Structural Modification of Calcium Hydroxyapatite Induced by Sorption of Cadmium Ions

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Sorption of cadmium ions from aqueous solutions on calcium hydroxyapatite was studied by chemical analysis and least squares refinement of X-ray diffraction patterns. Results show that Cd^{2+} ions are sorbed by exchanged with Ca^{2+} and Na^{2+} ions in the lattice of the apatite. In the concentration range studied, Cd is located in sites with symmetry *m* at $z = \frac{1}{4}$ or $\frac{3}{4}$. © 1994 Academic Press, Inc.

INTRODUCTION

During the last decades inorganic ions fixators have been much studied, because they seemed to be very promising for the treatment of waste industrial aqueous solutions. Among inorganic fixators, hydroxyapatites have potential exchange capacities for both cations and anions.

Hydroxyapatites are the major inorganic constituents of biological hard tissues such as bones and teeth and, consequently, their properties have been intensively investigated. Macromolecules may be adsorbed on the surface (1) while some ions may exchange with the ions of the hydroxyapatite lattice. Anion exchange reactions between the hydroxyl ions in the lattice and anions in the solution have been extensively studied (2–6). More recently, it was found that exchange reactions occur also for several cations (7–15). Among these studies, it was shown that hydroxyapatite exhibited high removal capacity through exchange between the Ca^{2+} ions in the lattice and heavy metals ions such as Pb^{2+}, Cu^{2+}, and Cd^{2+}, in water under ambient conditions (9–15). In these works, the molar ratio between the heavy metal retained in the solid and calcium released into the solution is reported as being very close to one. A complete replacement of Ca^{2+} by the heavy metals ions was reported in certain cases (11).

However, some questions arise after these results, and a pure lattice ion exchange could not be the unique process responsible for the sorption of heavy bivalent ions. It was observed that depending on the nature of the starting apatite and on the anion present in the solution (NO_3^-, Cl^-, or F^-), the sorption of Pb^{2+} could lead to a mixture of phases. In some cases, one of this phase is no more an apatite (15). Another fact is that the maximum of lead sorption is achieved at pH values for which hydroxyapatites exhibit a rather high solubility (11, 15).

In the present work we have tried to characterize more accurately the mechanism of bivalent ions sorption on calcium hydroxyapatite. For that purpose we have determined the crystal structure of hydroxyapatite in connection with the fixation of Cd^{2+} ions.

Cadmium is one of the toxic heavy metals, for which we need an efficient method of removal from industrial wastes. It was chosen for the present study, because its ionic radius is close to that of calcium.

EXPERIMENTAL

Materials

We used a synthetic hydroxyapatite for liquid chromatography from Bio-rad, referenced DNA Grade Bio-Gel HTP. The solid was sieved under water flow. The particles of diameter ranging from 36 to 71 μm were selected for further experiments.

Observation by scanning electron microscopy shows hexagonal-shaped crystals. The mean length along the diagonals of the crystals is 50 μm and the thickness about 3 μm. The high crystallinity was confirmed by X-ray diffraction. This crystallinity was the reason for the choice of this product compared to other commercial hydroxyapatites.

Chemical Analysis

The chemical composition for Ca, Na, and P of the starting hydroxyapatite was determined by inductively coupled plasma atomic emission spectroscopy (ICP/AES). During the experiments of cadmium fixation on

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apatite from aqueous solution, Cd, Ca, Na, and P were determined in the solution by the same method.

Thermogravimetry was also used for the analysis of the starting material.

X-ray Diffraction

The crystal structures were determined from the diffraction line intensities collected on a step scan diffractometer fitted with a curved monochromator in the diffracted beam, a scintillation counter and a pulse-height analyzer. CoK_α has been used with a scanning step of $0.005°$ 2Θ in the range $15° < 2\Theta < 80°$.

The reliability factor,

$$R = \frac{\Sigma|F_0 - K F_c|}{\Sigma|F_0|},$$

where K is the scale factor, F_0 and F_c, the observed and calculated structure factors, was obtained after least squares refinement of the crystallographic parameters (AFFINE computer code) (16). Due to the limited set of available data, some of the temperature factors of the atoms could not be allowed to vary during the least squares refinements. Interatomic distances were computed with the ORFFE code (17).
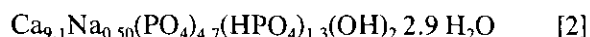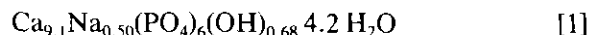
Cadmium Fixation Experiments

The amount of cadmium retained in the solid was determined by "batch experiments". A cadmium solution of 0.9 mg · liter^{-1} was prepared by dissolving the metal in nitric acid. Batches of 100 mg hydroxyapatite were introduced into several 20 ml fractions of the cadmium solution. These conditions were chosen in order to have approximately 2 mole of Cd per mole of apatite. Suzuki et al. (11, 15) observed that the retained quantity of lead ions was maximum for pH 3. However, our experiments on solubility showed that the hydroxyapatite used in the present work, becomes very soluble below pH 4. Therefore we performed the sorption experiments near pH 4.5. The pH was adjusted by addition of sodium hydroxide to the cadmium solution. pH values measured after the sorption experiments ranged between 4.4 and 4.7. In this range we did not observe a significant influence of pH on the cadmium sorption. The solutions with apatites were shaken at 20°C for different time intervals. The solutions were then filtered and analyzed for Cd, Ca, Na, and P.

RESULTS

Chemical Composition of the Starting Hydroxyapatite

The results are given in Table 1. The concentrations are calculated as mean values from two emission lines of

each element determined in three samples. This apatite contains a certain amount of sodium. It is deficient in cations. This deficiency could be compensated either by a lower amount of OH$^-$ ions compared to the stoichiometric formula, or by the presence of a certain amount of HPO$_4^{2-}$ ions, as already proposed (18). Therefore, two formulae may be proposed for the apatite used here:

$$Ca_{9.1}Na_{0.50}(PO_4)_6(OH)_{0.68}\,4.2\,H_2O \qquad [1]$$

$$Ca_{9.1}Na_{0.50}(PO_4)_{4.7}(HPO_4)_{1.3}(OH)_2\,2.9\,H_2O \qquad [2]$$

In fact, the actual composition may be between these two formulae. This point will be discussed later.

Sorption Kinetics

As shown in Fig. 1 the amount of Cd^{2+} retained in the apatite increases with time and reaches an equilibrium value after about 100 hr. The maximum uptake of cadmium is of 0.8 mole/mole which has to be compared to 2 mole/mole, quantity of Cd introduced into the solution.

The amount of Cd^{2+} ions sorbed into hydroxyapatite is greater than the amount of Ca^{2+} released into the solution. If we add the initial quantity of sodium in the solid to the quantity of released calcium (both quantites in equivalents per mole of solid), the obtained curve (noted Ca + Na in Fig. 1) agrees well with the concentration of sorbed cadmium equivalents. Therefore, the sorption of cadmium occurs with an equivalent ratio Cd/Ca + Na very close to 1. Furthermore, sodium is released in the earlier stages of the sorption.

The quantity of phosphorus released into the solution is always less than 0.5% of the initial quantity in the solid.

X-Ray Study

The calcium hydroxyapatite crystallizes in the hexagonal system with the space group $P6_3/m$. A detailed description of its structure was provided by Beevers and McIntyre in 1945 (19) and more recently by many other authors (20, 21). Ca^{2+} ions occupy two different crystallographic sites. Ca(1) is found on ternary axes at $x = \frac{1}{3}$, $y = \frac{2}{3}$, Ca(2) at sites with symmetry m at $z = \frac{1}{4}, z = \frac{3}{4}$. OH$^-$ ions are found in channels along the hexagonal screw-axes, at $z = 0.198$.

In order to know the localization and population of cations we have determined the crystal structure of the hydroxyapatite before and after fixation of Cd^{2+} ions. If an exchange reaction occurs, the population of cations in the hydroxyapatite will be modified after the introduction of Cd^{2+} ions.

The main crystallographic parameters including the reliability factor R are given in Table 2. Table 3 summarizes the cation distribution. The most important interatomic distances are reported in Table 4.

TABLE 1

Chemical Composition of the Hydroxyapatite Used for Cadmium Fixation Experiments

Elements	Ca	Na	P
Concentration, mole per 100 g of apatite	0.879 ± 0.013	0.0485 ± 0.0005	0.5802 ± 0.0075
Concentration, mole per 6 mole of phosphorus	9.09 ± 0.18	0.501 ± 0.009	6

In Sample I (initial hydroxyapatite), Ca(1) are entirely occupied while Ca(2) sites are only partially occupied (Table 2). Taking into account the error intervals, the total population of Ca^{2+} in both sites (8.9(5) atoms per unit cell, where 5 is the standard deviation on the last digit) agrees with the concentration found by ICP/AES (9.1(1) Ca^{2+}). In sample II (hydroxyapatite with 0.8 Cd^{2+} and 8.55 Ca^{2+} ions per mole), when the refinement is performed with the scattering factor of calcium, the total found population for this element (9.8(5) Ca^{2+}) exceeds the actual value found by analysis (8.55(9) Ca^{2+}).

We must point out that structure analysis gives only the electron density; two cations of a different nature located in the same site cannot be distinguished from each other. Assigning a site to several cations was essentially based on the chemical analysis and on the evolution of the population found by the refinement. So we can assume that in Sample II, the population of cations which effectively occupy Ca(2) sites is in fact: 0.8(1) Cd^{2+} + 3.7(5) Ca^{2+} (Table 3). The total population of Ca^{2+} ions deter-

mined by X-ray analysis (7.9(8) Ca^{2+}) is in agreement with the value determined by ICP/AES (8.55(9) Ca^{2+}), taking into account the error intervals. When both population and scattering factors are too low, the localization

TABLE 2

Crystallographic Data for Initial and Exchanged Samples

		Sample I	Sample II
P	X	$0.397(6)^a$	$0.392(6)$
(6h)	Y	$0.372(6)$	$0.372(6)$
	Z	$\frac{1}{4}$	$\frac{1}{4}$
	B	$1.9(9)$	$1.6(9)$
O(1)	X	$0.349(8)$	$0.325(8)$
(6h)	Y	$0.503(8)$	$0.493(7)$
	Z	$\frac{1}{4}$	$\frac{1}{4}$
	B	2	2
O(2)	X	$0.591(7)$	$0.586(6)$
(6h)	Y	$0.475(7)$	$0.463(5)$
	Z	$\frac{1}{4}$	$\frac{1}{4}$
	B	2	2
O(3)	X	$0.356(5)$	$0.350(5)$
(12i)	Y	$0.269(5)$	$0.267(5)$
	Z	$0.063(3)$	$0.060(3)$
	B	$2.3(9)$	$1.6(9)$
Ca(1)	X	$\frac{1}{3}$	$\frac{1}{3}$
(4f)	Y	$\frac{2}{3}$	$\frac{2}{3}$
	Z	0.0014	0.0014
	B	$1.8(9)$	2
	P	$4.2(2)$	$4.2(3)$
	OF	1	1
Ca(2)	X	$0.244(4)$	$0.249(4)$
(6h)	Y	$-0.005(4)$	$-0.010(4)$
	Z	$\frac{1}{4}$	$\frac{1}{4}$
	B	2	$2.0(9)$
	P	$4.7(3)$	$5.6(2)$
	OF	0.81	0.91
H_2O	$X = Y$	0	0
(4e)	Z	$0.40(1)$	$0.39(1)$
	B	2	2
	P	$2.0(6)$	$2.4(6)$
	OF	0.5	0.6
R		0.09	0.09
a		$9.46(1)$	$9.46(1)$
c		$6.88(1)$	$6.88(1)$

^{a} Standard deviation on the last digit.

Note. Atomic coordinates, $X\,Y\,Z$; population, P; occupancy factors, OF; temperature factors, B (Å^2); reliability factor, R; and unit cell parameters a and c (Å).
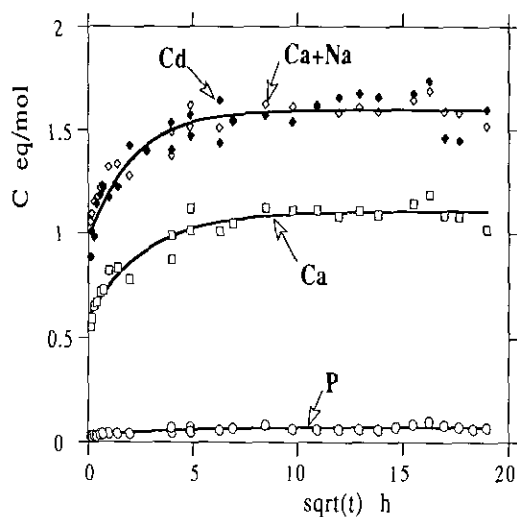

FIG. 1. Sorption kinetics of cadmium ions on calcium hydroxyapatite. Variation of the concentration C of cadmium in the solid (Cd), of calcium released from the solid (Ca), of the sum of calcium released and initial concentration of sodium in the solid (Ca + Na), and of phosphorous released from the solid (P), as a function of the square root of time. All concentrations are expressed as ion equivalents per mole of hydroxyapatite.

TABLE 3
Cation Distribution in Hydroxyapatite before (Sample I) and after (Sample II) Cadmium Fixation

	Sample I $(Ca_{9.1}Na_{0.50}-HA)$	Sample II $(Cd_{0.8}Ca_{8.55}-HA)$
Ca(1) (4f)	4.2(2) Ca^{2+} Na$^+$?	4.2(3) Ca^{2+}
Ca(2) (6h)	4.7(3) Ca^{2+} Na$^+$?	0.8(1) Cd^{2+} + 3.7(5) Ca^{2+}

becomes impossible. Thus Na^+ ions cannot be localized (Table 3).

During the refinement process, scattering matter was found in the channels at $z = 0.40$ and not at $z = 0.198$, where OH^- are generally localized. This matter was attributed to water molecules. This point will be discussed later. We observe also that, after Cd^{2+} ions fixation, there is no variation of the unit cell parameters "a" and "c."

DISCUSSION

First, some features about the structure of the hydroxyapatite used as starting product have to be discussed. The value of the unit cell parameter $a = 9.46$ Å is slightly higher than that generally found in the literature ($a = 9.41–9.43$ Å) (19–25). Our product is a deficient calcium hydroxyapatite (Ca/P = 1.515). Such products have generally a parameter "a" smaller than 9.41 Å. For instance, in the apatite $Ca_9(PO_4)_6$ $2H_2O$, a is equal to 9.25 Å (26).

We also notice a slight increase of the P–O distances

compared to the values determined by other authors on natural or synthetic single crystals of hydroxyapatites (Table 4). This increase could be interpreted by the presence of HPO_4^{2-} groups substituting for PO_4^{3-} as it was already advanced to explain calcium deficiency (18). This substitution is known to cause a lengthening of the a parameter, as in our measurements (27). In all cases the c parameter is never significantly affected. Therefore, it seems that the composition of this apatite is more probably close to the formula (2).

Structural refinement has shown the presence of scattering matter in the channels at $z = 0.40$. Assigning this matter to H_2O molecules remains arbitrary but seems quite reasonable. We can notice that the population of water in the channel represents a weight fraction near 4%, smaller than the weight loss at 873°C (7%). Total weight loss likely includes also surface adsorbed water, and HPO_4^{2-} (even OH^-) content (8, 28). In fact the localization of H_2O molecules at $z = 0.40$ does not allow us to exclude the presence of OH^- ions at $z = 0.198$. It is very difficult to distinguish scattering matter in very near sites, moreover with a too low occupancy factor. There are necessarily OH^- ions as in both proposed formulae [1] and [2]. A similar composition with both OH^- groups and H_2O molecules was proposed in a previous work (29).

Considering the results of chemical analysis alone, characterized by a 1/1 Cd/Ca + Na equivalent ratio, the fixation mechanism could be either an ion exchange or a dissolution–precipitation process. Structural considerations clearly indicate an ion exchange process. Exchanged Cd^{2+} ions are located in Ca(2) sites, while the concentration of Ca^{2+} ions in Ca(1) sites remains unchanged. This result is different from the observations reported in a recent work on calcium–cadmium hydroxyapatites pre-

TABLE 4
Interatomic Distances in Hydroxyapatite before (Sample I) and after (Sample II) Cadmium Sorption: Comparison to Literature Values

	Hughes *et al.* (20)	Kay *et al.* (21)	Our work	
			Sample I	Sample II
P–O(1)	1.534	1.538	1.52(4)	1.56(4)
P–O(2)	1.537	1.547	1.59(4)	1.59(4)
P–O(3)	1.529	1.529	1.54(3)	1.57(3)
Ca(1)–O(1)	2.404	2.408	2.36(5)	2.34(4)
Ca(1)–O(2)	2.452	2.454	2.50(5)	2.45(5)
Ca(1)–O(3)	2.802	2.808	2.72(4)	2.76(4)
Ca(2)–O(1)	2.711	2.707	2.92(7)	2.70(6)
Ca(2)–O(2)	2.353	2.358	2.31(6)	2.36(6)
Ca(2)–O(3)	2.343	2.345	2.34(6)	2.27(6)
Ca(2)–O(3)	2.509	2.514	2.59(3)	2.65(3)

pared by precipitation (30). In this last study, cadmium preferentially occupies the Ca(2) sites, but a certain amount is also found in Ca(1) sites. Therefore, it seems that ion exchange and precipitation lead to different distributions of cadmium in crystallographic sites. However, the comparison between these works is limited by the fact that the composition of hydroxyapatites were slightly different.

If we admit that the composition of the starting apatite is close to the formula [2], the product after cadmium fixation, could have the following composition:

$$Ca_{8.55}Cd_{0.8}(PO_4)_{4.7}(HPO_4)_{1.3}(OH)_2 \cdot xH_2O \qquad [3]$$
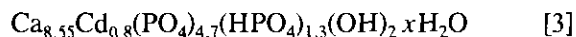
As already pointed out, this formula is hypothetical concerning the amount of OH^- and HPO_4^{2-}.

Observations by electron micrography after cadmium fixation show no modification of the crystallites and no occurrence of a new phase. This also confirms the ion exchange mechanism.

In a work on the structures of mixed calcium–cadmium hydroxyapatite (31), a variation of the unit cell parameters was observed as the Cd/Ca ratio increases in the solid. In our case, this ratio is too small to induce a significant modification of cell parameters.

CONCLUSION

In the case of a well crystallized calcium–sodium hydroxyapatite, and in a pH range near 4.5, our experiments clearly demonstrate that Cd^{2+} ions are sorbed by an ion exchange process which involves Na^+ and Ca^{2+} ions of the solid. For the cadmium concentration ranges used, the lattice is not modified. Cadmium is located in a characteristic crystallographic site (m symmetry at $z = \frac{1}{4}$ or $\frac{3}{4}$). Concerning the sorption capability, a distribution coefficient of $1.6 \ 10^2$ liter · kg^{-1} was measured at equilibrium. It is a promising value for an eventual use of hydroxyapatites as sorbents for decontamination of liquid industrial wastes. Further work has to be done in order to find the optimum conditions for the fixation of cadmium and other heavy metals such as lead, mercury, or uranium.

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