Experimental studies of apatite crystallization in parts of the system $CaO–P_2O_5–H_2O$ at 1000 bars

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Summary. Solid–liquid–vapour phase equilibria for the join $Ca(OH)_2$–$Ca_3(PO_4)_2$–H_2O at 1000 bars are determined in the temperature range 700 to 950° C. The isobaric invariant equilibrium portlandite + hydroxyapatite → liquid on the join $Ca(OH)_2$–$Ca_3(PO_4)_2$ involves a liquid with the composition 96 wt. % $Ca(OH)_2$, 4 wt. % $Ca_3(PO_4)_2$ and occurs at 765° C. The isobaric invariant equilibrium portlandite + hydroxyapatite + vapour → liquid on the join $Ca(OH)_2$–$Ca_3(PO_4)_2$–H_2O is encountered at 735° C, and involves a liquid containing 92 wt. % $Ca(OH)_2$, 4 wt. % $Ca_3(PO_4)_2$, and 4 wt. % H_2O. The apatites are shown by X-ray diffraction techniques to vary in composition with changes in the bulk composition from which crystallization occurred.

The apatite liquidus is steep; apatite is the first mineral to crystallize from calcium-hydroxide-rich liquids containing as little as 4 wt. % $Ca_3(PO_4)_2$ (1·8 % P_2O_5) at temperatures as low as 735° C in the presence of vapour at 1000 bars pressure; and rapid crystal settling of apatite was experimentally noted. These observations suggest that concentrations of apatite in carbonatites are the result of crystal accumulation from liquids relatively poor in P_2O_5.

A STUDY of the crystal–liquid equilibria of carbonatites would involve a complex system with at least the components $CaO–MgO–CO_2–SiO_2–P_2O_5–FeO–Fe_2O_3–CaF_2–H_2O$. In the system $CaO–CO_2–H_2O$, Wyllie and Tuttle (1960) refer to liquids as 'synthetic carbonatite magmas' and present research is directed at extending the system $CaO–CO_2–H_2O$ to include CaF_2 and P_2O_5 and thus encompassing the compositions of fluorapatite and hydroxyapatite.

The determination of phase equilibria in parts of the system $CaO–P_2O_5–H_2O$ at 1000 bars was chosen as a starting-point for the study of the more complex systems involving P_2O_5. The system $CaO–P_2O_5–H_2O$ (fig. 1) has been extensively studied at atmospheric pressure (van Wazer, 1958) and is of considerable chemical and mineralogical interest in view of the variations in compositions and properties of phases described as hydroxyapatite. At elevated pressures much of the previous work has been performed at 1000 bars and once data are obtained for this pressure a few important equilibria will be followed to other pressures. The binary system $CaO–H_2O$ was determined by Wyllie

and Tuttle (1960), and Wyllie and Raynor (1965). A preliminary report of the present work was given by Biggar and Wyllie (1962) and a preliminary report by Simpson and Roland (1962) refers to the joins $Ca_3(PO_4)_2$–H_2O and $Ca_2P_2O_7$–H_2O at pressures from 500 to 1500 bars and at temperatures up to $750°$ C.

In the system CaO–P_2O_5–H_2O, liquids on the join $Ca(OH)_2$–$Ca_3(PO_4)_2$–H_2O that are rich in calcium hydroxide are regarded as simplified models
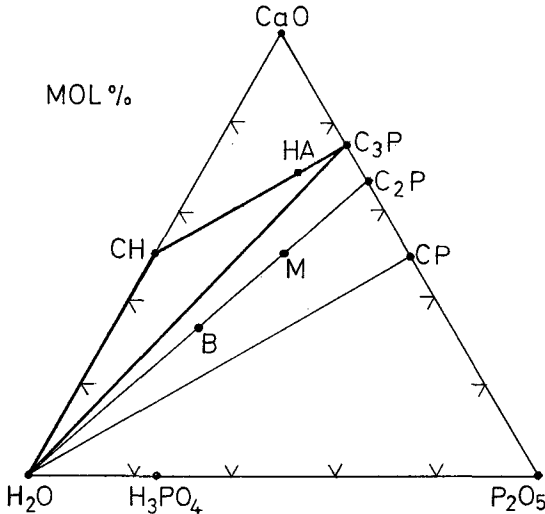

FIG. 1. Compounds in the system CaO–P_2O_5–H_2O in mole %. The abbreviations used are calcium hydroxide CH, hydroxyapatite HA, tricalcium phosphate C_3P, dicalcium phosphate C_2P, monetite M, brushite B, calcium metaphosphate CP.

of more complex liquids, those rich in calcium fluoride or calcium carbonate, that are the compositions expected for carbonatite magmas. The join dicalcium-phosphate–water was studied to a limited extent and vapours rich in P_2O_5 were encountered.

Compounds in the system CaO–P_2O_5–H_2O are illustrated in mole % in fig. 1. For the sake of simplicity the following abbreviations are used, portlandite $= CH$, hydroxyapatite $= HA$, tricalcium phosphate $= C_3P$, dicalcium phosphate $= C_2P$, liquid $= L$, and vapour $= V$. The experimental techniques used to determine phase equilibrium diagrams at 1000 bars pressure and at temperatures up to $950°$ C are described and with the exception of fig. 1 all diagrams and compositions are quoted in weight %.

Experimental methods and materials. Standard equipment for hydrothermal studies at high pressures and temperatures was employed (e.g. Wyllie and Tuttle, 1960). Thermocouples were carefully calibrated using the melting-point of sodium chloride, 800° C, and temperature measurements were accurate to $\pm 5°$ C. Pressures were measured on Bourdon gauges to ± 50 bars. The duration of experiments was from one hour to thirty days. For given temperature and pressure conditions the same phase assemblage was encountered by approach from a lower or from a higher temperature and this reversibility is evidence that the results represent equilibrium conditions.

The method given by St. Pierre (1953) for the preparation of tricalcium phosphate was adopted. The starting materials were analytical grade calcium carbonate and phosphoric acid and the resultant α-tricalcium phosphate was analysed by Dr. O. von Knorring (Department of Geology, University of Leeds) with the result CaO 54·25 %, P_2O_5 45·88 % (theory CaO 54·23 %, P_2O_5 45·77 %). Dicalcium phosphate was obtained at an intermediate stage of this preparation. The calcium hydroxide was supplied by Johnson Matthey Co., and described by them as extra pure. Mixtures of the required compositions on the $CH-C_3P$ join were prepared by homogenizing known weights of the starting materials in a mechanical shaker. These mixtures, with or without a known weight of water, were sealed within small gold or platinum capsules, which were then maintained at constant pressure and temperature in cold-seal pressure vessels for a length of time believed sufficient for the attainment of equilibrium. The pressure vessel was then quenched and the product examined by optical and X-ray examination of the crushed sample.

Phase identification and interpretation. The phases encountered were portlandite, hydroxyapatite, dicalcium phosphate, a liquid, and a vapour. After quenching, at constant pressure, the capsules were examined with a binocular microscope. If a vapour phase had been present there was a large depression on the surface of the capsule formed by the collapse of the capsule walls as the vapour condensed during quenching.

The capsules were opened and the charge examined with the binocular microscope. If a differentiation of material was observed the separate fractions were broken from the charge and examined in turn. Subsolidus charges in the absence of vapour were compacted into thin wafers of hard material and in the presence of vapour charges were distributed irregularly throughout the capsule. In the presence of liquid the charges

were thin wafers of soft friable material and it was often possible to isolate a bottom fraction of apatite-rich material formed by crystal settling. In the presence of liquid and vapour a frozen meniscus was often preserved.

Fragments of each charge were examined in immersion oils with a polarizing microscope and the phases identified by their optical properties. Refractive indices were measured to an accuracy of ± 0.003 using sodium light. Portlandite formed rounded plates in sub-solidus phase fields and above the solidus it was only encountered as a quench product similar to that identified by Wyllie and Tuttle (1960). Hydroxyapatite formed irregular crystals in subsolidus regions but developed as equant or slightly elongated hexagonal prisms with pyramidal terminations in the presence of liquid. These prisms ranged in size up to 0.25×0.10 mm and the maximum elongation observed was 4 : 1 although 2 : 1 was more usual. Dicalcium phosphate was identified from its X-ray diffraction pattern.

Liquids that were found on the join $CH-C_3P-H_2O$ could not be quenched to a glass but formed instead a crystalline mixture of portlandite and hydroxyapatite in which the habit of the hydroxyapatite was distinctive. The quench hydroxyapatite consisted of numerous thin needles set in quench portlandite. Elongations of 20 : 1 were observed for the apatite needles and a variety of skeletal features were evident. By slowing the rate of the quench to five or more minutes (one minute was normal from 800° C to 90° C) it was found that the apatite needles became shorter and less abundant. A full description and photographs of the quench apatites appear in Wyllie, Cox, and Biggar (1962). In addition to the previously noted settling of the apatite crystals in charges containing liquid, some charges had a small upper fraction with relatively few apatite needles. This suggests that the first needles produced during the quench sank. To allow this to happen during a normal quench the viscosity of the melt must have been low.

A detailed comparison of the apatites formed from different bulk compositions was made by measuring the positions of the 231 and 140 apatite peaks using the 311 peak of calcium fluoride as an internal standard. Six scans of each sample were made using an X-ray counter diffractometer; the accuracy of the determinations was $\pm 0.02°$ of 2θ.

Results

The join $HA-H_2O$. The experimental data for the join $HA-H_2O$ are listed in table I along with the $\Delta 2\theta$ values ($\Delta 2\theta = 2\theta_{311, CaF_2} - 2\theta_{HA}$) of

the apatite products. When dry charges of the HA composition were maintained at 700 to 950° C and 1000 bars pressure the product was black and had a brown or grey coating due to reaction with the gold or platinum; the X-ray diffraction pattern showed the presence of apatite

TABLE I. The joins HA–H_2O, C_3P–H_2O, and C_2P–H_2O at 1000 bars.
Temperatures to $\pm 5°$ C; $\Delta 2\theta$ to $\pm 0.02°$

| Composition | | | | | Apatite | |
Wt. % HA	Wt. % H_2O	Temp.	Time, days	Result	$\Delta 2\theta_{140}$	$\Delta 2\theta_{231}$
100	0	850° C	$6\frac{1}{4}$	*HA	4·51°	5·29°
77	23	850	30	$HA+V$	4·54	5·31
53	47	755	13	$HA+V$	4·54	5·31
C_3P						
100	0	755	4	*C_3P+HA tr	—	—
75	25	905	3	$HA+C_2P+V$	4·52	5·31
C_2P						
100	0	825	10	*C_2P+HA tr	—	—
74	26	825	10	$C_2P+HA+V$	4·49	5·27
48	52	825	10	$HA+V$	4·50	5·26
24	76	825	10	$HA+V$	4·51	5·30

* reaction with capsule.

only. With water present there was no attack on the capsule and microscopic examination showed that the apatite obtained was a pseudomorph after the tricalcium phosphate, although rare apatite crystals of hexagonal outline up to 0·01 mm long were also present. The difference in $\Delta 2\theta$ between the composition HA and the compositions $HA+H_2O$ may be due to the contamination of the charge in the dry runs or to the presence of water in the hydroxyapatite structure (to an extent greater than that required by the formula) in the runs with water present.

The join C_3P–H_2O. The experimental data for the join C_3P–H_2O are listed in table I. Dry charges gave a black product composed of the starting material and some apatite. With 25 % water present there was no attack on the capsule and the product was a mixture of apatite and β–C_2P.

The join CH–C_3P–H_2O. The critical results, at 1000 bars pressure for the temperature range 700 to 950° C, are shown in fig. 2 for the bounding join CH–C_3P. The results for the experiments in which 45–53 % water was present are shown in fig. 3 as the plane containing 50 % water. The experimental data are given in tables II and III

respectively and some results from table I are also plotted in figs. 2 and 3.

On the join $CH-C_3P$ there is a eutectic equilibrium $CH+HA \rightleftharpoons L$ at 765° C at 1000 bars pressure (fig. 2). The composition of the eutectic liquid was estimated at 96 % CH and 4 % C_3P.

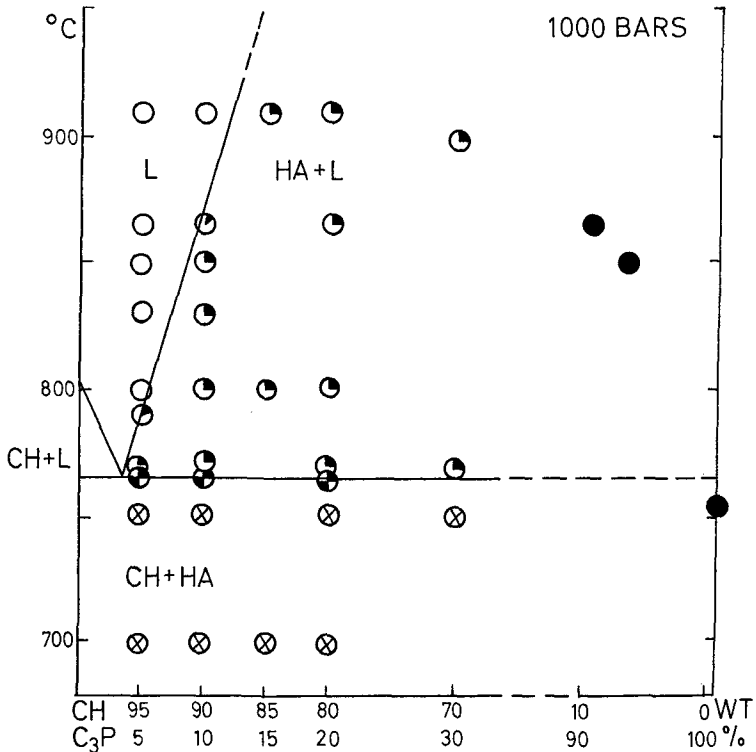FIG. 2. The join $CH-C_3P$ at 1000 bars; ○, L; ◑, $HA+L$; ◑, $CH+L$; ●, charge reacted with capsule; ⊗ subsolidus region. Phase boundaries between C_3P and HA are not shown in view of the reaction with the capsule.

On the section $CH-C_3P-50$ % H_2O there is an equilibrium $CH+HA+V \rightleftharpoons L$ at 735° C at 1000 bars pressure (fig. 3). The liquid composition in this reaction contains CH and C_3P in the weight ratio of 96 to 4 and a few % dissolved water.

A brief description of the changes observed in the hydroxyapatites as the bulk composition of mixtures varied from 100 % C_3P to 5 % C_3P follows and tables I and IV list the values of $\Delta 2\theta$ for these apatites.

TABLE II. The join $CH-C_3P$ at 1000 bars. Temperatures to $\pm 5°$ C

Wt. % CH	C_3P	Temp.	Time d.	hr.	Result				Wt. % CH	C_3P	Temp.	Time d.	hr.	Result		
95	5	700° C	3	0	CH	HA			95	5	800° C	3	0			L
90	10	700	3	0	CH	HA(1)*			90	10	800	3	0	HA		L
85	15	700	3	0	CH	HA(2)			85	15	800	3	0	HA(4)		L
80	20	700	3	0	CH	HA(3)			80	20	800	3	0	HA(5)		L
95	5	750		22	CH	HA			95	5	830	6	0			L
90	10	750		22	CH	HA			90	10	830	6	0	HA		L
80	20	750		22	CH	HA			95	5	852	1	0			L
70	30	750		22	CH	HA			90	10	852	1	0	HA		L
95	5	765	2	6	CH	HA	L		95	5	865	30	0			L
90	10	765	2	6	CH	HA	L		90	10	865	30	0	HA tr		L
80	20	765	2	6	CH	HA	L		80	20	865	30	0	HA		L
95	5	770	30	0		HA	L		70	30	865		20	HA		L
90	10	770	30	0		HA	L		95	5	910		5			L
80	20	770	30	0		HA	L		90	10	910		5			L
70	30	770	30	0		HA	L		85	15	910		5	HA		L
95	5	791	2	6		HA tr	L		80	20	910		5	HA		L

* Nos. (1) to (5) refer to table IV.

TABLE III. The section $CH-C_3P-50$ % H_2O

Ratio CH	: C_3P	Wt. % H_2O	Temp.	Time d.	hr.	Result			
90	10	51	720° C		22	CH	HA		V
80	20	50	720		22	CH	HA		V
70	30	49	720		22	CH	HA		V
95	5	50	730	2	18	CH	HA		V
85	15	50	730	2	18	CH	HA		V
95	5	48	740	30	0		HA	L	V
90	10	50	740	30	0		HA	L	V
80	20	50	740	30	0		HA	L	V
70	30	48	740	30	0		HA	L	V
95	5	50	762		22		HA	L	V
90	10	51	762		22		HA	L	V
95	5	48	775	7	0			L	V
90	10	50	775	7	0		HA	L	V
90	15	53	800	7	0		HA (6)*	L	V
80	20	46	800	7	0		HA (7)	L	V
95	5	53	815	7	0			L	V
90	10	50	815	7	0		HA	L	V
95	5	48	852	2	19			L	V
90	10	46	852	2	19		HA tr	L	V
80	20	45	852	2	19		HA	L	V
90	10	48	910		5			L	V
80	20	50	910		5		HA	L	V
70	30	48	910		5		HA	L	V
95	5	43	932		5			L	V
90	10	49	932		5			L	V
85	15	52	932		5		HA	L	V
80	20	47	932		5		HA	L	V
10	90	50	865	30	0		HA (8)	L tr	V

* Nos. (6) to (8) refer to table IV.

Charges of C_3P and of $HA(C_3P$ 92·6 % CH 7·4 %) are described above. Charges with the composition C_3P 90 % CH 10 % and with 50 % water present were composed of hexagonal crystals of hydroxyapatite up to 0·02 mm long rimmed with portlandite. No pseudomorphs of C_3P remained. The portlandite rims represent the quenched liquid which,
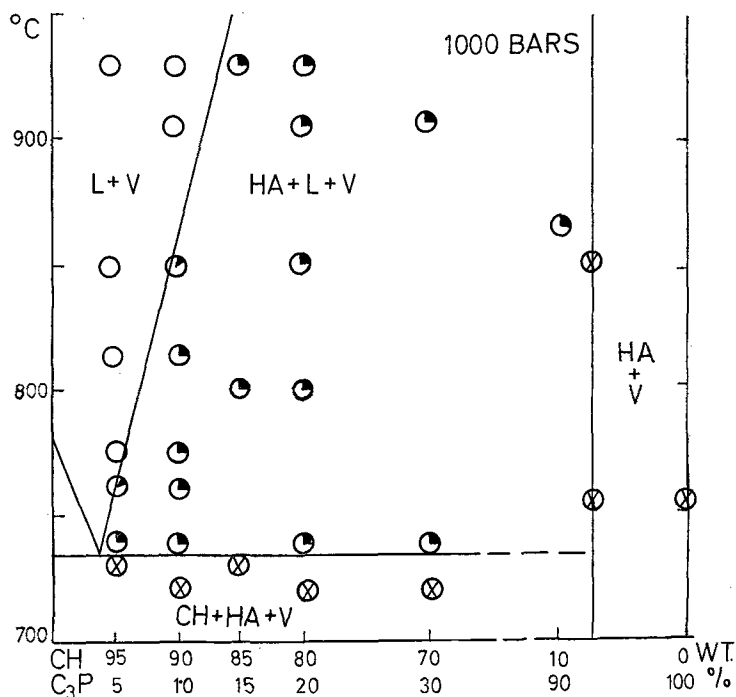

FIG. 3. The join CH–C_3P–H_2O at 1000 bars with approximately 50 wt. % water; $\bigcirc$, $L+V$; $\ominus$, $HA+L+V$; $\otimes$, subsolidus region.

although present in only very small amounts, acted as a solvent (or flux or mineralizer) for the recrystallization of the apatite. Larger apatite crystals up to 0·25 mm long grew in charges rich in portlandite with or without water and it was often possible to isolate an apatite rich layer from the bottom of the charge. Tables I and IV show that the $\Delta 2\theta$ values of the apatites formed from bulk compositions rich in CH on the join CH–C_3P–H_2O differ from the $\Delta 2\theta$ values obtained for compositions rich in C_3P, indicating that the presence of CH alters the apatite composition although no systematic variation was noted.

Liquids rich in portlandite did not form a glass on quenching but formed instead a crystalline mixture of portlandite and thin needles of apatite. The optical properties of these apatites formed during the quench and of the large apatite crystals grown at the temperature of the experiment were identical and sharp single X-ray diffraction peaks were obtained from mixtures of the two types.

TABLE IV. X-ray diffraction results for apatites from tables II and III

Table	No.	$\Delta 2\theta_{140}$	$\Delta 2\theta_{231}$
II	1	4·44	5·19
II	2	4·50	5·28
II	3	4·48	5·28
II	4	4·45	5·22
II	5	4·47	5·26
III	6	4·42	5·26
III	7	4·45	5·27
III	8	4·50	5·28

Data for the join CH–C_3P (fig. 2) and the section CH–C_3P–50 % H_2O (fig. 3) can be combined to construct isobaric isothermal planes for the join CH–HA–H_2O. Such a plane at 795° C is shown with a distorted scale in fig. 4. Data for the join CH–H_2O were taken from Wyllie and Raynor (1965) who reported a vapour of almost pure water and a liquid of composition CH 95 % H_2O 5 %. The crosses in fig. 4 are the experimental points from which the isothermal diagram was constructed. The tie-lines were not determined experimentally but were sketched in. In the field $HA + L$ the tie lines are shown to converge on HA. The X-ray evidence indicates a variable apatite composition but because the nature of the variation is not known the diagram is drawn showing HA of constant composition. Diagrams similar to fig. 4 can be constructed for other temperatures from figs. 2 and 3. The liquid and vapour corners of the three phase triangles $CH + L + V$, $CH + HA + L$ and $HA + L + V$ (the latter appears in fig. 4) generate, with changing temperature, liquidus and vaporus field boundaries, which are shown in projection in fig. 5. The liquid corners of these three triangles meet at the composition of the ternary isobaric invariant liquid which was estimated to contain CH 92 %, C_3P 4 %, H_2O 4 %; four phases, CH, HA, L, and V coexist at the invariant temperature, 735° C. The invariant temperatures and liquid compositions are shown in fig. 5.

The join C_2P–H_2O. The results of a few experiments with compositions on the join C_2P–H_2O at 825° C and 1000 bars pressure are shown in table I. Dry dicalcium phosphate reacted with the capsule to give

a black product with a diffraction pattern of $\beta\text{-}C_2P$ and traces of apatite. In the presence of 26 % water the product was C_2P and an apatite, and with more than 52 % water the product was an apatite only. The formation of an apatite from a charge of C_2P and water requires either that P_2O_5 is present in the vapour or that the apatite formed is deficient in calcium.
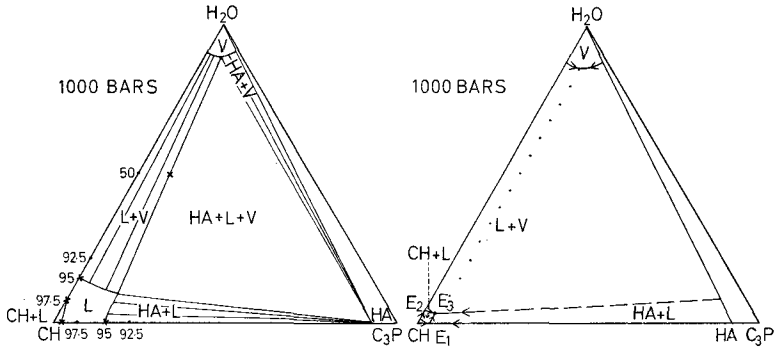
FIGS. 4 and 5. FIG. 4 (left). Isothermal section (795° C) for the region $CH\text{-}HA\text{-}H_2O$ at 1000 bars with distorted scale. The apatites are not stochiometric HA (see text). FIG. 5 (right). Liquidus (true scale) and vaporus (distorted scale) field boundaries for the join $CH\text{-}HA\text{-}H_2O$ at 1000 bars, projected on to $CH\text{-}C_3P\text{-}H_2O$. The in-variant temperatures and liquid compositions are E_1, 765° C, CH 96 % C_3P 4 %; E_2, 785° C, CH 95 % H_2O 5 %; E_3, 735° C, CH 92 % C_3P 4 %, H_2O 4 %.

The join $CaO\text{-}P_2O_5\text{-}H_2O$. Approximate phase relationships of this join can be deduced from the data for the join $CH\text{-}HA\text{-}H_2O$ and from the limited data available from the joins $C_3P\text{-}H_2O$ and $C_2P\text{-}H_2O$ as shown in fig. 6, which is an estimate of the isothermal section at 825° C. The apatites labelled A_1 and A_2 in fig. 6 are arbitrarily chosen. It is known from the X-ray evidence (tables I and IV) that they are not exactly HA but their actual composition is unknown. The vapours labelled V_1 and V_2 are shown on the join $H_2O\text{-}P_2O_5$ but they will have a small CaO content. The possible range of their H_2O and P_2O_5 contents is limited by the experimental points and the probability that A_1 and A_2 will be closer to HA than illustrated. The isothermal section indicates that for mixtures with bulk compositions on the CaO side of the composition line $HA\text{-}H_2O$ the P_2O_5 content of the vapour is low but for mixtures with bulk compositions between the composition line $HA\text{-}H_2O$ and the composition line $C_2P\text{-}H_2O$ the vapour may contain up to 20 % P_2O_5.

Discussion and conclusions. It was not found possible to synthesize hydroxyapatite directly from a charge of stoichiometric composition due to reaction with the capsule. Data relating to the contaminated product are listed in table I but should be read with caution. Previous authors have observed an attack on platinum by phosphate (van Wazer, 1959, pp. 177, 780; Eitel, 1924).
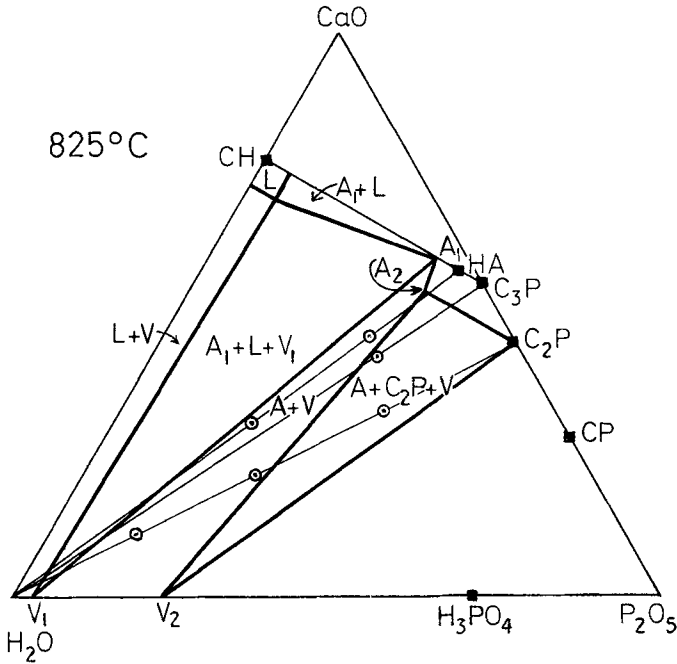

FIG. 6. Estimated isothermal section at 825° C for parts of the join $CaO-P_2O_5-H_2O$ at 1000 bars. Data for the region $CH-HA-H_2O$ are taken from figs. 2 and 3 and other experimental points are shown as circles. The compositions A_1 and A_2 are estimates but V_1 and V_2 are determined (subject to the qualifying statements in the text) by the experimental points.

The hydroxyapatites formed in the presence of various solvents (water, calcium hydroxide, water with calcium hydroxide, and water with dicalcium phosphate) had diffraction peaks at different angular positions and it is unlikely that any one of these is stoichiometric hydroxyapatite. In general the presence of excess calcium displaced the 140 and 231 peaks to smaller $\Delta 2\theta$ values (larger 2θ angle and hence smaller d-spacing) and water had the opposite effect. The presence of

a solvent greatly increased the size of the apatite crystals in the product and previous hydrothermal syntheses have employed such a technique (Perloff and Posner, 1956; Hayek *et al.*, 1958). However, in these syntheses the effect of the varying quantities of solvent, even if only water, on the composition of the apatite was not ascertained. The apatite lattice accepts, or has been postulated to accept, many substitutions and formulae such as $Ca_9H_2P_6O_{24}(OH)_2$ (Dallemagne *et al.*, 1949) represent calcium-deficient apatites with a water content greater than normal. The change in the position of the diffraction peaks in the presence of excess calcium hydroxide is less easily accounted for but limited solid solution of portlandite in hydroxyapatite is a possibility.

Liquids on the join $CH–C_3P–H_2O$ can be regarded as simple carbonate magmas and, although the join is remote from compositions of direct interest to the geologist, it provides the essential groundwork for studies in four-component systems formed by the addition of calcium fluoride or calcium carbonate, which will be the subject of later papers. The experimental facts to emerge that may be of geological significance are: the low solubility of apatite in the liquids at the point of final solidification (4 % C_3P or 4·5 % HA); the steep rise of the apatite liquidus with temperature to a value of, for example, 13·5 % HA at 900° C; the very rapid settling of the apatite crystals observed experimentally; and the formation of acicular apatites during rapid cooling. If operative in geological environments these effects would infer that carbonatites with more than, say, 15 % apatite have been enriched in that mineral by crystal accumulation and that this level would be reduced to as little as 4·5 % apatite at the lowest temperature (735° C) at which liquids were encountered in the present experiments. The finding of an increasingly acicular habit of the apatite as the chilled margin of a carbonatite dyke is approached is a possibility predicted by the experimental work.

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