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Structure Refinements of Pb^{2+} Ion-Exchanged Apatites by X-Ray Powder Pattern-Fitting

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The crystal structures of Pb^{2+} ion-exchanged hydroxyapatite (OHAp), chlorapatite (ClAp), and fluorapatite (FAp) in aqueous solutions with low pH value of 3.0 or 4.0 have been investigated by X-ray powder pattern-fitting methods. The site occupancy factors of Pb atoms for the M1 (column site) and M2 sites were determined to be 0.72 and 0.77 for $Pb_{7.5}Ca_{2.5}$–OHAp, 0.69 and 0.86 for $Pb_{7.9}Ca_{2.1}$–ClAp, and 0.60 and 0.52 for $Pb_{5.5}Ca_{4.5}$–FAp, respectively. These results imply that Ca^{2+} ions in calcium hydroxyapatite are exchanged for Pb^{2+} ions in acidic aqueous solution regardless of whether they occupy M1 or M2 sites.

Introduction

It is well known that calcium hydroxyapatite $[Ca_{10}(PO_4)_6OH_2]$ is the major inorganic constituent of bones and teeth as well as the main constituent of mineral phosphates. From investigations of the cation-exchange characteristics of synthetic calcium hydroxyapatite (Ca–OHAp) (*1–3*), we have found (*4*) that Pb^{2+} ions in aqueous solutions containing various counteranions (NO_3^-, Cl^-, and F^-) can be easily exchanged with Ca^{2+} ions of Ca–OHAp. This process occurs for low pH values (3.0, 4.0, and 5.0) at room temperature; Pb^{2+} ion-exchanged hydroxyapatite (OHAp), Pb^{2+} ion-exchanged chlorapatite (ClAp), and Pb^{2+} ion-exchanged fluorapatite (FAp) were formed depending on the counteranions of NO_3^-, Cl^-, and F^- present in the acidic aqueous solutions.

In this paper, the interesting crystal structures of Pb^{2+} ion-exchanged OHAp, ClAp, and FAp were refined by X-ray powder pattern-fitting method in order to clarify the site preference of Pb atoms in apatites.

Experimental

The Ca–OHAp sample used was prepared by dropwise titration of phosphoric acid solution into a boiling calcium hydroxide solution according to the method of Aunimelech *et al.* (*5*) and McDowell *et al.* (*6*). Pb^{2+} ion-exchanged OHAp, ClAp, and FAp were obtained by reacting 0.5 g of Ca–OHAp with aqueous solution of $Pb(NO_3)_2$, $PbCl_2$, and PbF_2 at concentrations of 5 mmole/100 cm^3. Operating conditions were kept at a pH of 4.0 or 3.0 at 25°C for 2 hr using the normal batch method described elsewhere (*3*). The pH values were controlled by a pH-stat (HSM-10A, TOA, Japan) using aqueous solutions of HNO_3, HCl, and HF, respectively. The residual Ca–OHAp was removed by dissolution into HNO_3 aqueous solution. All chemicals

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were of analytical reagent grade and were used without further purification. Quantitative analysis of the various ions was carried out using the EDTA titration method, the ion-electrode method, and by the atomic absorption technique.

The structural changes occurring in the apatite samples before and after the uptake of Pb^{2+}, Cl^-, and F^- ions were investigated using powder X-ray diffraction and infrared absorption spectroscopy. Intensities of the Pb^{2+} ion-exchanged OHAp, ClAp, and FAp for the X-ray powder pattern-fitting method were measured on a Shimazu X-ray diffractometer in the range from $2\theta = 15.0$ to $80.0°$, with Cu$K\alpha$ radiation monochromated with a balanced filter. Measurements were made using the step-scanning technique at fixed time intervals of 40 sec per 0.05° in 2θ. A total of 1301 data points were obtained.

Results

The chemical compositions for Pb^{2+} ion-exchanged OHAp, ClAp, and FAp were determined to be $Pb_{7.5}Ca_{2.5}(PO_4)_6OH_2$, $Pb_{7.9}Ca_{2.1}(PO_4)_6Cl_2$, and $Pb_{5.5}Ca_{4.5}(PO_4)_6F_2$ by quantitative analysis. The infrared absorption spectra show the existence of OH^- ions in Pb^{2+} ion-exchanged OHAp.

The crystal structure refinement of each Pb^{2+} ion-exchanged apatite was carried out with an X-ray powder pattern-fitting program (*7, 8*). The positional parameters, multiplicity, and isotropic temperature factors, together with profile parameters (background, unit cell dimensions, and half-width and asymmetry parameters), were refined using the 1301 observed intensities. The starting atomic parameters were given by Sudarsanan and Young (*9*) for OHAp, by Sudarsanan and Young (*10*) for ClAp, and by Sudarsanan *et al.* (*11*) for FAp. The unit cell dimensions, isotropic temperature factors, and half-width and asymmetry parameters for CaF_2 were refined together with all parameters for Pb^{2+} ion-exchanged FAp. This was done since the CaF_2 simultaneously produced by the ion-exchange reaction between PbF_2 aqueous solution and Ca–OHAp could not be successfully separated from Pb^{2+} ion-exchanged FAp. In the refinement, the orientations of the crystallites in powder specimen were assumed to be random. The occupancies of Pb and Ca atoms on two cation sites (M1 and M2) were allowed to vary with the chemical compositions 7.5 Pb + 2.5 Ca for OHAp, 7.9 Pb + 2.1 Ca for ClAp, and 5.5 Pb + 4.5 Ca for FAp. The site occupancy factor for the Pb atom on the M1 site for OHAp, x, was employed as a parameter. The factors for the Ca atom on the M1 site, and the Pb and Ca atoms on the M2 site were reset as $1 - x$, $(7.5 - 4x)/6$, and $1 - (7.5 - 4x)/6$, respectively. The atomic scattering factors for neutral atoms were taken from the International Tables for X-Ray Crystallography (*12*). After several cycles of the least-squares refinement, the discrepancy factors R_p and R_{wp} converged to 0.082 and 0.119 for Pb^{2+} ion-exchanged OHAp, 0.046 and 0.059 for Pb^{2+} ion-exchanged ClAp, and 0.073 and 0.105 for Pb^{2+} ion-exchanged FAp, respectively. Here R_p and R_{wp} are defined as

$$R_p = \sum_i |y_{obs}(2\theta_i) - y_{cal}(2\theta_i)| / \sum_i y_{obs}(2\theta_i)$$

and

$$R_{wp} = \left\{ \sum_i w_i[y_{obs}(2\theta_i) - y_{cal}(2\theta_i)]^2 / \sum_i w_i y_{obs}(2\theta_i)^2 \right\}^{1/2},$$

where $y_{obs}(2\theta_i)$ and $y_{cal}(2\theta_i)$ are the observed and calculated intensities at the ith step in the pattern, w_i is the reciprocal of the variance for each observation, and the summation is carried out over all observations. The observed and calculated profiles of each Pb^{2+} ion-exchanged apatite are shown in Figs. 1–3, together with the difference

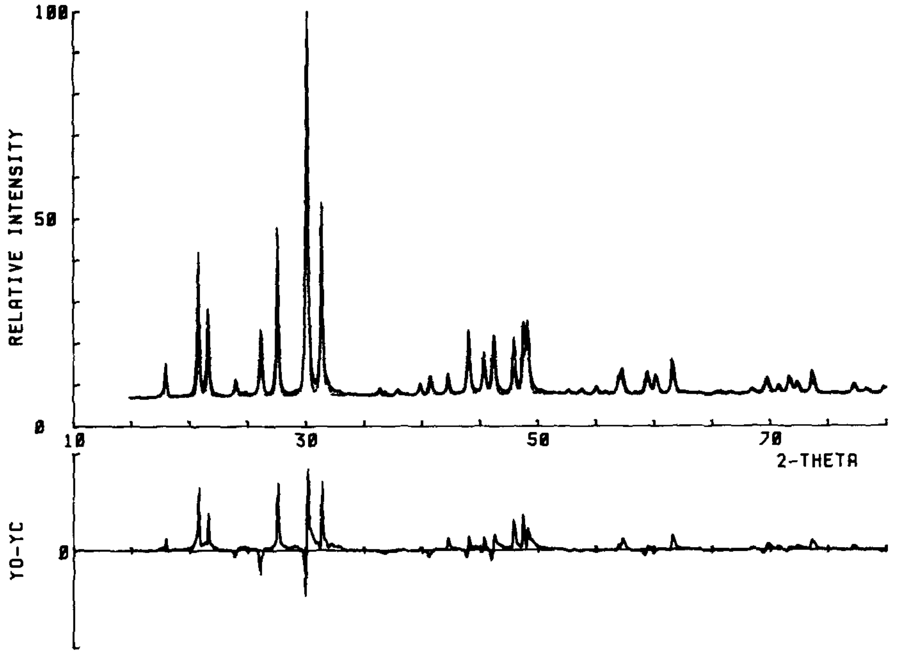

FIG. 1. X-Ray diffraction profiles of Pb$_{7.5}$Ca$_{2.5}$–OHAp. In the upper diagram, the observed profile (——) is shown together with the calculated one (– – –). The lower diagram is a plot of the difference on the same scale as above.

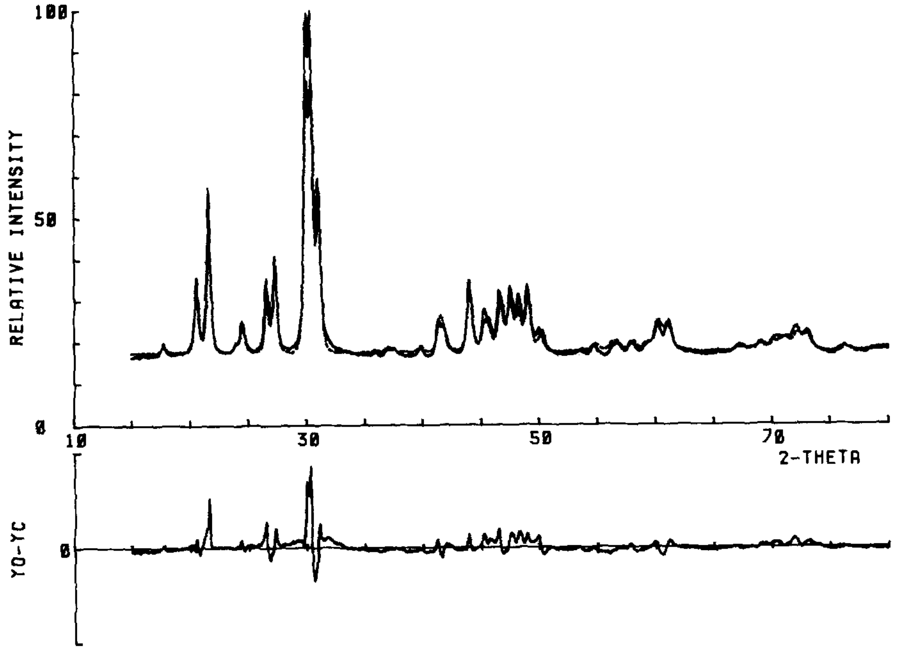

FIG. 2. X-Ray diffraction profiles of Pb$_{7.9}$Ca$_{2.1}$–ClAp. In the upper diagram, the observed profile (——) is shown together with the calculated one (– – –). The lower diagram is a plot of the difference on the same scale as above.

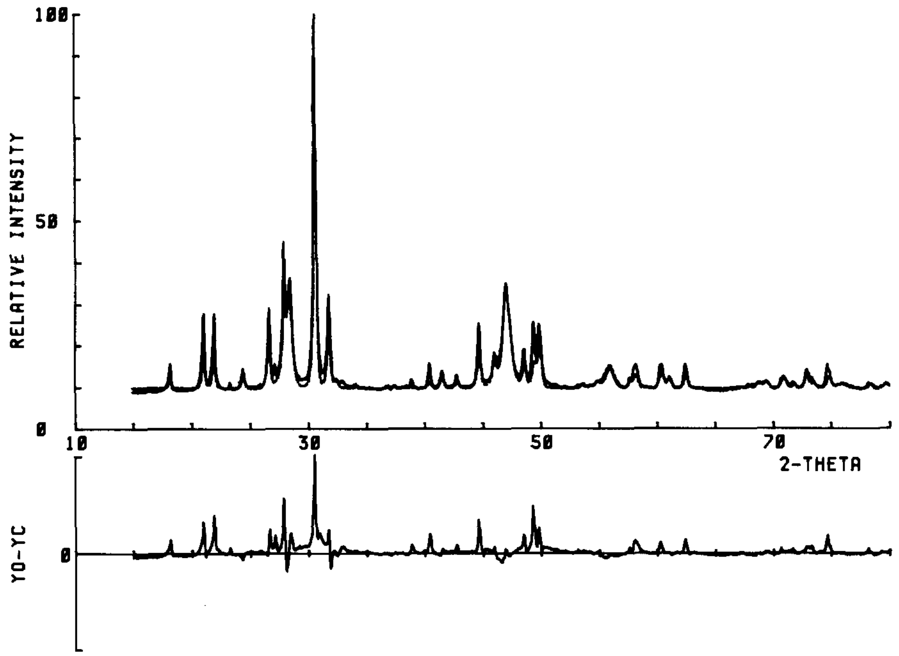

FIG. 3. X-Ray diffraction profiles of $Pb_{5.5}Ca_{4.5}$–FAp. In the upper diagram, the observed profile (——) is shown together with the calculated one (---). The lower diagram is a plot of the difference on the same scale as above.

between the two values on the same scale. The positional and thermal parameters are listed in Table I. The unit cell dimensions so determined are a = 9.880(3) and c = 7.417(2) Å for OHAp, a = 9.990(2) and c = 7.276(2) Å for ClAp, and a = 9.759(3) and c = 7.291(3) Å for FAp, respectively. The cell dimensions of Pb^{2+} ion-exchanged apatites are larger than those of the corresponding Ca apatites and close to those of the Pb apatites.

Discussion

There are 10 cations arranged on two nonequivalent sites, four on M1 (column site), and six on M2, in the hexagonal unit cell of apatite. The M1 atoms is surrounded by nine O atoms [three O(1), three O(2), and three O(3)], whereas the M2 atom is surrounded by six O atoms [O(1), O(2), and four O(3)] and by the X atom (X = OH, Cl, or F). The interatomic distances and bond angles were calculated by the program UNICS (*13*). The mean bond lengths of M1–O and M2–O are 2.75 and 2.60 Å (excepting M2–OH) for OHAp, 2.76 and 2.59 Å for ClAp, and 2.70 and 2.56 Å for FAp, respectively. The mean values are nearly equal to the sums of the ionic radii of Pb^{2+} and O^{2-}, where the Pb atom is surrounded by six or nine O atoms (*14*); they are also close to those in $Pb_9(PO_4)_6$ (*15*). The M2–X bond lengths are 2.54, 2.85, and 2.44 Å for OHAp, ClAp, and FAp, respectively. The side lengths of the M2 triangles are 4.32, 4.36, and 4.23 Å for OHAp, ClAp, and FAp, respectively, whereas that of $Pb_9(PO_4)_6$ (*15*) is 4.30 Å. The M–O and M–M interatomic distances in FAp are shorter than those in OHAp and ClAp because of the smaller concentration of Pb^{2+} ions in FAp. The P–O bond lengths have mean values of 1.58, 1.60, and 1.59 Å for OHAp,

TABLE I

POSITIONAL AND THERMAL PARAMETERS IN Pb^{2+} ION-EXCHANGED OHAp, ClAp, AND FAp

		OHAp	ClAp	FAp
M1	Pb	0.72(3)[a]	0.69(3)	0.60(5)
	Ca	0.28	0.31	0.40
	x	0.333	0.333	0.333
	y	0.667	0.667	0.667
	z	0.006(6)	0.013(3)	0.009(9)
	B	2.7(4)	2.6(5)	2.4(8)
M2	Pb	0.77	0.86	0.52
	Ca	0.23	0.14	0.48
	x	0.252(3)	0.254(2)	0.250(4)
	y	0.999(3)	1.003(3)	1.000(6)
	z	0.25	0.25	0.25
	B	2.1(3)	2.2(4)	2.1(6)
P	*x*	0.393(6)	0.403(4)	0.402(8)
	y	0.373(6)	0.365(4)	0.374(8)
	z	0.25	0.25	0.25
	B	0.9(4)	1.6(3)	0.8(6)
O(1)	*x*	0.323(9)	0.322(6)	0.313(12)
	y	0.482(9)	0.481(7)	0.477(10)
	z	0.25	0.25	0.25
	B	3.0(8)	2.9(7)	2.6(14)
O(2)	*x*	0.579(9)	0.577(7)	0.583(13)
	y	0.480(8)	0.486(7)	0.480(13)
	z	0.25	0.25	0.25
	B	1.1(6)	1.7(5)	1.4(11)
O(3)	*x*	0.349(6)	0.353(5)	0.351(8)
	y	0.267(8)	0.267(3)	0.271(8)
	z	0.075(9)	0.069(6)	0.066(11)
	B	2.7(5)	3.7(5)	2.5(10)
X	*x*	0.0	0.0	0.0
	y	0.0	0.0	0.0
	z	0.188(15)	0.066(9)	0.25
	B	1.7(11)	3.7(5)	3.5(9)

[a] Numbers in parentheses are calculated standard errors and refer to the last digit quoted.

ClAp, and FAp, respectively. The mean distances are long, compared to those of Ca–OHAp (*16*), 1.54 Å, and $Pb_9(PO_4)_6$ (*15*), 1.56 Å.

In Pb^{2+} ion-exchanged OHAp, the OH^- ion is not located at the center of the M2 triangle (0, 0, ¼), but shifted above or below the center of the triangle, as in Ca–, Sr–, and Cd–OHAp, (*16, 9, 17*). The Cl^- ion slightly deviates from the (0, 0, 0) position along the *c* axis in Pb^{2+} ion-exchanged ClAp, which is near the center of the O(3) triangle. In the structures of chlorapatites, the Cl^- ion occupies the (0, 0, 0) position when the metallic ion is larger than the Ca^{2+} ion (*10, 18*) and the (0, 0, ¼) position when it is smaller than the Ca^{2+} (*19, 20*). In Ca–ClAp, the Cl^- ion occupies the (0, 0, 0.06) position (*21*). The position of the Cl^- ion in Pb^{2+} ion-exchanged ClAp is similar to that in Ca–ClAp. The F^- ion is located at the center of the M2 triangle in Pb^{2+} ion-exchanged FAp. The X^- ion shifts away from the M2 triangle with increasing effective ionic radii of the X^- ions in Pb^{2+} ion-exchanged apatites.

From the pattern-fitting results, the site occupancy factors of Pb atoms on the M1 and M2 sites are found to be 0.72 and 0.77 for OHAp, 0.69 and 0.86 for ClAP, and 0.60 and 0.52 for FAp, respectively. Compared to the results of $Pb_{6.4}Ca_{3.6}(PO_4)_6OH_2$ (*4*), i.e., 0.75 and 0.57 on the M1 and M2 sites, respectively, both site occupancy factors of the Pb atoms on the M1 site for Pb^{2+} ion-exchanged OHAp are nearly equal and that of the M2 site increases with increasing amount of Pb^{2+} ions taken up by Ca–OHAp. The analytical results imply that the Pb^{2+} ions are ion-exchanged to almost the same degree whether Ca^{2+} ions occupy the M1 or the M2 sites, although the amount of Pb^{2+} ions taken up by Ca–OHAp depends on the counteranions in aqueous solution and on the pH values. In $Ca_{10-x}Pb_x$–OHAp solid solution series synthesized at pH 12.0 by Andres-Verges *et al.* (*22*), the cation distribution based on the relative intensities of the suitable reflections in diffractograms suggested that the Pb atom has a preference for the M2 site. The disagreement with our results is probably due to the difference between the Pb^{2+} ion-exchanged OHAp in acidic aqueous solution with pH value of 4.0 and the synthetic $Ca_{10-x}Pb_x$–OHAp in basic aqueous solution with a pH value of 12.0.

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