

## FORMATION OF $\beta$ -TRICALCIUM DI(ORTHOPHOSPHATE) FROM MIXTURES OF HYDROXYAPATITE AND CALCIUM HYDROGEN ORTHOPHOSPHATE

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### ABSTRACT

The decomposition of mixtures of hydroxyapatite and calcium hydrogen phosphate has been studied by X-ray diffraction, infrared spectroscopy and temperature programmed reaction. It is shown that hydroxyapatite and calcium pyrophosphate, resulting from the thermolysis of calcium hydrogen phosphate, are the two phases involved in the reaction of formation of  $\beta$ -tricalcium phosphate in the range 750–1000°C.

### INTRODUCTION

$\beta$ -Tricalcium phosphate [ $\beta$ -tricalcium bis(orthophosphate), noted here as  $\beta$ -TCP] is generally described either as a dehydration product of a calcium-deficient apatite with a Ca/P ratio of 1.5, or as a product of the high temperature solid–solid reaction between calcium oxide and dicalcium pyrophosphate (dicalcium diphosphate, referred to below as CPP) [1].

More recently [2], mineralogically pure  $\beta$ -tricalcium phosphate has been obtained by heating an equimolar mixture of hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , referred to below as HAP) and dicalcium phosphate (anhydrous calcium hydrogen orthophosphate, referred to below as DCP). It has been suggested [3], on the basis of infrared (IR) studies of octacalcium phosphate (OCP), that  $\beta$ -TCP could be a product of the reaction between HAP and CPP above 700°C.

The thermal analysis of dehydration (referred to below as TPR, for Temperature Programmed Reaction) has been applied to the study of hydrated DCP, HAP and OCP [4–6]. The aim of this note is to combine this method with X-ray diffraction (XRD) and IR spectroscopy to gain a better knowledge of the formation of  $\beta$ -TCP from HAP and DCP.

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## MATERIALS AND METHODS

Pure anhydrous calcium tri-orthophosphate, which proved to be hydroxyapatite, and anhydrous DCP, both from U.C.B., were used to prepare the three following mixtures: (A) 88 wt% HAP and 12 wt% DCP; B, 75 wt% HAP and 25 wt% DCP; C, 65 wt% HAP and 35 wt% DCP. Thus, small portions of the two solids were mixed vigorously in an agate mortar for about 5 min. The two pure phases were also examined separately. X-ray diffraction diagrams were recorded on a Philips-NORELCO PW 1130 diffractometer using  $\text{CuK}_\alpha$ , Ni filtered radiation ( $\lambda = 0.15418 \text{ nm}$ ).

Infrared spectra were recorded on KBr pellets with a Beckman IR 12 spectrometer. In order to allow a quantitative use of the spectra, the amounts of sample (20 mg) and of KBr (980 mg) were weighed accurately and mixed carefully in an agate mortar; the weight of each pellet was 120 mg. Cardboard with a rectangular perforation ( $1 \text{ cm}^2$ ) were used as pellet holders; the powder was placed in the perforation and pressed between two stainless steel plates.

For X-ray and IR analysis, small portions (1 g) of the sample were heated at different temperatures (560, 760, 900 and  $1000^\circ\text{C}$ ) for 1 h, in ambient atmosphere. The temperature programmed reaction technique (TPR) was used to follow thermal dehydration of all the samples. The TPR apparatus is similar to that proposed by Cvetanović and Amenomiya [7], and used previously by Sedlak and Beebe [8] for the thermal study of amorphous calcium phosphate. A detailed description of the experimental arrangement used in this work can be found in ref. 9. The solid is heated in a stream of inert carrier gas with a linear heating rate. The concentration,  $C$ , of water in the carrier gas is monitored by a thermal conductivity detector. The working conditions were: amount of sample, 130 mg (except for the DCP sample, 28.5 mg); heating rate,  $10^\circ\text{C min}^{-1}$ ; gas flow (argon),  $25 \text{ ml min}^{-1}$  (except for the DCP sample,  $50 \text{ ml min}^{-1}$ ). The reactor was of the tubular, flow through type (inner diameter = 0.10 cm).

## RESULTS AND DISCUSSION

The X-ray diffraction diagram of DCP corresponds to the ASTM card No. 9-80; the peaks are sharp, indicating a good crystallinity. On the other hand, as the pure HAP sample was heated at increasing temperatures, a sharpening of the peaks was observed, indicating an improvement of its crystallinity. The mean crystal size,  $t$ , has been estimated from the integral width  $\beta$  (radian) of the peak at  $2\theta = 25.9^\circ$ , using the Scherrer formula:

$$t = (K\beta)/\lambda \cos \theta$$

where  $t$  is in nm,  $K = 1$ ,  $\lambda = 0.1541\theta \text{ nm}$  and  $\theta$  is the Bragg angle. The crystal size estimated in this way varies from 14 nm, for the initial sample, to

about 30 nm after heating at 1000°C. The X-ray diffraction patterns of the heated mixtures indicate a reaction between HAP and DCP. For sample B, which corresponds to a nearly equimolar mixture, the reaction is quantitative and the sole phase detected is  $\beta$ -TCP. For samples A and C, either HAP or  $\beta$ -CPP, respectively, are found in excess.

The mineralogical composition has been estimated by measuring the intensity,  $I$ , of the characteristic peaks of the various phases, at  $2\theta = 30.9^\circ$  for  $\beta$ -TCP,  $2\theta = 29.1^\circ$  for  $\beta$ -CPP,  $2\theta = 31.8^\circ$  for HAP. Calibration curves have been established, using mixtures of either  $\beta$ -CPP or HAP with  $\beta$ -TCP. The pure phases were obtained respectively by calcining at 1000°C either DCP or HAP or an equimolar mixture of these products. The following calibration equations have been obtained:

$$\% \beta\text{-TCP} = -83.0 + 182.4I_{30.9}(I_{30.9} + I_{29.1})$$

with a confidence interval of  $\pm 1.4\%$  (confidence level = 0.95)

$$\% \beta\text{-TCP} = 11.6 + 88.9I_{30.9}(I_{30.9} + I_{31.8})$$

with a confidence interval of  $\pm 1.7\%$  (confidence level = 0.95). Figure 1 shows the weight % of  $\beta$ -TCP in samples A, B and C heated at 1000°C as a

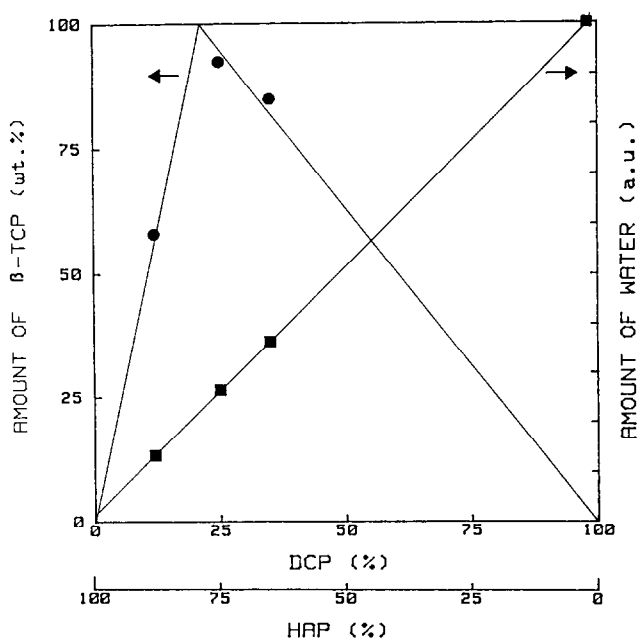


Fig. 1. Characteristic features of the samples versus their initial composition. (●) Amount of  $\beta$ -TCP produced after heating at 1000°C, as estimated from X-ray diffraction data. (■) Amount of water evolved during TPR experiments between 388°C and 612°C. The solid lines depict the expected values.

function of the weight composition of the initial mixtures; the straight lines give the composition expected on the basis of a stoichiometric reaction between HAP with DCP. The figure shows that the reaction is stoichiometric and complete after treatment of 1 h at 1000°C.

Figure 2 presents the TPR patterns of DCP, HAP and mixtures A, B and C. According to Füredi-Milhofer et al. [10], the band below 200°C is ascribed to a loss of molecular water (adsorption, crystallisation water from HAP). The peak observed near 500°C for DCP originates from the condensation of hydrogenphosphate groups to pyrophosphate ones:  $2\text{HPO}_4^{2-} \rightarrow \text{P}_2\text{O}_7^{4-} + \text{H}_2\text{O}$ . Its shape appears to change when DCP is mixed with HAP. The thermograms of samples B and C suggest a weak emission of water above 700°C. The amount of water ascribed to the condensation of hydrogenphosphate to pyrophosphate has been determined by measuring the area of the peak ranging from 388 to 612°C and normalizing it for the amount of sample and experimental conditions. Figure 1 shows that water is emitted in proportion to the DCP content.

The IR spectra of samples treated at increasing temperatures confirm the trend indicated by X-ray diffraction. In the 1000  $\text{cm}^{-1}$  range, a change is observed from the bands characteristic of HAP to those characteristic of  $\beta$ -TCP. In the OH stretching region, the spectra exhibit a broad band extending from 3000 to 3700  $\text{cm}^{-1}$ , to which a sharp peak at 3570  $\text{cm}^{-1}$  (full width at half maximum (FWHM) = 5  $\text{cm}^{-1}$ ) is superimposed, which is characteristic of HAP. This peak is hardly visible for the low temperature samples, due to the overlap of the broad band, but is clearly observed for the samples treated at 560°C and above. The height of the peak has been

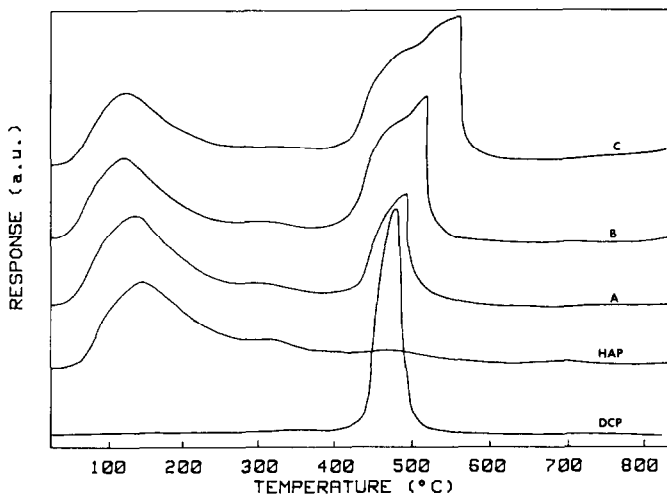


Fig. 2. TPR patterns of the starting HAP and DCP samples, and of their mixtures. The initial weight concentration of DCP in the mixture is: (A) 12%; (B) 25%; (C) 35%.

measured on absorbance spectra, by reference to a straight baseline drawn between its tails.

A band at  $725\text{ cm}^{-1}$  (FWHM =  $15\text{ cm}^{-1}$ ), characteristic of the pyrophosphate anion, appears for the samples heated at  $560^\circ\text{C}$ . Its intensity has been estimated from absorbance spectra by measuring the area under the band (absorbance unit  $\times\text{cm}^{-1}$ ). The intensities of the two bands can be compared from one sample to another, as the thickness of the KBr pellets and the sample content have been kept constant. Their variations as a function of the pretreatment temperature, are shown in Fig. 3. Except for the OH band of sample A, which goes through a maximum at  $760^\circ\text{C}$ , the intensities of both bands decrease above  $560^\circ\text{C}$ , indicating that the reaction between HAP and CPP is starting. The reaction rate increases above  $760^\circ\text{C}$  and extensive conversion is obtained at  $900^\circ\text{C}$ . The persistence of an OH band

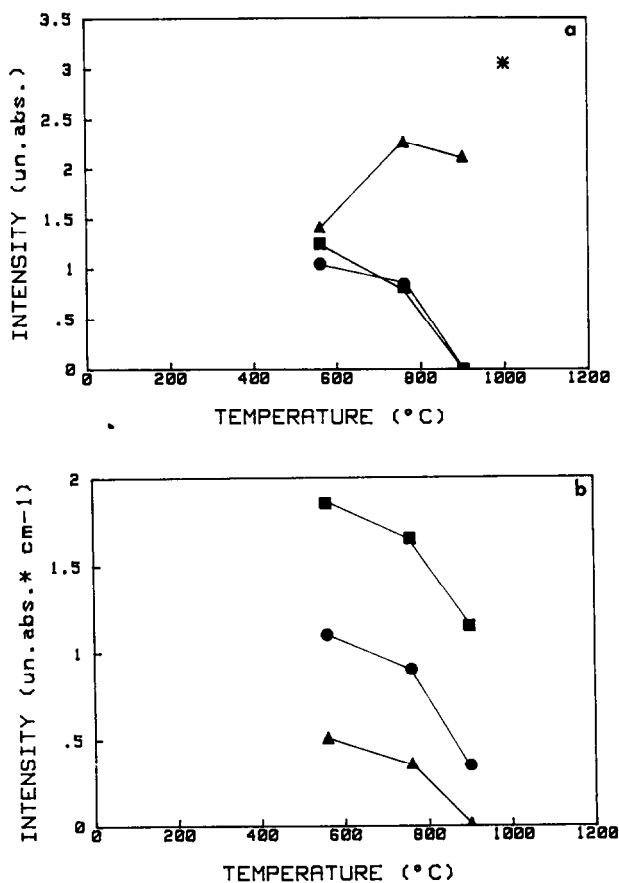


Fig. 3. Intensities of the characteristic IR bands of samples (▲) A, (●) B, (■) C and (\*) HAP, versus their heating temperature. (a) OH stretching band at  $3570\text{ cm}^{-1}$ ; (b) pyrophosphate band at  $725\text{ cm}^{-1}$ .

for sample A, and of a pyrophosphate band for sample B, is related to the excess of HAP and CPP, respectively, as evidenced by X-ray diffraction.

The occurrence of a reaction between HAP and CPP above 560°C should produce water according to the following reaction [3]:  $2\text{OH}^{-1} + \text{P}_2\text{O}_7^{4-} = 2\text{PO}_4^{3-} + \text{H}_2\text{O}$ . In order to check this, the following variation of the TPR experiment has been performed: standard TPR runs were stopped at 550°C and the samples were cooled down in situ. The temperature was then raised and maintained at 750°C, and the emission of water (gas flow = 12.5 ml min<sup>-1</sup>) was followed as a function of time until the response of the detector came back to the baseline. For samples A, B and C, the amount of water thus produced was about 0.12 wt.% of the sample, to be compared with expected values of 0.79, 1.34 and 1.17%, respectively. The emission of about the same amount of water by the three samples agrees well with the comparable decrease of the pyrophosphate IR band between 560 and 760°C, as depicted in Fig. 3(b). However, the amount of water released at 750°C remains still a small fraction of the amount expected for a complete reaction, in agreement with IR spectroscopic observations.

## CONCLUSION

X-ray diffraction results have shown that  $\beta$ -tricalcium phosphate was produced quantitatively upon heating for 1 h at 1000°C from mixtures of hydroxyapatite and dicalcium phosphate. TPR experiments and IR spectroscopic investigations have demonstrated that the reaction involved in fact hydroxyapatite and the thermolysis product of dicalcium phosphate,  $\beta$ -calcium pyrophosphate. The reaction starts at temperatures just above this thermolysis and becomes appreciable near 750°C.

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