Calcination Properties of Precipitated Basic Calcium Phosphates

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Abstract

Basic calcium phosphates with varying Ca/P ratio, 1.53-1.67 were prepared from lime suspension and phosphoric acid, or from calcium nitrate and ammonium phosphate solutions under various precipitation conditions, including agitation by ultrasonic vibration. Condensed phosphate formation has been studied by igniting the basic calcium phosphates, octacalcium phosphate and mixed phosphates with and without steam. Some precipitates have been examined by X-ray diffraction, infrared, petrographic microscopic techniques. These techniques did not reveal apparent separate phases in the precipitates.

Only one correlation between the amount of pyrophosphate equivalent formed and Ca/P ratio was found and it was independent of procedure and raw materials. The correlation is the case that calcined products consist of hydroxyapatite and calcium pyrophosphate only. The view is discussed that variation in Ca/P for some basic calcium phosphates is caused by simultaneous presence of hydroxyapatite with some other calcium phosphates. Constituents can be interlayered or poorly crystalline dicalcium phosphate, octacalcium phosphate and/or amorphous calcium phosphates without definite chemical identities mixed with hydroxyapatite.

This communication is concerned with properties of basic calcium phosphates, mainly calcining properties. In particular, a single pyrophosphate-Ca/P ratio correlation is presented, which is different from those of defective apatite models. Most of the samples of basic calcium phosphate (BCP) were prepared from lime suspension and phosphoric acid.

BCP or "hydroxyapatite" has found considerable industrial application as a flow conditioning agent for fine solids, as an anticaking agent for salt, as a mold coat for copper ingot casting, as a medium for suspension polymerization, etc. These applications arise from unique physical and chemical properties of BCP; very small particle size, large surface area, and/or water-adsorbing power, and low electrical conductivity[1] of BCP particles.

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Large volume production of BCP is based on a process of neutralizing lime suspension with phosphoric acid. No fundamental work has been reported on BCP made from lime suspension. Since the solid phase of $Ca(OH)_2$ is present throughout the precipitation process, the mechanism of precipitation may be different from that of solution precipitation. The objectives of this study were (1) to characterize properties, composition of BCP precipitated from lime suspension and phosphoric acid and (2) to study the effects of precipitation conditions on composition (measured by pyrophosphate) and properties of BCP.

Literature

The so-called non-stoichiometric apatites having lower Ca/p ratio than hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ have been the subjects of many investi-

gators[2-11]. A controversy has developed over the nonstoichiometric properties of basic calcium phosphates. Three different theories have emerged:

a) Adsorption model...There exists only one chemically defined compound, HA, and calcium phosphates having low ratios are caused by the adsorption of acid phosphates[12, 13] on the surface of the precipitated HA.

b) "Mixture" models...McConnel[9] has proposed that the low ratios result from "fine grained" (poorly crystalline) mixtures of dicalcium phosphate dihydrate (DCPD), dicalcium phosphate anhydrous (DCPA), octacalcium phosphate (OCP), and HA.

Alternatively, Brown[4] et al. proposed a structural model based on epitaxial growth of stoichiometric HA on OCP crystalline interlayered or lamellar mixtures analogous to clays.

c) Defective apatite models...Continuous series of compositions based on the defect apatite lattice concept have been proposed by a number of investigators[3, 5, 8, 11].

i) Posner[5] et al. proposed that Ca^{2+} ions were statistically missing from the apatite lattice of HA. In order to balance the charge, two protons enter into the lattice...$Ca_{10-n}H_{2n}(PO_4)_6(OH)_2$.

ii) Winand et al. [11] and subsequent investigators [2, 3, 5, 8] have proposed an alternative concept that the charge was balanced by the addition of one proton and the removal of one structural OH per missing Ca^{++} ions $Ca_{10-n}(HPO_4)_n (PO_4)_{6-n}(OH)_{2-n}$.

iii) Kuhl and Nebergall[8] have proposed yet further series with the general formula...$Ca_{10-x-y}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x-y}$ where $y=1-(x/2)$.
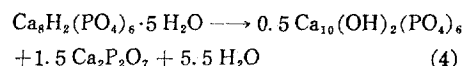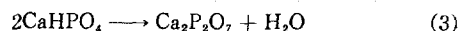
A number of investigators[2, 3, 7, 8, 10, 11, 14, 15, 16] studied pyrophosphate formation upon pyrolyzing BCP or bone at elevated temperatures. Acid phosphate groups such as HPO_4^{2-} in BCP precipitates or bones undergo a condensation reaction as follows:

$$2HPO_4^{2-} \longrightarrow P_2O_7^{4-} + H_2O \tag{1}$$
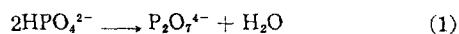
Winand et al. [11] and subsequent in vestigators postulated that the HPO_4 in defective apatites was molecularly dehydrated:

$$Ca_{10-n}(HPO_4)_n(PO_4)_{6-n} \longrightarrow Ca_{10-n}(P_2O_7)_{n/2}(PO_4)_{6-n}$$

$$(OH)_{2-n} + \frac{n}{2} H_2O \tag{2}$$
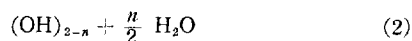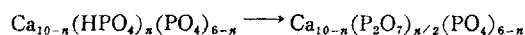
The sources of HPO_4^{-2} were also postulated to be DCP[7, 15] and OCP[4, 16] Thus:

$$2CaHPO_4 \longrightarrow Ca_2P_2O_7 + H_2O \tag{3}$$

$$Ca_8H_2(PO_4)_6 \cdot 5 H_2O \longrightarrow 0.5 Ca_{10}(OH)_2(PO_4)_6$$
$$+ 1.5 Ca_2P_2O_7 + 5.5 H_2O \tag{4}$$

In the calcining process, there is also a competing reaction[3, 15, 16] to consume the formed $Ca_2P_2O_7$ and HA to yield $\beta\text{-}Ca_3(PO_4)_2$.

$$Ca_2P_2O_7 + Ca_{10}(OH)_2(PO_4)_6 \longrightarrow 4Ca_3(PO_4)_2$$
$$+ H_2O \tag{5}$$
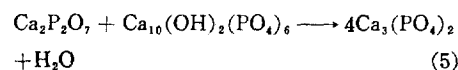
Reactions (3) and (4) take place over wide temperature ranges, 325-600°C[14]. The rate of pyrophosphate formation is reported to be much slower than that of the single phase reaction[3, 7]. The time required for maximum pyrophosphate formation varies widely: 15-240 hours[3, 7, 14] even at 600°C. Reaction (5) appears to begin at a low temperature and continues to 800°C. Thermogravimetric data[2] indicated that Reaction (5) proceeds quantitatively between 750-800°C. The temperature at which Reaction (5) first occurs appears to vary from sample to sample and varies with the method of calcination.

Even though the chemistry of BCP calcination is not well established, this method has been used to obtain quantitative information on the amount of HPO_4^{-2} radicals in precipitates. As a matter of fact, the pyrophosphate determined was one of the bases to propose some of the general formulas for calcium deficient apatite.

Fowler[16], in his study of OCP pyrolysis, demonstrated the possibility of maximizing pyrophosphate formation by calcining in a steam atmosphere. By injecting steam, Reaction (5) was assumed to be suppressed. In this study, condensed phosphate formation has been studied after calcining BCP precipitate with or without steam.

Experimental

Precipitation

Basic calcium phosphates were prepared by the slow addition of 1M H_3PO_4 into 0.6 - 1.2% lime suspension at room temperature under a variety of conditions; variable time of equibration (4 hours to 2 days), varying degree of agitation including ultrasonic vibration (Model S-75 sonifier of Branson Instruments Company, Stamford, Connecticut), and boiling after precipitation. The Ca/P molar ratio was varied by adjusting the amount of P_2O_5 equivalent added to lime suspension. The precipitate was filtered or centrifuged followed by washing.

Basic calcium phosphates were also prepared from ~0.5 M $Ca(NO_3)_2 \cdot 4H_2O$ and ~0.25 M $(NH_4)_2HPO_4$ solutions by rapid addition, slow addition of one solution to the other with ammoniation. The pH was maintained between 7 and 9. After the desired time for equilibration, the precipitate was washed thoroughly by centrifuging or decanting-settling procedures. The precipitates were dried in a 105°C oven for 24 hours.

Two commercial samples of tribasic calcium phosphate (reagent grade and NF grade) were included in the calcination study.

In order to study the calcination reaction, octacalcium phosphate (OCP) and hydroxyapatite (HA) were prepared by the methods[16,17] reported in the literature. The prepared calcium phosphates had the following Ca/P ratios as analyzed and as confirmed by XRD and IR.

Ca/P

	Analyze4	Theoretical
OCP A	1.329	1.333
OCP B	1.320	1.o33
HA	1.676	1.667

All the raw materials used were reagent grade, bearing certificates of analysis on impurity levels. Lime suspensions were prepared by hydrating CaO just before precipitation. The CaO was prepared from Fisher Ceritified $CaCO_3$(C-65) by calcining it at 900 °C for 24 hours. Lime handling, lime hydration, and precipitation were carried out in CO_2 free atmosphere

by using a dry box and by flowing N_2 gas on the top of the reactor.

Emission spectroscopy showed that the metal contamination level of the precipitate was about 0.1% by weight. The contminant consisted mainly of sodium and strontium believed to have come from phosphoric acid and calcium carbonate respectively. Some precipitates were also contaminated with carbonate even though every precaution was taken to prevent carbonate contamination. Most precipitates contained 0.1 - 0.2% CO_2 and the maximum level observed was 0.7% by weight. These chemical impurities at the levels observed are believed to have only a small influence on the properties or the results obtained for the condensed phosphate formation.

Analytical

CaO was determined[18] gravimetrically as CaO after precipitation as CaC_2O_4. P_2O_5 was determined[19] by the ammonium phosphomolybdate method. The CaO and P_2O_5 contents for a sample were analyzed in duplicate and the average was used to determine the ratio of Ca/P.

The precipitates (sample size 0.5 - 1.0 g) were calcined in an electric muffle furnace maintained at 550 °C ($\pm$10°C) for about 120 hours with or without steam injection. The calcined solid, 0.2 - 0.5 g, was dissolved with precooled ~0.2N HCl contained in an ice bath to minimize possible hydrolysis of condensed phosphates which had been formed during pyrolysis.

The P_2O_5 distribution in the solution was analyzed by the ion exchange method[20] which was modified for calcium phosphate samples.

Results

1. Characteristics of Precipitates

Electron photomicrographs of BCP from lime suspension are presented in Figure 1. Figure 1 (a) shows typical particles exhibiting poor crystallinity. The particles consist of crystallites, predominantly $0.02\mu \times 0.15\mu$, with sharp ends. Figure 1 (b) is the

Fig. la Electron-micrograph of Basic Calcium Phosphate Precipitated from Lime Suspension and Phosphoric Acid (poorly crystallized)

Fig. lb Electron-micrograph of Basic Calcium Posphate Precipitated from Lime Suspension and Phosphoric Acid (well crystallized)

photomicrograph of a better crystallized BCP. The crystallites appear as well defined prisms predominantly $0.015\mu \times 0.12\mu$ in size. The size distribution appears to be narrow. The crystallite size observed

in this study was of the same order of magnitude as that observed by Bett et al[2].

They prepared their samples from lime solution and phosphoric acid. The BET surface area of the precipitates ranged from 50 to $100m^2/g$. Ultrasonic agitation did not produce crystallites significantly different from that made by ordinary agitation. High temperature (boiling) treatment produced more crystalline precipitates.

Some samples were examined under a petrographic microscrope (McCrone Associates, Inc., Chicago, Illinois). According to their report, all the samples were typical gel particles and showed no birefringence or other indications of discrete phases of calcium phosphates. By the technique of dispersion staining the values of mean refractive index were determined as presented in Table 1. Mean refractive indices fall between those of OCP and HA.

Table 1. Refractive Indices of Some Precipitates

Sample	Ca/P	Refractive Index nD^{25}
6A*	1.624	1.594
6B	1.627	1.625
143421	1.596	1.615
8A*	1.593	1.596
OCP	1.333	1.576 – 1.585
HA	1.667	1.640 – 1.646

*Poorly crystalline.

The variation of refractive index within the samples was about ± 0.005. No apparent correlations exist between refractive index and Ca/Pratio. The refractive index may vary with the content of non-essential water and crystallinity.

A number of the BCP samples were examined by X-ray diffraction. All patterns were entirely apatitic in the range of Ca/P 1.53–1.67 observed. Poorly crystallized samples showed line broadening as well as poorly resolved peaks.

Several samples were examined by infrared spectroscopy using a Beckman Model IR 4 and 7. Infrared spectra of the samples were obtained by the KBr pellet technique. One typical spectrum of a BCP sample having Ca/P=1.593 is presented in Figure 2. The spectrum is in agreement with previous
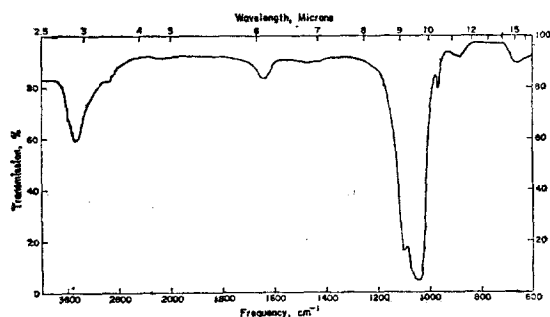
Fig. 2 IR Specturm of a Basic Calcium Phosphate (Ca/P= 1.593)

work[3],[21]. Comparison of spectra with distinguishing frequencies of brushite, monetite and octacalcium phosphate did not show apparent discrete phases of these compounds. The frequencies used to identify these phases are listed in Table 2. It apeaars that BCP has its own configuration. Details of absorption bands differed from sample to sample.

Table 2. Frequencies Used to Identify other Calcium Phosphates[16]

|	Frequencies, cm^{-1}
DCPD	984
	788
	1,132
	1,215
DCPA	892
	992
	1,128
OCP	910
	1,190
	1,280
β TCP	1,120
	972
	945

2. Condensed Phosphate Formation

There was always the formation of condensed phosphates other than pyrophosphate upon ignition. A typical example of condensed phosphate formed is given in Table 3.

Non-pyro condensed phosphates must have formed by local variation of Ca/P ratio in the solid during the calcination reaction. Thus, non-pyro portions were converted into pyro equivalent assuming the following stoichiometry after Kühl and Nebergall[6].

Table 3. Condensed Phosphate Formation on Ignition of BCP

Run 6A		Pyro Equivalent	
trimeta	0.21		0.42
tripoly	0.42		0.56
pyro	5.52		5.52
ortho	93.85	Total	6.50
Recovery	99.47		

$$2 P_2O_7{}^{4-} \rightarrow P_3O_{10}{}^{5-} + PO_4{}^{3-}$$
$$P_2O_7{}^{4-} \rightarrow PO^{3-} + PO_4{}^{3-}$$
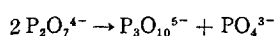
The amount of non-pyro condensed phosphates formed were from 6 % to as much as 15 % of the total pyrophosphate equivalent. An unsuccessful attempt was made to correlate P_2O_5 distribution with preparatory procedures. It was observed, however, that BCP from lime suspension produced more non-pyro condensed phosphates (10 % as an average) than those from $Ca(NO_3)_2$ and $(HN_4)_2HPO_4$ solutions (6 % average).

The time required to obtain a maximum amount of pyro phosphate equivalent varied depending upon samples. Table 4 presents the rate of formation for two samples. These are plotted in Figure 3. One sample (Sample 3P) showed a maximum amount at
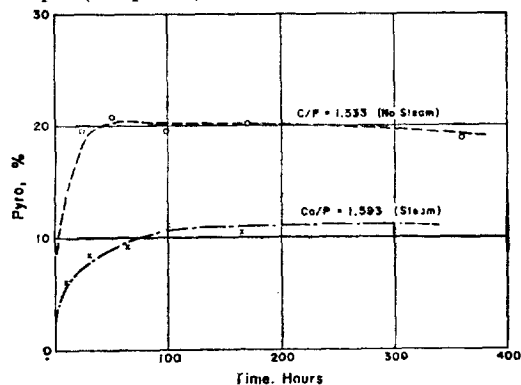

Fig. 3 Pyrophosphate Formation vs. Time (at5 50C°)

about 50 hours, while the other sample reached a maximum after 100 hours. It is also noted that with steam the pyro content did not appear to diminish with time. Based on the contention that steam did suppress Reaction (5), it was decided the samples should be calcined for more than 100 hours for pyrophosphate determinations with steam.

Table 4. Pyrophosphate Formation vs. Heating Time

a) Sample 3P (No steam) b) Sample 8A (steam)

Ca/P = 1.533 Ca/P = 1.593

Time, hr.	pyro%	Time, hr.	pyro%
10	10.1	10	6.1
24	19.5	31	8.5
50	20.8	64	9.2
98	19.4	100	11.1
170	20.1	165	10.4
360	18.8	300	10.8

3. Pyrophosphate Formation vs. Ca/P Molar Ratio

Table 5 summarizes the Ca/P molar ratio vs. pyrophosphate equivalent formed. The pyrophosphate values are based on 100-130 hours calcination time except two samples for which the maximum values observed arepresented. The data are arranged in the order of increasing Ca/P molar ratio. The pyro-
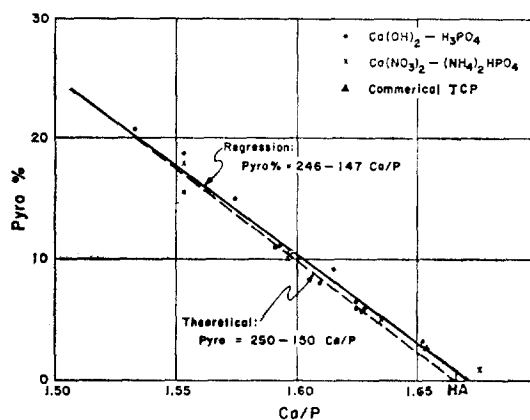

Fig. 4 Pyrophosphate Formation vs. Ca/P Ratio

phosphate data including commercial tribasic calcium phosphates are plotted in Figure 4. Even though data points are scattered, the amount of pyrophosphate formed increased linearly with the decrease of Ca/P ratio. The following regression equation was obtained independent of preparatory procedures and raw

Table 5. Pyrophosphate Formation vs. Ca/P Ratio (100-130 hours)

Sample	Ca/P ratio	Pyrophosphate equivalent formed, %	Non-pyrocon-** densed phosphate formed, %	Surface Area, m²/g
A. Lime suspension and H_3PO_4				
3P	1.533	20.8*	8.1	—
10A-S	1.553	15.5	9.8	85.8
10B-S	1.553	18.8	9.1	63.8
11-S	1.574	15.0	—	—
8B	1.591	10.8	8.5	—
8A-S	1.593	11.1*	9.3	94.9
9A-S	1.610	8.1	9.3	95.1
9B-S	1.615	9.2	10.3	67.1
6A	1.624	6.5	15.1	—
7B-S	1.625	5.9	8.6	57.9
6B	1.627	5.8	10.4	—
7A-S	1.628	6.0	8.3	87.2
12-S	1.652	3.1	—	—
B. $(NH_4)_1HPO_4$ and $Ca(NO_3)_2$				
143434-S	1.553	18.0	—	—
143421	1.596	10.2	5.6	—
143433-S	1.635	5.1	6.5	—
143429	1.676	0.4	—	—
C. Commerical				
Fisher certified TCP-S	1.597	10.4	9.0	39.1
Baker, technical	1.653	2.9	7.0	46.4

*maximum observed

** relative to total pyrophosphate equivalent formed

S: calcination in steam

materials.

$$\text{Pyro formed}(\%) = 245 - 146 \, \text{Ca/P} \qquad (6)$$

$$r^2 = 0.978$$

S. E. about regression $= 0.876$

error range $= \pm 1.75\%$ at the 95 % confidence level

A calcined sample (127 hours, steam) containing about 16 % P_2O_5 as pyrophosphate was examined by X-ray and infra red techniques. Both techniques revealed the presence of separate phases of β-$Ca_2P_2O_7$ and HA. In particular, the IR spectrum showed distinct absorption bands at 1210, 1186, 1155, 1140, 1003, 972 cm^{-1} frequencies characteristics of β-$Ca_2P_2O_7$. No β-$Ca_3(PO_4)_2$ was detected.
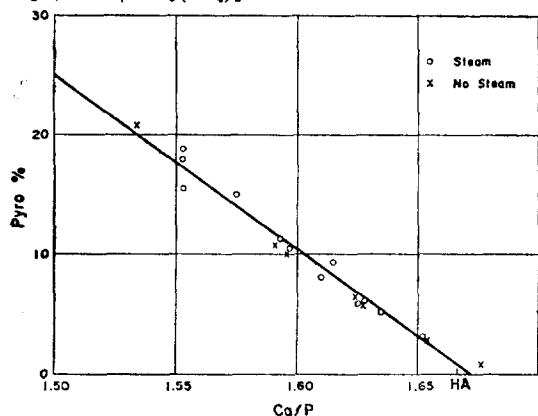

Fig. 5 Effect of Steam Injection on Pyrophosphate Formation

The effect of steam on pyro values appears to be negligible as shown in Fig. 5.

If we assume that the calcined product from BCP consists of only HA and $Ca_2P_2O_7$, the theoretical line of pyro vs. Ca/P ratio (see DISCUSSION) can be expressed as follows:

$$\text{pyro} (\%) = 250 - 150 \, \text{Ca/P} \qquad (7)$$

$$1 \leq \text{Ca/P} \leq 1.67$$

The experimentally determined line is in close agreement with the theoretical line defined by Eq. 7.

4. Calcination of OCP and Mixed Phosphates

In an attempt to verify Equation 7 in the low Ca/P ranges and the stoichiometry of Reaction 4 upon calcining octacalcium phosphate (as a special case of Equation 7), a calcining test was conducted for OCP, hydrolyzed OCP and mixed phosphates. The result is
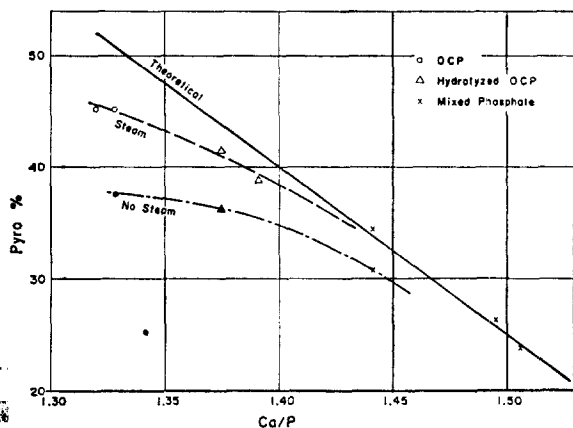

Fig. 6 Pyrophosphate Formation on Ignition of OCP And Mixed Phosphates

Table 6. Calcination of OCP and Mixed Phosphates

Sample	XRD	Ca/P	Pyrophosphate formed, % without steam	with steam
OCP A	OCP	1.329	37.5	44.9
OCP B	OCP	1.320	—	45.2
Partially hydrplyzed OCP-1*	OCP	1.375	36.5	43.7
Partially hydrolyzed OCP-2*	OCP	1.391	—	41.1
OCP-6B mixture	—	1.506	—	23.7
OCP-HA mixture	—	1.495	—	26.2
BCP	HA+ DCPD	1.441	30.4	33.4

summarized in Table 6 and graphically presented in Fig. 6.

The partially hydrolyzed OCP were obtained by hydrolyzing finely ground DCPD in IM solution of sodium acetate. The XRD patterns were still that of OCP but the intensity of the 2.67Å line was considerably diminished.

The OCP-BCP mixtures were prepared by mixing accurately weighed amounts of constituents in a laboratory sample grinder.

Without steam injection, pure OCP yielded only 74% of the amount predicted by Reaction 4. However, in a steam atmosphere, it yielded 89 % of the predicted values. These results are in close agreement with the results of Fowler[16] who calcined OCP at 500°C. For the partially hydrolyzed OCP having higher Ca/P ratios than OCP, the yield increased to ca 95%. This observation suggested that Reaction 5 was concurrently occuring with Reaction 4 during

calcination when concentraction of $Ca_2P_2O_7$ is high. To prove this conjecture, two mechanical mixtures were prepared from OCP and BCP. The pyro yields from these mixtures were close to theoretical pyrophosphate values. The calcined product of OCP contained a small amount of condensed phosphate (about 1% of total pyro equivalent), mostly tripolyphosphate.

One BCP sample having $Ca/P = 1.441$ and showing diffused XRD peak of DCPD (7.62Å line) was calcined with or without steam. Only with steam was the theoretical pyrophosphate formation obtained. The effect of steam is significant in the Ca/P range below 1.5.

The result of this test series verifies that Reaction 4 is quantitative if OCP is calcined in steam and properly diluted. If BCP contains OCP, Reaction 4 would proceed quantitatively when calcined in a steam atmosphere.
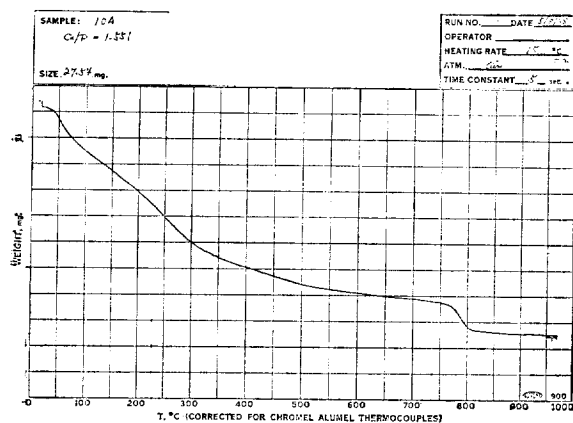

Fig. 7 Thermogravimetric Analysis of a Basic Calcium Phosphate

5. Thermogravimetric Analysis

Fig. 7 shows a typical thermogravimetric analysis (TGA)curve obtained with a BCP. Up to 700°C there was no sharp break in weight loss indicating no discrete phases in the precipitate. As previously observed[2,3], there was a sharp break between 750–800°C. Fig. 8 shows the weight loss observed in TGA curves together with the calculated weight loss based on the assumptions:

a. At 700°C on the curve, only chemical species present are $Ca_2P_2O_7$ and HA.
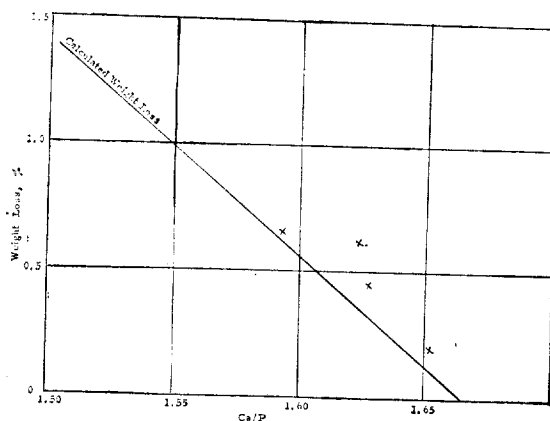

Fig. 8 Weight Loss Observed Between 700 and 900°C in TGA Analysis (With respect to the weight at 700°C)

b. Reaction 5 proceeds quantitatively between 750–800°C.

c. The amount of pyrophosphate at 700°C was calculated from Equation 7.

Data points fall near the calculated line in most cases supporting HA-pyrophosphate mixture as the final produt. All the points fall above the line indicating that, under the dynamic heating conditions in TGA analysis, pyrophosphate formation may not have been completed at 700°C.

Discussion

In the Ca/P range of $1.0 - 1.67$ in the $CaO - P_2O_5 - H_2O$ system at elevated temperature (pertinent to the calcining experiment), only three chemical species are crystallographically well defined and thermodynamically stable:

$$Ca_2P_2O_7 (Ca/P = 1.0)$$
$$Ca_3(PO_4)_2 (Ca/O = 1.5)$$
$$Ca_{10}(OH)_2(PO_4)_6 (Ca/P = 1.67)$$
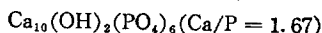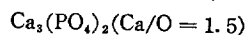
After a BCP is calcined for a long period to yield pyrophosphate, the nominal composition of the calcined product may be expressed by varying the proportion of these three compounds. The presentation can be made conveniently in a triangular diagram as shown in Fig. 9. In the figure, iso Ca/P lines and iso pyro lines are plotted. We observe the following:

Side	Ca/P range	Composition	Pyrophosphate for a given Ca/P	Note
AB	1 - 1.67	$Ca_2P_2O_7$ + HA	maximum	stable under water vapor
AC	1 - 1.5	$Ca_2P_2O_7$ + $Ca_3(PO_4)_2$	minimum	equilibrium mixture without water vapor[1,32]
CB	1.5 - 6.7	$Ca_3(PO_4)_2$ + HA	none	″

Fig. 9 Pyrophosphate and Composition

Fig. 10 Pyrophosphate Formation vs. Ca/P Ratio (Literature)
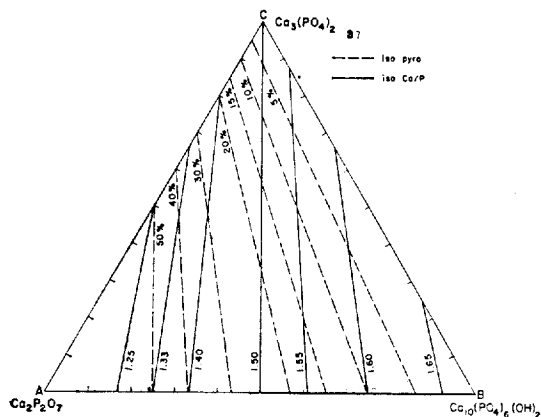
Side AB represents the stable mixture under water vapor. The pressure required for the stability is not known. As Fowler[16] observed and data of this study showed, water vapor of about 1 atm suppresses Reaction 5. For this case, pyrophosphate can be predicted from Ca/P as follows:

$$\text{pyro } (\%) = 250 - 150 \text{ Ca/P} \qquad (7)$$

$$1 < \text{Ca/P} < 1.67$$

Equation 7 predicts 25 % pyrophosphate at Ca/P = 1.5. Reaction 4, which is the disproportionating reaction of OCP into HA and $Ca_2P_2O_7$, is embodied by Equation 7.

Our pyrophosphate data are the case of maximum pyrophosphate formation indicating we have obtained a mixture of $Ca_2P_2O_7$ and HA after calcination. Our pyrophosphate data are consistently higher than most of those reported in the literature.

In the literature, various models of BCP and pyrophosphate formation therefrom have been discussed[2,3,7,8,10]. This is summarized Table 7 and graphically presented in Figure 10. Our pyro data fall very close to the line represented by mixture models I and II.
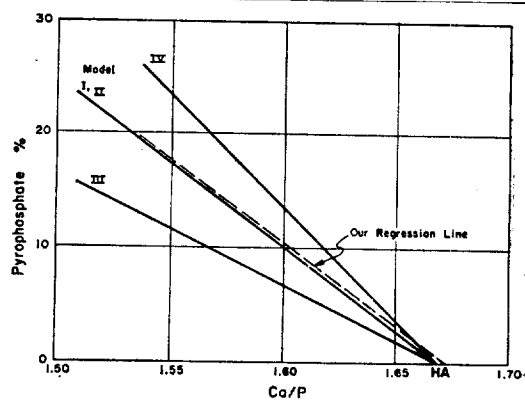
Our pyro data including pyro formation from OCP related phosphates indicate that our BCP probably consist of DCP and/or OCP mixed with HA. However, we cannot preclude other possibilities.

From the view that DCPD and OCP are sparingly soluble and easily occurring species metastable[4,25,26] to thermodynamically stable DCPA and HA, it is not unreasonable to assume that our BCP consist of all these calcium phosphates. DCPD and OCP may not be the most stable chemical species under the condition of BCP preparation. However, these metastable phases can be precipitated rapidly in preference to HA due to favorable conditions prevailing locally and instantaneously under most precipitation conditions. These initial precipitates are subsequently altered to HA[4,27]. One BCP (Ca/P = 1.441) prepared from $(NH_2)_2HPO_4$ and $Ca(NO_3)_2$ equilibrated for only two hours at pH = 9 showed a very diffused brushite 7.62Å line by XRD indicating some DCPD was precipitated initially. If the precipitate were left long, all brushite peaks must have disappeared. We also observed that the Ca/P ratio of the solid phase increased with equilibration time accompanied

Table 7. Various Models of BCP and Pyro Formation (Literature)

Model	Ca/P(molar)	P pyro/P total	Special Case Ca/P = 1.5**	
I. DCP-HA Mixture[7]				Pyro%
$Ca_{10}(PO_4)_6(OH)_2 \cdot nCaHPO_4$	$\dfrac{10+n}{6+n}$	$\dfrac{n}{6+n}$	$n=2$	25
II. OCP-HA interlayered mixture[4]				
$Ca_{10}(PO_4)_6(OH)_2 \cdot nCa_8H_2(PO_4)_6$	$\dfrac{10+8n}{6+6n}$	$\dfrac{3n^*}{6+6n}$	$n=1$	25
III. Defective apatite[3,11]				
$Ca_{10-n}(PO_4)_6 - n(HPO)n(OH)_{2-n}$	$\dfrac{10-n}{6}$	n *	$n=1$	16.6
IV. Defective apatite[5]				
$Ca_{10-n}(PO_4)_{6-n}(HPO_4)_{2n}(OH)_2$	$\dfrac{10-n}{6}$	$\dfrac{2n}{6}$	$n=1$	33.3

*Assuming Reaction (4)
**Corresponding to TCP, $Ca_3(PO_4)_2$ composition

by decrease in pH, indicating that initial phosphates were gradually hydrolyzed to HA on standing. From this standpoint, the intracrystalline mixture of DCP-OCP-HA as proposed by Brown et al is possible.

However, XRD, IR and microscopic observation did not show discrete phases. If we consider these metastable phosphates were already altered by hydrolysis, it may be impossible to detect constituents of an intracrystalline mixture by these means. Alternatively, they may be poorly crystalline DCP, OCP mixed with HA.

The fact that some BCP are poorly crystalline points out another possibility. Eanes et al[23] observed that the initial solid immediatelyl on mixing of reactants was "non-crystaline" calcium phosphate. They postulated irregular coordination complexes of Ca^{++} and HPO_4^{2-} large enough in size to separate from solution. The amorphous phase, though metastable to more ordered apatite configuration, was eventually converted to crystalline HA. As Newesley[28] pointed out, amorphous calcium phosphates are non-stoichiometric. A BCP may be an intermediate of this conversion process and may consist of this amorphous calcium phosphate mixed with HA.

In recent thermochemical studies on amorphous calcium phosphate Earnes[29] showed that he pyrophosphate formation was very low when calcined just below the crystallization point. The samples were prepared by with drawing the amorphous calcium phosphate from the reaction medium immediately after its formation. His results concluded that his calcium phosphate under specific chemical conditions was a hydrated tricalcium phosphate. M. D. Francis[30], on the hand, obtained basic calcium phosphate supporting the contention that it was mixtures of HA and DCPD. DCPD was precipitated first and converted to HA.

As Arnold[24] pointed out, no two preparations of BCP are likely to be identical. Thus, depending upon precipitation conditions, the composition of BCP would vary greatly. Thus, one BCP may contain mostly an interlayered mixture and another BCP may consist of more amorphous phase calcium phosphates.

The discusions lead to the conclusion that the cause of Ca/P variation in our BCP may be explained by the mixture concept rather than defective apatite models. The mixture concept here is that BCP is a mixture of HA with some calcium phosphates. Constituents can be interlayered or poorly crystalline DCP, OCP and/or amorphous calcium phosphates without definite chemical identities.

Summary and Conclusion

Basic calcium phosphates with varying Ca/P ratio, 1.53 - 1.67, have been prepared from lime suspension

and phosphoric acid under a variety of conditions; varying equibration time, degree of agitation, concentration. Precipitates were also prepared from calcium nitrate and ammonium phosphate solutions.

Condensed phosphate formation has been studied upon igniting the basic calcium phosphates, octacalcium phosphate and mixed phosphates with or without steam. Important results obtained are:

1. For basic calcium phosphates studies, only one correlation was found between pyrophosphate equivalent formed and Ca/P ratio, and it was independent of preparatory procedure and raw materials.

2. The correlation established is consistent with the case that the calcined product consists of hydroxyapatite and calcium pyrophosphate only. This is the case where maximum pyrophosphate formation is possible.

3. It has been demonstrated that octacalcium phosphate will yield hydroxyapatite and calcium pyrophosphate upon calcining in a steam atmosphere when the overall Ca/P ratio is 1.5 or above.

4. The correlation is also consistent with the literature interpretation that basic calcium phosphates consist of dicalcium phosphate and/or octacalcium phosphate mixed with hydroxyapatite. However, x-ray diffraction, infrared spectroscopy and petrographic examination could not reveal discrete phases of these calcium phosphates.

5 Variation of Ca/P in our basic calcium phosphates can be explained by the mixture concept that hydroxyapatite is mixed with some other calcium phosphates. Depending upon the preparatory procedure, constituents can be interlayered or poorly crystalline dicalcium phosphate, octacalcium phosphate and/or amorphous calcium phosphates without definite chemical identites.

Acknowledgements

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