Original Papers

Studies in the Basic Mineralizing System, CaO-P_2O_5-H_2O

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Equilibrium phase diagrams have been determined for the system CaO-P_2O_5-H_2O using hydrothermal synthesis techniques in the temperature range 300–600° and 2 Kb H_2O pressure. Well-crystallized hydroxyapatite has been produced and characterized. Small variations in unit cell parameters dependent on temperature of synthesis and bulk composition' of the starting materials have been determined. Precise chemical conditions were required to obtain apatite as the only solid phase in equilibrium with solution. Equilibrium phase diagram results are compared with previous synthetic investigations.

Key words: Hydroxyapatite — Mineral — Phase — Chemistry — Synthesis.

Des diagrammes de phase d'équilibre ont été déterminés pour le système CaO-P_2O_5-H_2O en utilisant des techniques de synthèse hydrothermique au cours de variatio nsde température allant de 300–600° et 2 Kb H_2O de pression. De l'hydroxyapatite bien cristallisé a été synthétisé et caractérisé. De faibles variations de paramètres de la maille cristalline, liées à la température de synthèse et composition globale du matériel initial, ont été déterminées. Des conditions chimiques précises sont nécessaires pour obtenir de l'apatite, en tant que seule phase solide en équilibre dans la solution. Les résultats de diagramme de phase d'équilibre sont comparés avec ceux obtenus dans des milieux synthétiques.

Es wurden Gleichgewichts-Phasendiagramme für das System CaO-P_2O_5-H_2O bestimmt, indem hydrothermale Synthese-Techniken im Temperaturbereich von 300—600° und bei einem Druck von 2 Kb H_2O verwendet wurden. Es wurde gut-kristallisiertes Hydroxyapatit erzeugt und charakterisiert. Es wurden geringe Unterschiede in den Parametern der Zelleinheiten festgestellt, welche von der angewandten Temperatur und der Zusammensetzung des Startmaterials abhingen. Es waren genaue chemische Bedingungen nötig, um Apatit als die einzige feste Phase im Gleichgewicht mit der Lösung zu erhalten. Die Resultate der Gleichgewichts-Phasendiagramme werden mit früheren Untersuchungen mit der Synthesetechnik verglichen.

Introduction

The dominant mineral species of vertebrate hard tissues, teeth and bone, is known to be hydroxyapatite. Although hydroxyapatite is a ubiquitous, naturally occurring calcium phosphate mineral, the material that is precipitated in low temperature environments, such as the physiological conditions of hard tissues, is not well defined nor understood. The extremely fine grain size of the precipitate virtually precludes accurate identification of the phase(s) present and hinders the attempts to understand mineral reactions. It is not surprising therefore that investigators turn to synthetic situations, where the chemical and physical conditions can be controlled, to learn about the mineral system.

For reasons not generally understood, hydroxyapatite of "ideal" composition is not easily synthesized. Synthetics, usually precipitated from solution and then heated to increase "crystallinity", often exhibit variable chemical composition. Sometimes the synthetics are a mixture containing more than one mineral species. Often an apatite phase is produced which gives variable unit cell parameters depending on temperature of heating or starting composition. Elements other than Ca, P, O and H required for "ideal" (stoichiometric) hydroxyapatite, Ca_{10} $(PO_4)_6(OH)_2$, are usually present in the starting solutions and it is known that the apatite crystal lattice can incorporate many of them (Cockbain, 1968; Deer, W.A., et al., 1963). The properties of the hydroxyapatite phase (HA) have not been determined directly on pure $Ca_{10}(PO_4)_6(OH)_2$ because well crystallized material of this composition was unavailable. It seemed essential to obtain pure material, in good crystals, in order to properly evaluate the phase and to understand its stability and reactions in the biological system.

Using a method known to give relatively large crystals of hydroxyapatite (Hayek, 1958; Posner and Perloff, 1958) investigations were undertaken in the system CaO-P_2O_5-H_2O. The hydrothermal synthesis method used in these investigations has many advantages. The solid products are well crystallized and, by systematic examination of a range of compositions, the relationships between apatite, solution, and other calcium phosphate phases, can be determined.

Posner and Perloff (1958) used hydrothermal synthesis techniques to obtain well crystallized HA but did not make a systematic study of reactions. Hayek (1958) obtained well-crystallized HA at 400° over a pH range of 5 to 11 but starting materials usually contained Na, which was also found in the products. Neither of these authors considered the problems of attainment of equilibrium for their products and this is important in understanding the calcium phosphate system. High temperature studies, 700–900° at 1000 bars H_2O pressure have been carried out over a wide composition range, including F, but are only generally applicable (Biggar, 1966), and most of this report is outside the composition range appropriate for calcified tissues. The few experiments in the composition range cannot be extrapolated to physiologic conditions because under the physical conditions of the experiment the products of reaction are in the liquid portion of the system.

In the report that follows hydrothermal studies have been carried out at 2000 bars H_2O pressure over the range 300–600°. These physical conditions were chosen primarily to accelerate reactions to achieve equilibrium in a reasonable length of time. A systematic range of compositions in the chemical system CaO-P_2O_5-H_2O have been explored, in particular those areas where HA occurred as a stable phase. Experimental details and a technical discussion of the four phase diagrams drawn in the temperature interval studied have been presented elsewhere (Skinner, 1973). Hydroxyapatite crystals have been well characterized, and small variations in unit cell parameters dependent on temperature of synthesis and bulk composition of the starting materials have been accurately determined. The results emphasize the variability of HA even when produced in a simple chemical system. Secondly, precise chemical conditions were required to obtain apatite as the *only* solid phase in equilibrium with solution. The detailed relationships between HA and other phases in the basic chemical system

at equilibrium have been established. A brief outline of methods employed and two equilibrium phase diagrams are presented as background to the discussion of hydroxyapatite as a synthetic phase and as a constituent of mineralizing systems.

Methods

Solid CaO and water solutions of phosphoric acid (H$_3$PO$_4$) were individually accurately weighed and sealed into gold capsules of 4 mm diameter and approximately 1 cm in length. The chemicals reacted inside this inert container at elevated temperatures and pressures without contamination from atmospheric or extraneous solution components. The capsules were placed in a pressure vessel which was maintained at temperature. Water pressure was supplied by a constantly monitored pump system.

The length of time that samples of known composition were held at T and P was dictated by criteria that the products be at equilibrium. Equilibrium is operationally defined as that state where a phase no longer changes in response to its environment. For example: a sample of known composition, held at known T and P, might produce, after a few days, crystalline apatite and fluid. Examination of the solid phase by X-ray diffraction would then enable precise unit cell parameters of the apatite to be calculated (Skinner, 1968). Another sample of the same composition but held at T and P for longer time (say 3 or 20 weeks), would be analysed by X-ray diffraction and the paramenters of the apatite calculated; if these remained constant it was assumed that equilibrium had been reached. In the calcium phosphate system metastable products persisted. Some samples were held at T and P for periods up to 180 days to assure equilibrium.

About 500 samples were examined. Optical and X-ray diffraction analyses were used to identify the solid products. The fluid present was tested by pHydrion paper. Results of these determinations on each sample were located on a composition plot and equilibrium phase diagrams were constructed.

Before the results presented in Fig. 2 are discussed the sample plotting technique will be illustrated using the triangular diagram, Fig. 1.

Fig. 1 is a composition plot for the three component system, CaO, P$_2$O$_5$, H$_2$O. The three apices represent 100 wt% of each of the components. Pure water (H$_2$O) is plotted at the top. Using theoretical formulae of the phases that can occur in this system, the weight percent of the components in the compounds have been calculated. Table 1 gives 4 examples.

Table 1

Solid phase	Component formula	Wt%CaO	Wt%P$_2$O$_5$	Wt%H$_2$O
Ca(OH)$_2$	CaO $\cdot$ H$_2$O	75.7	—	24.3
Ca$_{10}$(PO$_4$)$_6$(OH)$_2$	10 CaO $\cdot$ 3P$_2$O$_5$.H$_2$O	55.8	42.4	1.8
2CaHPO$_4$	2CaO $\cdot$ P$_2$O$_5$ $\cdot$ H$_2$O	41.2	52.2	6.6
Ca$_2$P$_2$O$_7$	2CaO $\cdot$ P$_2$O$_5$	44.1	55.9	—

Anhydrous forms, such as Ca$_2$P$_2$O$_7$ plot along the CaO-P$_2$O$_5$ edge of Fig. 1. Ca(OH)$_2$ plots on the edge CaO-H$_2$O. All phases containing some of each of the three components will plot within the triangle.

Results

Fig. 1 depicts a number of solid phases, some of which are plotted on Fig. 2. The phases in Fig. 2A were the only stable compounds found in samples submitted to 300° and 2000 bars H$_2$O pressure. The phase diagrams (Fig. 2) have been constructed using samples of known composition (the percent of three components weighed into the capsule), subjected to temperature and pressure for the time required to obtain equilibrium (about four weeks for each sample under the con-
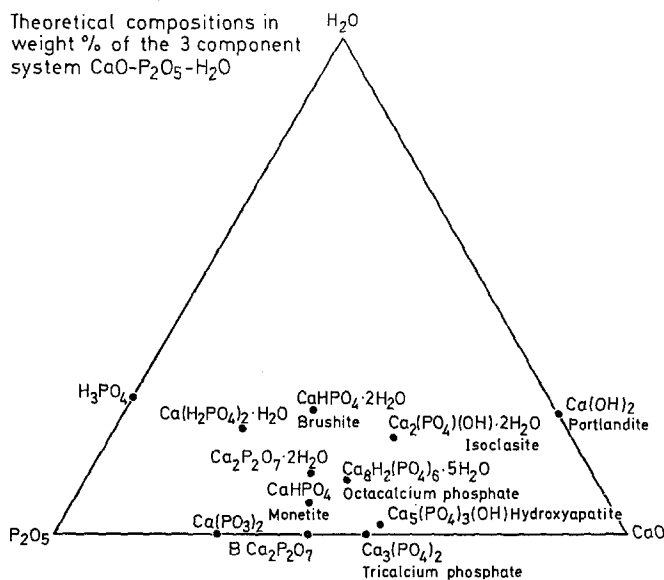
Fig. 1. Composition diagram for plotting phase equilibrium results. Theoretical compositions of possible solid phases in the system CaO-P_2O_5-H_2O are plotted

ditions of Fig. 2A). The products of each sample were plotted at the appropriate sample composition on the diagram. About 150 samples were examined to determine the relationships between composition and occurrence of phases at 300° and 2000 bars H_2O pressure.

The smaller triangular sub-areas within the composition plot are phase fields, defined by solid and/or dotted lines. For any starting composition within one of these fields the products at equilibrium at 300° and 2000 bars are the same. Samples of different bulk compositions falling within the field merely exhibit different proportions of the phases. Samples with an initial high H_2O composition contain a higher proportion of fluid. Each phase field has been numbered and the products listed. From the diagram, products for any sample composition can be predicted. In a three-component system no other phases should be found in the products provided the sample has reached equilibrium. To illustrate: for all starting compositions within phase field #4 (Fig. 2A) only two solid phases, monetite (CaHPO₄) plus HA and a fluid may occur. The composition of the monetite and HA is fixed at the compositions $CaHPO_4$ and $Ca_{10}(PO_4)_6(OH)_2$. X-ray diffraction analysis of the solid products from many samples in this field have shown that the solids are virtually ideal compounds (Skinner, 1973). The solids in the sample are expressed at the theoretical composition for the phases on the diagram. The composition of the fluid for samples in this phase field is expressed by the remaining apex of sub-triangle #4. The fluid has a composition close to water but contains a small amount of P_2O_5, and even less CaO, in solution. The compositions included in phase field #4 produce at equilibrium monetite, HA and a fluid. The solid phases are produced over a wide range of CaO/P_2O_5 and H_2O compositions.
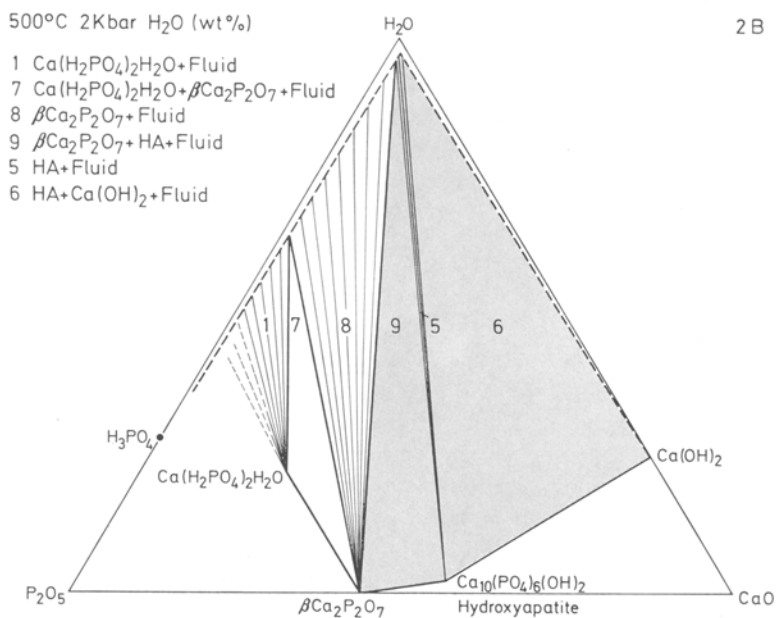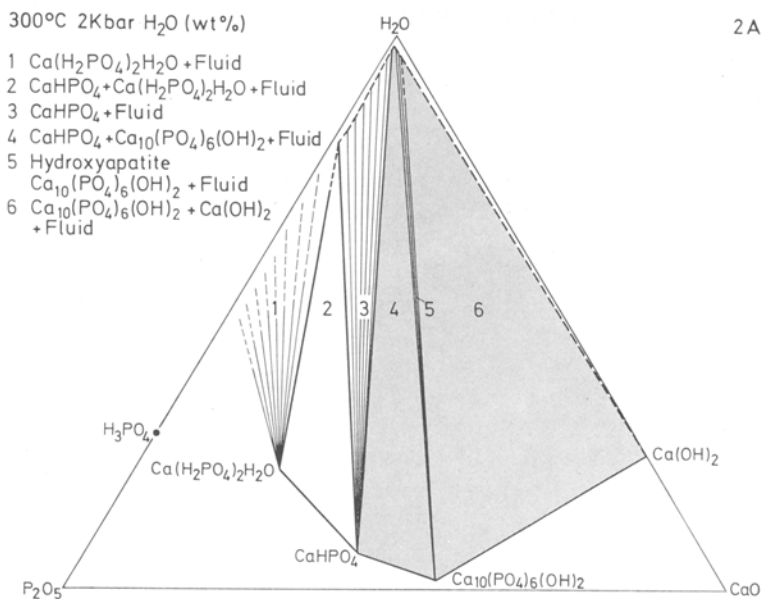
300°C 2Kbar H$_2$O (wt%)　　　　H$_2$O　　　　2 A

1　Ca(H$_2$PO$_4$)$_2$H$_2$O +Fluid
2　CaHPO$_4$+Ca(H$_2$PO$_4$)$_2$H$_2$O +Fluid
3　CaHPO$_4$ +Fluid
4　CaHPO$_4$+Ca$_{10}$(PO$_4$)$_6$(OH)$_2$+Fluid
5　Hydroxyapatite
　　Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ +Fluid
6　Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ +Ca(OH)$_2$
　　+Fluid

H$_3$PO$_4$

Ca(H$_2$PO$_4$)$_2$H$_2$O

Ca(OH)$_2$

CaHPO$_4$

P$_2$O$_5$　　　　Ca$_{10}$(PO$_4$)$_6$(OH)$_2$　　　　CaO

500°C 2Kbar H$_2$O (wt%)　　　　H$_2$O　　　　2 B

1　Ca(H$_2$PO$_4$)$_2$H$_2$O+Fluid
7　Ca(H$_2$PO$_4$)$_2$H$_2$O+βCa$_2$P$_2$O$_7$+Fluid
8　βCa$_2$P$_2$O$_7$+Fluid
9　βCa$_2$P$_2$O$_7$+HA+Fluid
5　HA+Fluid
6　HA+Ca(OH)$_2$+Fluid

H$_3$PO$_4$

Ca(H$_2$PO$_4$)$_2$H$_2$O

Ca(OH)$_2$

Ca$_{10}$(PO$_4$)$_6$(OH)$_2$
P$_2$O$_5$　　　βCa$_2$P$_2$O$_7$　　　Hydroxyapatite　　　CaO

Fig. 2A and B. Equilibrium phase diagrams CaO-P$_2$O$_5$-H$_2$O experimentally determined.
Shaded portion indicates area where HA occurs

It follows from the diagram that HA occurs as a stable solid phase over a
wide range of CaO/P$_2$O$_5$ ratios and H$_2$O compositions but usually in association
with a second solid phase. Under these T and P conditions the second phase is
either monetite or portlandite (Ca(OH)$_2$). Phase field #5 delineates the con-

ditions where there is only one solid phase in association with fluid: hydroxyapatite. The field is extremely restricted in CaO/P_2O_5 composition, except at high H_2O compositions.

The phase fields were accurately determined using close compositional control. It is known that samples with CaO/P_2O_5 greater than that required for "ideal" hydroxyapatite ($CaO/P_2O_5 = 1.315$, $Ca/P = 2.15$) will always contain two solid phases (HA and portlandite, $Ca(OH)_2$) no matter what the H_2O content of the sample. At CaO/P_2O_5 values below ideal HA, there is a small CaO/P_2O_5 composition range, but only at high H_2O content, where HA is the only solid phase. In order to stay in phase field $\neq 5$ (HA + fluid) at 50% H_2O, the CaO/P_2O_5 ratio may vary between 1.28–1.315, at 75% H_2O, CaO/P_2O_5 variation may be 1.18–1.315, at 90%, 1.05–1.315. At still lower CaO/P_2O_5 values HA occurs with a second solid phase. The phase varies depending on the temperature of the experiment; at 300° it is $CaHPO_4$. Fig. 2B, the phase diagram for 500°, 2000 bars H_2O pressure illustrates the effect of higher T: $Ca_2P_2O_7$ has replaced $CaHPO_4$ as the stable calcium phosphate phase. Note that the phase diagram at this temperature is virtually the same as at 300°: the phase field $\neq 5$ is extremely limited.

X-ray diffraction analysis of the solid products, especially apatite, was used to establish equilibrium conditions (see discussion below). It was found that apatites from fields $\neq 4$, 5 and 6 at equilibrium at 300°, and at 500° had reproducibly distinctive cell dimensions (Table 3).

Discussion

Comparison of equilibrium phase diagram results with previous synthetic work:

A. Elevated Pressure Hydrothermal Synthesis Method

In describing the hydrothermal synthesis of HA at 300°, 1250 lb/in², Posner (1958) stated that "at least 10 ml of H_2O for each 0.10 g of $CaHPO_4$ was necessary to obtain a complete reaction". At lower water contents the product was mixed $CaHPO_4$ and HA. Two solid phases could be the result of an incomplete reaction, or, from the phase diagram (Fig. 2A) it could be predicted that two solid phases were the stable assemblage for lower H_2O contents. Bulk composition, H_2O as well as CaO/P_2O_5, is important in determining the products. $CaHPO_4$ was used as the starting solid. $CaHPO_4$ has $CaO/P_2O_5 = 0.79$ (wt%), a low CaO content, and therefore the proportion of H_2O necessary to insure crystallization of HA only, field $\neq 5$, is high. Larger yields of crystalline HA could have been obtained by increasing the CaO wt% of the charge. The precise bulk composition required to produce HA can be predicted from the phase diagram. Well crystallized hydroxyapatite can be obtained from a range of compositions, but it is usually accompanied by a second solid phase.

B. Room Pressure Hydrothermal Synthesis

Table 2 compares several published methods of producing crystalline HA. Many of the preparative procedures are carried out at room pressures. A phosphate

Table 2. Synthesis of HA

Reference	Starting materials	Method	Results and comments
Wallaeys (1952)	Solid $Ca_3(PO_4)_2$ & $CaO+H_2O$ vapor	Heat at 850°	Very slow reaction
	Solutions H_3PO_4 & $Ca(OH)_2$	Mix at 100°, Calcine 800°	HA $a=9.403$ (1) $c=6.866$ (1)
		In cold saturated solutions dried at 80°	HA $a=9.410$ (5) $c=6.865$ (2)
Montel (1953)	Solutions of H_3PO_4 with CaO	Neutralize in hot water	Incomplete reaction produced "trical and bical" several days to complete reaction (HA)
Brasseur (1953)	$Na_2HPO_4 \cdot 2H_2O+CaCl_2$	Mix in NH_4 solution— dry at 70°	Produced hydrated trical
Brasseur (1954) Brasseur (1958)	$Ca_8H_2(PO_4)_6+H_2O$	Heat to 300° — Calcine at 1000°	Trical $a=9.387$ $c=6.846$ HA $a=9.406$ $c=6.873$
Hayek and Stadlmann (1955)	$(NH_4)_2HPO_4+$ $Ca(NO_3)_2$	Mix in NH_4 solution — Calcined 600°	pH $=12$ 0.05 μ crystals
Hayek et al. (1958)	NaOH and $Ca(OH)_2$ +Product of above	Recrystallized under H_2O P at 400° up to 72 h	Crystals 0.04 mm long 0.005 mm wide
Posner and Stephenson (1952)	$Ca_3(PO_4)_2$ solid and H_2O	200–300° at 1250 lb/in² H_2O	HA 0.3 mm long $a=9.42$–9.44 $c=6.87$–6.88
Posner and Perloff (1958) Posner, Perloff and Dorio (1958)	$CaHPO_4$ solid and H_2O	300° at 1250 lb/in² H_2O	$a=9.432$ $c=6.881$ +whitlockite
Bassett (1958)	$Ca+H_3PO_4$ solutions	100° mix in varying proportions	Low CaO $=$ HA$+$ $Ca_3(PO_4)_2 \cdot$ crystals High CaO $=$ HA $+Ca(OH)_2$
Trautz (1958) Trautz et al. (1961)	$Ca_3(PO_4)_2+$ $Ca(OH)_2$ solids and steam	Autoclave at 360° $+$ 200 ATM 16 h	HA $a=9.421$ $c=6.881$ $Ca_3(PO_4)_2$ present on calcining product

solution is saturated with $Ca(OH)_2$ or CaO. If the degree of saturation is incomplete or if the pH of the solution does not attain neutrality (see Montel, 1953; or Wallaeys, 1952, p. 835) the precipitate shows a CaO/P_2O_5 ratio lower than ideal HA. A mixed product of two solid phases is the result. The second phase in addition to HA depends on the temperature of mixing. At 100° $CaHPO_4 \cdot 2H_2O$ plus HA is produced, at 300° $CaHPO_4$ plus HA (Bassett, 1958). Material with low CaO/ P_2O_5 can be identified by the presence of a second solid phase using optical or X-ray diffraction analyses.
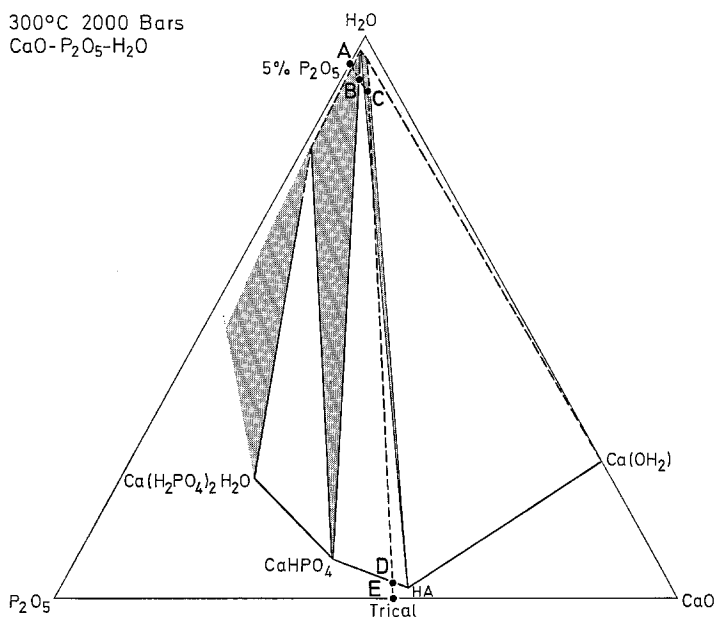
Fig. 3. "Path of crystallization" in terms of an equilibrium phase diagram

Whether a single phase, apatite, or apatite plus another phase, should be found provided the sample is at equilibrium can be predicted using the phase diagram. An initial dilute solution, a H_3PO_4-H_2O mixture, containing 5% P_2O_5 for example, will plot at A on Fig. 3. To add CaO move directly toward the CaO apex. A series of phase fields will be encountered reflecting the changing bulk composition of the sample. When the sample contains approximately 3 wt% CaO, HA could appear as a solid phase (B, Fig. 3). Supersaturation may be required for precipitation. The energy for nucleation and associated physical phenomena may delay the appearance of the solid phase. However, the first solid to form at RT is a fine-grained or amorphous precipitate. The actual structure in the latter case cannot be specified (Eanes *et al.*, 1965; Eanes and Posner, 1968) but it is probably analogous to opal and converts to crystalline HA in time (Eanes *et al.*, 1967).

Continued addition of CaO changes the sample bulk composition increasing the relative proportion of solid HA. At about 5 wt% CaO (sample bulk composition) the solid products should reflect the field in which two solid phases are present at equilibrium and the pH of the solution should be acidic. If H_2O is the major component, say 90% of the sample, and the $CaO/P_2O_5 = 1.0$, the equilibrium solid products at room T and P ought to be $CaHPO_4 \cdot 2H_2O$ + HA. At 300° Ca HPO_4 + HA are the solid phase products (Fig. 2A, 3). Between CaO/P_2O_5 ratio 1.0 and 1.315 HA should be the only phase at equilibrium.

C. Ignition of Samples

1. Formation of Phase $Ca_3(PO_4)_2$

Continuing the progress of the synthetic sample on Fig. 3 now at C ($CaO/P_2O_5 = 1.184$) the precipitate, which is probably poorly crystalline, may be removed from the aqueous surroundings, and in addition, heated to increase crystallinity. The bulk composition of the sample therefore changes again. The composition change can be expressed on the diagram by projection away from H_2O apex. On heating or harvesting the precipitate, the proportion of water should be the only chemical change, the CaO/P_2O_5 of the sample remains the same. Calcining at 800 or 900° will dehydrate the material rapidly. The appropriate anhydrous phase(s) for the CaO/P_2O_5 of the sample (1.184), $\beta Ca_3(PO_4)_2$ in the illustrated case, may nucleate and form. Partial dehydration will produce HA and $\beta Ca_3(PO_4)_2$; the sample composition will plot at D close to the $CaO-P_2O_5$ edge of the diagram. If dehydration is complete, only $\beta Ca_3(PO_4)_2$ should be expressed and the sample would plot on the $CaO-P_2O_5$ edge at the appropriate CaO/P_2O_5 ratio (E). $\beta Ca_3(PO_4)_2$ is the only phase which should appear at $CaO/P_2O_5 = 1.184$ (Tromel and Moller, 1932). It follows from the diagram that only one CaO/P_2O_5 composition will retain single phase HA material through precipitation from aqueous solutions and calcination, that CaO/P_2O_5 is 1.315, the ideal stoichiometric ratio of HA.

2. P_2O_7 (Pyrophosphate) Formation

Ignition of a precipitate with $CaO/P_2O_5 = 0.79–1.315$ usually produces apatite plus another solid phase. The second phase expressed depends on the temperature of ignition.

Gee and Dietz (1955) related Ca/P ratio (or CaO/P_2O_5) and surface area of a series of synthetic precipitates with mineral phase(s) expressed after calcining. Herman and Dallemagne (1961) ignited precipitates with a range of Ca/P for varying times at different temperatures up to 600°. They state that the amount of P_2O_7 produced increased with the temperature of the ignition and the nature of the sample material. Referring to Fig. 2 B (500°–2000 bars H_2O pressure) the phase at equilibrium with HA on the low CaO side is $Ca_2P_2O_7$, field #9. The replacement of $CaHPO_4$, monetite, by $\beta Ca_2P_2O_7$ actually takes place at $322° + 2.5°$ (Skinner, 1970) at 2000 bars H_2O pressure. At temperatures above $322°$, $\beta Ca_2P_2O_7$ would be the stable second phase. Interpretation of the results of Herman and Dallemagne (1961) is that above about 300° P_2O_7 appears more rapidly in samples which have lowest Ca/P. Samples of tricalcium phosphate hydrate, CaO/P_2O_5 approximately 1.184, showed $Ca_2P_2O_7$ but required higher temperatures. $\beta Ca_2P_2O_7 + HA$ are the stable solids at low CaO/P_2O_5 compositions between 325–730°C in the hydrous system, $\beta Ca_2P_2O_7$ plus $\beta Ca_3(PO_4)_2$ in the anhydrous system (Tromel and Moller, 1932).

D. The Fluid Phase

The pH of the fluid phase in equilibrium with the solid phase(s) in the phase diagram have been determined. pH is distinctive for a particular phase field. Phase field #4 fluid pH = 3.7. Calcium phosphates precipitated at low pH

(Brasseur, 1953) usually form mixed products consisting of two solid phases. Early studies (Lorah *et al.*, 1929) showed that the point of equilibrium between tricalcium phosphate and "basic tricalcium phosphate" was on the acid side of neutrality. Wallaeys (1952) stressed the need to achieve neutral pH to assure a single product phase. Hayek (1951) presented a graph of variations in pH with CaO/P_2O_5 composition in aqueous calcium phosphate systems. All these experiments are an expression of the fact that HA can form over a wide pH range. If the conditions are such that the solution has a low or high pH a second solid may be present even though the expression and therefore identification of the second phase is difficult. Field #6 (HA + $Ca(OH)_2$ + fluid) has a pH of 12.0. Field #5 (HA + fluid) is the locus of rapidly changing fluid characteristics. Large pH changes are possible with small changes in CaO/P_2O_5 even at constant H_2O composition.

E. Equilibrium Considerations

To assure production of HA of constant composition, equilibrium conditions should be obtained. Skinner (1973) has shown that all equilibrium apatites from a phase field at one T and P have identical unit cell paramenters. Sample #300–121 (Table 3) from phase field #4 contained monetite and HA as the solid phases at equilibrium. The HA cell dimensions are different from the apatite produced in field #5 at the same temperature (300–115, Table 3), or in field #6. There may be slight variations in parameters of apatites hydrothermally produced in like fields at different temperatures, or in compositionally different fields at the same temperature.

In the experiment of Posner *et al.* (1958) using $CaHPO_4$ as starting material the cell dimensions determined are different than those given in Posner and Stephenson (1952) Table 2. In the latter paper tricalcium phosphate was used as starting material and treated at 1250 lb/in² H_2O pressure and 300°, for up to 7 days. The apatite products were somewhat better crystallized than the starting compound but variable lattice parameters were found which were dependent on the treatment times. The unit cell parameter variation is probably an expression of dis-equilibrium. The experimental conditions discussed herein used higher pressure (2000 bars = 30000 lb/in²) which should accelerate reaction rates. Demonstration of equilibrium in the products usually took about 4 weeks at 300°. Apatites with slightly larger cell dimensions were formed in the shorter duration experiments (Table 3).

Bassett (1958), who investigated this chemical system at 25° and *one atmosphere* (15 lb/in²) pressure concluded that even after 19 months he had not achieved equilibrium conditions.

Unit cell parameters can be used as a sensitive indicator of the type of apatite produced. The parameters determined on apatites synthesized by other methods and listed in Table 2 show a range of values even when starting materials were similar. Slightly different temperature or treatment times or dis-equilibrium could cause the observed variations. Unit cell parameter variation of synthetic apatites has already been discussed by McConnell (1960). The results presented here emphasize his suggestion that investigators are not necessarily dealing with the same compound and may not have been sufficiently aware of the wide variety

Table 3. Unit cell parameters of HA synthesized at 2000 bars H$_2$O pressure

Sample #	Composition			Field #	Apatite cell parameters	
	CaO	P$_2$O$_5$	H$_2$O		a	c
300–121	5.24	7.19	87.57	4	9.417 (1)[a]	6.879 (2)[a]
300–115	14.18	11.88	73.94	5	9.422 (2)	6.880 (2)
300–120	15.45	11.25	73.30	6	9.426 (1)	6.877 (3)
Disequilib.	300°C	HA+Fluid field			9.443	6.890
500–120	5.56	7.14	87.30	4	9.4249 (7)	6.8866 (7)
500–38	21.45	15.04	63.51	5	9.417 (2)	6.874 (3)
500–131	9.55	6.82	83.63	6	9.423 (1)	6.882 (1)

[a] Number in parenthesis is the measurement standard error. It is applicable to the final decimal figure of the determined value, i.e. 9.417 ± 0.001

of substitution of other elements within the apatite structure type (Cockbain, 1969). The apatites, therefore may be discretely different. Small unit cell variations are significant. The phase equilibrium study outlined here has demonstrated that unit cell variations can take place in response to temperature, composition field of synthesis or non-attainment of equilibrium in the products. Substitution of other elements into the basic apatite structure adds other variables to influence apatite cell parameter changes.

Synthesis of pure HA can be achieved by precipitation from solution using H$_3$PO$_4$ and CaO or Ca(OH)$_2$. Variations in temperature or bulk composition (including H$_2$O) leading to crystallization in different phase fields are potential sources of minor differences in the solid product which can be detected by unit cell parameter measurements. Calcining a low temperature precipitate should recrystallize the HA without creating a second solid phase but only if the CaO/P$_2$O$_5$ is precisely 1.315. The production of a unique, ideal or stoichiometric, Ca$_{10}$(PO$_4$)$_6$ (OH)$_2$ requires stringent chemical conditions in respect to all three components: CaO, P$_2$O$_5$ and H$_2$O, and strict adherance to equilibrium attainment to achieve reproducability of the product. Hydrothermal synthesis techniques (elevated temperatures and pressures) increase reaction rates and have been used to produce equilibrium crystalline HA in a time of approximately one month.

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