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Lattice Parameters and Cation Distribution of Solid Solutions of Calcium and Lead Hydroxyapatite

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Summary. Solid solutions of calcium hydroxyapatite (CaOHA) and lead hydroxyapatite (PbOHA) of the formula $Ca_{10-x}\ Pb_x\ (PO_4)_6\ (OH)_2$ were prepared by coprecipitation followed by heating at 800°C in a stream of CO_2-free water vapor of 1 atm. The samples were apatitic in the range $0 < x < 6$ and contained lead phosphates as a second phase at higher Pb/Ca ratios. Lattice parameters and cation distribution of the apatitic samples were determined by X-ray diffraction. The lattice parameters varied linearly with x in the range considered, whereas all Pb^{2+} were located in the sixfold position for cations. There was a miscibility gap in the apatite series of solid solutions in the range $1 < x < 4$, whereas apatites in the range $6 < x < 10$ were not stable under the conditions of preparation. It is concluded that apatites in the range $4 < x < 6$ represent a minimum in the free energy of solid solutions between CaOHA and PbOHA.

Key words: Calcium hydroxyapatite — Lead hydroxyapatite — Cation distribution — Lattice parameters — Solid solutions.

Exposure to lead in food and the environment in general or in industry in particular can cause anemia [1], renal insufficiency [2, 3], and encephalopathy [4], the latter resulting in disturbed behavior [5]. Lead is retained in liver, kidneys, and blood, and especially in bone, teeth, and brain [6]. Infants have a relatively high retention as compared to adults [7]. Indications have been found that lead interferes with the metabolism of calcium [8–16], magnesium [17], strontium [9], copper [1, 18], iron [18, 19], zinc [20], phosphorus [8, 15], and sulfur [21, 22]. The disappearance curves for lead excretion in blood, plasma, hematic cells, and some other soft tissues can be expressed as sums of exponential functions. In contrast, lead is removed from bone tissue at a constant and extremely slow rate [23]. For this reason time integrals of body burdens of lead may well be diagnosed by determination of the lead content in bones and teeth [23–31], whereas momentary body burdens of lead should be derived rather from analyses of biochemical factors [32–34]. When lead ions are injected in the form of lead acetate, they not only interact with the calcified tissues [35, 36], but they also induce ectopic calcification [37, 38]. The strong capacity of lead ions to induce calcification is clearly illustrated by a case study reporting arthritis of the hip secondary to retained bullet fragments which corroded when in contact with synovial fluid [39].

Little is known about the physicochemical background of the interaction of lead ions with calcified tissues. It might be assumed that lead ions are incorporated in the apatite phase of the minerals in these tissues, as the existence of lead apatite has been established. However, Kato and Ogura [38] have shown that the first lead-containing mineral in the ectopic calcifications formed after injection of lead acetate in the rat is lead pyrophosphate. That the intensity of the characteristic X-ray diffraction peaks diminishes with time [38] might indicate that this pyrophosphate dissolves slowly whereby the dissolved ions react as yet with the apatitic mineral present in the calcification. In order to gain more insight into these processes, more basic physicochemical studies should be carried out.

Some investigators have prepared solid solutions of calcium hydroxyapatite (CaOHA) and lead hydroxyapatite (PbOHA). According to Müller [40], Narasaraju et al. [41], and Rao [42], the lattice parameters of these solid solutions both vary linearly

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with composition between those of the pure end members. On the contrary, Engel et al. [43] found that the variation of the c parameter with composition deviates markedly from Vegard's law. This was attributed to the preference of Pb^{2+} for the sixfold position of the cation sublattices of apatite. Unfortunately, Engel et al. [43] determined the cation distribution only in one sample. In order to check this hypothesis and as a start for a systematic physicochemical study on the interaction of lead ions with CaOHA, the present investigation was undertaken. In this study the lattice parameters and the cation distribution of solid solutions of CaOHA and PbOHA were determined in the most relevant composition range.

Theoretical Considerations

In the apatite structure two sublattices occur for the cation. Position I is fourfold and its Wyckhoff notation is f, whereas position II is sixfold and is denoted by h. Therefore, if the chemical formula of a solid solution of lead and calcium hydroxyapatite is given by

$$Ca_{10-x}Pb_x(PO_4)_6(OH)_2 \qquad 0 < x < 10 \qquad (1)$$

its structural formula can be written as

$$Ca_{4-\alpha x}Pb_{\alpha x}(Ca_{6-(1-\alpha)x}Pb_{(1-\alpha)x})\ (PO_4)_6(OH)_2 \qquad (2)$$

At the temperature of preparation, the equilibrium

$$Ca(I) + Pb(II) \rightleftharpoons Ca(II) + Pb(I) \qquad (3)$$

may be reached [44]. A distribution coefficient K can then be defined as

$$K = \frac{[6 - (1 - \alpha)x]\,[\alpha x]}{[4 - \alpha x]\,[(1 - \alpha)x]} \qquad (4)$$

If the Pb and Ca ions have no preference for either the sixfold or the fourfold position, their distribution over the corresponding sublattices will be at random whereby K = 1. However, a preference of Pb for the sixfold position II and hence a preference of Ca for the fourfold position I, as suggested by Engel et al. [43], would result in $K << 1$. In that case the cation distribution is most accurately determined on samples with $x \leq 6$. A constant value for K throughout the composition range $0 < x < 10$ would mean that the solid solutions are ideal in the thermodynamic sense [44]. In that case K is identical to the equilibrium constant for equation (3). Both PbOHA [45, 46] and CaOHA [47] have the space group $P6_3/m$. The structure is hexagonal. Literature values for the lattice parameters a and c of PbOHA are summarized in Table 1. For those of CaOHA, see [48].

Materials and Methods

Pure CaOHA and solid solutions of CaOHA and PbOHA were prepared according to the method described by Wright [51] for the preparation of solid solutions of PbOHA and strontium hydroxyapatite. The apatites were precipitated from a boiling aqueous solution of piperidine at pH 12 by the simultaneous and slow addition of a solution containing the appropriate amounts of $Ca(NO_3)_2$ and $Pb(NO_3)_2$ and a H_3PO_4 solution. The pH of the latter was adjusted to pH 12 by the addition of piperidine. Reagent grade chemicals were used throughout. Further details on the method of preparation can be found elsewhere [51]. Finally, the samples were pressed into bars under 2×10^7 N m^{-2} and heated at 800°C in a stream of CO_2-free water vapor of 1 atm. After 4 h the samples were quenched in air, crushed, and powdered in an agate ball mill. The calcium and lead contents of the single-phase samples were determined by atomic absorption spectrometry and are summarized in Table 2.

X-ray diffraction was carried out in the Philips Guinier XDC-700 camera. The camera constant was determined with α-Al_2O_3 as an internal standard. $CuK_{\alpha 1}$ radiation was used for an exposure time of about 8 h. The films were developed in the usual way. Densitograms were recorded on the Lin/Log Densitometer DD2 (Kipp) having logarithmic sensitivity.

The densitograms were analyzed for the occurrence of second phases by comparing the d values of eventual extra peaks with those of known compounds in the quaternary system CaO-PbO-P_2O_5-H_2O. The cell parameters a and c of the apatite phase were determined by measuring the position of as many apatite peaks as possible (n). A least-squares calculation on these positions

Table 1. Literature values for the lattice parameters of pure lead hydroxyapatite

Substance	a	c	Reference
PbOHA	9.34	6.87	Narasaraju et al. [41]
	9.86	7.22	Rao [42]
	9.84–9.88	7.40–7.42	Bhatnagar [50]
	9.89	7.28	Müller [40]
	9.868	7.430	Wright [51]
	9.877	7.429	Engel [49]
	9.879	7.434	Engel [46]
	9.878	7.432	Negas and Roth [52]
	9.877	7.247	Blakeslee and Condrate [53]

Preparations of the above substances have been different and may have affected the results

Table 2. Chemical composition and substitution degree x of the CaOHA-PbOHA solid solutions

x_{theor}	wt % Pb	wt % Ca	x_{exp}
1	15.2	28.8	0.93
2	29.6	24.8	1.88
3	40.5	20.6	2.76
4	47.5	15.2	3.77
5	56.1	11.3	4.90
6	60.2	8.09	5.90

Table 3. Phase composition and lattice parameters of the apatite phase in samples prepared in this study

x_{theor}	Second phase	a	c	N^b
0	Absent	9.416	6.885	16
1	Absent	9.442	6.910	30
2	Absent	9.48[a]	6.94[a]	20
3	Absent	9.54[a]	7.01[a]	10
4	Absent	9.572	7.014	27
5	Absent	9.625	7.051	31
6	$Pb_8P_2O_{13}$ (trace)	9.661	7.099	24

[a] Nearly all peaks were very broad or even double
[b] Number of reflections used to calculate the lattice parameters

Table 4. Mean values and corresponding variances for the cation distribution parameter α and distribution coefficient K of the CaOHA-PbOHA solid solutions

x_{theor}	$\bar{\alpha}(x)$	$\sigma^2_{\alpha(x)}$	$\bar{K}(x)$	$\sigma^2_{K(x)}$
1	0.152	0.0135	0.279	0.0579
2	0.153	0.0056	0.230	0.0236
4	0.091	0.0058	0.084	0.0077
5	0.075	0.0034	0.041	0.0023
6	0.055	0.0032	0.013	0.0004

produced the best fitting values for a and c. In those instances where $n > 25$, the accuracy is estimated to be better than 0.003 and 0.002 Å for a and c, respectively.

In the single-phase apatitic samples the cation distributions were determined from the relative intensities of the suitable reflections in diffractograms obtained without addition of the internal standard. Peak area was taken as a measure for peak intensity. The combination of the film sensitivity and the logarithmic sensitivity of the densitometer gives an overall linear relationship between peak and reflection intensity.

As standardization of all steps in the intensity measurements is difficult, intensity ratios of pairs of reflections were used to determine the cation distribution. These pairs were chosen so that a certain preference of Pb ions for a certain sublattice would have an opposite effect on their intensity and so that the absorption correction and the temperature factor could be neglected. For each x value and for each of the 12 chosen pairs of reflections, theoretical intensity ratios were calculated for values of α ranging from minimum to maximum. Lorentz polarization, multiplicity, and structure factor were taken into account. For each chosen pair of reflections the value of the distribution parameter α corresponding to the measured intensity ratio was then obtained by comparison with these theoretical intensity ratios. In this way 12 values for α and K were obtained for each sample at a given x.

Results

Since the samples with $x_{theor} > 6$ were found to contain fairly large amounts of certain lead phosphates as a second phase, they were not examined further. The phase composition and the lattice parameters a and c of the apatite phase in the other samples prepared in this work are summarized in Table 3. At $x_{theor} = 6$ a trace of second phase was observed which could be identified by comparison with data of Brixner and Foris [54]. Samples at x_{theor} values of 2 and 3 showed broad and even double peaks suggesting the occurrence of a miscibility gap of the apatites in the range $1 < x_{theor} < 4$. However, when calculated from the position of the most sharp reflections, the estimated lattice parameters of these samples as given in Table 3 fit reasonably well within the rest of the values. The latter vary within experimental error linearly with x according to

$$a = (9.410 \pm 0.005) + (0.043 \pm 0.001)x \quad \text{with } \sigma_a = 0.006 \tag{5}$$

and

$$c = (6.880 \pm 0.005) + (0.036 \pm 0.001)x \quad \text{with } \sigma_c = 0.006 \tag{6}$$

where σ represents the standard deviation of estimate.

In Table 4, the cation distribution parameter α and the distribution coefficient K are summarized. Each value represents the mean of 12 determinations corresponding to 12 selected intensity ratios. The respective variances σ^2_α and σ^2_K are also given. From the table it is seen that within the experimental error all Pb ions occupy the sixfold position II. The fact that two apatite phases are probably present at $x = 2$ and 3 means that K and α for these samples in Table 4 are a sort of average for these two apatite phases, as the intensities of the X-ray diffraction peaks are monotonous functions of α and K.

Discussion

The cell parameters for our heat-treated samples both vary linearly with x within the limits of experimental error. The a parameter at $x = 10$ as extrapolated from Eq. (5) agrees fairly well with literature values commonly reported for PbOHA (Table 1). However, there is considerable disagreement between the extrapolated value for c at $x = 10$ [Eq. (6)] and the c parameter of PbOHA (Table 1). Such deviation from Vegard's law indicates that K [Eq. (4)] differs markedly from unity. This is corroborated by the results in Table 4 showing the strong preference of the Pb ions for the sixfold position II in the apatite lattice and confirming the opinion of Engel et al. [43]. On this basis no ideal behavior can be expected for these solid solutions [44]. The preference of Pb^{2+} ions for the sixfold position II may

be related to the fact that there is somewhat more space in position II than in position I [57].

The values for the lattice parameters of the PbOHA-CaOHA solid solutions in Table 3 are generally 0.03 Å lower than those reported by Engel et al. [43]. A calculation based on the results of Engel [46] shows that the dehydration degree of pure PbOHA at 800°C and for a partial water vapor pressure of 760 mm Hg amounts to 3% maximum. Since the dehydration tendency of PbOHA-CaOHA solid solutions decreases with increasing calcium content [43], it is unlikely that the lower a and c values in this study are due to a partial dehydration of the samples. The discrepancy most probably is related to a different crystal-chemical constitution of heat-treated and hydrothermally treated solids as is shown for CaOHA [53, 55].

The fact that for x_{theor} values of 2 and 3 there was a doubling of most lines in the X-ray diffraction pattern is interpreted as the occurrence of a miscibility gap in the range $1 < x_{theor} < 4$. The formation of a superstructure around $x = 3$ is not likely as it would have resulted in extra lines rather than in a doubling of lines. Moreover, such extra lines would have appeared only in a narrow compositional range around $x = 3$. A miscibility gap is not uncommon in series of apatites with isomorphous substitution [56] and means that there is a maximum in the free energy of the apatites within that range. Further, the fact that our preparations in the range $6 < x_{theor} < 10$ contained fairly large amounts of certain lead phosphates as a second phase is an indication that apatites in that range are not very stable either.

Therefore, we conclude that apatites in the range $4 < x_{theor} < 6$ represent a minimum in the free energy between CaOHA and PbOHA. Hence one should expect that incorporation of Pb^{2+} ions in bone and teeth results in the formation of a separate (Pb,Ca)OHA phase somewhere in the range $4 < x_{theor} < 6$, at least as far as the minerals in bone and teeth can be compared with CaOHA. In the following study we will carry out solubility determinations on the apatites prepared in this study in order to investigate whether this hypothesis is correct for in vivo conditions or whether other, eventually hydrated solid phases (e.g., $PbHPO_4$) interfere in the control of the solubility behavior.

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