Journal of Solid State Chemistry **148,** 308–315 (1999)
Article ID jssc.1999.8452, available online at http://www.idealibrary.com on IDEAL®

Behavior in Wet Atmosphere of an Amorphous Calcium Phosphate with an Atomic Ca/P Ratio of 1.33

A. Rodrigues and A. Lebugle

Laboratoire des Matériaux, Equipe de Physico-Chimie des Phosphates, INPT-ENSCT, UPRES-A 5071, 38, rue des 36 Ponts, 31400 Toulouse, France

Received April 6, 1999; in revised form June 21, 1999; accepted July 22, 1999

This study deals with the behavior, in a wet atmosphere at 40, 60, and 80°C, of an amorphous calcium phosphate with an atomic Ca/P ratio of 1.33. The wet atmosphere treatment leads to the formation of a thin film of water on the sample surface, allowing its maturation. At 40 and 60°C, the upper surface, rich in adsorbed water, crystallizes into triclinic OCP, a compound with structural water. The other deeper part leads to apatitic OCP. Whatever the temperature, both types of crystal decompose with time, in various stages, to finally lead to a mixture of hydroxyapatite and monetite. © 1999 Academic Press

Key Words: **wet atmosphere; octocalcium phosphate; amorphous; crystallization; decomposition.**

I. INTRODUCTION

What is generally considered as amorphous calcium phosphate (ACP) is calcium phosphate with an atomic Ca/P ratio of 1.50. Different studies have shown that it is a precise compound. It is synthesized in aqueous medium at 25°C at a pH of about 10 (1). However, other authors have shown that there is another amorphous calcium phosphate with a lower Ca/P ratio close to that of triclinic OCP (OCPt). Zahidi *et al.* (2) synthesized an amorphous compound with a Ca/P ratio of 1.33 at 37°C in water–ethanol medium from solutions of $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ with a Ca/P ratio of 1.00. After freeze-drying, the product obtained was amorphous and presented the formula $Ca_8(HPO_4)_2(PO_4)_4 \cdot nH_2O$. Christoffersen *et al.* (3) also obtained an amorphous calcium phosphate with a Ca/P ratio close to 1.33 in aqueous medium. The synthesis was performed between 30 and 42°C from aqueous solutions of $CaCl_2$ and K_2HPO_4 with a Ca/P ratio equal to those of hydroxyapatite and a pH adjusted to 7.40. In order to avoid any confusion with ACP, the amorphous calcium phosphate with the same Ca/P ratio as OCPt will be noted OCPam in the text.

The maturation of ACP (Ca/P = 1.50) was studied in various conditions. As a moist cake, it crystallizes into nonstoichiometric apatite. It is apatitic tricalcium phosphate (TCPap) (4). With water, ACP was shown to readily transform to apatite by way of OCPt or OCPt-like phases (5, 6). In wet atmosphere, it converts into TCPap as very long crystallites (7).

The evolution of OCPam was studied in various conditions too. Zahidi *et al.* showed that the gel of OCPam obtained in water–ethanol medium and oven-dried at 80°C leads to an apatitic compound with a Ca/P ratio equal to 1.33 (2). It is the most nonstoichiometric apatite so far obtained and presents the formula $Ca_8(HPO_4)_{2.5}(PO_4)_{3.5}(OH)_{0.5}$. The OCPam obtained by Christoffersen *et al.* (3) evolves into OCPt in synthesis solutions.

During calcification, an amorphous calcium phosphate with an atomic ratio of about 1.33 forms in the first step. Then it crystallizes into an apatite and not into the triclinic system.

Our aim was to study the evolution of OCPam with limited quantities of water (treatment in wet atmosphere) to see which crystalline structure (apatitic or triclinic) is favored. Thus, the global composition of the solid will be preserved. The wet atmosphere treatment was selected because it covers the sample with a thin film of water as shown by Lasserre and Lebugle (8) in a study carried out on apatitic OCP. This work studied the influence of temperature on OCPam prepared as reported by Zahidi *et al.* (2). The method has the advantage of allowing precise control of the Ca/P ratio of the compound and providing large quantities of product essential for a complete study.

II. EXPERIMENTAL

The OCP gel was obtained by double decomposition, at 37°C, by adding a solution of calcium (A) to a basic solution of orthophosphate (B). Solution A contained 30 mmoles of calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$)) dissolved in 100 ml of deionized water and 100 ml of ethanol. Solution B contained 30 mmoles of di-ammonium hydrogenophosphate, $(NH_4)_2HPO_4$ in 250 ml of deionized water, 45 ml of ammonia (11 M), and 295 ml of ethanol (pH 10.3). After formation, the precipitate was immediately filtered and washed with

0022-4596/99 $30.00

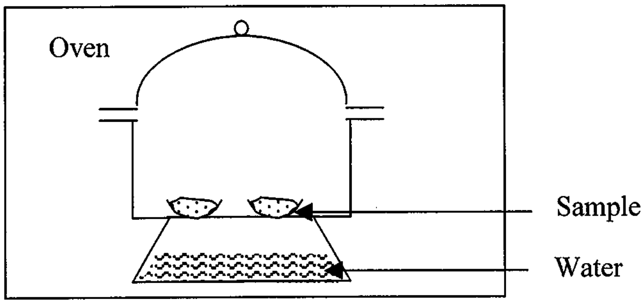

FIG. 1. Experimental system for wet atmosphere study.

a solution containing 180 ml of deionized water, 30 ml of ammonia (11 M), and 210 ml of ethanol (pH 12.0). Then, the gel was freeze-dried to give the amorphous product.

The amorphous compound was exposed to an atmosphere saturated in water vapor using a reactor in an oven (Fig. 1). The temperature was fixed at 40, 60, or 80°C. The reactor contained water to saturate the atmosphere. Powder was spread out on watch glasses and put into the reactor for various times (from a few hours to some months). First, the samples were put at the study temperature for 30 minutes to avoid any condensation caused by the introduction of a cold body into an atmosphere saturated in water vapor. After the various periods of time, the sample was removed from the reactor and dried at the study temperature for 1 hour. This precaution was taken to avoid any further evolution caused by surface adsorbed water.

The initial sample was first characterized after acidic dissolution by chemical analysis (volumetric titration of calcium (9, 10) and by colorimetric titration of orthophosphate ions (11)). The atomic Ca/P ratio was equal to 1.33.

The initial and the treated samples were analyzed by X-ray diffraction (XRD) with a CPS 120 INEL diffractometer using the $K\alpha 1$ radiation line emitted by a cobalt anticathode ($\lambda = 1.78892$ Å). In some cases, a Seifert diffractometer was used because it allows acquisition at small angles to display OCPt (copper anticathode, $\lambda = 1.5405$ Å). The study also used infrared spectroscopy (Perkin Elmer FTIR 1600), SEM (Jeol JSM-6400), and titration of HPO_4^{2-} ions. The hydrogenophosphate ions were titrated after heating the sample to 600°C for 20 minutes. During this heating, the HPO_4^{2-} ions present condensed into pyrophosphate ions according to the reaction

$$2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O.$$

Then, the orthophosphate ions were titrated in the heated sample before and after acid hydrolysis (1 hour at 100°C) (12). The difference gives the hydrogenophosphate ion content.

III. RESULTS

III.1. X-Ray Diffraction

Samples treated under the wet atmosphere were examined by XRD. The various phases observed are reported in Table 1.

At 80°C, the initially amorphous sample crystallized into apatite after 0.5 hour of treatment. From 6 hours, three additional lines appeared at $d = 3.35$, 3.13, and 2.96 Å (Fig. 2). These lines correspond to monetite (DCPA, $CaHPO_4$). Their intensity increased with time and the apatite lines became thinner.

At 60°C, OCPam crystallization was observed after only 1 hour. After 6 hours, near the apatite lines, those of OCPt appeared. This was clearly shown by the main line at small angles ($d = 18.7$ Å, i.e., $2\theta = 4.74°$ with a copper anticathode) (Fig. 3). The other lines of OCPt were hard to see because they are close to those of apatite. The main line was observed for samples treated from 6 to 24 hours, but its intensity decreased with time. At the same time as this decrease, monetite appeared and its intensity increased with time. After 3 days, only the lines of apatite and monetite were present.

At 40°C, crystallization occurred after 6 hours of treatment but here again, near the apatite lines, there were also OCPt lines. The intensity of the OCPt lines increased between 6 and 24 hours. Then, it decreased and after 3 days the lines were no longer detectable. At the same time that OCPt disappeared (i.e., after 24 hours), brushite (DCPD), detectable by its most intense line (020), increased. From 3 days, the brushite lines decreased while monetite lines appeared and increased with time.

TABLE 1
XRD Phases Observed in Samples Treated at 80, 60, or 40°C for Various Times

Time	40°C	60°C	80°C
0 hour	Amorphous	Amorphous	Amorphous
30 minutes	Amorphous	Amorphous	*Apatite (Ap)*
1 hour	Amorphous	*Apatite*	*Apatite*
6 hour	*Ap + OCPt*	*Ap + OCPt*	**Ap + DCPA**
15 hour	*Ap + OCPt*	**Ap + DCPA + OCPt**	**Ap + DCPA**
24 hour	**Ap + OCPt + DCPD**	**Ap + DCPA + OCPt**	**Ap + DCPA**
3 days	**Ap + DCPD + DCPA**	**Ap + DCPA**	**Ap + DCPA**
6 days	**Ap + DCPD + DCPA**	**Ap + DCPA**	**Ap + DCPA**
15 days	**Ap + DCPD + DCPA**	**Ap + DCPA**	**Ap + DCPA**
1 days	**Ap + DCPA**	**Ap + DCPA**	**Ap + DCPA**
4 months	**Ap + DCPA**	**Ap + DCPA**	**Ap + DCPA**

Note. Roman, Amorphous; Italic, Crystallization; Bold, Decomposition.

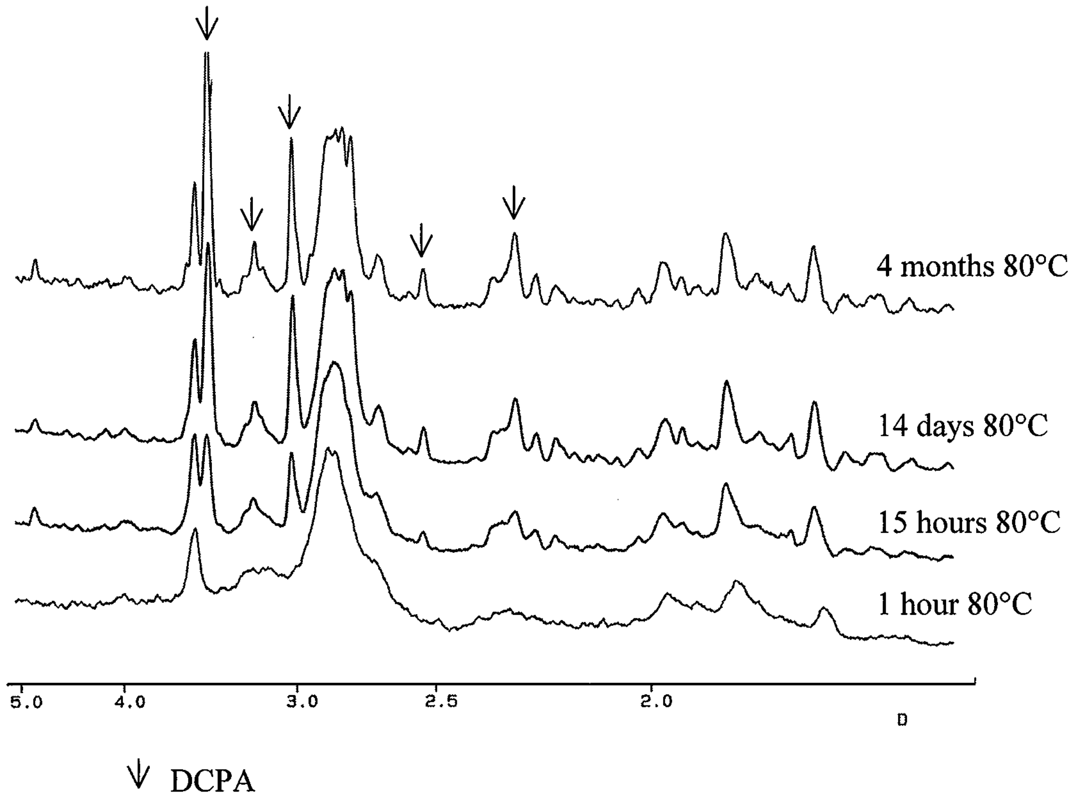

FIG. 2. XRD diagrams of OCPam treated in a wet atmosphere at 80°C for 1 h, 15 h, 14 days, and 4 months.

III.2. Infrared Spectroscopy

The IR spectra of samples treated at 80°C are reported in Fig. 4. They indicate the same variations as those observed by XRD.

At 80°C, from the first 30 minutes of treatment of OCPam, crystallization was observed. Indeed, the band at 555 cm^{-1} splits into two bands at 600 and 560 cm^{-1}. This splitting is characteristic of the organization of PO_4^{3-} groups in an apatitic environment as is the shoulder at

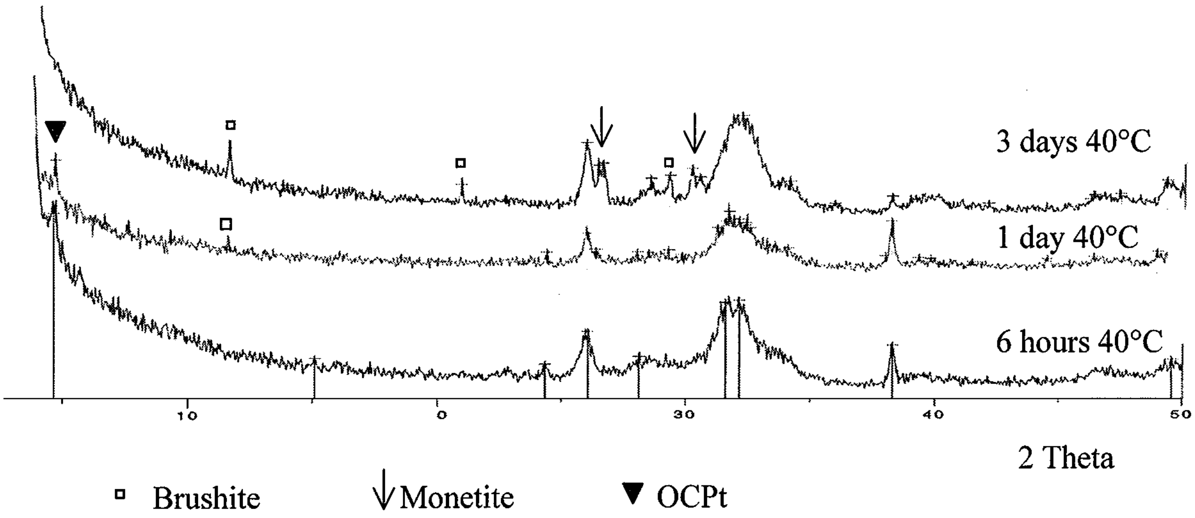

FIG. 3. XRD diagrams of OCPam treated in a wet atmosphere at 40°C for 6 h, 1 day, and 3 days ($\lambda = 1.5405$ Å).

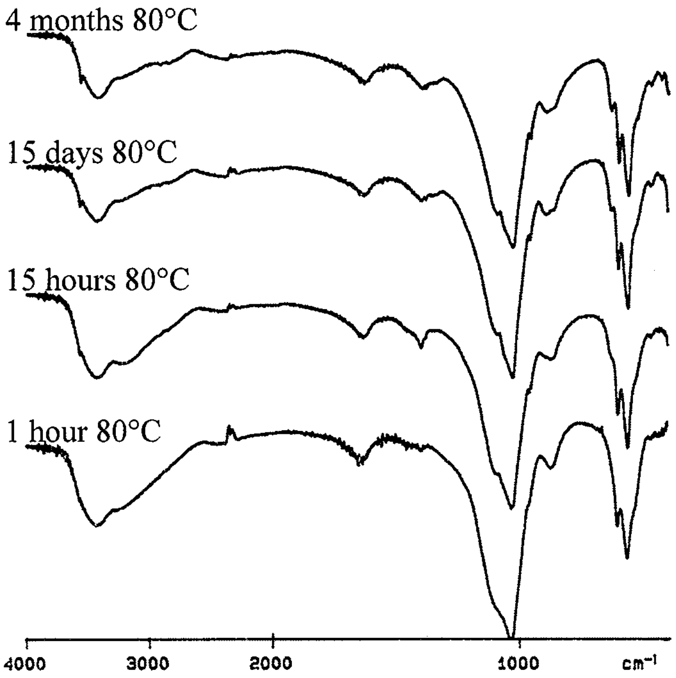

FIG. 4. IR spectra of OCPam treated in a wet atmosphere at 80°C for 1 h, 15 h, 14 days, and 4 months.

1100 cm^{-1} (13). With time, the two bands became thinner and the shoulder clearer. The OH$^-$ ion bands at 3560 and 630 cm^{-1} were detectable after 15 hours and their intensity increased with time. Furthermore, the band at 875 cm^{-1}, characteristic of the HPO_4^{2-} groups present in OCPam, broadened. At the same time, a shoulder appeared at 1060 cm^{-1}. These two phenomena could be ascribed to monetite, which presents bands at 880 and 1060 cm^{-1}.

At 60 and 40°C, the spectra varied in similar ways but the changes were shifted in time. Furthermore, additional shoulders appeared at 1035, 1055, and 1075 cm^{-1} (Fig. 5). They are characteristic of OCPt, as also shown by XRD.

III.3. Level of Condensable Phosphates

The level of phosphate in the condensed form (pyrophosphate) was determined in various treated samples. The level of condensable phosphate is plotted versus time in Fig. 6.

Whatever the wet treatment temperature, different stages were seen in the variation of the HPO_4^{2-} level.

At 80°C, the curve was composed of three parts. First of all, the HPO_4^{2-} level increased rapidly from 33.2 to 44.7%, between 0 and 3 days. Then, it remained stable at 44.7% between 3 and 6 days. Finally, it increased gradually to reach 48.5% after 4 months.

At 60°C, three stages appeared too: the HPO_4^{2-} level increased rapidly from 33.2 to 42% between 0 and 15 hours; between 15 hours and 6 days, it remained stable; then, it increased again to 46.3% over 4 months.

At 40°C, the level of condensable phosphate varied with time in 4 stages. First of all, it increased rapidly from 33.2 to 40.7% between 0 and 6 hours and then it remained stable for 6 hours. Afterward, it increased to 42% and kept this value between days 1 and 14. Finally, it increased to reach 44.7% after 4 months.

FIG. 5. IR spectrum of OCPam treated in a wet atmosphere at 40°C for 6 h.

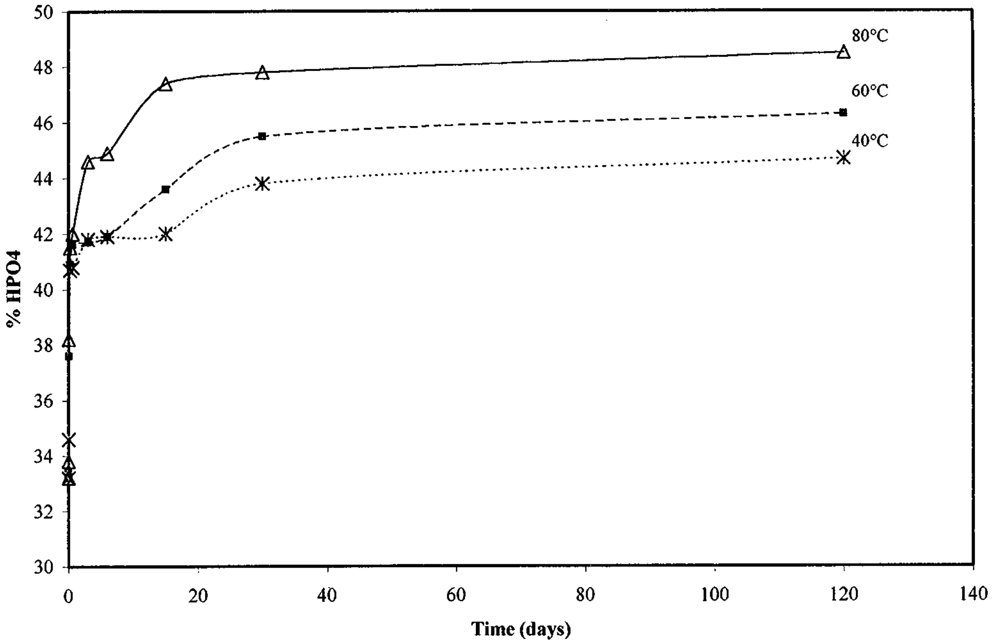

FIG. 6. Levels of condensable phosphates versus time for samples treated in wet atmosphere at 80, 60, and 40°C.

III.4. SEM

Photographs of the initial sample and of samples treated at 80°C for 15 hours and 14 days are reported in Fig. 7.

The amorphous initial sample was in the form of granules. After 15 hours, small plaques were observed. They increased in size with time. A similar morphology was already reported by Lasserre and Lebugle (8) for the decomposition of apatitic OCP treated under a wet atmosphere. The plaques were ascribed to monetite as indicated by XRD.

At 60°C, different morphologies were observed (Fig. 8). Indeed, at 15 hours, the sample was composed of needles. After a long period of treatment, the needles disappeared and only plaques closely connected to the granule phase were observed.

At 40°C, the changes in sample morphology with time were similar (Fig. 9). The needles present for short times disappeared to give plaques and granules.

IV. INTERPRETATION–DISCUSSION

The study shows that amorphous OCP, treated under wet atmosphere, evolves via various stages whatever the temperature; the length of the stages depends on the temperature.

The first stage is crystallization. It occurs earlier at higher temperatures and the type of crystal formed changes with temperature.

At 40°C, X-ray diffraction shows that amorphous OCP crystallizes, after 6 hours, into two crystallographic forms, an apatite and OCPt. Since OCPt presents an atomic Ca/P ratio of 1.33, it can be deduced that the apatitic phase is apatitic octocalcium phosphate, OCPap, reported by Zahidi *et al.* (2) and Lebugle *et al.* (14). According to Fowler *et al.* (15), OCPt is composed of an apatitic layer ($Ca_3(PO_4)_2 \cdot 0.5H_2O$) and a hydrated layer ($CaHPO_4 \cdot 2H_2O$). Van der Waals forces and hydrogen bonds link these layers. Moreover, the crystalline parameters of OCPt are very close to those of a double apatitic unit cell (2a, b, c) (Table 2).

So, it follows that amorphous OCP could lead, under a wet atmosphere, to both OCPt and OCPap. Moreover, the upper surface of the OCPam powder, in greatest contact with water and thus with a large quantity of adsorbed water molecules, can crystallize, leading to OCPt. The deeper part of the OCPam undergoes the hydrolysis/crystallization reaction described by Lebugle *et al.* (14) for OCPap and by Heughebaert and Montel (4) for TCPap to lead to OCPap. These interpretations are in line with the observations of Christofferssen *et al.* (3) and Zahidi *et al.* (2). Indeed, Christoffersen *et al.* studied the behavior of OCPam in large quantities of water and showed that OCPam crystallizes into OCPt. On the other hand, Zahidi *et al.* studied the crystallization of the OCPam gel in an oven. In these conditions, the quantities of water in the gel being smaller and as the water is rapidly eliminated during drying, OCPam crystallizes into OCPap. In the present case, the quantity of

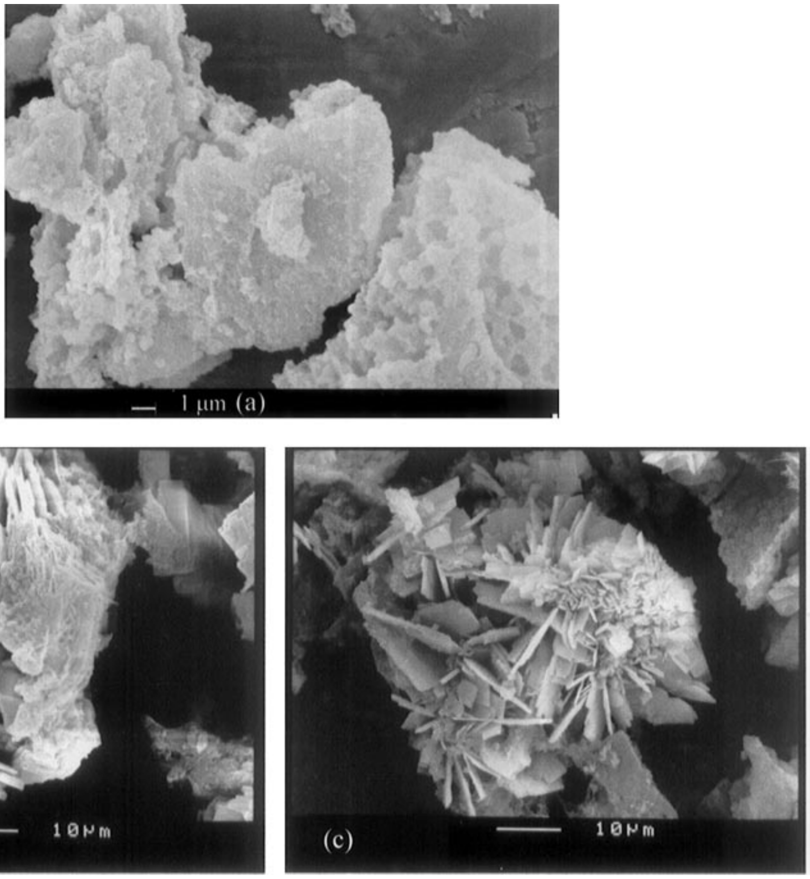

FIG. 7. Photographs of initial OCPam (a) and samples treated for 15 h (b) and 14 days (c) at 80°C under a wet atmosphere.

water varied according to the depth in the powder and the crystalline structure of OCPt and OCPap being close, both varieties were observed. So, the reaction scheme is thought to be

$$\mathrm{Ca_8(HPO_4)_2(PO_4)_4} \xrightarrow{+\mathrm{H_2O}} x\mathrm{Ca_8(HPO_4)_{2.5}(PO_4)_{3.5}(OH)_{0.5}} + (1-x)\mathrm{Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O}. \quad [1]$$

The OCPt is necessarily formed from OCPam because its intensity increases during a given period and then decreases. If it formed from OCPap by a dissolution/reprecipitation mechanism, the quantities would increase continually with time.

The proportion of OCPt formed can be deduced from the condensable phosphate level determined in samples after treatment then heating to 600°C (40.7%). Indeed this level is

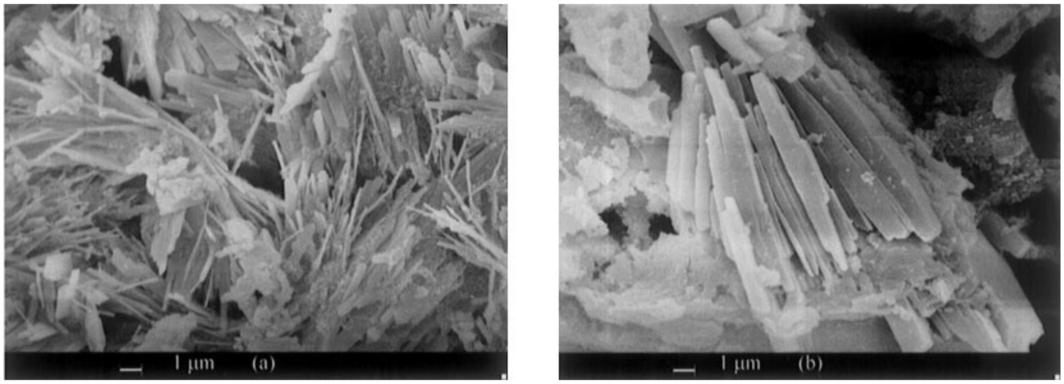

FIG. 8. Photographs of OCPam samples treated for 15 h (a) and 14 days (b) at 60°C under a wet atmosphere.

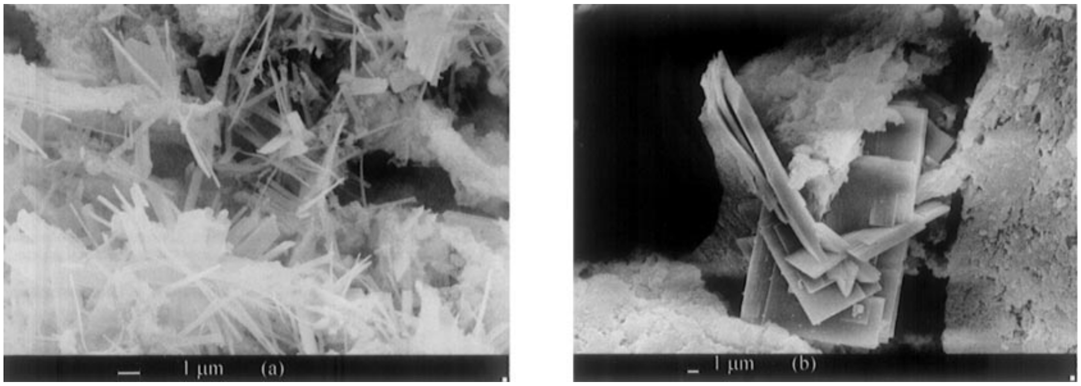

FIG. 9. Photographs of OCPam samples treated for 15 h (a) and 14 days (b) at 40°C under a wet atmosphere.

due to OCPap on the one hand and to OCPt on the other hand. The level of condensable phosphate in OCPt is equal to 33.3% and that of OCPap to 41.5% (maximum level of hydrolysis). It is easy to show that at 40°C, the crystallized samples were composed of 0.87 moles of OCPap and of 0.13 moles of OCPt. This mixture of crystallized phases remained stable for 6 hours at least 40°C.

At 60°C, crystallization occurred more rapidly (1 hour) but the level of condensable phosphate observed at 6 hours indicates that OCPap and OCPt were present in the same proportions as at 40°C.

In addition, the SEM study performed at 40 and 60°C showed needles. The needles had a similar morphology to those observed by Legeros (17, 18) for OCPt. They most probably correspond to the OCPt observed by XRD, particularly as they are located at the surface of the samples, where this variety of crystal forms preferentially. OCPap, generally present in the form of granules, cannot be observed because it occurs in the deeper layers.

At 80°C, XRD shows only the apatitic variety after 0.5 hour. The lack of OCPt can be explained by the fact that it is not stable at this temperature because it loses two structural water molecules at 75°C (19). The proportion of condensable phosphate in the sample treated for 1 hour was 38.2%. This value is lower than that observed when hydrolysis was complete. So the OCPap obtained did not have time to hydrolyze completely, probably because the product decomposed before hydrolysis was complete, as discussed later.

TABLE 2
Crystalline Parameters of OCPt and Hydroxyapatite (16)

Crystalline parameters	OCPt	HAP
a (Å)	19.692	9.418
b (Å)	9.523	9.418
c (Å)	6.835	6.881
α (°)	90.13	90
β (°)	92.19	90
γ (°)	108.36	120

The second stage is observable at 40°C between 1 and 14 days and at 60°C between 14 hours and 6 days. This stage is characterized by the disappearance of OCPt and by the appearance of brushite at 40°C or monetite at 60°C as shown by XRD, SEM, and variation of the condensable phosphate level. It corresponds to OCPt decomposition already observed by Yesinowski and Eckert (20).

At 40°C, the brushite formation can explain OCPt decomposition according to a topotactic mechanism similar to that seen with OCPap. Such a mechanism is particularly possible given that, according to Fowler *et al.* (15), there is a brushite layer in OCPt. These layers could be eliminated from the OCPt structure by topotactic reaction and so lead to the observed brushite. Its progressive disappearance at 40°C to yield monetite can be explained by the fact that from a kinetic point of view this phase could form at this temperature but it is thermodynamically unstable above 37°C (21).

The decomposition of OCPt parallels the increase of condensable phosphate from 40.7 to 42%. This variation is interpreted by considering that OCPt decomposes according to a scheme similar to that of OCPap (8) except that brushite forms instead of monetite:

$$\mathrm{Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O} \xrightarrow{+\mathrm{H_2O}} 2/3\ \mathrm{Ca_9(HPO_4)(PO_4)_6(OH)} + 2\ \mathrm{CaHPO_4 \cdot 2H_2O}. \qquad [2]$$

However, the level of condensable phosphate in the products of such a decomposition [2] is 44.4%. But it must be taken into account that the sample is composed of 0.13 moles of OCPt and 0.87 moles of OCPap. In these conditions, the level of condensable phosphate will be equal to $(0.87 * 41.5 + 0.13 * 44.4)\%$, which makes 42.6%. (Note that the level of 41.5% corresponds to nondecomposed OCPap.)

The calculated value is close to that obtained experimentally.

At 60°C, the previously described OCPt decomposition occurs too but the brushite is not observed because it is thermodynamically unstable at this temperature becoming dehydrated as soon as it is formed (21).

The third stage corresponds to the decomposition of OCPap into monetite and apatitic tricalcium phosphate. It is evidenced by the appearance of monetite at 40, 60, and 80°C and by an increase of the level of condensable phosphate to 44%. These observations can be interpreted by considering the decomposition of OCPap according to the following reaction scheme:

$$3\ \mathrm{Ca_8(HPO_4)_{2.5}(PO_4)_{3.5}(OH)_{0.5}} \xrightarrow{+\mathrm{H_2O}} 2\ \mathrm{Ca_9(HPO_4)(PO_4)_5(OH)} + 6\ \mathrm{CaHPO_4}. \qquad [3]$$

During this stage, the level of condensable phosphate varies from 41.5 to 44.4%.

This decomposition is accelerated by temperature. At 80°C, it occurs before complete hydrolysis of OCPap. Indeed, after 6 hours, although the level of condensable phosphate is equal to 41.5%, monetite is already observed by XRD.

The fourth stage corresponds to the decomposition of TCPap formed during previous stages. It occurs only at 80 and 60°C. It leads to hydroxyapatite and monetite according to the scheme proposed by Lasserre and Lebugle (8):

$$2\ \mathrm{Ca_9(HPO_4)(PO_4)_5(OH)} \xrightarrow{+\mathrm{H_2O}} 3/2\ \mathrm{Ca_{10}(PO_4)_6(OH)_2} + 3\ \mathrm{CaHPO_4}. \qquad [4]$$

This stage is approximately finished after 4 months of treatment at 80°C. Indeed, the proportion of condensable phosphate (48.7%) is close to the theoretical value calculated from the global reaction:

$$2\ \mathrm{Ca_8(HPO_4)_{2.5}(PO_4)_{3.5}(OH)_{0.5}} \xrightarrow{+\mathrm{H_2O}} \mathrm{Ca_{10}(PO_4)_6(OH)_2} + 6\ \mathrm{CaHPO_4}. \qquad [5]$$

It is clear that the calculated proportion of condensable phosphate is equal to 50% (6/12).

At 60°C, this fourth stage is still not finished after 4 months of treatment. Indeed, the experimental level only reached 46.3%.

Finally, it seems to be very slow to start at 40°C. After 4 months, the level of condensable phosphate was 44.7%, a value close to that determined from reaction [3].

V. CONCLUSION

The study shows the determining role of the quantity of water on the type of crystal appearing as amorphous OCP crystallizes under a wet atmosphere. On the surface on the powder, richest in adsorbed water, OCPt, a compound containing structural water, forms. On the other hand, in the less superficial regions, apatitic OCP crystallizes.

It was also seen that the two crystalline varieties of OCP decompose in several stages to both lead to the same final stage, a mixture of hydroxyapatite and monetite.

REFERENCES

1. J. C. Heughebaert and G. Montel, *Bull. Soc. Chim. Fr.* **8–9,** 2923 (1970).
2. E. Zahidi, A. Lebugle, and G. Bonel, *Bull. Soc. Chim. Fr.* **4,** 523 (1985).
3. M. R. Christoffersen, J. Christoffersen, and W. Kibalczyc, *J. Cryst. Growth* **106,** 349 (1990).
4. J. C. Heughebaert and G. Montel, *Calcif. Tissue Int.* **34,** S103 (1982).
5. E. D. Eanes, J. D. Termine, and M. U. Nylen, *Calcif. Tissue Res.* **12,** 143 (1973).
6. N. Eidelman, L. C. Chow, and W. E. Brown, *Calcif. Tissue Int.* **41,** 18 (1987).
7. J. Puech, J. C. Heughebaert, and G. Montel, *J. Cryst. Growth* **56,** 20 (1982).
8. V. Lasserre and A. Lebugle, *Ann. Chim. Fr.* **21,** 205 (1996).
9. J. L. Meyer and E. D. Eanes, *Calcif. Tiss. Res.* **23,** 259 (1978).
10. G. Charlot, "Les méthodes de la chimie analytique; analyse quantitative et minérale," 5th ed. Masson, Paris, 1966.
11. A. Gee and V. R. Deitz, *Anal. Chem.* **25,** 132 (1953).
12. A. Gee and V. R. Deitz, *J. Am. Chem. Soc.* **77,** 2961 (1955).
13. S. J. Gadaleta, E. P. Paschalis, F. Betts, R. Mendelsohn, and A. L. Boskey, *Calcif. Tissue Int.* **58,** 9 (1996).
14. A. Lebugle, E. Zahidi, and G. Bonel, *Reactivity of Solids* **2,** 151 (1986).
15. B. O. Fowler, M. Markovic, and W. E. Brown, *Chem. Mater.* **5,** 1417 (1993).
16. M. Mathew, W. E. Brown, L. W. Schroeder, and D. Dickens, *J. Cryst. Spectrosc. Res.* **18,** 235 (1988).
17. R. Z. Legeros, *Calcif. Tissue Int.* **37,** 194 (1984).
18. R. Z. Legeros, *J. Dent. Res.* **65,** 292 (1986).
19. A. Biji, G. Cojazzi, M. Gazzano, A. Ripamonti, and N. Roveri, *J. Inorg. Biochem.* **40,** 293 (1990).
20. J. P. Yesinowski and H. Eckert, *J. Am. Chem. Soc.* **109,** 6274 (1987).
21. R. I. Martin and P. W. Brown, *J. Am. Ceram. Soc.* **80,** 1263 (1997).