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## Lattice Parameters and Cation Distribution of Solid Solutions of Calcium and Strontium Hydroxyapatite

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**Summary.** Solid solutions of strontium and calcium hydroxyapatite were synthesized by solid-state reaction. Lattice parameters of these compounds were determined using two types of Guinier cameras. They vary linearly with the molar percentage of strontium hydroxyapatite. The distribution of Ca and Sr ions over the fourfold and sixfold positions in the apatite structure was determined by comparing experimental and calculated values for the intensity ratios of suitable reflections. A slight, although significant, preference of Sr for the sixfold position was found. An ideal behavior is predicted for these solid solutions.

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

### Introduction

When strontium occurs in the diet of man or animal, it is incorporated partially in bone and tooth tissues. It is thought [1-3] that it replaces calcium in the apatite lattice in these tissues. This might be doubted as small amounts of other phases such as octocalcium phosphate and brushite can occur in addition to apatite in biominerals [4], whereas the apatite phase itself contains a large amount of  $\text{Na}^-$  and  $\text{CO}_3^-$  ions as well as vacancies [5] and thus is not pure hydroxyapatite.

It has been reported that strontium can cause rickets in bone [6-8] and increases the duration of bone abnormalities caused by scurvy [12]. Likins, McCann, and Posner [9] reported a preferential release of skeletally deposited strontium, whereas

Feith et al. [10] describe strontium as a bone-seeking ion. Jowsey and Balasubramaniam [11] reported that strontium retention in bone is increased by adding phosphate to the diet. Joseph, Gedalia, and Fuks [13] found that strontium occurring in the diet of rats increased their susceptibility to caries. This is in line with the finding that treatment with strontium chloride increases the rate of dissolution of dental enamel [14]. Rosenthal, Austin, and Moreno Eves [15] found that dentin contains more strontium than enamel and that carious enamel contains more strontium than sound enamel. Before we can understand these phenomena, further research is necessary on the interaction of strontium with the calcium phosphates occurring in biominerals and on the stability and solubility of the strontium analogs.

Although Sanfourche and Focet [16] concluded from wet-chemical studies that the system  $\text{SrO-P}_2\text{O}_5\text{-H}_2\text{O}$  behaves analogously to the system  $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ , the strontium analogs of octocalcium phosphate and brushite do not exist [17, 18]. Lorah, Tartar, and Wood [19] were able to synthesize strontium hydroxyapatite  $\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$ , whereas Schnell et al. [18] found that this apatite can incorporate large amounts of carbonate like the biological calcium hydroxyapatite.

Collin [20] and Hayek and Petter [21] were able to prepare solid solutions of strontium hydroxyapatite ( $\text{SrOHA}$ ) and calcium hydroxyapatite ( $\text{CaOHA}$ ). Their lattice constants were found to vary linearly with composition between those of the pure end members. Similar results have been found for the analogous fluoroapatites [22]. Collin [20] reported that the apatitic solid solutions had a much smaller Sr/Ca ratio than the aqueous solutions from which they were precipitated. This is in agreement with solubility measurements on solid solutions carried out by Narasaraju, Chickerur, and Singh [23], who found that strontium incorporation causes increased solubility. On the other hand, synergistic

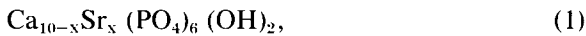
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effects for fluoride and strontium are reported on calcium hydroxyapatite dissolution [24–26], which should indicate that the apatite phase would prefer incorporation of strontium over that of calcium.

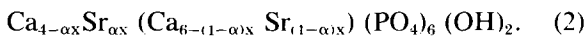
These contradictory reports necessitate a reinvestigation of pure and crystalline SrOHA and CaOHA solid solutions. In this study their lattice parameters and cation distribution are reported. In a separate study [27] their solubility behavior will be described.

### Theoretical Considerations

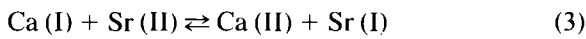
In the apatite structure two sublattices occur for the cations. Position I is fourfold and its Wyckhoff notation is f, whereas position II is sixfold and is denoted by h. Therefore, if the chemical formula of a solid solution is given by



its structure formula can be written as



At the temperatures of preparation, the equilibrium



will be reached.

A distribution coefficient  $K$  can be defined as

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

If the Sr and Ca ions have no preference for either the sixfold or the fourfold position, their distribution over the according sublattices will be at random whereby  $K = 1$ . A value of  $K < 1$  would indicate a preference of strontium for the fourfold position I and, vice versa, a preference of calcium for the sixfold position II. A constant value for  $K$  throughout the composition range  $0 < x < 10$  would mean that the solid solutions are ideal in a thermodynamic way [28]. In that case  $K$  is identical to the equilibrium constant for equation (3). Both SrOHA and CaOHA have the space group  $P_{6/3m}$  [29]. The structure is hexagonal. Literature values for the lattice parameters  $a$  and  $c$  of these ternary components are summarized in Table 1.

### Materials and Methods

Pure CaOHA and SrOHA were prepared by titrating a boiling slurry of calcium and strontium hydroxide, respectively, with phosphoric acid according to the procedure described by Avnimelech, Moreno, and Brown [30]. Reagent grade chemicals were used throughout. The purity and stoichiometry of the samples were confirmed by chemical analysis.

**Table 1.** Lattice parameters for pure calcium hydroxyapatite (CaOHA) and pure strontium hydroxyapatite (SrOHA) compared to literature values (Å)

Substance	a	c	Reference
CaOHA	9.424	6.879	Sudarsanan and Young [31]
	9.418	6.884	De Wolff [34a]
	9.432	6.881	Posner et al. [32]
	9.418	6.883	Collin [20]
	9.423	6.884	Lagergren and Carlström [33]
	9.418	6.880	Sudarsanan and Young [37]
	9.403	6.866	Wallaeyts [38]
	9.416	6.875	Philips camera, this work
	9.415	6.878	Nonius camera, this work
	SrOHA	9.760	7.284
9.761		7.277	Lagergren and Carlström [33]
9.745		7.256	Ropp [34b]
9.767		7.288	Bhatnagar [39]
9.745		7.265	Sudarsanan and Young [37]
9.743		7.266	Akhavan Niaki [40]
9.763		7.280	Philips camera, this work
9.758		7.280	Nonius camera, this work

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

Solid solutions of CaOHA and SrOHA at  $x = 1, 2, 4, 5, 6, 8,$  and  $9$  were prepared by solid-state reaction of the respective ternary apatites at  $1200^\circ\text{C}$  in a stream of  $\text{CO}_2$ -free water vapor of  $1$  atm. After 2 days the temperature was fixed at  $900^\circ\text{C}$  for 1 consecutive day. Then the samples were slowly cooled, crushed, and powdered. Further details of the preparation can be found elsewhere [27]. For internal consistency the pure CaOHA and SrOHA were subjected to the same high temperature treatment as their solid solutions prior to X-ray diffraction.

Determination of the lattice parameters was carried out by X-ray diffraction in the Philips Guinier XDC-700 and in the Nonius Guinier-de Wolff camera. As the film position in the Philips camera is very reproducible, it is not necessary to add an internal standard. The camera constant was determined with  $\alpha\text{-Al}_2\text{O}_3$ . In the Nonius camera an internal standard of  $\alpha\text{-Al}_2\text{O}_3$  was added. In the Philips camera  $\text{CrK}\alpha_1$  and in the Nonius camera  $\text{CuK}\alpha_1$  radiation was used for an exposure time of approximately 30 min. The films were developed in the usual way.

Densitograms were recorded on the Lin/Log Densitometer DD2 (Kipp) with logarithmic sensitivity.

The cell parameters were determined by measuring the position of at least 28 reflections for each sample. A least-squares calculation on these positions produced the best fitting values for the two cell parameters  $a$  and  $c$  for each sample. The accuracy is estimated to be better than  $\pm 0.003$  and  $\pm 0.002$  for  $a$  and  $c$ , respectively.

The cation distributions were derived from the relative intensities of the reflections 002, 210, 300, 202, 222, 312, 213, 321, and 410. 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. For the sample at  $x = 6$ , a diffractogram was measured as well in order to check the photographic procedure for intensity measurements.

As standardization of all steps in the intensity measurements is difficult, intensity ratios of pairs of reflections were used to determine the cation distribution. Seven pairs were chosen so that a

certain preference of Sr ions for a certain sublattice would have opposite effects on their intensity. These were 210/002, 300/002, 222/002, 002/202, 321/202, 321/410, and 213/312. For each  $x$  value and for each pair of reflections, theoretical intensity ratios were calculated for values of  $\alpha$  ranging from minimum to maximum. Lorentz polarization, multiplicity, and structure factor were taken into account. Absorption correction and temperature factor were neglected, as they are not of primary concern in the selected intensity ratios.

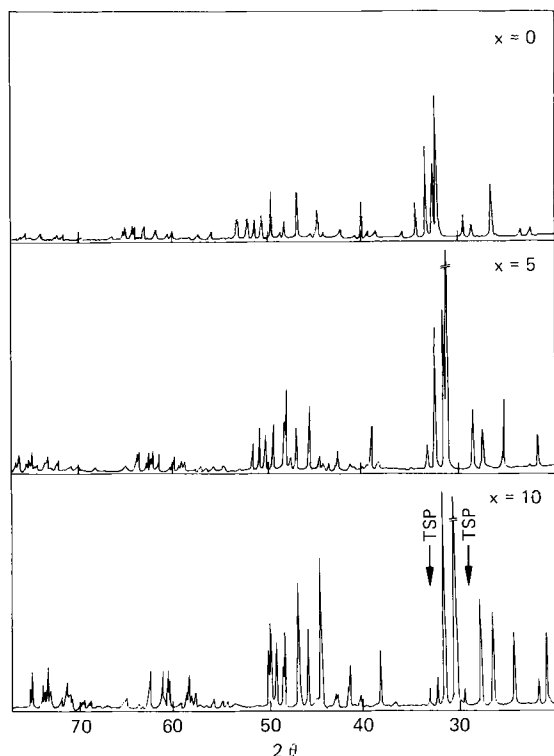
The value of the distribution parameter  $\alpha$  corresponding to the measured intensity ratio was then obtained by comparing with these theoretical intensity ratios. In this way seven  $\alpha$  and  $K$  values were obtained from each set of seven intensity ratios.

## Results

X-ray diffraction showed that all specimens were well crystalline as shown in Figure 1. In the specimens at  $x = 8, 9$ , and  $10$ , small amounts of  $\text{Sr}_3(\text{PO}_4)_2$  were found as a second phase. The cell parameters  $a$  and  $c$  of the apatite phase are summarized in Tables 1 and 2 as a function of  $x$  together with the  $c/a$  ratio and the unit cell volume,  $V$ . The parameters vary linearly with  $x$ , within experimental error, according to

$$a = 9.422 + 0.0340 x \quad \text{with } \sigma_a = 3.7 \cdot 10^{-3} \quad (5)$$

$$c = 6.879 + 0.0402 x \quad \text{with } \sigma_c = 2.2 \cdot 10^{-3} \quad (6)$$



**Fig. 1.** X-ray diffractograms of 3 samples ( $x = 0, 5$ , and  $10$ ) of the series of CaOHA-SrOHA solid solutions. Second phase peaks have been indicated by TSP (tertiary strontium phosphate, see text)

where  $\sigma$  is the standard deviation of estimate. Further evidence of this behavior is found in the variation of the  $c/a$  ratio and of the cell volume with  $x$  according to

$$\begin{aligned} c/a &= 0.73015 \\ &+ 0.00158 x \quad \text{with } \sigma_{c/a} = 1.8 \cdot 10^{-4} \end{aligned} \quad (7)$$

and

$$V = 528.5 + 7.20 x \quad \text{with } \sigma_V = 0.52. \quad (8)$$

The standard deviations  $\sigma_{c/a}$  and  $\sigma_V$  agree well with the anticipated errors  $3 \cdot 10^{-4}$  and  $0.4$ , respectively.

In Table 3,  $\alpha$  and  $K$  are listed for the compositions  $x$  considered. Each value is the mean of 7 determinations, corresponding to the 7 selected in-

**Table 2.** Lattice parameters of CaOHA and SrOHA solid solutions obtained with Philips and Nonius Guinier<sup>a</sup> cameras as a function of  $x$  (Å)

$x$	$a$	$c$	$c/a$	$V$
1	9.463	6.924	0.7316	537.0
1 <sup>a</sup>	9.458	6.917	0.7314	535.9
2	9.493	6.960	0.7331	543.1
2 <sup>a</sup>	9.491	6.961	0.7334	543.1
4	9.563	7.043	0.7365	557.7
4 <sup>a</sup>	9.560	7.041	0.7366	557.3
5	9.594	7.081	0.7381	564.5
5 <sup>a</sup>	9.592	7.081	0.7382	564.2
6	9.624	7.119	0.7398	571.0
6 <sup>a</sup>	9.624	7.119	0.7397	571.0
8	9.695	7.203	0.7430	586.4
8 <sup>a</sup>	9.692	7.200	0.7429	585.8
9	9.727	7.240	0.7443	593.2
9 <sup>a</sup>	9.730	7.243	0.7444	593.9

**Table 3.** Values of the cation distribution parameter  $\alpha$  and the distribution coefficient  $K$  obtained for solid solutions of CaOHA and SrOHA together with their respective experimental variances

$x$	$\alpha(x)^a$	$\sigma_{\alpha(x)}^2$	$K(x)$	$\sigma_{K(x)}^2$
1	0.281	0.0254	0.665	0.22
2	0.406	0.0193	1.286	1.07
4	0.373	0.0045	0.905	0.19
5	0.376	0.0021	0.868	0.11
6	0.378	0.0056	0.983	0.39
6	0.356	0.0034	0.719	0.11
6	0.382 <sup>b</sup>	0.0013	0.877	0.08
6	0.362 <sup>c</sup>	0.0024	0.741	0.10
8	0.371	0.0031	0.962	1.12
9	0.378	0.0010	0.685	0.39

<sup>a</sup> Unless stated otherwise tracings of the films of the Philips camera were used

<sup>b</sup> Derived from film of Nonius camera

<sup>c</sup> Derived from a diffractometer recording

tensity ratios. The respective variances  $\sigma_\alpha^2$   $\sigma_K^2$  are also given. Variance analysis at the 99% confidence level shows that the  $\sigma_{K(x)}^2$  of the subgroups are homogeneous with  $\sigma_{K(x)}^2 = 0.23$ , and there is no significant difference in  $K(x)$  for the samples considered. Hence,  $K$  was estimated as the mean from all determinations giving  $\bar{K} = 0.847 \pm 0.087$ .

## Discussion

Table 2 shows a gradual change of the cell parameters for increasing  $x$ , and all samples were single phase. It confirms the results of Collin [20] and Hayek and Petter [21] who also obtained continuous miscibility so that the apparent miscibility gap in the samples of Lagergren and Carlström [33] must be due to incorrect preparation. The present method of preparation has the advantage over coprecipitation and subsequent heating [20, 21] that the cation/phosphate and the Ca/Sr ratio can be controlled by proportionate weighing while a quick equilibration and homogenization is preserved by application of adequate ceramic techniques.

The cell parameters of our slowly cooled samples varied linearly with  $x$  within the limits of experimental error, except for the  $a$  and  $c$  values of pure CaOHA (see Table 1), which were both slightly smaller than expected on the basis of the observed linear behavior.

Despite the content of second phase, the  $a$  and  $c$  values for  $x = 8, 9$ , and  $10$  conformed well to a linear behavior. The accuracy of the chemical analysis was such that the Sr/P molar ratio in SrOHA was  $1.662 \pm 0.0005$ . Therefore, the content of second phase at  $x = 10$  might have been 3% maximum. It certainly was smaller at  $x = 8$  and  $9$ . If the Ca/Sr ratio in the second phase would not deviate much from that in the main apatitic phase, a possible deviation from linearity of the cell parameters due to second phase formation should be even less than the expectation based on assuming pure tertiary strontium phosphate as the second phase. Our data for the cell parameters of the second phase are, however, not conclusive as to Ca substitution in this phase.

In case of a strong preference of the Sr ions for either one of the cation sublattices in the apatite structure, probably both cell parameters would have shown a serious deviation from linear variation with composition. For comparison, in  $\text{Co}_3\text{O}_4$ - $\text{Mn}_3\text{O}_4$  solid solutions the distribution coefficient deviates appreciably more from unity and still the parameters appear to vary linearly with composition [35]. As the size of the Sr ion is considerably larger than that of Ca, the increase in the cell vol-

ume with  $x$  is as expected. If there is no preference for either sublattice, incorporation of larger cations will increase both the  $a$  and the  $c$  parameters [3]. The overall mean of the distribution constant  $K$  is so close to unity that no detectable deviation from linearity for the cell parameters can be expected.

The overall mean for  $K$  and its standard deviation are such that it can be concluded that Sr ions have a slight but significant preference for the sixfold position. However, the value of  $K$  does not depend on  $x$  within the limits of error so that an ideal behavior is expected for the solid solutions [5] and, hence,  $K$  may be called the equilibrium constant for the exchange reaction (3). For comparison, an ideal behavior is derived for  $\text{CaCO}_3$ - $\text{SrCO}_3$  solid solutions having aragonite structure from their precipitation behavior [36].

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