

Phase relationships in the join $\text{Ca}(\text{OH})_2\text{--CaCO}_3\text{--Ca}_3(\text{PO}_4)_2\text{--H}_2\text{O}$ at 1000 bars

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SUMMARY. Phase equilibria involving calcite, apatite, portlandite, liquid, and vapour were determined at 1000 bars. Calcite, apatite, and portlandite melt at 654 °C to form a liquid of composition (wt %), $\text{Ca}(\text{OH})_2$ 53 %, CaCO_3 46 %, $\text{Ca}_3(\text{PO}_4)_2$ 1 %. With water present melting occurs at 635 °C to form a similar liquid with a low water content. The X-ray diffraction patterns of the equilibrium apatites were not significantly different from synthetic hydroxyapatite.

CALCITE and apatite are commonly associated in carbonatites and the join $\text{Ca}(\text{OH})_2\text{--CaCO}_3\text{--Ca}_3(\text{PO}_4)_2\text{--H}_2\text{O}$ is one of the simplest in which to study the experimental behaviour of compositions that are possibly close to the natural compositions from which calcite and apatite crystallize. The join also embraces some of the suggested formulae of the much studied but little understood carbonate apatite. Little is known of the stability range of this mineral.

The equipment and the techniques used including the X-ray diffractometry methods are adequately described by Biggar.¹ Calcium carbonate of AnalaR grade was required for the present work. The following abbreviations are used subsequently in the text and figures: portlandite CH, tricalcium phosphate C_3P , calcite CC, apatite A, hydroxyapatite HA, fluorite CF, liquid L, and vapour V.

The join $\text{CH--CC--C}_3\text{P}$ was determined in the temperature range 600–950 °C at 1000 bars by studying a selection of compositions lying on lines parallel to the join CH--CC and containing 5 %, 10 %, 20 %, and 30 % C_3P . The experimental results obtained from these compositions are shown as isobaric TX sections in fig. 1 and the critical experiments used to determine the figures are listed in table I. The smoothed curves from the TX sections were used to construct the projection shown in fig. 2, which illustrates the contoured liquidus surfaces for the primary phases A, CH, and CC. The ternary eutectic $\text{CH+CC+A} = \text{L}$ was placed at a nominal temperature of 654 °C since it was not experimentally distinguished from the eutectic in the binary system CH--CC for which a temperature of 655 °C was obtained from data given in table I. From fig. 2 the composition of the ternary liquid at 655 °C was estimated to be CH 53 %, C_3P 1 %, and CC 46 %. The directions of the contours on the calcite liquidus surface are unusual and probably reflect experimental failures. Calcite crystals settle to the bottom of the charge and may be lost during opening of the capsule, resulting in failure to record the correct assemblage or, as is shown later, the presence of water modifies the calcite liquidus surface to an extreme extent and despite

¹ G. M. Biggar, *Min. Mag.* 1966, 35, 1110.

TABLE I. *The join CH-CC-C₃P at 1000 bars*

Composition			Temp. °C ±5	Time d hr	Result			Composition			Temp. °C ±5	Time d hr	Result						
CH	CC	C ₃ P			CH	CC	C ₃ P	CH	CC	C ₃ P			CH	CC	C ₃ P				
70	30	—	650	6	CH	CC													
50	50	—	650	1	2	CH	CC												
			660	2	—		CC	L		65	25	10	640	3	—	CH	CC	A	L
			645	5	—	CH	CC	A					660	3	—	CH		A	L
			745	1	17	CH		A	L				695	3	—	CH		A	L
90	5	5	770	6	—			A	L				715	3	—			A	L
			800		22			A	L				900	4	—			A	L
			645	5	—	CH	CC	A	L	55	35	10	760	5	—	CH		A	L
			745	1	17	CH		A	L				920		3			A	L
80	15	15	785		16			A	L				640	4	—	CH	CC	A	L
			875		7			A	L				660	3	—		CC	A	L
			650	3	—	CH	CC	A	L	45	45	10	740	3	—		CC	A	L
			660	3	—	CH		A	L				770	6	—			A	L
70	25	5	715		20	CH		A	L				920		3			A	L
			745	1	17			A	L				825	1	—		CC	A	L
			650	1	2	CH	CC	A	L	40	50	10	850		12			A	L
			660	2	—	CH		A	L				650	3	—	CH	CC	A	L
			680	5	—	CH		A	L				660	3	—		CC	A	L
60	35	5	690	2	—			A	L				910		3		CC	A	L
			780	1	8			A	L				725	4	—	CH		A	L
			805	1	—			A	L				750	4	—			A	L
			875		7			A	L				920		5			A	L
			650	1	2	CH	CC	A	L				648	6	—	CH	CC	A	L
52½	42½	5	660	2	—	CH		A	L				660	21	—	CH		A	L
			670	2	—			A	L				710	3	—	CH		A	L
			780	1	8			A	L				725	4	—			A	L
			650	1	2	CH	CC	A	L				670	3	—	CH		A	L
			660	2	—		CC	A	L				710	3	—			A	L
45	50	5	715		20		CC	A	L				900	4	12			A	L
			755	4	—			A	L				670	3	—		CC	A	L
			800	1	—			A	L				750	3	—		CC	A	L
			850		12		CC	L					775	2	8			A	L
			870		18			L					890		4		CC	A	L
35	60	5	850		12			A	L				925		4			A	L
15	80	5	650	6	—	CH	CC	A	L				725	4	—	CH		A	L
			640	3	—	CH	CC	A	L				750	4	—	CH		A	L
			660	3	—	CH		A	L				770	4	—			A	L
			750	3	—	CH		A	L				900	5	—			A	L
85	5	10	770	6	—			A	L				640	21	—	CH	CC	A	L
			850	2	—			A	L				660	3	—	CH		A	L
			900		4			A	L				725	4	—	CH		A	L
			650		6	CH	CC	A	L				675	2	—	CH		A	L
			660	3	—	CH		A	L				750	3	—		CC	A	L
75	15	10	750	3	—			A	L				795	3	—			A	L
			850	2	—			A	L				890	4	—		CC	A	L
			900		4			A	L				925	4	—			A	L

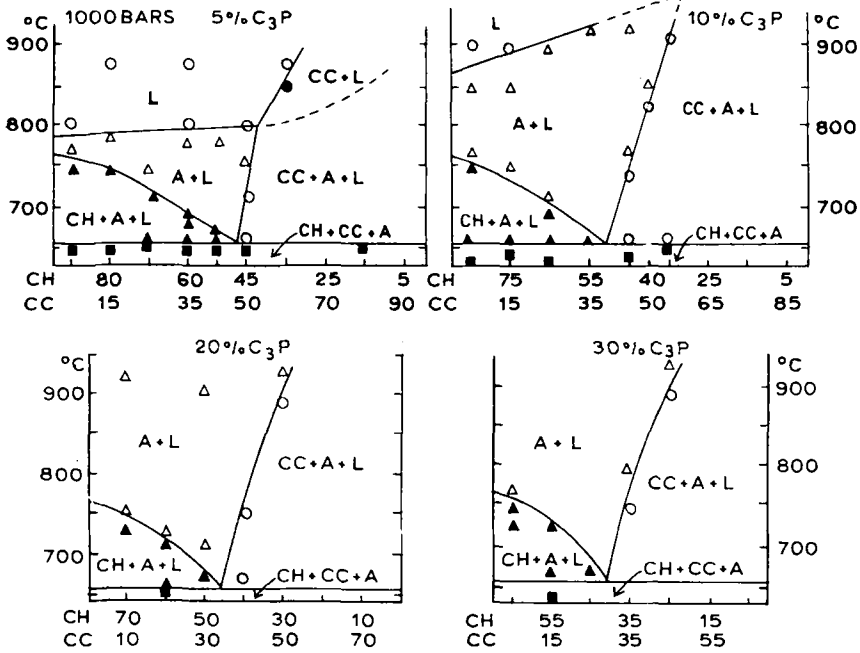


FIG. 1. Experimentally determined TX sections for the join CH-CC-C₃P at 1000 bars, at 5 %, 10 %, 20 %, and 30 % C₃P. ○, L or CC+A+L; △, A+L; ▲, CH+A+L; ●, CC+L; ■, CH+CC+A.

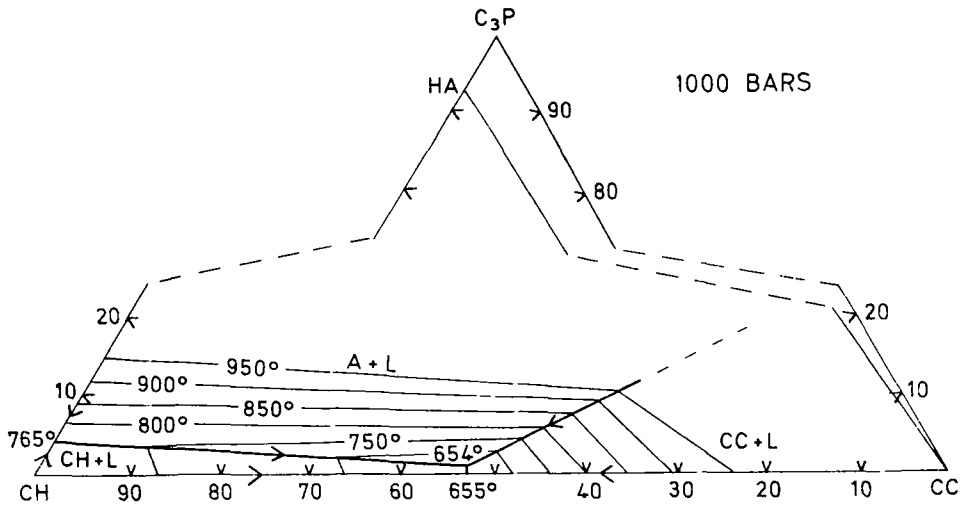


FIG. 2. The join CH-CC-C₃P in projection at 1000 bars showing liquidus field boundaries and thermal contours for liquidus surfaces.

precautions in drying samples of starting materials traces of water may be absorbed during experimental procedures.

Apatites from several compositions in the join were measured using the previously described X-ray diffractometry method, but the results were not meaningful. The maximum shift in the angular position of the 140 and 231 peaks was 0.06° of 2θ which

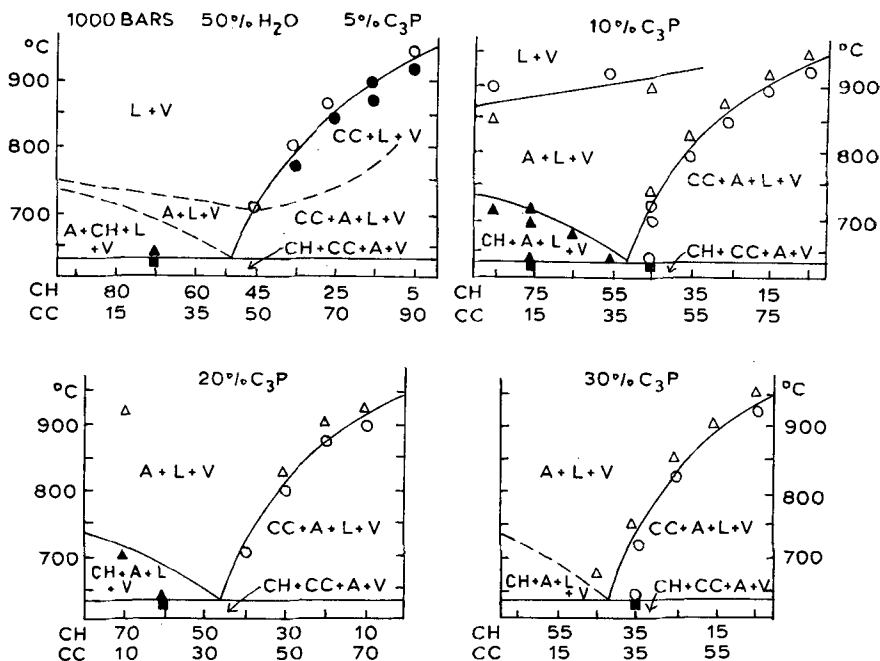


FIG. 3. Experimentally determined TX sections for the join $CH-CC-C_3P-H_2O$ at 1000 bars and at $50 \pm 5\%$ water. The four sections contain constant C_3P contents of 5%, 10%, 20%, and 30% of the solids. \circ , $L+V$ and $CC+A+L+V$; Δ , $A+L+V$; \blacktriangle , $CH+A+L+V$; \bullet , $CC+L+V$; \blacksquare , $CH+CC+A+V$.

is just greater than the range found for defect apatites from the join $CH-C_3P-H_2O$ (Biggar, loc. cit.). If CO_2 enters the apatite lattice at the experimental temperatures and pressures its effect or its amount is small and apatite compositions could not be determined with the X-ray techniques used. In view of the occurrence of carbonate apatites in low-temperature environments it is presumed that the equilibrium apatite is close to HA and subsequent diagrams are plotted on this basis.

The join $CH-CC-C_3P-H_2O$. A section through this join at $50 \pm 5\%$ water was studied using compositions on the 5%, 10%, 20%, and 30% C_3P composition planes. The experimentally determined TX sections at 1000 bars are shown in fig. 3 and the data appear in table II. The temperature of the eutectic $CH+CC+A+V = L$ was $635^\circ C$ and the liquid was probably close in composition to that formed in the join $CH-CC-C_3P$ but with a few per cent water present. The nature of the vapour phase is

discussed shortly. The range of angular positions of the X-ray diffraction peaks of apatites from these sections was just greater than the range for defect apatites and so afforded no clue of the true nature of the apatites.

The nature of the phase fields in the join $\text{CH-CC-C}_3\text{P-CO}_2\text{-H}_2\text{O}$ are most easily visualized in an isothermal pentahedron with these components as apices and the

TABLE II. *The section containing $50 \pm 5\%$ H_2O in the join $\text{CH-CC-C}_3\text{P-H}_2\text{O}$ at 1000 bars*

Composi- tion wt %			Temp. °C	Time d hr	Result				Composi- tion wt %			Temp. °C	Time d hr	Result													
CH	CC	C ₃ P	±5						CH	CC	C ₃ P	±5															
70	25	5	630	1	—	CH	CC	A	V	35	55	10	795	3	—	CC	A	L	V								
																				640	1	—	CH	A	L	V	
45	50	5	715	3	—	CC	CC	L	V	25	65	10	850	3	—	CC	A	L	V								
																				780	1	8	CC	L	V		
35	60	5	800	20	—	L	L	V	—	15	75	10	900	3	—	CC	A	L	V								
																				850	12	—	CC	L	V		
25	70	5	875	7	—	L	L	V	—	5	85	10	925	3	—	CC	A	L	V								
																				875	7	—	CC	L	V		
15	80	5	900	3	—	L	L	V	—	70	10	20	710	5	—	CH	A	L	V								
																				925	3	—	CC	L	V		
5	90	5	950	1	—	L	L	V	—	60	20	20	630	1	—	CH	CC	A	V								
																				715	7	—	CH	A	L	V	
85	5	10	850	7	—	A	L	V	—	40	40	20	710	5	—	CC	A	L	V								
																				900	4	—	CC	A	L	V	
75	15	10	630	1	—	CH	CC	A	V	30	50	20	825	1	—	A	L	V	—								
																				640	1	—	CH	A	L	V	
																				695	7	—	CH	A	L	V	
																				715	7	—	A	L	V		
65	25	10	675	7	—	CH	A	L	V	20	60	20	900	3	—	CC	A	L	V								
																				900	3	—	CC	A	L	V	
55	35	10	635	2	—	CH	CC	A	L	V	10	70	925	3	—	A	L	V	—								
																				920	5	—	CH	CC	A	L	V
45	45	10	630	1	—	CH	CC	A	V	35	35	30	630	1	—	CH	CC	A	V								
																				640	1	—	CH	CC	A	L	V
																				640	4	—	CC	A	L	V	
																				700	3	—	CC	A	L	V	
																				720	3	—	CC	A	L	V	
																				740	3	—	A	L	V		
900	5	—	A	L	V																						
25	45	30	825	1	—	CC	A	L	V	15	55	30	900	3	—	A	L	V	—								
																				850	2	—	A	L	V		
15	55	30	925	3	—	CC	A	L	V	5	65	30	925	3	—	CC	A	L	V								
																				950	1	—	A	L	V		

pentahedron at 900 °C is shown in fig. 4c. It was constructed from the data in tables I and II and from the isothermal sections at 900 °C for the join $\text{CH-CC-C}_3\text{P}$ and for the 50 % water section shown respectively in figs. 4a and 4b. The section for the join $\text{CH-CC-C}_3\text{P}$, fig. 4a, is fairly normal. In the presence of water calcite loses considerable quantities of CO_2 to the vapour phase leading to an unusual isothermal section at 50 % water, which is only correctly described within the join $\text{CH-CC-C}_3\text{P-CO}_2\text{-H}_2\text{O}$ as indicated by the dashed lines in figs. 4c and 4b. The departure of the vapour composition from pure water is clearly seen in fig. 4c. A consequence of the changing vapour composition is a considerable lowering of the temperature at which apatite

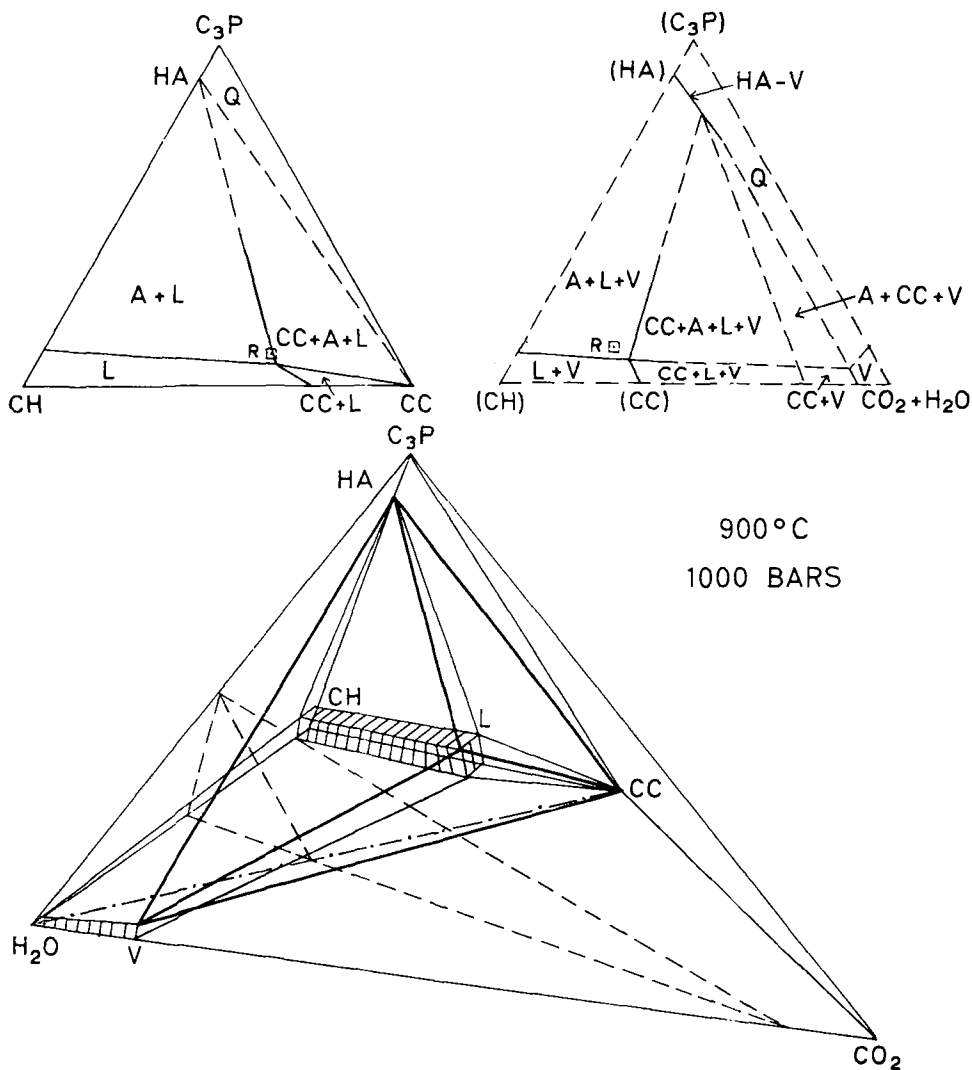


FIG. 4. Isothermal sections at 900°C. Fig. 4a (top left) the join CH-CC-C₃P. Fig. 4b (top right) the section at 50% water of the join CH-CC-C₃P-H₂O but distorted and plotted in terms of the system CH-C₃P-CC-H₂O-CO₂, the plane of the plot being shown as dashed lines in fig. 4c and the parentheses in fig. 4b indicate points that contain 50% H₂O. Q indicates phase fields that were not studied and were presumed to contain defect apatites. Fig. 4c (bottom). Partial isothermal section for the join CH-CC-C₃P-H₂O-CO₂ showing clearly the departure of the vapour from pure water. The liquidus surfaces L(A), L(CC), L(V) are shown shaded and the vaporous surface which coexists with liquid V(L) is shown, other vaporous surfaces are omitted.

and calcite crystallize together. As an example apatite and calcite commence to co-crystallize at 910°C from a composition R, fig. 4a, but the two minerals do not appear together until the temperature drops to 810°C for the composition R+50% water, fig. 4b. Isothermal sections at lower temperatures become more complex as the four-phase tetrahedra ($\text{CH}+\text{A}+\text{L}+\text{V}$ and $\text{CH}+\text{CC}+\text{L}+\text{V}$) develop and at 635°C the liquid and vapour apices of these tetrahedra meet at the eutectic condition where the phases CH, HA, CC, L, and V coexist. At lower temperatures these tetrahedra are replaced by the subsolidus assemblage $\text{CH}+\text{A}+\text{CC}+\text{V}$.

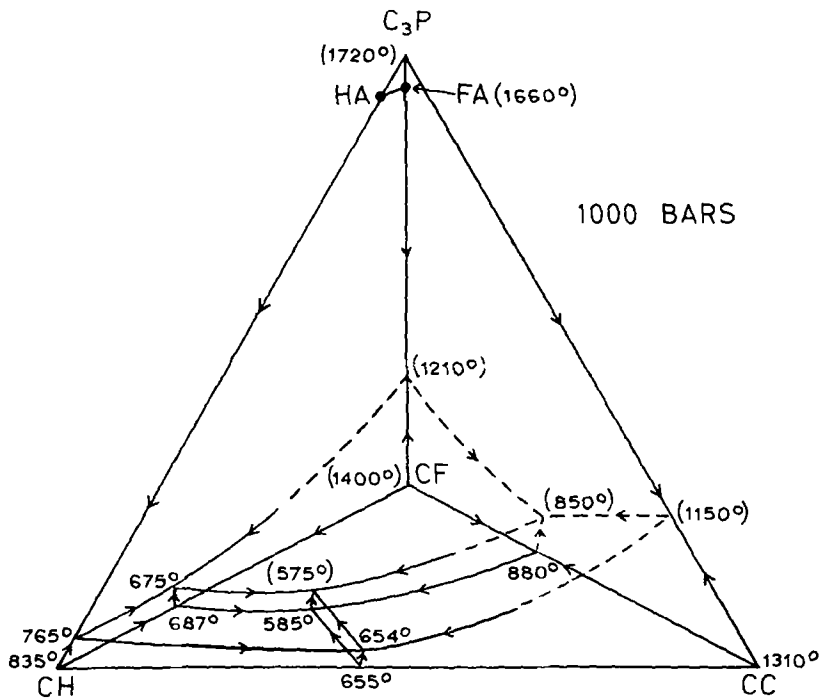


FIG. 5. Schematic diagram of the liquidus phase relationships in the system CH-CC-CF- C_3P at 1000 bars, estimated temperatures are shown in parentheses.

Discussion. The experimental data demonstrate that liquids in the system that initially contain more than a few per cent of P_2O_5 begin to crystallize apatite before calcite and that with an increase in the amount of water present there is an increase in the temperature interval between the onset of apatite and the onset of calcite crystallization. Calcite and apatite do, nevertheless, co-crystallize over a temperature interval at least as large as 300°C (fig. 3). In common with related systems a constant feature of the experimental results was the marked settling of primary crystals to the bottom of the charge. These features in a natural environment would be expected to give rise to segregations with various relative contents of apatite and calcite in response to changing temperatures, pressures, and water contents.

The study of the join CH-CC-C₃P completes the study of the ternary systems that bound the quaternary system CH-CF-CC-C₃P and allows an estimate to be made of the quaternary system at 1000 bars as shown in fig. 5. The addition of water to form a quinary system has the effect of creating a water-rich vapour as a coexisting phase and in general this is accompanied by a lowering of temperature of the order of 10-40 °C, except that close to the calcite apex, where the vapour contains an increasing amount of CO₂ derived from the decomposition of calcite, the field boundaries leave the simplified system and it is necessary to describe phase relationships within the system CaO-CaF₂-CO₂-P₂O₅-H₂O. It seems certain that calcite, fluorite, and apatite coexist with liquid at temperatures below 600 °C and this suite of minerals in various proportions obtainable by crystal settling and differentiation can account for, in a simplified manner, very many of the non-siliceous rock types associated with carbonatite complexes.

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