cristbl., tridymite, glass
						1262	40	cristbl., C_3P, clinoenst., glass
						1228	50	clinoenst., C_3P, cristbl.

* diopsidic pyroxene
Abbreviations; $C_3P=\beta\text{-}3CaO\cdot P_2O_5$, M_2S=Forsterite, Cristbl.=Cristobalite, Clinoenst.=Clinoenstatite.

These compositions are on the four lines joining No. 23 (60 C_3P—40 SiO_2) with No. 25, 15, 4, or 31 along the C_3P—MS. Fig. 4 was obtained as the phase diagram of this system in which two quintuple points occur, the one at 49% C_3P, 17% M, 34% S and 1246±3°C (alteration point), and the other at 50.5% C_3P, 15% M, 34.5% S and 1230±4°C (the ternary eutectic of the system C_3P—MS—S). It is to be noted that the tie line C_3P—MS may not intersect the boundary curve (alteration curve) between the clinoenstatite and forsterite fields. X-ray examinations of samples No. 42 and No. 47, quenched from 1200°C, gave the β-tricalcium phosphate and clinoenstatite patterns with faint forsterite in the case of the former.

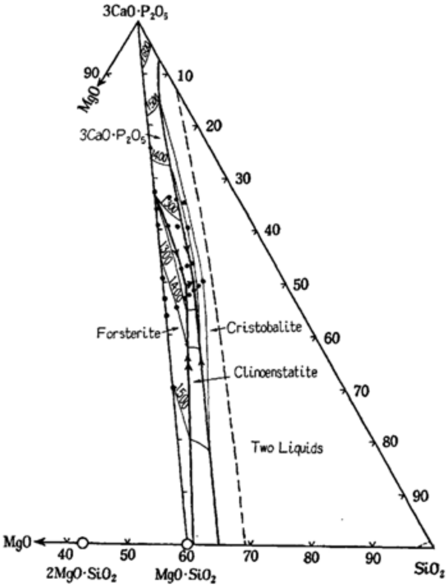

Fig. 4. The system tricalcium phosphate-magnesium metasilicate-silica.

Summary

The phase relationship in the system $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$—SiO_2 was investigated by the usual quenching method. In the partial system $3CaO\cdot P_2O_5$—SiO_2, the existence of solid solution and the change of the transition temperature of α—β tricalcium phosphate were not found by X-ray examinations.

The partial system $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$ is pseudo-binary, whose eutectic is at 1246°C and 40% $3CaO\cdot P_2O_5$. In this system, $\beta\text{-}3CaO\cdot P_2O_5$, always appeared in quenched samples, has a maximum solid solubility of 7±2% $MgO\cdot SiO_2$.

The system $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$—SiO_2 has two quintuple points, the one an alteration point and the other a ternary eutectic at 50.5% $3CaO\cdot P_2O_5$, 15.0% MgO, 34.5%SiO_2 that melts at 1230±4°C.

This system is of great importance to the manufacture of the fused phosphatic fertilizer and the bone ash magnesia porcelain. For instance, in this system, the lower liquidus groove lies at higher silica side along $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$, in accord with the results of cone fusion and melting point measurements already obtained by Kiyoura and Sata[1,2].

The author acknowledges the constant help and encouragement given by Professor Dr. R. Kiyoura, Tokyo Institute of Technology, and also much helpful advice supplied by Professor, Dr. H. Yamada and Assistant Professor S. Kawakubo, Tokyo Institute of Technology. This work was conducted as a part of a program to investigate the corrosion problems of various refractory bricks in the manufacture of fused phosphatic fertilizer.

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