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Preparation of octacalcium phosphate by the hydrolysis of α-tricalcium phosphate

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A new simple method of preparation for the thermodynamically unstable octacalcium phosphate [$Ca_8H_2(PO_4)_6 \cdot 5H_2O$; OCP] has been developed using the hydrolysis of α-$Ca_3(PO_4)_2$ instead of the conventional hydrolysis of $CaHPO_4 \cdot 2H_2O$. The hydrolysis experiments were carried out by treating an α-$Ca_3(PO_4)_2$(1 g)–H_2O(50 m) suspension for 3 h at temperatures in the range 40 to 80° C and at pHs in the range 3 to 7.5. The formation of OCP was limited to within a narrow region between formation regions of other phosphates. Favourable conditions for OCP preparation were, for example, 70° C, pH4.5 to 5.0 and 60° C, pH5.0. Particles of OCP were composed of tight aggregates of strip-like microcrystals growing probably along the [001] and (100) plane of the OCP structure. Nearly stoichiometric OCP was obtained under the most suitable conditions with good reproducibility. Pyrolytic processes of OCP were approximately consistent with the data published so far. However, the temperatures of the appearance and disappearance of pyrolytic crystalline phases and ionic species deviated slightly from the published data. Thermal dehydration up to 150° C without destruction of OCP and decomposition reactions above 300° C resulted in changes in surface area and average pore radius of OCP.

1. Introduction

The crystal structure and spectroscopic properties of octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$, Ca:P atomic ratio of 1.33 and 11.0% H_2O, hereafter called OCP) have been well characterized by X-ray diffraction and infrared absorption methods [1, 2]. The OCP is frequently encountered in the dissolution or precipitation chemistry related to bone, tooth, nonstoichiometric or Ca-deficient hydroxyapatite (e.g. $Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z} \cdot nH_2O$, Ca:P = 1.50 to 1.67, H_2O = 5.8 to 1.79%; DAp), brushite ($CaHPO_4 \cdot 2H_2O$) and phosphate fertilizers [1, 3–6]. From studies and reviews on OCP [7–9], it can be concluded that most of the studies have been done with the intention of clarifying calcification phenomena *in vivo*. In other words, OCP has not been appreciably noted as a possible material for some other application. On the other hand, DAp resembling OCP in chemical composition and crystal structure is well known as a useful separator of proteins and nucleic acids, and also as a catalyst for dehydrating alcohols. Therefore, OCP might exhibit such properties. Spencer [10] tested OCP for chromatography and suggested that OCP was a possible material for separating polynucleotides. In preparing OCP, the principle idea is that the aqueous solution media used for the preparation must contain fairly low Ca^{2+} and PO_4^{3+} concentrations in order to avoid the formation of DAp and brushite [9]. For example, the hydrolysis method of brushite, which has been widely used, utilizes the slight water-solubility of brushite. Although the hydrolysis is not so fast at low temperatures, Spencer [10] succeeded in preparing OCP at a reasonable rate by conducting the hydrolysis at 80° C and pH 6.

In the present work, a new simple hydrolysis method has been developed using powdered α-$Ca_3(PO_4)_2$ instead of brushite. The OCP samples obtained have been characterized in detail.

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2. Experimental procedure

Powdered α-$Ca_3(PO_4)_2$ was prepared by heating an equimolar mixture of thermally synthesized γ-$Ca_2P_2O_7$ and reagent grade $CaCO_3$ at 1000° C for 5 days with mixing at intervals. Subsequently heating at 1300° C for 2 h, followed by air-quenching, and then grinding to a 200 inch-mesh was carried out. The γ-$Ca_2P_2O_7$ was prepared by heating reagent grade brushite at 500° C for 10 h. Hydrolysis experiments were carried out as follows.

1 g of α-$Ca_3(PO_4)_2$ was suspended in 50 ml of preheated hot water maintained at temperatures of 40 to 80° C and bubbled thoroughly by a nitrogen gas stream. The hot suspension was quickly adjusted to a pH of 3 to 7.5 with dilute HNO_3 or aqueous NH_4OH and kept for 3 h at the fixed temperature (± 1° C) and pH (± 0.1). The temperature and pH were automatically controlled by using a thermostat and pH-stat assembly. Throughout the hydrolysis experiments the suspension was stirred vigorously by a magnetic stirrer and a nitrogen gas stream. After that the solid part of the suspension was separated by filtration, washed with water and ethanol and dried under suction at room temperature. The solid thus obtained was identified by X-ray diffraction using Cu*Kα* radiation. OCP and DAp were distinguished by noting characteristic X-ray diffraction peaks such as 4.7° in 2θ (18.7 Å-spacing), 9.35° (9.45 Å) and 9.75° (9.06 Å) for OCP, and 10.8° (8.2 Å) for DAp, and infrared absorption bands such as 910 and 860 cm^{-1} for OCP, and 3570, 865 and 630 cm^{-1} for DAp [9]. Particles of OCP were observed by scanning electron microscopy (SEM). After a synthetic diagram for OCP was made, approximately 30 g of OCP was newly prepared under the most favourable conditions and used for the following analyses and measurements. CaO was determined by standard EDTA titration and P_2O_5 by spectrophotometric phosphovanadomolybdate method. H_2O was estimated thermogravimetically or by subtracting CaO and P_2O_5 amounts from the total amount weighed for the analysis. Thermogravimetric curves were obtained using a heating rate of 5° C min^{-1} in a nitrogen gas stream of 150 ml min^{-1}. Thermal changes in OCP were investigated in the crystalline phase by X-ray powder diffractometry, ionic species by infrared spectroscopy, and surface area and average pore radius by nitrogen adsorption at 77 K using conventional volumetric apparatus.

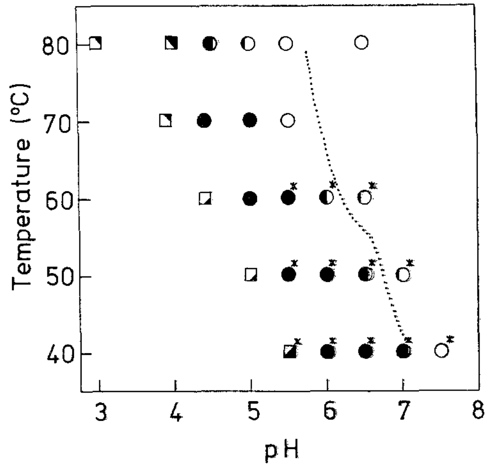

Figure 1 Synthetic diagram for OCP. ●: OCP, ◐: OCP + DAp, ○: DAp, ◨: $CaHPO_4$ + OCP, ◩: $CaHPO_4 \cdot 2H_2O$ + OCP, *: Hydrolysis incomplete (part of α-$Ca_3(PO_4)_2$ remained unreacted). Boundary between OCP and DAp determined in "homogeneous precipitation system" by Newesely [14].

3. Results and discussion

3.1. Synthetic diagram for OCP

Fig. 1 shows the correlation between temperature, pH and crystalline products in the hydrolysis system of α-$Ca_3(PO_4)_2$. The formation of OCP was limited to within a considerably narrow region between the formation regions of DAp and $CaHPO_4$ ($\gtrsim$ 70° C) or $CaHPO_4 \cdot 2H_2O$ ($\lesssim$ 60° C). At temperatures below 60° C and pH above 5.5, part of the α-$Ca_3(PO_4)_2$ still remained in the products after 3 h of treatment. Products at 80° C were composed of mixtures of OCP and DAp or $CaHPO_4$ i.e. OCP single phase could not be obtained. As OCP is a thermodynamically unstable phase compared with brushite or hydroxyapatite [9, 11–13], the products at 80° C might be a result of partial transformation of OCP to much more stable phases. The dotted line in Fig. 1 is a boundary between OCP and DAp according to Newesely [14]. The experiment for obtaining the dotted line was conducted by mixing two aqueous solutions with comparatively high concentrations of calcium and phosphate salts. Therefore, considering the principle idea mentioned in the introduction, OCP was supposed to form through steps such that a slightly water-soluble substance such as amorphous calcium phosphate [$Ca_3(PO_4)_2 \cdot xH_2O$] precipitated and then it transformed to OCP.

From the above results, 70° C, pH4.5 to 5.0, 3 h and 60° C, pH5.0, 3 h are examples of favour-

TABLE I Surface area and average pore radius of OCP and DAp samples

Sample[a]	Preparation conditions			Ca:P (atomic ratio, ± 0.01)	H_2O content (± 0.1%)	Surface area[c] (± 1, $m^2\,g^{-1}$)		Average pore radius[d] (± 1 nm)
	(° C)	pH	(h)			S_{BET}	S_{CI}	
OCP–I	70	4.7	3	1.35	11.0	24	26	17
OCP–II	70	4.7	3	1.35	11.1	21	22	19
OCP–III	65	4.7	3	1.35	10.9	25	26	16
DAp	80	8.0[b]	2	1.53	5.2	13	14	6
DAp	100	8.6[b]	12	1.54	4.0	15	17	5

a. OCP: octacalcium phosphate, DAp: Ca-deficient hydroxyapatite prepared according to the previous study [3]. Samples for measurement of surface area and pore radius were degassed thoroughly below 10^{-2} mm Hg at room temperature.
b. Initial pH value.
c. S_{BET} and S_{CI} mean the area by BET method and Cranston–Inkley method [19], respectively.
d. Obtained by $2 \times Vg/S_{BET}$, where Vg is total amount of nitrogen adsorbed at $P/P_0 \approx 1$.

able conditions for OCP preparation at an α-$Ca_3(PO_4)_2$:H_2O ratio of 1 g:50 ml. Nearly stoichiometric OCP samples were prepared under these conditions with a good reproducibility (see Table I).

3.2. Observation of OCP particles

Fig. 2 shows the particle textures of OCP obtained under different conditions. Particles of OCP consisted of tight aggregates of strip-like microcrystals. The strip-like microcrystals tended to become longer on raising the temperature of hydrolysis. However, microcrystals of OCP formed at 80° C resembled the blade-like shape [3, 15] of DAp. These microcrystals were presumed to grow along the [0 0 1] and (1 0 0) plane of the OCP structure [1, 3].

3.3. Thermal changes

Thermal dehydration and structural changes in OCP have been studied by many investigators [7, 8, 16, 17]. Summarizing them, OCP decomposes on heating as follows

$$Ca_8H_2(PO_4)_6\cdot 5H_2O \xrightarrow[(\sim 100^\circ C)]{-mH_2O} Ca_8H_2(PO_4)_6\cdot(5-m)H_2O \xrightarrow[(150^\circ C \sim)]{-(4-m)H_2O} \tfrac{1}{2}Ca_{10}(PO_4)_6(OH)_2$$

$$+\ 3CaHPO_4 \xrightarrow[(200^\circ C \sim)]{-1.5H_2O} \tfrac{1}{2}Ca_{10}(PO_4)_6(OH)_2 + \tfrac{3}{2}Ca_2P_2O_7 \xrightarrow[(600^\circ C \sim)]{-0.5H_2O} 2Ca_3(PO_4)_2 + Ca_2P_2O_7$$

where the temperatures are not necessarily the determined temperatures. For example, the heating dehydration curve of OCP by Fowler *et al.* [8] has a steep dehydration step at 600 to 700° C, and the curve by Anderson *et al.* [17] shows a similar step at 700 to 800° C. If the steps are due to the decomposition of apatite to $Ca_3(PO_4)_2$, the OCP samples used by them may have originally contained some DAp, or have produced a DAp-like phase in the course of heating, because DAp gives a similar tep at 700 to 800° C due to the same decomposition [18].

Pyrolysis reactions of the OCP prepared here were followed by X-ray diffraction patterns, infrared spectra and measurement of weight losses. Fig. 3 shows a typical thermogravimetric curve of OCP in comparison with that of DAp. The curves below 600° C were similar to curves in the literature [8, 17]. The curve above 600° C suggested that the above final reaction proceeded slowly. Table II lists changes in crystalline phase and ionic species of OCP with heating. Weight losses up to 100 and 150° C corresponded to $m \approx 2.4$ and $m \approx 3.3$, respectively, since the products were only OCP having the (1 0 0) reflection (18.7 Å). At 200 to 250° C the 18.7 Å spacing contracted to 18.4 and 17.0 Å, and further to 15.7 Å, with the appearance of OH^- and reduction of HPO_4^{2-}. An apatitic phase appeared above 250 to 300° C with both a further increase of OH^- and disappearance of HPO_4^{2-}. Subsequently, PO_4^{3-} of β-$Ca_3(PO_4)_2$ appeared above 500° C; in other words, the decomposition of the apatitic compound to β-$Ca_3(PO_4)_2$ started gradually from *ca* 500° C. The thermogravimetric curve above 500° C supported this gradual decomposition. Finally, OCP decomposed to form a mixture of β-$Ca_3(PO_4)_2$ and

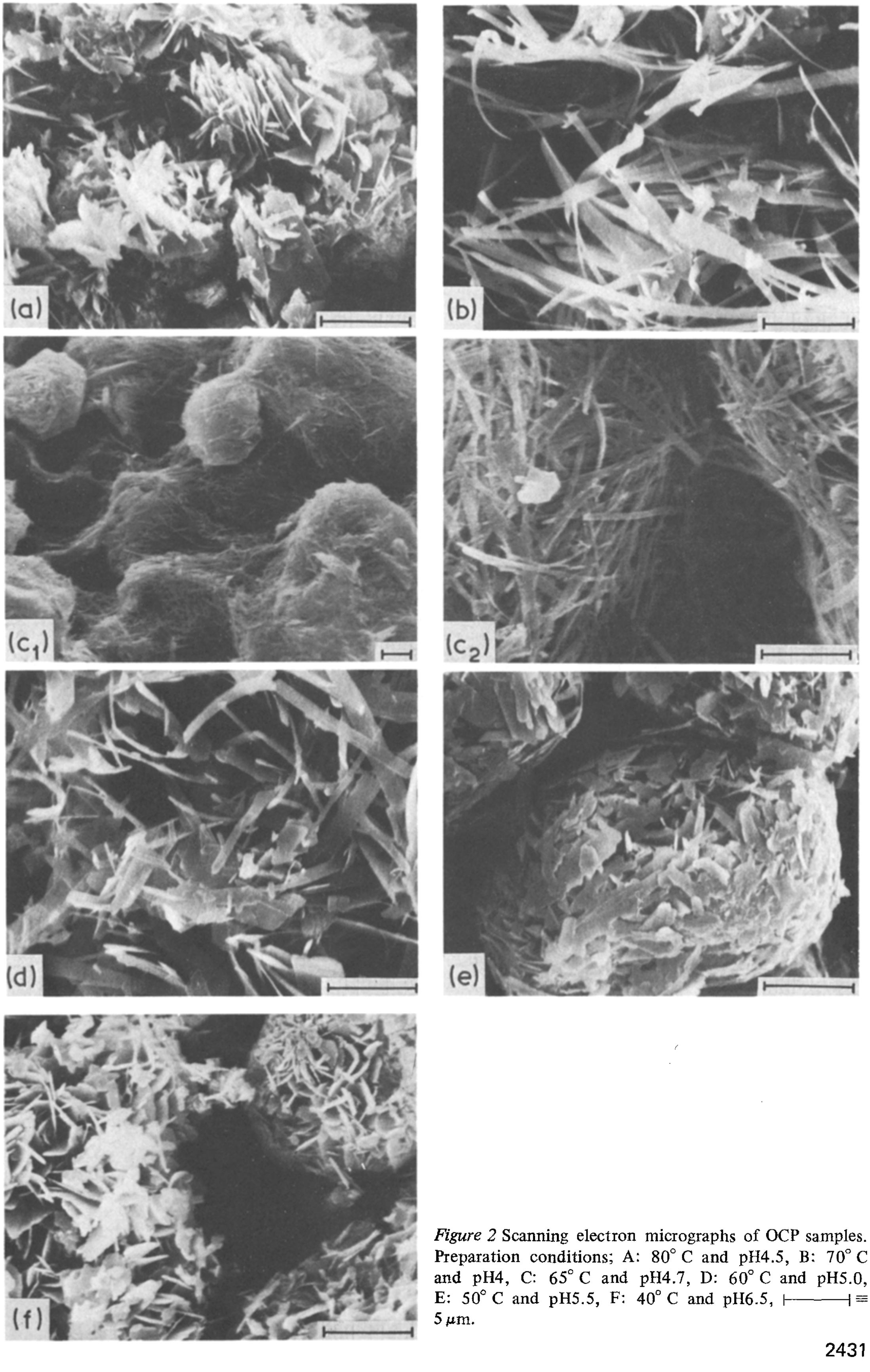

Figure 2 Scanning electron micrographs of OCP samples. Preparation conditions; A: 80° C and pH4.5, B: 70° C and pH4, C: 65° C and pH4.7, D: 60° C and pH5.0, E: 50° C and pH5.5, F: 40° C and pH6.5, ⊢——⊣ ≡ 5 μm.

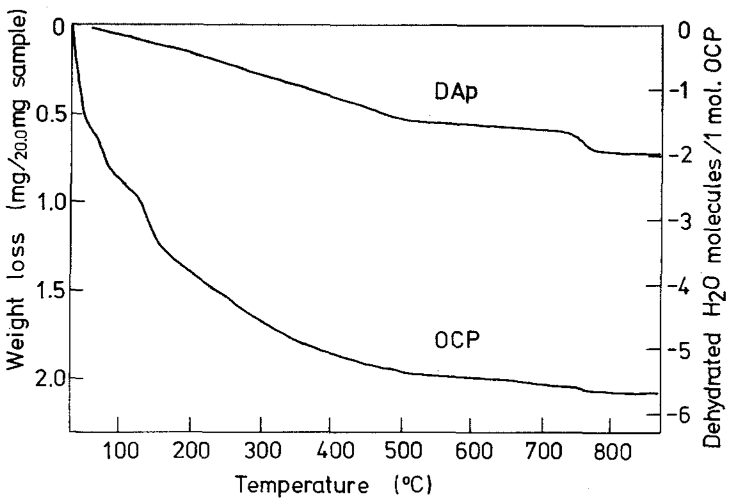

Figure 3 Typical thermogravimetric curves of OCPand DAp.

β-$Ca_2P_2O_7$. An intermediate, $CaHPO_4$, could not be detected as a distinct phase. These results were approximately consistent with data in the literature [7, 8, 16, 17]. However, the temperatures of the appearance and disappearance of crystalline phases and ionic species deviated slightly from the literature data. These slight discrepancies might be due to the different conditions of OCP preparation or to different heating conditions.

Table I lists surface areas and average pore radii of three OCP samples and two DAp samples prepared according to the previous study [3], with their preparation conditions and chemical compositions. Comparing the surface areas and pore radii of OCP and DAp, OCP particles were evaluated to be composed of smaller but more smooth-faced microcrystals than those of DAp.

Isothermal adsorption and desorption of nitrogen at 77 K were measured for OCP-I (see Table I) and its heated samples. Some of the curves are shown in Fig. 4. OCP dried at room temperature had a small hysteresis similar to that [20] of DAp. The degree of the hysteresis was maintained approximately constant up to 300 to 400° C, and then decreased with temperature, and became negligible above 600° C. Fig. 5 shows thermal changes in surface area and average pore radius of OCP. Thermal dehydration up to 150° C

TABLE II Thermal changes in crystalline phase and ionic species of OCP

Temp. (° C)	Time (h)	Phase by X-ray	Ionic species by infrared[b]			
			OH	HPO_4	P_2O_7	PO_4 of T[a]
r.t.	240	OCP	X	○	X	X
100	1	OCP	X	○	X	X
150	1	OCP, M (?)	X	○	X	X
200	1	OCP′	Δ	Δ	X	X
250	1	OCP″	○	X	○	X
300	1	Ap	○	X	○	X
400	1	Ap	○	X	○	X
500	1	Ap	○	X	○	○
500	20	Ap, T	○	X	○	○
600	1	Ap, T, P′ (?)	○	X	○	○
600	20	Ap, T, P	○	X	○	○
700	1	Ap, T, P	○	X	○	○
700	20	T, P, Ap	○	X	○	○
800	1	T, P	X	X	○	○
800	20	T, P	X	X	○	○

a. OCP: octacalcium phosphate having 18.7 Å (strong), OCP′: OCP having 17.0 Å (middle) and 18.4 Å (weak) instead of 18.7 Å, OCP″: OCP having 15.7 Å (weak), M: monetite ($CaHPO_4$), Ap: apatitic phase, T: β-tricalcium phosphate, P: β-calcium pyrophosphate, P′: γ- or β-calcium pyrophosphate.

b. X: not detected, Δ: detected (trace), ○: detected.

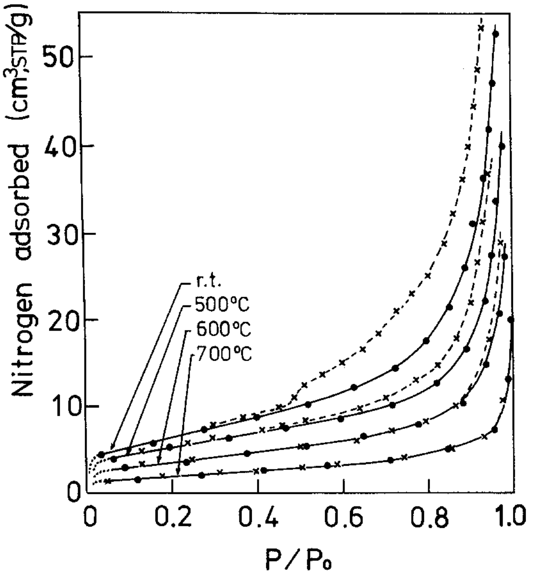

Figure 4 Nitrogen isotherms of 77 K of OCP and its heated samples. Sample: OCP–I. ●: adsorption, X: desorption.

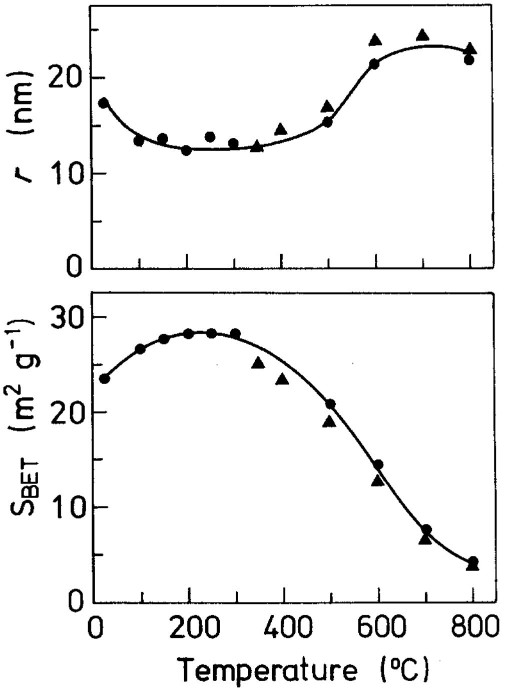

Figure 5 Thermal changes in surface area (S_{BET}) and average pore radius ($\bar{r}$) of OCP. Sample: OCP–I. Prior to measurements, samples below 300° C were heated and degassed at each temperature to below 10^{-2} mm Hg (●), and samples above 350° C were heated in air at each temperature and then degassed to below 10^{-2} mm Hg at room temperature (▲) or at 300° C (●).

without destruction of OCP reflected an increase in surface area and decrease in pore radius. After that, up to 300° C there was no appreciable change. Above 300° C at which decomposition reactions of OCP proceeded definitely, the surface area began to decrease and the pore radius began to increase with temperature.

4. Conclusion

(1) Nearly stoichiometric octacalcium phosphate (OCP) was obtained by using the hydrolysis of α-$Ca_3(PO_4)_2$ with good reproducibility. The OCP samples prepared under favourable conditions gave Ca:P atomic ratios of 1.35 ± 0.01, H_2O contents of $11.0 \pm 0.1\%$, surface areas of 21 to 26 $m^2\,g^{-1}$ and average pore radii of 16 to 19 nm.

(2) Particles of OCP were composed of tight aggregates of strip-like microcrystals growing probably along the [0 0 1] and (1 0 0) plane of OCP structure.

(3) Thermal dehydration up to 150° C without destruction of OCP and decomposition reactions above 300° C resulted in an increase or decrease in surface area and average pore radius of OCP.

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