

## Thermal Behavior of Cadmium-Containing Apatites

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The behaviour of cadmium hydroxy- and fluorapatites at 500–1000°C and under low or high water vapor pressure were examined by X-ray diffraction and IR spectrometry. Heat treatment induces decomposition of both hydroxyapatites and fluorapatites. The decomposition temperature and the nature of the crystalline phases (cadmium oxide, tetracadmium phosphate, trimetallic phosphate) are strongly dependent on water vapor pressure and the nature and cadmium content of the initial compounds. Fluorapatites appear to be more stable than hydroxyapatites; a cadmium rate increase destabilizes the apatitic structure and high water vapor pressure stabilizes the hydroxyapatites. © 1993 Academic Press, Inc.

### Introduction

Natural apatitic phosphates never occur as pure compounds: ores contain a large number of metallic elements which can be valuable (e.g., U, V, Ti) or unwanted impurities (e.g., Cd, As, Mg) (1, 2); biological apatites are hydroxyapatites modified by various ions such as  $Mg^{2+}$ ,  $CO_3^{2-}$ , and  $HPO_4^{2-}$  (3–5).

The apatites form a large family of phosphate compounds whose fluorapatite,  $Ca_{10}(PO_4)_6F_2$ , is the well-known representative term. They generally crystallize in the hexagonal system (space group  $P6_3/m$ ) (6). The almost compact assembly of orthophosphate ions  $PO_4$  defines two channels in which the cations are localized. One of the main characteristics of the apatitic structure is to allow large and varied substitutions for both the cations or anions: in the cationic  $Ca^{2+}$  sites, and in the anionic  $PO_4^{3-}$  sites or in the channel  $F^-$  sites (7).

The amounts of cadmium in cultivated soils, due to phosphate fertilization, increase every year (8). The new norms imposed by the European Economic Commu-

nity are fixed at less than 18 ppm for technical grade phosphoric acid (9–11). So, it is necessary to limit or to eliminate cadmium from phosphate ores and from fertilizers. Some processes are proposed using liquid–liquid or ionic flotation methods to eliminate the cadmium from the phosphoric acid (12, 13). Another method is to remove cadmium directly from phosphate rocks by heat treatment. It appears that fundamental studies are necessary.

In this paper, we have studied the temperature effect on thermal stability of cadmium-containing hydroxy- and fluorapatites, at low and high water vapor pressure. To approximate conditions of phosphate ores, thermal treatment of apatites containing very low amounts of cadmium was also studied.

### Materials and Methods

The cadmium-containing hydroxyapatites were prepared using a double decomposition method in a boiling aqueous medium (14). Fluorapatites were obtained by two synthetic methods: precipitation by a

similar method to hydroxyapatite preparation in the presence of a large excess of fluoride ions or by a solid-gas reaction at 600°C between a previously prepared hydroxyapatite and hydrogen fluoride.

For the hydroxyapatite, a solid solution exists between calcium hydroxyapatite and cadmium hydroxyapatite with the general formula  $\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6(\text{OH})_2$  with  $0 \leq x \leq 10$ .

For the fluorapatite, the solid solution only exists in the range  $0 \leq x \leq 6$ , the general formula being  $\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6\text{F}_2$ . When the  $\text{Ca}/(\text{Ca} + \text{Cd})$  atomic ratio is greater than 6 (i.e.,  $x \geq 6$ ), the precipitated compounds are mixed hydroxy-fluoroapatites, and the amount of hydroxide ions increases with the amount of Cd ions; compounds prepared by a solid-gas reaction are a mixture of various phases.

All the apatitic samples were well crystallized pure apatitic phases, with a Cation/P atomic ratio close to the stoichiometric one: 1.667. The  $a$ - and  $c$ -axis lattice constants of cadmium-calcium apatites vary linearly with composition according to Vegard's law. The slight shift to lower wavenumbers of the  $\text{PO}_4$  and  $\text{OH}$  infrared bands is due to the contraction of the unit cell and to the cation-oxygen interactions.

The treatment atmosphere has a large influence on the decomposition temperature of apatites; this was demonstrated by treatment in the presence or absence of water vapor. The behavior of all cadmium-containing hydroxyapatites was examined at various temperatures and at high and low water vapor pressure (respectively  $p_{\text{H}_2\text{O}} = 46 \times 10^3$  Pa and  $p_{\text{H}_2\text{O}} = 658$  Pa). Fluoroapatites were treated only at the low water vapor pressure.

The samples were placed in a boat, then into a silica laboratory tube, in which nitrogen containing a varying amount of water vapor circulated. After 1 hr of treatment, the samples were cooled and examined by X-ray diffraction, IR-spectroscopy, and chemical analysis.

X-ray diffraction (INEL powder diffrac-

tometer CPS 120) was carried out at room temperature using  $K\alpha 1$  radiation. The  $a$  and  $c$  lattice constants were determined from diffractometric data by a least-squares refinement.

IR-spectrometry (Perkin-Elmer FTIR 7700) was performed in the range 4000–400  $\text{cm}^{-1}$ . The technique used was to finely mix the powdered samples with 300 mg of KBr (I.R. grade) and pelleted under vacuum.

Calcium and cadmium contents were determined using a Perkin-Elmer 5000 atomic absorption spectrophotometer (15). Phosphorus was determined colorimetrically as phosphovanadomolybdic complex using the Gee and Deitz method (16).

## Experimental Results

### *Thermal Behavior of Hydroxyapatite*

Previous experiments showed that for a fixed temperature and a fixed duration, the stability of cadmium-containing hydroxyapatite was dependent on water vapor pressure. For example, hydroxyapatite  $\text{Ca}_2\text{Cd}_1(\text{PO}_4)_6(\text{OH})_2$  heated for 1 hr at 900°C (Fig. 1) in a dry atmosphere ( $p_{\text{H}_2\text{O}} \approx 0$  Pa) completely decomposed into  $\beta$ -tricalcium phosphate and cadmium oxide. In a slightly humid atmosphere ( $p_{\text{H}_2\text{O}} = 658$  Pa), just a very low amount of apatite was decomposed and only traces of  $\beta$ -tricalcium phosphate appeared. The decomposition rate strongly depended on the water vapor pressure.

X-ray diffraction allows the determination of the different crystalline phases formed during the heat treatment and, thus, the stability of the initial compound to be checked. Nevertheless, it was not possible to make a quantitative evaluation of the relative amounts of each phase due to frequent superimpositions of the X-ray lines and to the lack of accurate calibration curves.

Between room temperature and 500°C, no decomposition phase appeared whatever the initial apatitic composition or the water vapor pressure. Just a very slight decrease of the intensity of the  $\text{OH}$  IR band at 3560  $\text{cm}^{-1}$  was observed: this is in agreement

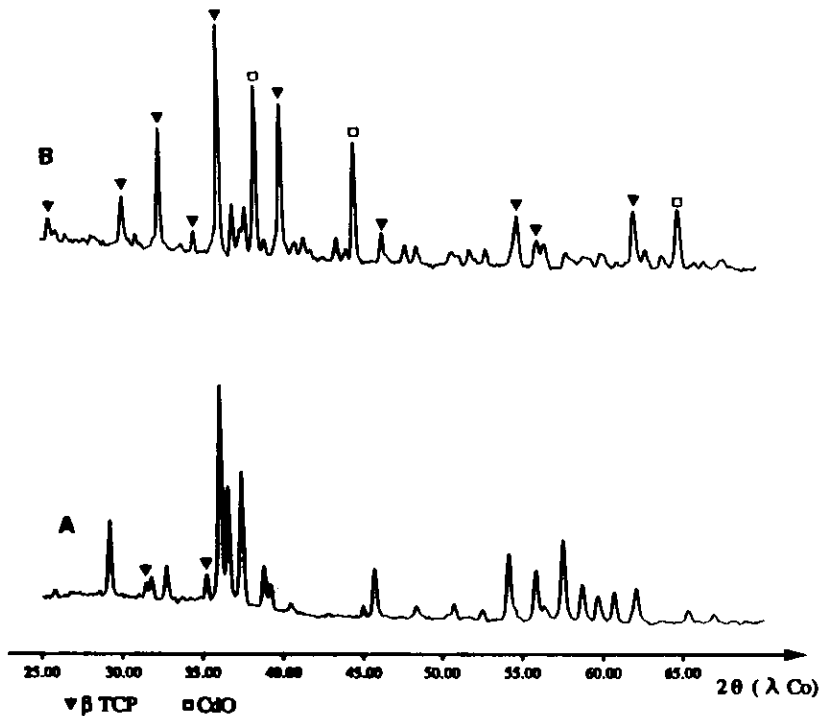


FIG. 1. X-ray diffraction patterns of hydroxyapatite  $\text{Ca}_9\text{Cd}_1(\text{PO}_4)_6(\text{OH})_2$  treated at  $900^\circ\text{C}$  for 1 hr: (A)  $p_{\text{H}_2\text{O}} = 658$  Pa and (B)  $p_{\text{H}_2\text{O}} \approx 0$  Pa.

with the loss of  $\text{OH}^-$  ions from the structure. This process was more sensitive when the cadmium content was increased.

The main results of treatments over  $500^\circ\text{C}$  at high or low water vapor pressure are reported in Table I.

At  $600^\circ\text{C}$ , the treatment did not decompose the apatitic compounds whatever the water vapor pressure or the cadmium content, except for cadmium hydroxyapatite  $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$  treated at low water vapor pressure, where tetracadmium phosphate  $\text{Cd}_4\text{P}_2\text{O}_9$  and  $\beta'$ -tricadmium phosphate  $\text{Cd}_3(\text{PO}_4)_2$  appeared.

At  $800^\circ\text{C}$ , all the apatites treated at high water vapor pressure were stable except cadmium hydroxyapatite. At low water vapor pressure, apatites containing less than four cadmium ions (atomic ratio:  $\text{Cd}/(\text{Ca} + \text{Cd}) < 0.4$ ) were stable; other ones (atomic ratio:  $\text{Cd}/(\text{Ca} + \text{Cd}) > 0.4$ ) were decomposed into tetracadmium phosphate and  $\alpha$ -trimetallic phosphate  $(\text{Ca}, \text{Cd})_3(\text{PO}_4)_2$ .

At  $900^\circ\text{C}$ , all the apatites were decomposed except the one containing 0.005 cadmium atoms per cell. The nature of the decomposition phases depends on the initial apatitic composition: for atomic ratio  $\text{Cd}/(\text{Ca} + \text{Cd}) \leq 0.4$ , apatite decomposed into  $\alpha$ - or  $\beta$ -trimetallic phosphate and cadmium oxide  $\text{CdO}$ , for atomic ratio  $0.5 \leq \text{Cd}/(\text{Ca} + \text{Cd}) \leq 0.8$  into tetracadmium phosphate, and  $\alpha$ -trimetallic phosphate, and for cadmium hydroxyapatite (atomic ratio  $\text{Cd}/(\text{Ca} + \text{Cd}) = 1$ ) into tetracadmium phosphate and  $\beta'$ -tricadmium phosphate.

Thermogravimetric analysis of hydroxyapatite samples was carried out until  $1000^\circ\text{C}$  ( $360^\circ\text{C hr}^{-1}$ ) in an air atmosphere. Three different weight losses were observed:

—The first one (1–2%), in the temperature range  $60$ – $300^\circ\text{C}$ , was the usual loss of absorbed water.

—The second one occurs over various temperature ranges depending on the apatite composition. The weight loss also depends

TABLE I  
THERMAL HYDROXYAPATITE BEHAVIOR: A,  $p_{\text{H}_2\text{O}} = 658 \text{ Pa}$ ; B,  $p_{\text{H}_2\text{O}} = 46 \times 10^3 \text{ Pa}$

Cd/(Ca + Cd) (solution)	600°C		800°C		900°C	
	A	B	A	B	A	B
0	Stable	Stable	Stable	Stable	Stable	Stable
0.0005	Stable	Stable	Stable	Stable	Stable	Stable
0.05	Stable	Stable	Stable	Stable	Unstable <sup>d</sup>	Unstable <sup>a</sup>
0.1	Stable	Stable	Stable	Stable	Unstable	Unstable
0.2	Stable	Stable	Stable	Stable	Unstable	Unstable
0.3	Stable	Stable	Stable	Stable	Unstable	Unstable
0.4	Stable	Stable	Unstable <sup>d</sup>	Stable	<sup>b</sup>	<sup>b</sup>
0.5	Stable	Stable	<sup>c</sup>	Stable	<sup>c</sup>	<sup>c</sup>
0.6	Stable	Stable	<sup>c</sup>	Stable	<sup>c</sup>	<sup>c</sup>
0.8	Stable	Stable	<sup>c</sup>	Stable	<sup>c</sup>	<sup>c</sup>
1.0	Unstable <sup>d</sup>	Stable	<sup>d</sup>	Unstable <sup>d</sup>	<sup>d</sup>	<sup>d</sup>

<sup>a</sup>  $\beta$ -TCP + CdO.

<sup>b</sup>  $\alpha$ -TCP + CdO.

<sup>c</sup>  $\text{Cd}_4\text{P}_2\text{O}_9$  +  $\alpha$ -TCP.

<sup>d</sup>  $\text{Cd}_4\text{P}_2\text{O}_9$  +  $\beta'$ - $\text{Cd}_3(\text{PO}_4)_2$ .

on the amount of cadmium in the hydroxyapatite. It can be correlated to  $\text{OH}^-$  ion elimination from the structure; the experimental values are in good agreement with the theoretical losses (Fig. 2, Table II).

—The third one begins at a same temperature (960°C) whatever the hydroxyapatite.

#### Thermal Behavior of Fluorapatite

The stability of different cadmium-containing fluorapatites was examined (Table III).

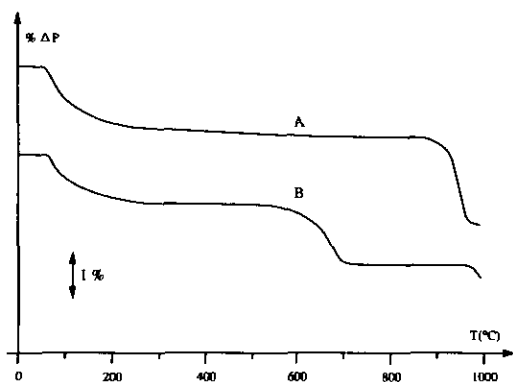


FIG. 2. Thermogravimetric analysis curves: (A)  $\text{Ca}_2\text{Cd}(\text{PO}_4)_6(\text{OH})_2$  and (B)  $\text{Ca}_2\text{Cd}_8(\text{PO}_4)_6(\text{OH})_2$ .

The decomposition temperature of the fluorapatites was strongly dependent on the initial composition of the apatites. So at 800°C, only the limit compound of the solid solution (atomic ratio:  $\text{Cd}/(\text{Ca} + \text{Cd}) = 0.6$ ) decomposed; at 900°C apatites with  $\text{Cd}/(\text{Ca} + \text{Cd}) \geq 0.3$  and at 1000°C all apatites with  $\text{Cd}/(\text{Ca} + \text{Cd}) \geq 0.1$  decomposed.

X-ray diffraction showed that on heat treatment, fluorapatites were converted into  $\alpha$ - or  $\beta$ -trimetallic phosphate and calcium or cadmium fluorides.

For a fixed temperature and a fixed cadmium — concentration the amount of decomposed apatite appeared to be lower for fluorapatite than for hydroxyapatite.

TABLE II  
THERMOGRAVIMETRIC ANALYSIS

Cd/(Ca + Cd) (solution)	Second loss weight		
	T (°C)	$\Delta P$ (%) (Exp.)	$\Delta P$ (%) (theor.)
0.1	900–960	1.65	1.67
0.8	570–720	1.13	1.16

TABLE III  
THERMAL FLUORAPATITE BEHAVIOR  
( $p_{\text{H}_2\text{O}} = 658 \text{ Pa}$ )

Cd/(Ca + Cd) (solution)	800°C	900°C	1000°C
0	Stable	Stable	Stable
0.0005	Stable	Stable	Stable
0.05	Stable	Stable	Stable
0.1	Stable	Stable	Unstable <sup>a</sup>
0.2	Stable	Stable	Unstable <sup>a</sup>
0.3	Stable	Unstable <sup>a</sup>	Unstable <sup>a</sup>
0.5	Stable	<sup>b</sup>	<sup>b</sup>
0.6	Unstable <sup>b</sup>	<sup>b</sup>	<sup>b</sup>

<sup>a</sup>  $\beta$ -TCP.

<sup>b</sup>  $\alpha$ -TCP.

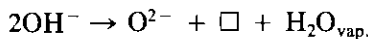
### Interpretation and Discussion

Fluorapatites appear to be more stable than hydroxyapatite over all the cadmium concentration range. This is in agreement with the well-known decomposition temperatures of pure calcium fluor- and hydroxyapatites. So, the introduction of increasing amount of cadmium into the apatitic structure simultaneously decreases the stability of fluor- and hydroxyapatite.

Crystalline phases formed during heat treatment allow different mechanisms to be proposed, correlated both with the nature of the initial apatite (fluor or hydroxy) and with the cadmium content. It is interesting to note that the water vapor pressure does not modify the mechanism but only the temperature of decomposition.

#### Hydroxyapatite Decomposition

The first stage observed is the formation of oxyapatite due to  $\text{OH}^-$  ion condensation according to

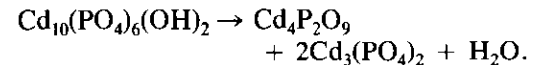


This is illustrated both by the weight loss measured by thermogravimetric analysis and by the decrease of the intensity of the infrared OH bands. One can notice that the temperature of  $\text{OH}^-$  ion condensation is strongly dependent on the atomic cation ra-

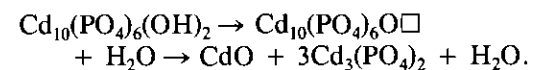
tio. When  $\text{Cd}/(\text{Cd} + \text{Ca}) = 1$ , i.e., cadmium hydroxyapatite, oxyapatite is formed from 500°C, when  $\text{Cd}/(\text{Cd} + \text{Ca}) = 0$ , i.e., calcium hydroxyapatite, oxyapatite is formed above 1000°C. Oxyapatites are well-known to be unstable compounds and one can understand that (i) a high water vapor pressure limits the condensation of OH ions and so increases the stability of hydroxyapatite and (ii) a high content of cadmium favors condensation of the  $\text{OH}^-$  ion, then oxyapatite formation, and finally apatite decomposition.

After decomposition, various phases appear (Fig. 3): cadmium oxide, tetracadmium phosphate (17), and trimetallic phosphate  $\text{Ca}_{3-u}\text{Cd}_u(\text{PO}_4)_2$ . The allotropic variety of the trimetallic phosphate depends on the cadmium content (18, 19); the phase with a high calcium content ( $u \leq 0.55$ ) is isomorphous to  $\beta$ -tricalcium phosphate, the one with a high cadmium content ( $2.33 \leq u \leq 3$ ) is isomorphous to  $\beta'$ -tricalcium phosphate and the intermediate one to  $\alpha$ -tricalcium phosphate. All these phases were detected after hydroxyapatite decomposition and correlated with the initial content in the apatitic compound. Different mechanisms of thermal decomposition can be proposed.

The simplest case is that of cadmium hydroxyapatite: this apatite is decomposed into tetracadmium phosphate and  $\beta'$ -tricalcium phosphate according to the reaction



Tetracadmium phosphate is formed, like tetracalcium phosphate, by different chemical reactions. First, the cadmium apatite forms oxyapatite and decomposes into cadmium oxide and tricalcium phosphate according to the reaction



Then, the cadmium oxide reacts with the apatite and/or with the tricalcium phosphate and forms tetracadmium phosphate according to the reactions

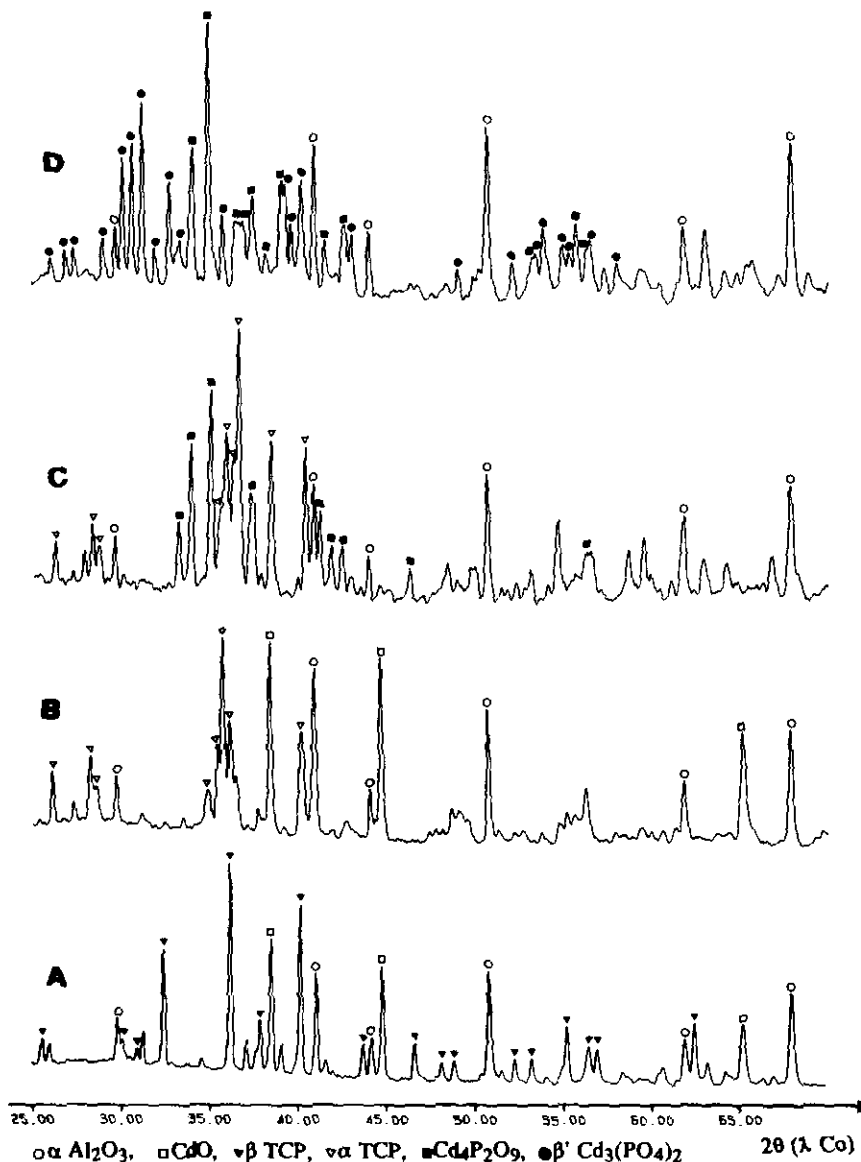
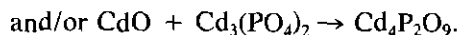
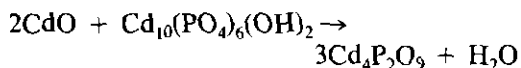
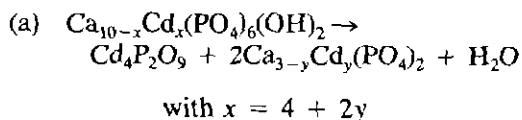


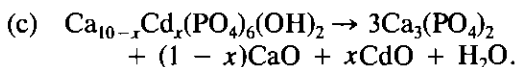
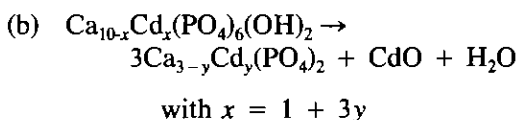
FIG. 3. X-ray diffraction patterns of hydroxyapatites with atomic ratio Cd/(Ca + Cd): (A) 0.2 (900°C), (B) 0.4 (900°C), (C) 0.8 (800°C), and (D) 1.0 (800°C).



For the calcium-cadmium apatites  $\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6(\text{OH})_2$ , three reactions can be foreseen which form either (a) tetracadmium

and trimetallic phosphate or (b) cadmium oxide and trimetallic phosphate or (c)  $\beta$ -tricalcium phosphate:





The range of existence of  $x$  and  $y$  coefficients can be determined.

—reaction (a) takes place if  $4 \leq x \leq 10$  and  $0 \leq y \leq 3$ ;

—reaction (b) takes place if  $1 \leq x \leq 10$  and  $0 \leq y \leq 3$ ;

—reaction (c) takes place if  $0 \leq x \leq 1$ .

Three ranges,  $0 \leq x \leq 1$ ,  $1 \leq x \leq 4$ , and  $4 < x \leq 10$ , can be defined.

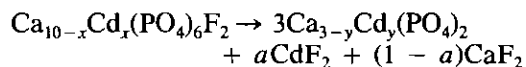
In the ranges  $0 \leq x \leq 1$  and  $1 \leq x \leq 4$  experiments verify that reactions (c) and (b), respectively, take place (Table I).

In range  $4 \leq x \leq 10$  the two equations (a) and (b) are possible; experiments show that only reaction (a) occurs. It is not possible to know if (a) reaction is favoured by kinetic or thermodynamic factors.

During heat treatment the low or high water vapor pressure does not modify either the nature of the crystalline phases formed or the decomposition mechanisms. It just modifies the temperature of the oxyapatite formation and thus the decomposition temperature.

### Fluorapatite Decomposition

The stability of cadmium-containing fluorapatites treated in the range 600–1000°C, for 1 hr, increases when the cadmium content decreases. In these conditions, they are partially decomposed and the lattice parameters of the remaining apatite are similar to those of the initial fluorapatite. It is a partial destruction without modification of  $\text{Cd}/(\text{Ca} + \text{Cd})$  of the apatite. The amount of collapsed apatite increases with temperature and with the  $\text{Cd}/(\text{Ca} + \text{Cd})$  ratio. The part which is decomposed is converted into different phases:  $\beta$ -TCP or  $\alpha$ -TCP,  $\text{CdF}_2$ , and  $\text{CaF}_2$  according the following equation:



$$\text{with } y = (x - a)/3 \quad \text{and } 0 \leq a \leq 1.$$

This equation is verified over the whole range  $0 \leq x \leq 6$ .

According to this equation it is not possible to foresee theoretically either the respective amounts of  $\text{CaF}_2$  or  $\text{CdF}_2$ , or the composition of the trimetallic phosphate.

The presence of all the phases was experimentally confirmed: at low concentrations of cadmium in the initial apatite, the trimetallic phase presents a low cadmium content and the allotropic variety formed is isomorphous to  $\beta$ -tricalcium phosphate; at higher concentrations ( $x > 3$ ) the allotropic variety is isomorphous to  $\alpha$ -tricalcium phosphate.

### Conclusion

The stability, at high temperature, of hydroxyapatites or fluorapatites which have a general formula  $\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6\text{Y}_2$  ( $Y = \text{OH}$  with  $0 \leq x \leq 10$ ;  $Y = \text{F}$  with  $0 \leq x \leq 6$ ) decreases with the cadmium content. However, for a given cadmium concentration the fluorapatites are more stable than the hydroxyapatites. Upon heat treatment, hydroxyapatites are first converted into oxyapatites.

The nature and the amounts of the decomposition phases depend on the nature of the anion in the channel (hydroxide or fluoride), on the initial composition, and on the treatment temperature. They can be foreseen by a theoretical calculation for hydroxyapatite.

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