Phase Equilibrium on Liquidus Surface of the System $3CaO \cdot P_2O_5 - CaO \cdot MgO \cdot 2SiO_2 - MgO \cdot SiO_2$

By Toshiyuki Sata

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As a continuation of the author's preceding reports, which were on the phase relationship in the systems 3CaO·P₂O₅- $MgO \cdot SiO_2 - SiO_2^{1}$ and $3CaO \cdot P_2O_5 - CaO \cdot MgO \cdot$ 2SiO₂-SiO₂²⁾, an equilibrium study on the system 3CaO·P₂O₅-CaO·MgO·2SiO₂-MgO· SiO₂, a side plane of a tetrahedron of a system 3CaO·P₂O₅-CaO·MgO·2SiO₂-MgO· SiO₂-SiO₂, was carried out by the usual quenching method. On the phase relationship of this 3-component system, no paper has ever been presented.

Of the three component system concerned, data of the two partial systems, $3CaO \cdot P_2O_5 - CaO \cdot MgO \cdot 2SiO_2$ and $3CaO \cdot P_2O_5 -$ MgO·SiO₂, were already given by the author's reports. Another partial system investi-CaO·MgO·2SiO₂-MgO·SiO₂ was gated by Bowen³⁾. In his phase diagram, it is characterized that forsterite is a primary phase at 22~100% of MgO·SiO₂. However, in the phase diagram published in 1952 by Atlas⁴⁾, who studied the matter by adding LiF, the primary phase may be a solid solution at overall range, which is decomposed to a clinoenstatite, diopside, protoenstatite or rhombic enstatite solid solution in a crystalline phase. In this report the author followed Bowen's diagram, and constructed the phase diagram on the liquidus surface of this system.

Experimental

The nine compositions taken on the system CaO·MgO·2SiO₂-MgO·SiO₂ are listed in Table I. Then on the line joining these nine compositions with 3CaO·P₂O₅ point, thirty-two sample points were taken in the system 3CaO·P₂O₅-CaO·MgO· 2SiO2-MgO·SiO2 and plotted in Fig. 1.

Powdered batches of these compositions, prepared by quenching into a glass after being kept at above their melting points, were again held at constant temperatures in a silicon carbide resister furnace and then quenched in water. Thenceforth the equilibrium phases found therein were determined by optical and X-ray examination. For measuring the temperature a thermocouple of platinum-platinum rhodium (10%) was used. Details of the experimental procedures are similar to those already described in the preceding report1).

TABLE I. COMPOSITIONS OF SAMPLES TAKEN FROM THE SYSTEM CaO·MgO·2SiO2-MgO·SiO2

No.	CaO·MgO·2SiO ₂ wt.			
225	85	15		
240	80	20		
	75	25		
209	70	30		
230	60	40		
210	50	50		
238	40	60		
211	20	80		

Results

Data on the quenching runs for this 3-component system are listed in Table II,

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

T. Sata, ibid, 32, 105 (1959).

³⁾ N. L. Bowen, Z. anorg. u. allgem. Chem., 90, 1-66 (1914).

⁴⁾ L. Atlas, J. Geology, 60, 140 (1952).

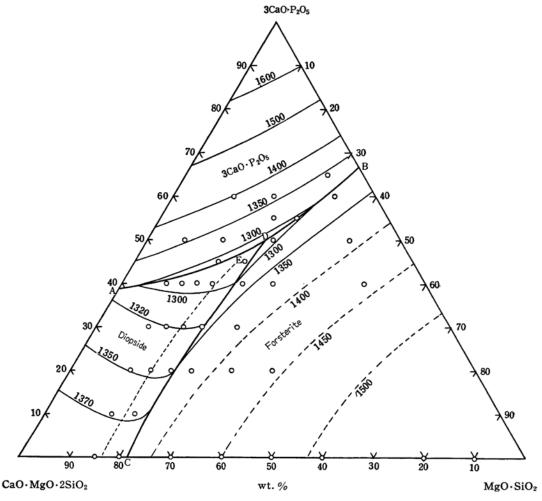


Fig. 1. The system 3CaO·P₂O₅-CaO·MgO·2SiO₂-MgO·SiO₂. (A: 1314°C, B: 1308°C, C: 1390°C)

from which the equilibrium diagram on the liquidus surface was constructed as shown in Fig. 1. Primary crystals in this system are tricalcium phosphate (α or β), diopside and forsterite, respectively, and forsterite occupies a wide field. Accordingly it is found that this system is not a ternary one.

A lower liquidus temperature range is located in the center of this triangle, its minimum temperature being 1277±5°C. A temperature minimum at 1389°C in the system CaO·MgO·2SiO₂-MgO·SiO₂ falls slowly toward the neighborhood of this lowest point as shown by a dotted line. However, it can not be decided in this report whether this valley of temperature attains to this point or not. Clinoenstatite does not appear as a primary crystal on

the liquidus surface. Hence a decomposition of pyroxene solid solution to colinoenstatite may occur under the liquidus.

Summary

The phase relationship on the liquidus surface of the system $3\text{CaO} \cdot P_2 O_5$ –CaO·MgO·2SiO₂–MgO·SiO₂ was investigated by the usual quenching method. The three primary crystals are α - or β -tricalcium phosphate, diopside and forsterite, and the range of the lowest temperature is located at the center of this triangle (1277°C). From these results, it is found that this system should be considered as a partial system in the 4-component system 3CaO·P₂O₅–CaO·MgO·2SiO₂–2MgO·SiO₂–SiO₂.

Table II. Quenching data in the system $3CaO \cdot P_2O_5 - CaO \cdot MgO \cdot 2SiO_2 - MgO \cdot SiO_2$

	Composition				Holding			
No.	wt.	0/-	C ₃ P	CMS ₂	MS*	temp. °C	time min.	Phases present
		o. 225		wt. %		• •	min.	
226	50	50	50	42.5	7.5	1347	30	gl.*
220	00	50	30	42.0	7.0	1340	30	β-C ₃ P, gl.
227	40	60	40	51.0	9.0	1307	30	gl.
221	40	00	40	01.0	5.0	1298	30	faint diopside, gl.
						1290	40	diopside, gl.
						1282	40	all crystal
228	30	70	30	59.5	10.5	1332	60	gl.
	00		•	00.0	10.0	1325	30	small diopside, gl.
						1290	30	diopside, gl.
						1282	30	all crystal
235	20	80	20	68.0	12.0	1356	30	gl.
200	20	00	20	00.0	12.0	1347	30	faint diopside, gl.
236	10	90	10	76.5	13.5	1372	30	gl.
200	10	30	10	70.0	10.0	1364	30	diopside, gl.
						1340	30	diopside, small gl.
	C ₃ P N	o. 240				1340	30	diopside, sman gr.
241	40	60	40	48	12	1307	30	faint diopside, gl.
.241	40	00	40	40	12	1290	30	diopside, gl.
242	30	70	30	56	14		60	
242	30	70	30	30	14	1332 1325	30	gl.
							30	small diopside, gl. diopside, gl.
243	20	80	20	64	16	1307 1356	20	gl.
240	20	80	20	04	10			•
244	10	90	10	72	18	1347	30	small diopside, gl.
244	10	90	10	72	18	1372	30	gl.
						1364	30	diopside, gl.
245**			40	45	15	1302	30	small diopside, gl.
						1294	30	diopside, gl.
						1286	30	diopside, gl.
246**			30	52.5	17.5	1314	40	gl.
						1307	40	diopside, gl.
247**			20	60	20	1357	50	gl.
						1347	30	faint diopside, gl.
	C ₃ P N	o. 209						, 6
212	60	40	60	28	12	1356	40	gl.
						1348	40	β -C ₃ P, gl.
						1282	40	β -C ₃ P, gl.
213	50	50	50	35	15	1330	40	gl.
						1307	40	small C ₃ P, gl.
						1282	40	β -C ₃ P, gl.
						1273	30	all crystal
221	45	55	45	38.5	16.5	1307	30	gl.
•						1282	30	small C ₃ P, gl.
						1274	50	all crystal
214	40	60	40	42	18	1302	30	gl.
		- •				1294	30	faint diopside, gl.
						1286	30	small diopside, gl.
						1273	30	all crystal

^{*} Abbreviations: $C_3P=3CaO \cdot P_2O_5$; $CMS_2=CaO \cdot MgO \cdot 2SiO_2$; $MS=MgO \cdot SiO_2$; gl.=glass.

^{**} No. 245, 246, 247 were prepared from 1:1 mixture of No. 241—No. 214, No. 242—No. 222, No. 243—No. 229, respectively.

ebruary,	1960]	Phase	3CaO	·P ₂ O ₅ -Ca	Liquid aO·MgO	us Surface 0·2SiO ₂ -Mg	O·SiO ₂	System	219
222	30	70	30	49	21	1324	40	gl.	
						1314	40	faint diopside, gl.	
						1282	40	diopside, small gl.	
229	20	80	20	56	24	1407	30	gl.	
						1397	40	small forsterite, gl.	
						1340	50	forsterite, gl.	
						1332	60	forsterite, diopside, gl.	
						1322	60	forsterite, diopside, gl.	
	C ₃ P N	0. 230							
001	•		45	00	00	1000	00		
231	45	55	45	33	22	1290	30	gl.	
						1282	30	small diopside, gl.	
						1272	30	diopside, β-C ₃ P, gl.	
000	40	40	40		0.4	1265	30	all crystal	
232	40	60	40	36	24	1323	60	gl.	
						1314	60	small forsterite, gl.	
						1299	60	forsterite, gl.	
						1290	40	forsterite, diopside, gl.	
233	30	70	30	42	28	1397	40	gl.	
						1390	30	small forsterite, gl.	
						1323	30	forsterite, gl.	
						1314	60	forsterite, small diopside,	gl.
						1250	60	forsterite, diopside, β -C ₃ P	
234	20	80	20	48	32	1460	30	gl.	
						1450	30	small forsterite, gl.	
	C_3P N	o. 210							
215	60	40	60	20	20	1348	40	gl.	
						1340	40	very small C ₃ P, gl.	
						1332	40	small C ₃ P, gl.	
223	55	45	55	22.5	22.5	1314	40	gl.	
	• • • • • • • • • • • • • • • • • • • •					1307	30	small C ₃ P, gl.	
216	50	50	50	25	25	1298	30	gl.	
	**	••				1290	30	faint forsterite, gl.	
						1282	20	forsterite, gl.	
						1277	30	forsterite, C ₃ P, gl.	
217	40	60	40	30	30	1365	50	gl.	
						1356	40	small forsterite, gl.	
237	20	80	20	40	40	1499	15	gl.	
						1480	20	small forsterite, gl.	
	C ₃ P N	0 238							
000				10		1005	00	C. L. C. D. Co. et al. C. d.	
239	55	45	55	18	27	1297	30	faint C ₈ P, forsterite, gl.	
						1290	30	C ₂ P, forsterite, gl.	
	C ₃ P N	o. 211							
224	65	35	65	28	7	1340	30	gl.	
						1332	40	small C ₃ P, gl.	
						1299	30	β-C ₃ P, gl.	
						1290	30	β -C ₃ P, forsterite, gl.	
218	60	40	60	32	8	1314	40	gl.	
						1307	50	small forsterite, C3P, gl.	
219	50	50	50	40	10	1422	30	gl.	
						1407	30	small forsterite, gl.	
						1365	50	forsterite gl.	
						1250	60	forsterite, β-C ₃ P, diopside	
220	40	60	40	48	12	1479	15	gl.	
						1460	20	small forsterite, gl.	
						1432	20	forsterite, gl.	
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220 [Vol. 33, No. 2

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