Phase Relationship in the System $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$—$SiO_2$

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According to the present writer's published studies[1,2], slowly cooled specimens of fused phosphatic fertilizer and of bone-ash magnesia porcelain are composed of β-tricalcium phosphate, apatite, diopsidic pyroxene, and silica minerals. The equilibrium study of the system composed of these minerals, therefore, must be of great importance for the industrial manufacture of these products. Henceforth the author constructed the phase diagrams of the ternary system $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$—$SiO_2$, on which no paper has ever been presented. This investigation is continued from his preceding report on the system $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$—SiO_2[3].

Experimental

Of the three-component system concerned, data of the two partial systems, $3CaO \cdot P_2O_5$—SiO_2

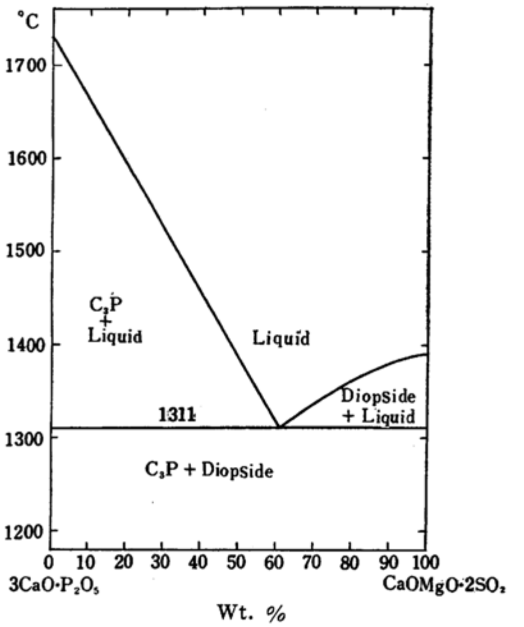

Fig. 1. The system $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$

and $CaO \cdot MgO \cdot 2SiO_2$—$SiO_2$, were given by other authors, the former by Pierre[4] and Wojciechowska[5], and the latter by Bowen[6]. Another partial system $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$ and the three-component system were investigated by usual quenching method in this study.

Powdered batches of selected compositions, prepared by quenching into glass after being kept at above their melting points, were again held at constant temperatures in a silicon carbide resistor furnace and then quenched in water. Thenceforth the equilibrium phases found therein were determined by the optical and the X-ray examination. For measuring the temperature a thermocouple of platinum-platinum rhodium (10%) was used. Details of experimental

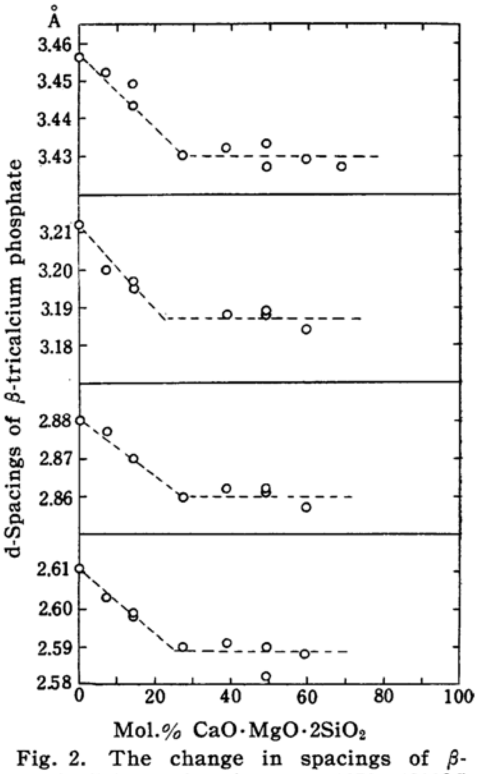

Fig. 2. The change in spacings of β-tricalicium phosphate at 1250～1300°C (pure tricalicium phosphate at 1100°C)

1) T. Sata and R. Kiyoura, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 63 (1959).
2) T. Sata and R. Kiyoura, *J. Cer. Assoc., Japan* (*Yogyo Kyokai Shi*), **66**, 294 (1958).
3) T. Sata, This Bulletin, **31**, No. 4 408 (1958).
4) D. D. S. St Pierre, *J. Am. Cer. Soc.*, **37**, (6) 243 (1954), **39**, (4) 147 (1956).
5) J. Wojciechowska et al., *Roczniki Chem.*, **30**, 743 (1956).
6) N. L. Bowen, *Am. J. Sci.*, (4) **38**, 207 (1914), *Z. anorg. allgem. Chem.*, **90**, 1 (1914).

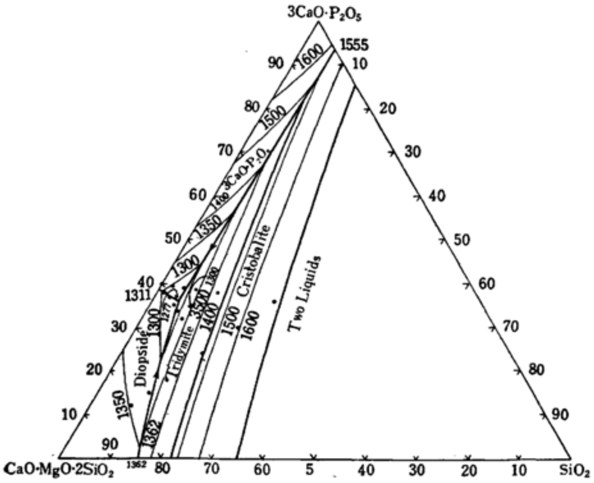

Fig. 3. The system $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$—$2SiO_2$

procedures are similar to those already described in the author's preceding report[3].

Results

The system $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$. —Data on the quenching runs for this two-component system are listed in Table I, from which the equilibrium diagram was constructed as shown in Fig. 1. It is found that this system seems to be perfectly described as a binary one, whose eutectic is located at 39% of $3CaO \cdot P_2O_5$ and 61% of $CaO \cdot MgO \cdot 2SiO_2$, melting point at 1311±4°C. In the region rich in $3CaO \cdot P_2O_5$ (over 80%), the following facts were observed. (1) The crystallization of diopside did not take place when samples were kept for about 1 hr. even under the eutectic temperature. (2) The transition temperature of tricalcium phosphate from

TABLE I
QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$

No.	Composition wt.%		Holding		Phases present
	C_3P	CMS_2*	temp. °C	time min.	
248	95	5	1500	45	α-C_3P, glass
			1400	120	α-C_3P, β-C_3P, glass
			1292	60	β-C_3P
113	90	10	1500	30	α-C_3P, glass
			1450	60	α-C_3P, small β-C_3P, glass
			1400	60	β-C_3P, glass
			1292	300	β-C_3P, diopside
100	80	20	1600	20	small α-C_3P, glass
			1520	30	α-C_3P, β-C_3P, glass
			1450	60	β-C_3P, glass
			1307	30	β-C_3P
			1272	70	β-C_3P, small diopside
112	70	30	1314	30	β-C_3P, glass
			1302	30	β-C_3P, trace diopside
			1292	50	β-C_3P, diopside
99	60	40	1455	30	glass
			1422	30	very small β-C_3P, glass
			1314	40	small β-C_3P, glass
			1307	40	β-C_3P, diopside, glass
111	50	50	1382	30	very small β-C_3P, glass
			1357	30	small β-C_3P, glass
98	40	60	1324	40	glass
			1314	60	small β-C_3P, glass
			1307	40	β-C_3P, diopside, glass
			1282	40	all crystal
119	35	65	1314	40	small diopside, glass
118	30	70	1340	20	glass
			1324	30	trace diopside, glass
			1314	30	diopside
97	20	80	1364	30	glass
			1358	40	diopside, glass

* Abbreviations: $C_3P = 3CaO \cdot P_2O_5$, $CMS_2 = CaO \cdot MgO \cdot 2SiO_2$

TABLE II

QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$—$SiO_2$

No.	Composition wt.%		C_3P wt.%	CMS_2 wt.%	S* wt.%	Holding Temp. °C	Holding Time min.	Phases present
	CMS_2	No. 23						
195	80	20	12	80	8	1340	30	glass
						1334	30	diopside, glass
						1304	30	almost crystal
200	75	25	15	75	10	1330	60	glass
						1323	40	very small diopside, glass
196	70	30	18	70	12	1354	30	cristbl.,* glass
						1314	60	cristbl., glass
						1304	30	cristbl., diopside, glass
						1237	120	β-C_3P, diopside, cristbl.
197	60	40	24	60	16	1354	30	cristbl., glass
						1294	60	cristbl., glass
						1284	60	cristbl., diopside, glass
						1279	60	cristbl., diopside, small glass
						1274	60	all crystal
198	50	50	30	50	20	1354	30	cristbl., glass
						1284	60	cristbl., glass
						1279	60	all crystal
199	40	60	36	40	24	1292	40	β-C_3P, cristbl., glass
						1277	60	all crystal
						1237	120	β-C_3P, diopside, cristbl., tridymite
	No. 197	No. 98						
203	50	50	32	60	8	1299	40	small cristbl., glass
						1282	50	cristbl., glass
						1273	50	all crystal
204	40	60	33.6	60	6.4	1290	50	diopside, cristbl., glass
						1282	50	almost crystal
205	30	70	35.2	60	4.8	1290	50	glass
						1281	60	diopside, glass
206	19.4	80.6	36.9	60	3.1	1290	50	glass
						1281	60	diopside, glass
	No. 199	No. 98						
202	50	50	38	50	12	1315	40	cristbl., glass
201	30	70	38.8	54	7.2	1315	40	very small cristal., glass
						1299	40	cristbl., glass
						1282	50	cristbl., β-C_3P, glass
						1277	50	all crystal
207	20	80	39.2	56	4.8	1290	50	very small C_3P, glass
						1282	50	diopside, almost crystal
208	10	90	39.6	58	2.4	1290	50	small β-C_3P, glass
						1282	50	diopside, almost crystal

* Abbreviations; S=silica, cristbl.=cristobalite

β to α increased with diopside content, 1350$\sim$1400°C with 5%, 1450$\sim$1450°C with 10%, and 1450$\sim$1520°C with 20% of diopside (the transition temperature of pure tricalcium phosphate is 1180°C). (3) The spacings for diffraction lines in β-tricalcium phosphate decreased with diopside contents as indicated in Fig. 2, showing apparent formation of solid solution with some diopside (25±2 mol.% or 19±2 wt.%). These facts occurring in the region rich in tricalcium phosphate will be discussed with more data in the near future.

The system $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$—$SiO_2$.—This three-component system is a perfect ternary one, and its eutectic was decided from the quenching data of the 14 samples shown in Table II, whose compositions lie along the tie lines connecting No. 23 (C_3P60—SiO_240) with $CaO \cdot MgO \cdot 2SiO_2$ corner and No. 98 (C_3P40—$CaO \cdot MgO \cdot 2SiO_260$) with No. 197 or No. 199, as plotted in Fig. 3. The ternary eutectic is located at 36±1% C_3P, 59±1% $CaO \cdot MgO \cdot 2SiO_2$, and 5±1% SiO_2, and at 1277±3°C, which is close to the $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$ join. Accordingly the silica field covers over a very wide area. The isotherms on the liquidus surface were approximately represented in the ternary system.

Summary

The phase relationship in the system $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$—$SiO_2$ was investigated by the usual quenching method. The two partial systems $3CaO \cdot P_2O_5$—SiO_2 and $CaO \cdot MgO \cdot 2SiO_2$—$SiO_2$ have already been reported by previous investigators. Another partial system $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$ seems to be approximately binary, whose eutectic is located at 39% of $3CaO \cdot P_2O_5$ and 61% of $CaO \cdot MgO \cdot 2SiO_2$, and at 1311±4°C. In the region rich in $3CaO \cdot P_2O_5$, it was observed that the crystallization velocity of diopside is rather slow under the solidus temperature, that the transition temperature of tricalcium phosphate is considerably increased with diopside content, and that β-tricalicium phosphate apparently makes solid solution with diopside (19 wt.%).

The system $3CaO \cdot P_2O_5$—$CaO \cdot MgO \cdot 2SiO_2$—$SiO_2$ is of a perfect ternary one, whose eutectic is at 36% of $3CaO \cdot P_2O_5$, 59% of $CaO \cdot MgO \cdot 2SiO_2$ and 5% of SiO_2, and at 1277±3°C. Its isotherms of the liquidus surface were approximately represented.

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