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X-ray diffraction study of cadmium hydroxyapatite

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Abstract. Solid solutions of cadmium and calcium hydroxyapatite [$\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6(\text{OH})_2$ ($0 \leq x \leq 10$)] were synthesized by a wet process in a basic medium. The lattice dimensions of these compounds vary linearly with the atom percent cadmium. The distribution of the calcium and cadmium ions between two non-equivalent crystallographic sites, (1) and (2), were determined by the Rietveld method. The site-occupancy factors of atoms indicate a slight preference of cadmium for site (2) in the apatite structure.

1. INTRODUCTION

Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, presents a good model of biological apatite only if it is modified by the presence of many other ions (Mg^{2+} , CO_3^{2-} , HPO_4^{2-}) [1,2]. It constitutes the inorganic phase of teeth and bones. The apatitic structure can accommodate a great variety of substituents both in anionic and cationic sites. Cadmium is one of the ions which can be found in biological apatite. It is a toxic element which follows the food chain and can induce serious bone troubles, e.g. Itai-Itai illness and osteoporosis [3,4]. The amount of cadmium in cultivated soils, due to phosphate fertilization, is increasing every year

[5] although processes have been proposed to eliminate it from phosphate ores and from fertilizers. So in order to understand the action of cadmium, the interactions of this element with calcium phosphates have to be studied.

The hexagonal unit-cell of hydroxyapatite contains ten cations distributed between two crystallographic sites : four on type (1) sites and six on type (2) sites. Ca(1) ions present a C_2 site symmetry and are surrounded by nine oxygen atoms (three O(1), three O(2) and three O(3)). Ca(2)

ions present a Cs symmetry and are surrounded by six oxygen atoms ; one O(1), one O(2), four O(3) and one OH⁻ ion.

The calcium-cadmium substitution studies and the localisation of those cations in the hydroxyapatite structure are of biological and economic interest. In order to determine the preferential site for cadmium we analysed various samples of solid solution calcium-cadmium apatite, by powder X-ray diffraction using the Rietveld method.

2. MATERIALS AND METHOD

The cadmium-containing hydroxyapatites were prepared using a double decomposition method in a boiling basic aqueous medium [6]. A cation solution [Ca(NO₃)₂·4H₂O-Cd(NO₃)₂·4H₂O] was added to the boiling phosphate solution and refluxed for 1 h in the mother solution, then filtered and finally dried at 80° C for 15 h.

Different samples were characterized by X-ray diffraction (INEL powder diffractometer CPS 120), IR-spectrometry (Perkin-Elmer FTIR 7700) and chemical analysis.

A continuous solid solution exists between calcium hydroxyapatite and cadmium hydroxyapatite : Ca_{10-x}Cd_x(PO₄)₆(OH)₂ with $0 \leq x \leq 10$. All the samples crystallize in a pure apatitic phase, with a Cation/P atomic ratio close to the stoichiometric one : 1.667. The cell parameters (a and c) and the unit cell volume (V) vary linearly with composition according to Vegard's law; the slight shift to lower wavenumbers of the PO₄ and OH IR bands is due to the contraction of the unit cell and to the cation- oxygen interactions.

3. EXPERIMENTAL RESULTS

3.1 Structural analysis

The compounds being only obtained in powder form, the structural investigations were performed using the Rietveld technique. A powder sample of particle size between 40 and 90 nm was packed in a cylindrical alumina holder of 24 mm diameter and 0.5 mm depth. The pattern was recorded on a Seifert XRD3000TT diffractometer of Bragg Brentano geometry equipped with a rear graphite monochromator. Copper radiation was used to measure a theta range of 5 to 80°. The hydroxyapatite structure [7] was used as a model to start the structural determination process. Young and wiles [8] recommend, after a systematic study, the pseudo-Voigt (pV) profile function.

The parameters relevant to the profile (zero of the pattern, coefficient of the polynomial used for background simulation, scale factor, width of the profile function, mixing parameters between the

Lorentzian and Gaussian parts of the profile function, asymmetry of the line, preferential orientation) were fitted for every compound. Then, the atomic parameters (coordinates, thermal parameters, and site occupancy of calcium and cadmium) were fitted too. The levels of cadmium and calcium in each site gave full occupancy of the sites.

The calculations were performed using the DBW3.2S program of Wiles and Young [9]. The ionic structure factors included in the program were taken to describe the atoms involved in the compound.

The calculated R-factors for all samples containing cadmium at different levels are given in Table 1.

Table 1. Rietveld refinement.

Cd/cell	0.0	0.5	1.0	2.0	4.0	6.0	8.0	9.0	10.0
R_p	11.0	9.9	9.4	8.8	7.0	10.9	9.5	12.2	13.4
R_{wp}	15.2	13.2	12.4	11.5	10.2	14.7	12.6	16.2	18.2
R_B	6.2	6.5	6.3	6.4	5.2	6.0	5.4	6.1	6.7
R_F	6.0	4.7	4.8	5.1	4.5	6.7	6.2	6.9	7.8

3.2 Cadmium distribution between the two sites

The X-ray diffraction patterns of hydroxyapatites containing 0 and 10 Cd atoms per cell are shown in

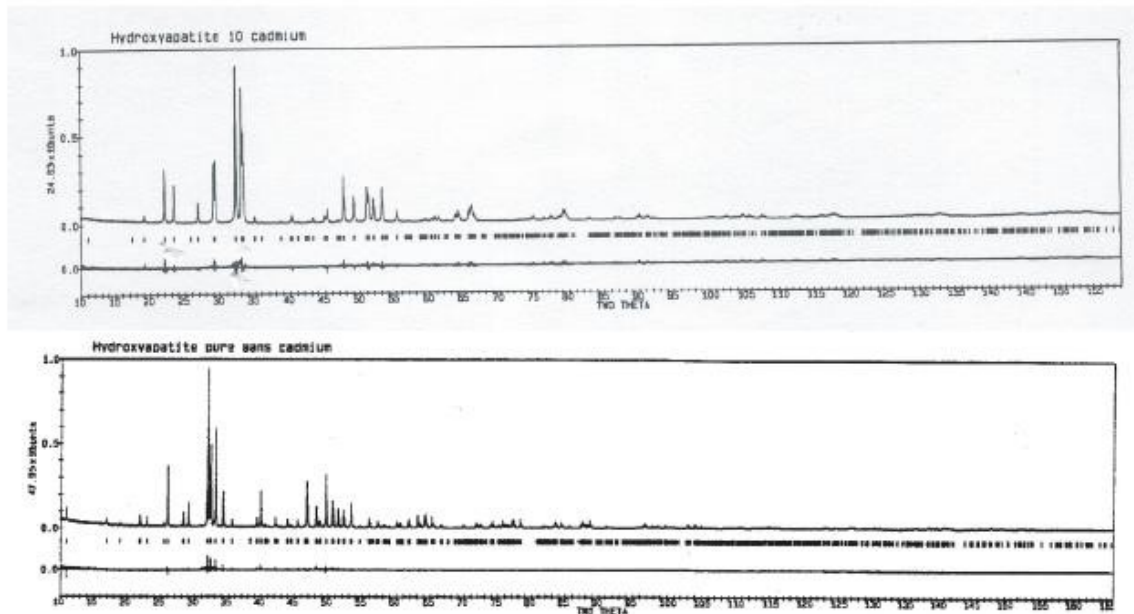


Fig.1. The lower pattern in each case is the difference between observed and calculated patterns.

The distribution of the cadmium ions at both sites is reported in Table 2. The total amount of cadmium found during refinement is in good agreement with the analytical data.

As shown, the values determined differ from the random distribution. Table 2 shows the cadmium distribution percentage versus the atomic ratio $\text{Cd}/(\text{Ca}+\text{Cd})$; the occupation level of cadmium is the ratio of the numbers of Cd^{2+} ions in a site to the total number of ions in the same site (4 for site (1) and 6 for site (2)). In a random distribution, the occupancy percentage is the same for both sites (an apatite with x randomly distributed Cd atoms per cell contains $4x/10$ atoms in site (1) and $6x/10$ atoms in site (2), i.e. $10x\%$ for any given site (1) or (2)).

Whatever its amount in the apatite, cadmium is located simultaneously in the two cationic sites but slightly prefers type (2) sites. The deviation from random distribution decreases when the cadmium

Figure 1. The observed powder diffraction patterns for hydroxyapatites containing 0 and 10 Cd atoms per cell. concentration increases (Table 2, $|(A-B)/B|$). At low concentrations (0.48 Cd/cell), 0.19 Cd are expected in site (1) but only 0.11 were observed, i.e. 40% less. At higher concentrations, (9.17 Cd/cell), 3.67 Cd are expected in site (1) but only 3.50 atoms, i.e. 5% less were observed. The richer the apatites are in cadmium the closer the distribution is to random. For low Cd contents, extrapolation is delicate; it can be assumed that in cadmium-poor hydroxyapatites, the cadmium is almost entirely located in site (2).

Cd/cell (affin.)	Cd/cell (chem.)	Distribution by affinement A		Random distribution B		(A - B)/B	
		site I	site II	site I	site II	site I	site II
0.480	0.470	0.115	0.365	0.192	0.288	-0.401	+0.267
1.032	0.980	0.0253	0.779	0.413	0.619	-0.387	+0.258
1.944	1.980	0.541	1.403	0.778	1.166	-0.304	+0.203
3.948	3.900	1.227	2.721	1.579	2.369	-0.223	+0.148
6.087	5.930	2.021	4.066	2.435	3.652	-0.170	+0.113
7.830	7.600	2.864	4.966	3.132	4.698	-0.086	+0.057
9.170	9.012	3.505	5.665	3.668	5.502	-0.044	+0.030
10.000	10.000	4.000	6.000	4.000	6.000	0.000	0.000

Table 2. Distribution of cadmium between cationic sites (1) and (2).

3.3 Structural parameter refinement

The corresponding interatomic distances and bond angles were calculated using the ORFFEC program [10]. The mean interatomic distances for P-O, Ca(1)-O, Ca(2)-O decrease with

increasing cadmium content in hydroxyapatite (Table 3). One can correlate this effect to the decrease of unit cell volume resulting from the substitution of Ca ions by Cd ions whose ionic radius is smaller. The decrease of the d_{Ca-O} distance must therefore be correlated with the lattice parameter shortening.

Introduction of Cd in the lattice induces modifications of the bond lengths: Ca(1)-O(1), Ca(1)-O(3) and Ca(1)-Omean. Bond lengths decrease with increase of Cd content, at the opposite the Ca(1)-O(2) bond does not vary in a regular way: it remains constant up to 2 Cd atoms per cell then increases until 6 Cd atoms, remaining constant again until 10 Cd atoms per cell. It can be noticed that the main disturbance of bond lengths occurs for small amounts of Cd in calcium hydroxyapatite or small amounts of Ca in cadmium hydroxyapatite.

Table 3. The mean interatomic distances.

Cd/cell	0.0	0.5	1.0	2.0	4.0	6.0	8.0	10.0
P-O	1.552(5)	1.547(6)	1.541(7)	1.534(7)	1.530(8)	1.506(9)	1.522(9)	1.478(9)
Ca(1)-O	2.570(5)	2.561(6)	2.562(6)	2.553(6)	2.548(7)	2.542(9)	2.533(9)	2.514(9)
Ca(2)-O	2.437(5)	2.438(5)	2.435(5)	2.434(5)	2.424(5)	2.430(8)	2.414(7)	2.424(7)

4. DISCUSSION CONCLUSION

The results of the powder-fitting structure refinements show that whatever its amount in the apatites cadmium is located simultaneously in both cation sites. Nevertheless, in the hydroxyapatite structure, a slight preference of cadmium ions for site (2) is indicated.

For seven-fold coordination, the coordination of the Ca(2) site in apatite, Shannon [11] gives a radius of 1.03 Å for [7] Cd²⁺, in contrast to a value of 1.06 Å for [7] Ca²⁺. For nine-fold coordination, approximating the crystal field for the Ca(1) site in apatite, values are not available for Cd.

The structural data show that the mean Ca(1) interatomic distances are longer than for Ca(2) and that the volume is greater by 38%. So, it could be thought that ions larger than Ca²⁺ would substitute primarily in the Ca(1) site while smaller substitutional ions would preferentially substitute for Ca(2).

However, various studies have shown that this is in disagreement with experience. Small Mn²⁺ ions (0.80Å), prefer site (1) in the case of calcium fluorapatite and become randomly distributed between the two sites in calcium chlorapatite [12].

In consequence, the nature of the anion located in the channel and the charge and the strength of the cation-anion bond are of great importance for filling sites. For instance, the location of rare-earth in site (2) satisfies the charge balance and allows the formation of a strong rare-earth-oxygen bond [13].

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