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Synthesis and Thermal Behavior of Well-Crystallized Calcium-Deficient Phosphate Apatite

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Large crystals (0.5 × 0.5 × 10 μm) of calcium-deficient hydroxyapatites (DAp's) have been synthesized by aqueous precipitation under controlled conditions of pH and temperature. The samples have been characterized using chemical analysis, temperature-programmed dehydration (TPR), X-ray diffraction, IR spectroscopy, and transmission electron microscopy. They show that very well-crystallized DAp's with Ca/P close to 1.50 can be obtained under well-selected synthesis conditions. The specimens presented typical TPR patterns, consisting of a diffuse evolution of water in the range 300–700°C and a sharper one in the range 700–900°C. The maximum temperatures of the TPR bands were found to be markedly higher for the DAp specimen having the largest crystal size. © 1989 Academic Press, Inc.

Introduction

Hydroxyapatite, as the main mineral constituent of hard tissues (bones, teeth), is of importance in the biomedical field as a raw material for the preparation of artificial bone graft. Stoichiometric hydroxyapatite $Ca_5(OH)(PO_4)_3$ (denoted below as HAp) has a Ca/P atomic ratio of 1.67. Hydroxyapatites prepared by precipitation from aqueous solutions are usually obtained with lower Ca/P ratios, which may range from 1.67 to 1.33. They present generally the characteristic X-ray diffraction pattern of hydroxyapatite, although the broadening of the diffraction lines often points to poorly crystallized solids. Precipitates having the lowest ratio often present a diffraction line at 18.7 Å (*1*). The corresponding compound, called octacalcium phosphate (OCP), is best described by the formula $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ (*2*). Compounds with a composition intermediate between HAp and OCP are conventionally called calcium-deficient apatites (DAp's) and have been the object of many studies (*2–12*). Their commonly accepted formula is:

$$Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z} \cdot nH_2O.$$

It corresponds to an apatite structure involving Ca defects and substitution of some HPO_4^{2-} groups for PO_4^{3-} ones. A number of

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methods have been used for preparing DAp. However, there is still no agreement as to a method for the simple and reproducible preparation of well-crystallized DAp having a fixed Ca/P ratio.

This paper reports the synthesis of well-crystallized DAp's obtained by controlled hydrolysis of either monetite ($CaHPO_4$, referred to as DCP) or brushite ($CaHPO_4 \cdot 2H_2O$, referred to as DCPD) in aqueous suspension (*13*). This reaction is limited by the following equilibrium:

$$CaHPO_4 + 2.5H_2O \Leftrightarrow Ca_9(HPO_4)(PO_4)_5(OH) + 4H_2PO_4^- + 4H^+.$$

This equilibrium can be shifted to the right by neutralizing the acidity produced. This has been achieved by the slow hydrolysis of urea added to the suspension, which will occur at temperatures above 80°C (*14*), resulting in the homogeneous production of ammonia and carbon dioxide.

Temperature-programmed dehydration studies (also known as effluent gas thermal analysis, EGTA, and referred to below as temperature-programmed reaction, TPR) of calcium phosphate precipitates have already been performed in the past (*15–17*). However, TPR has never been used until now for characterizing DAp samples. This note will present TPR patterns of the synthesized DAp samples, together with the result of their characterization by conventional techniques like X-ray diffraction and IR spectroscopy.

Materials and Methods

Materials

Two DAp samples have been synthesized by hydrolysis of DCP (UCB p.a.) or DCPD (Merck p.a.), in the presence of urea (Merck p.a.).

The desired amount of solid reactant (10 g/liter) was suspended in distilled water, after adjusting the pH using a 1 *M* HNO_3 solution. The desired amount of urea was then added (1.8 g/liter). The suspension (5 liter) was placed in a double-jacket Pyrex reactor and continuously stirred at a constant rate (100 rpm). The temperature of the reactor was controlled by a programmable circulation thermostat (Lauda KP 20 D). The temperature was raised linearly so as to reach the desired value (80 or 90°C) within 1 hr. The pH of the solution then increased progressively as a result of the hydrolysis of urea (*14*).

The precipitates were filtered, thoroughly washed with distilled water, and freeze dried. The dry samples were stored in a desiccator. The preparation conditions of the individual samples are summarized in Table I.

Methods

The Ca/P atomic ratios of the samples have been estimated from the conventional elemental analysis of Ca and phosphorus (*18*), using $CaCO_3$ and KH_2PO_4, respectively, as standards for Ca and P. The atomic absorption determination of Ca was performed on a Varian Techtron Model A-5 apparatus, while P was determined colorimetrically as the molybdenum blue complex, using a Baush & Lomb Spectronic 700 apparatus.

X-ray diffraction patterns were recorded on a Philips-Norelco PW 1130 diffractometer using Cu*Kα*, Ni-filtered radiation (λ = 0.15418 nm).

Infrared spectra were recorded employing KBr pellets with a Beckman IR 12 spectrometer.

TABLE I
PREPARATION CONDITIONS OF THE SAMPLES

Sample	Starting material	pH Initial	pH Final	Temperature (°C)	Time (hr)
DAP24	DCPD	4.0	6.6	80	94
DAP33	DCP	4.0	6.8	90	71

The TPR technique was used to follow thermal dehydration of the samples. Details on the TPR apparatus and the operating conditions were given previously (*19*). The samples (about 65 mg) were heated in a stream of argon (50 ml/min) with a linear temperature program (10°C/min). The reactor was of the tubular, flow-through type (inner diameter = 0.10 cm).

Electron microscopy specimens were prepared by dispersing the powdered samples in distilled water and depositing a droplet of the obtained suspension on an athene 483-type copper grid (Agar Aids Ltd), covered with a thin carbon film. After drying in a desiccator, the specimens were observed using an AEI transmission electron microscope (EM6G type) operated with an acceleration voltage of 100 kV.

Results and Discussion

Both samples were found by chemical analysis to have a Ca/P of 1.53 ± 0.03 (95% confidence interval).

Before thermal treatment, they presented the characteristic diffraction pattern of well-crystallized HAp, free of any other sparingly soluble calcium phosphate (Fig. 1). After heating for 1 hr at 1000°C, both samples presented the characteristic pattern of pure β-tricalcium phosphate (β-TCP), free of any detectable amounts of either β-calcium pyrophosphate (β-CPP) or HAp.

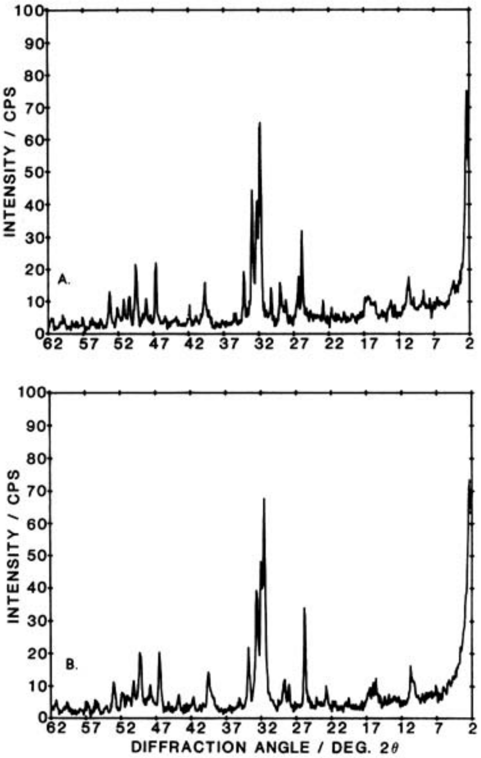

FIG. 1. Characteristic XRD patterns of the DAp samples: (A) DAP24 and (B) DAP33.

IR spectra of the fresh DAp samples were characteristic of well-defined HAp, partially substituted with HPO_4^{2-} (bands at 875, shoulders at 1180 and 1200 cm^{-1}) (*11, 12, 20*) and containing traces of carbonate groups substituted for PO_4^{3-} (very small bands at 1410 and 1450 cm^{-1}) (*20*). After heating for 1 hr at 1000°C, both samples produced IR spectra characteristic of pure β-TCP and free of any detectable hydroxyl or pyrophosphate groups. According to (*20*), and assuming the detection limits to be 2 wt% for HAp in β-TCP–HAp mixtures according to X-ray diffraction measurements and 0.5 wt% for β-CPP in β-CPP–β-TCP mixtures according to IR measurements, it is concluded from the above results that the Ca/P ratios of both sample are in the range 1.498–1.503.

Electron micrographs of the samples (Fig. 2) show that the DAp's are obtained in the form of very elongated acicular crystal, with average size dependent strongly on the synthesis conditions: 0.25 × 10 μm for sample DAP33, 0.1 × 2 μm for sample DAP24.

The characteristic TPR patterns of the samples are presented in Fig. 3. An intense band around 100°C is observed on sample DAP24. A second, very broad band appears in the 300–600°C range for sample DAP24, with a maximum at 420°C; the same band is found in the range 300–680°C for sample DAP33, with its maximum at 560°C. Finally

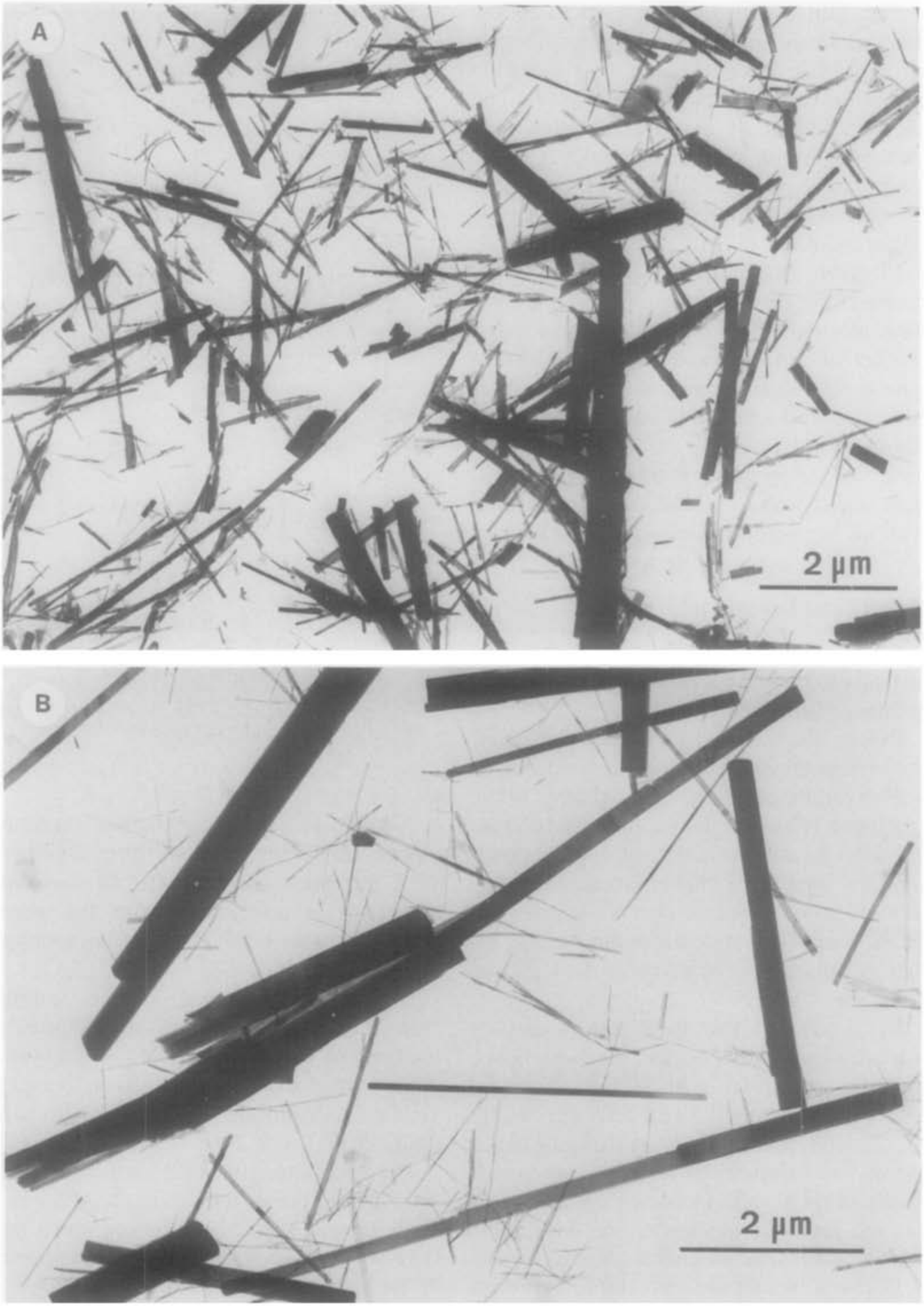

FIG. 2. Electron micrographs of the DAp samples: (A) DAP24 and (B) DAP33.

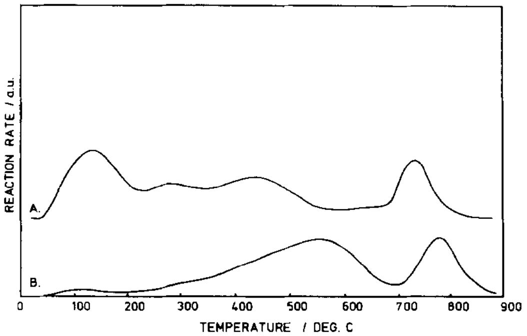

FIG. 3. TPR patterns of the DAp samples: (A) DAP24 and (B) DAP33.

a high-temperature band is observed, with maximum temperature 700°C for sample DAP24 and 780°C for sample DAP33. According to the literature data (*13, 15, 20, 21*), the first band corresponds to the evolution of adsorbed water. The intermediate band is due to a very progressive release of water as a result of the reaction:

$$2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O. \qquad (A)$$

The latter is characteristic of the DAp–β-TCP thermal transformation, during which:

$$P_2O_7^{4-} + 2OH^- \rightarrow 2PO_4^{3-} + H_2O. \quad (B)$$

The TPR observation indicates that both processes are the slowest for the DAp having the largest crystallite size, Reaction (A) being the most sensitive to crystal size variation.

In conclusion, the present results show that pure, very well-crystallized deficient apatites having a Ca/P ratio very close to 1.50 can be synthesized in the form of crystals with sizes which can vary widely. They exhibit characteristic TPR patterns, the peak temperatures of which are affected by their particle size.

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