

Thermal Stability of Cadmium–Calcium Hydroxyapatite Solid Solutions

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A continuous series of solid solutions of cadmium and calcium hydroxyapatite has been prepared from aqueous solution and characterized by X-ray diffraction and i.r. spectroscopic analyses. The lattice dimensions and the i.r. frequencies of the solid solutions vary linearly with the atom % of the cadmium. Upon heat treatment these solid solutions are converted into the β and α forms of cadmium-substituted tricalcium phosphate. Cadmium promotes these thermal conversions, having a destabilizing effect on the apatite structure. This effect cannot be explained by the small differences in the ionic radius of cadmium and calcium ions, but instead to differences in the nature of the cation–oxygen interactions.

Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, represents a good model system for natural apatites only when appropriately impure. Mineral as well as biological apatites contain many other ions.^{1–4} Some of these ions are known to substitute for calcium in synthetic calcium hydroxy- and halogeno-apatites, while others replace calcium only in fluoro- and chloro-apatites.^{5–7} In biological apatites many cations have been assumed to be adsorbed only on the apatite surface and not part of the structure.⁸ The replacement of calcium with other cations in calcium apatite induces changes in the apatite lattice parameters which can generally be related to the ionic radius of the cation compared to that of calcium.^{1,4,9–11} It should be noted that, due to the simultaneous presence of many ions in biological apatites, it is difficult to assess the individual effect of these ions on the apatite structure.¹² Among the ions which can be associated with biological apatites, cadmium is of interest because of its possible role in caries and osteoporosis.^{13–15} Although the crystal structures of cadmium hydroxy-, chloro-, and fluoro-apatites are well known,^{16–18} cadmium-substituted calcium hydroxyapatites have not been studied in similar detail.

LeGeros *et al.*¹⁹ obtained calcium hydroxyapatite in which the calcium was partially substituted by cadmium (less than 10 atom %) and found a slight contraction of the lattice parameters. We have carried out a crystallographic and spectroscopic study of cadmium-substituted calcium hydroxyapatite in order to investigate the effect of cadmium substitution on the thermal stability of the hydroxyapatite structure.

Experimental

Synthetic hydroxyapatites were prepared by dropwise addition of a calcium and cadmium acetate solution to a stirred solution of sodium monohydrogenphosphate in a CO_2 -free atmosphere. The reaction was carried out at 100 or 25 °C. The solution compositions were varied in steps from pure calcium acetate to pure cadmium acetate. The total cation concentration in the acetate solution was 0.06 mol dm^{-3} and the phosphate concentration was 0.051 mol dm^{-3} . The precipitate was stored overnight in contact with the mother-liquor then filtered off, washed with distilled water, and dried at 100 °C. Part of the products so obtained was heat treated at different temperatures up to 1300 °C for about 15 h.

X-Ray diffraction analysis was carried out by means of a Philips powder diffractometer using nickel-filtered Cu-K

radiation. The 2θ diffraction range was 10–65° at a scanning speed of 0.5° min^{-1} . The lattice constants were determined from diffractometric data by least-squares refinements.

For i.r. absorption analysis, *ca.* 1 mg of the powdered samples was intimately mixed with 300 mg of KBr (i.r. grade) and pelletized under vacuum. The pellets were analysed using a Perkin-Elmer 390 i.r. grating spectrophotometer, range 4000–400 cm^{-1} , with a normal slit and a scanning speed of 72 $\text{cm}^{-1} \text{min}^{-1}$.

Calcium and cadmium contents were determined using a Perkin-Elmer 373 atomic absorption spectrophotometer. Phosphorus was determined spectrophotometrically as molybdovanadophosphoric acid.²⁰

Results

The lattice constants a and c of the apatite phases obtained by reactions of calcium and cadmium acetate solution with phosphate solution at 100 °C are plotted in Figure 1 against the cadmium concentration in the solid phase. These parameters vary linearly with the composition, within experimental error, according to equations (1) and (2) obtained by least-squares

$$a = 9.429 - 0.00097x \text{ \AA} \quad \sigma(a) = 2.5 \times 10^{-3} \text{ \AA} \quad (1)$$

$$c = 6.879 - 0.00210x \text{ \AA} \quad \sigma(c) = 2.5 \times 10^{-3} \text{ \AA} \quad (2)$$

fitting, where x is the cadmium concentration expressed in atom % and σ is the standard deviation. The cell volume (V) varies with the composition according to equation (3). The (Ca +

$$V = 529.6 - 0.267x \text{ \AA}^3 \quad \sigma(V) = 0.3 \text{ \AA}^3 \quad (3)$$

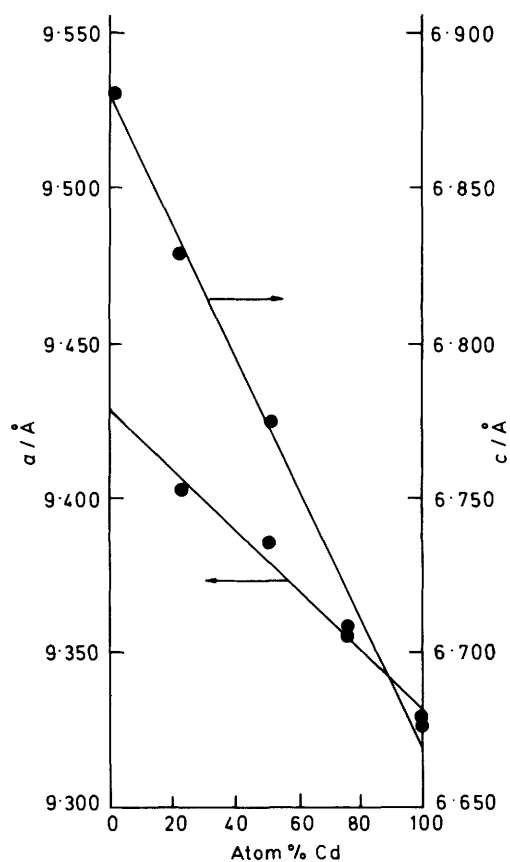
Cd)/P mol ratio of the apatite phases does not change appreciably with the cadmium content of the samples and its average value is 1.69.

The i.r. absorption spectrum of a sample of pure cadmium hydroxyapatite is shown in Figure 2(a). The main absorption bands are at 3540, 1070, 1010, 950, 715, 590, 560, and 470 cm^{-1} . On decreasing the cadmium content of the samples, these absorption bands shift towards those characteristic of calcium hydroxyapatite, as can be seen in Figure 2(b) (75.5 Cd atom %) and 2(c) (0 Cd atom %). The intensity of the OH bands at 3572 and 630 cm^{-1} for calcium hydroxyapatite, which are shifted to

Table 1. Crystalline phases obtained by heat treatment at different temperatures of cadmium–calcium hydroxyapatite solid solutions synthesized at 100 °C

Atom % Cd	Heat treatment temperature (°C)					
	100	500	700	900	1 100	1 300
0	hap	hap/ β -tcp*	β -tcp/hap	β -tcp/hap	β -tcp/hap	β -tcp/ α -tcp
23.5	hap	hap/ β -tcp	β -tcp/hap	β -tcp	β -tcp/ α -tcp	α -tcp
50.3	hap	hap/ α -tcp	α -tcp/hap	α -tcp	α -tcp	α -tcp
75.5	hap	hap/ α -tcp	α -tcp	α -tcp	α -tcp	α -tcp
100.0	hap	$\text{Cd}_3(\text{PO}_4)_2$	$\text{Cd}_3(\text{PO}_4)_2/\text{Cd}_4\text{P}_2\text{O}_9$	$\text{Cd}_3(\text{PO}_4)_2/\text{Cd}_4\text{P}_2\text{O}_9$	α -tcp	α -tcp

* hap and tcp indicate hydroxyapatite and tricalcium phosphate respectively. The same abbreviations have been used when cadmium replaces calcium in the crystalline phases. The first reported phase is that present in higher relative amount.

**Figure 1.** Plot of the lattice constants of cadmium–calcium hydroxyapatite solid solutions against the atom % of cadmium

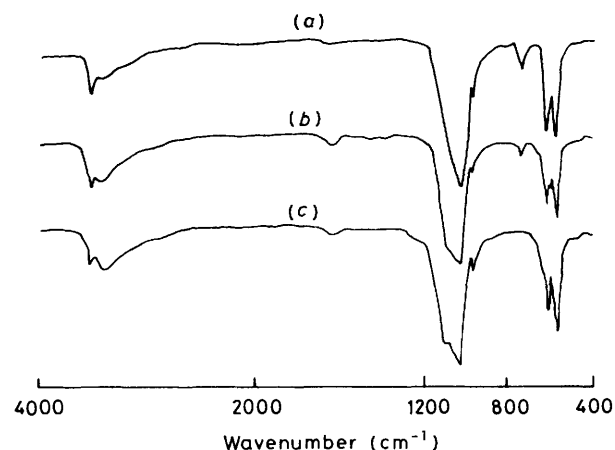
3 540 and 715 cm^{-1} respectively for the cadmium compound, increases with cadmium atom concentration.

The crystalline phases present in the samples after heat treatment at different temperatures are reported in Table 1 together with the cadmium concentration in the sample. When more than one phase is present, a quantitative evaluation of the relative amount of each phase is made difficult because of the superposition of many of their characteristic diffraction maxima. However, a rough estimate of the relative amounts of the different phases has been made from the areas of the diffraction maxima characteristic of each phase. The first reported phase is that which is present to the largest amount in the sample.

Whereas heat treatment of calcium hydroxyapatite results in

Table 2. Crystal lattice constants of α - and β -tricalcium phosphate obtained by heat treatment of cadmium–calcium hydroxyapatite solid solutions

Atom % Cd	β -Tricalcium phosphate		α -Tricalcium phosphate		
	a/Å	c/Å	a/Å	b/Å	c/Å
0	10.433(2)	37.298(5)	15.46(4)	20.55(5)	9.33(3)
23.5	10.401(3)	37.159(8)	15.36(4)	20.45(5)	9.24(4)
50.3			15.25(3)	20.33(5)	9.12(3)
75.5			15.17(6)	20.20(7)	9.01(6)
100.0			15.03(6)	20.10(7)	8.92(5)

**Figure 2.** Infrared spectra of cadmium–calcium hydroxyapatite solid solutions. Atom % of cadmium: (a) 100, (b) 75.5, and (c) 0

β -tricalcium phosphate and then the corresponding α form, the products of thermal conversion of cadmium hydroxyapatite are $\text{Cd}_3(\text{PO}_4)_2$, which is not isostructural with any known form of tricalcium phosphate, $\text{Cd}_4\text{P}_2\text{O}_9$, and α -tricalcium phosphate. Calcium hydroxyapatite partially substituted by cadmium for calcium is converted into α - and β -tricalcium phosphate and the temperature at which these conversions occur decreases with increasing cadmium content in the sample.

The lattice parameters of α - and β -tricalcium phosphate obtained by thermal conversion of cadmium–calcium hydroxyapatites are reported in Table 2 together with the cadmium content in the solid phase. The values do not appreciably change with the heat treatment temperature and are averages for samples treated at different phase. It is evident that the lattice constants decrease as the cadmium content of the solid phase increases.

Table 3. Crystalline phases obtained by heat treatment at different temperatures of the solid products synthesized at 25 °C

Atom % Cd	Heat treatment temperature (°C)					
	100	500	700	900	1 100	1 300
0	hap	β -tcp/hap	β -tcp	β -tcp	β -tcp	β -tcp/ α -tcp
23.3	hap	β -tcp	β -tcp	β -tcp/ α -tcp	β -tcp/ α -tcp	α -tcp/ β -tcp
51.6	hap	α -tcp	α -tcp	α -tcp	α -tcp	α -tcp
76.0	Amorphous	$\text{Cd}_3(\text{PO}_4)_2/\alpha$ -tcp	$\text{Cd}_3(\text{PO}_4)_2/\alpha$ -tcp	$\text{Cd}_3(\text{PO}_4)_2/\alpha$ -tcp	α -tcp	α -tcp
100.0	Amorphous	$\text{Cd}_3(\text{PO}_4)_2/\text{Cd}_4\text{P}_2\text{O}_9$	$\text{Cd}_3(\text{PO}_4)_2/\text{Cd}_4\text{P}_2\text{O}_9$	$\text{Cd}_3(\text{PO}_4)_2/\text{Cd}_4\text{P}_2\text{O}_9$	α -tcp	α -tcp

The X-ray diffraction patterns of the products obtained by reaction of cadmium and calcium acetate with sodium monohydrogenphosphate at 25 °C and dried at 100 °C are characteristic of an apatite phase for the samples of low cadmium concentration, whereas the samples with a high content of cadmium are amorphous. The low degree of crystallinity, which decreases further as the cadmium content increases, does not allow a reliable evaluation of the lattice constants. On increasing the cadmium content in the sample the (Ca + Cd)/P mol ratio of these products decreases from 1.61 to 1.50, and the i.r. bands become more and more broad.

The crystalline phases present in the X-ray diffraction patterns of the samples synthesized at 25 °C and heat treated at different temperatures are listed in Table 3 together with the cadmium content in the sample. When more than one phase is present, that first reported is the one present in largest amount. Calcium hydroxyapatite synthesized at 25 °C is converted completely into β -tricalcium phosphate by heat treatment at 700 °C. The apatite phase containing 23.3 atom % of cadmium is completely converted into this phosphate at 500 °C, whereas that containing 51.6 atom % of cadmium is completely converted into α -tricalcium phosphate. The main product of thermal conversion of samples of higher cadmium contents is $\text{Cd}_3(\text{PO}_4)_2$.

The lattice constants of α - and β -tricalcium phosphate change with cadmium content in the sample in a way very similar to that reported in Table 2.

Discussion

We have investigated by X-ray diffraction and i.r. absorption analysis the substitution of cadmium for calcium in hydroxyapatite structures prepared from aqueous solutions. Cadmium and calcium hydroxyapatite form a continuous series of solid solutions with cell parameters which vary linearly with the cadmium atom concentration according to the law of Vegard. The replacement of calcium by cadmium in the apatite structure induces a contraction of the lattice constants in agreement with the smaller ionic radius of cadmium with respect to that of calcium. However, this difference in ionic radius (0.99 Å for calcium, 0.97 Å for cadmium) appears too small to justify the observed contraction of the unit-cell parameters. On the other hand, it should be noted that the shortening of the cation-oxygen interatomic distances in cadmium hydroxyapatite is greater than that expected from the variation of ionic radius. The mean values of the Cd-O interatomic distances in cadmium hydroxyapatite are Cd(1)-O 2.382 Å and Cd(2)-O 2.391 Å,¹⁸ and those in calcium hydroxyapatite are Ca(1)-O 2.430 Å and Ca(2)-O 2.451 Å.²¹

The frequencies of the vibrational modes of cadmium-calcium hydroxyapatite solid solutions assume values lying on a straight line joining the characteristic frequencies of the pure end members. The shift of the frequencies of the OH vibrational modes as a function of cadmium atom % is coherent with the decrease in ionic radius on passing from calcium to cadmium.

Furthermore, the increase in the intensity of the OH bands with increasing cadmium atom concentration is in agreement with the data on calcium, strontium, and barium apatites reported by Fowler²² who related the differences in intensities to differences in OH bonding. On the other hand, cadmium apatite shows a greater band splitting and deviation of the internal PO frequencies from the nearly linear relation between the cation mass and the frequencies observed for the apatites of Ca, Sr, and Ba. According to Klee and Engel²³ this can be explained by the more covalent character of the cation-anion bond in cadmium apatite than in calcium, strontium, and barium apatites. This view is in agreement with the shortening of the mean interatomic distances between the cation and the oxygen atoms on passing from calcium to cadmium hydroxyapatite.^{18,21}

The thermal behaviour of cadmium-calcium hydroxyapatite solid solutions shows clearly the destabilizing effect of cadmium on the apatite structure. Cadmium promotes the thermal conversion of hydroxyapatite into α - and β -tricalcium phosphate. The contraction of the lattice parameters of these phosphates with increasing cadmium content shows that cadmium replaces calcium. Upon heat treatment at temperatures higher than 1 000 °C, pure cadmium hydroxyapatite is converted into a crystalline phase, α - $\text{Cd}_3(\text{PO}_4)_2$, which has never been reported before and appears to be isostructural with α -tricalcium phosphate. α -Tricalcium and α -tricalcium phosphate form a continuous series of solid solutions with lattice parameters which vary linearly with the composition according to Vegard's law. Upon heat treatment at temperatures less than 1 000 °C, cadmium hydroxyapatite is converted into $\text{Cd}_4\text{P}_2\text{O}_9$, and $\text{Cd}_3(\text{PO}_4)_2$ which is not isostructural with any form of tricalcium phosphate.

The destabilizing effect of cadmium on the apatite structure is even more evident from the analysis of the products obtained at 25 °C. These products exhibit a (Ca + Cd)/P mol ratio which decreases to 1.5 with increasing cadmium content; this value coincides with the stoichiometric value of tricalcium phosphate. Furthermore these products show a low degree of crystallinity which decreases with increasing cadmium content, and a lower thermal stability than that of cadmium-calcium apatite solid solutions.

In conclusion, cadmium replaces calcium in the hydroxyapatite structure over the whole range of composition. The destabilizing effect of this ion on the apatite structure is evident from the thermal behaviour of the solid solutions and the formation of amorphous tricalcium phosphate at high cadmium concentration. This effect, which cannot be explained by the small difference in the ionic radii of cadmium and calcium ions, should be attributed to differences in the nature of the cation-oxygen interaction.

Acknowledgements

We thank the Consiglio Nazionale delle Ricerche and the Ministero della Pubblica Istruzione, Italy, for financial support.

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Received 24th January 1985; Paper 5/133