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Isomorfic Substitutions of Calcium by Strontium in Calcium Hydroxyapatite

H. Christensen

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ISOMORPHIC SUBSTITUTIONS OF CALCIUM BY STRONTIUM IN CALCIUM HYDROXYAPATITE

by Hans Christensen

Summary:

By means of homogeneous precipitation it has been possible to synthetize crystalline solid solutions of calcium strontium hydroxyapatite from aqueous solutions.

The lattice constants for the solid solutions were measured in the range $CA_9Sr(PO_4)_6(OH)_2$ - $CaSr_9(PO_4)_6(OH)_2$.

The investigations show that the discrimination of strontium against calcium is considerably smaller than reported elsewhere (1).

Strontium is preferentially built into the c-axis direction of the apatite lattice.

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CONTENTS

1. Introduction

To find out more about the mechanism underlying the separation of strontium from aqueous solutions by means of basic calcium phosphates (2), it is of interest to know whether calcium can be substituted by strontium in calcium hydroxyapatite (CaHA).

Previous experiments show a considerable discrimination of strontium in the precipitation of calcium strontium hydroxyapatite. After heating his samples to 950 ^{o}C for four hours Collin (1) obtained X-ray patterns which gave no detectable line broadening. However, samples dried at 110 ^{o}C gave X-ray patterns with a varying line breadth that would suggest fluctuations in homogeneity.

Lagergren and Carlström (3) were not successful in their experiments to form solid solutions over the whole range $Ca_9Sr(PO_4)_6(OH)_2$ - $CaSr_9(PO_4)_6(OH)_2$ They mixed stoichiometric amounts of the solid solutions of CaHA and strontium hydroxyapatite (SrHA) and attempted to attain a solid state reaction by heating the mechanical mixture to 1300 ^{o}C.

From X-ray crystallographic investigations it was shown that no solid solutions could be formed in the region $Ca_7Sr_3(PO_4)_6(OH)_2$ - $Ca_3Sr_7(PO_4)_6(OH)_2$.

2. Experimental

2.1 Conditions

To attain a gradual substitution of calcium ions by strontium ions in the unit cell of CaHA, it is essential to work under such conditions during the precipitation reaction that the precipitates show no interference in the lattice, i. e. are crystalline.

Crystalline solid solutions of CaHA were obtained by Rathje (4) and Hayek (5). However, neither method was suitable for the substitution experiments.

Crystalline homogeneous solid solutions of CaHA and SrHA can be synthetized from aqueous solutions by means of homogeneous precipitation if the ratio of the reaction in equation (1) is maintained:

$$10Me(NO_3)_2 + 6KH_2PO_4 + 14NaOH = Me_{10}(PO_4)_6(OH)_2 + 20KNO_3 + 12H_2O \quad (1).$$

2.2 Process

All chemicals were of reagent grade.

Concentration of the solutions:

a)	47.24 g $Ca(NO_3)_2 \cdot 4\,H_2O$	per liter solution
b)	42.34 g $Sr(NO_3)_2$	" " "
c)	15.70 g KOH	" " "
d)	16.34 g KH_2PO_4	" " "

1 ml of each solution (a or b, c and d) corresponds to the stoichiometric amounts needed to form apatite according to eq. (1).

A 2-liter 4-necked flask was equipped with a stirrer, a condenser and 2 dropping funnels. 500 ml of water was used as receiver. By synthetizing CaHA the solutions a, d and c were dropped to the boiling receiver at the same speed. The acidity of the reaction mixture was held constant at pH 6.2 (methyl red). It is unadvisable to carry out the precipitation reaction in more basic solution - at the color change interval of phenolphthalein - as the slow rate of crystallization of the apatite is still further deteriorated.

To get a crystalline precipitate of the apatite, the solutions must be very slowly added at the beginning. After an addition of about 5 ml of each solution the first crystals form. The rate of adding the solutions can now be increased to about 50 ml per 15 min. For one batch 300 ml of solutions a, c, d and b, c, d was used for CaHA and SrHA respectively. If the precipitation was done at pH 6.2, the consumption of solution c was 300 ml $\pm$ 2 ml for series of precipitations.

After the addition of the solutions, the reaction mixture was allowed to boil for about 15 min. The crystalline product was filtered on a Büchner funnel, washed carefully with water and dried at 105 - 110 ^{o}C.

For the substitution experiments, mixtures of the solutions a and b, corresponding to a ratio Ca/Sr = 9/1 to Ca/Sr = 1/9, were used in addition to the solutions c and d.

2.2.1 Analytical methods

Calcium and strontium were separated from phosphorus on a Dowex 50 x 8 column. The phosphorus was determined by means of quinoline phosphomolybdate (6). Calcium and strontium were determined from the same solution by means of a flame photometer (7).

The X-ray investigations were carried out with a Philips X-ray spectrometer PV 10 10 / 30, using nickel filtered copper radiation; λ = 1.5418 Å. The lattice constants a_o and c_o were determined for all samples by measuring the diffraction angles 2 0 for the planes (hkl), (112), (221), (312), (213).

3. Results and discussion

The results of the investigations will be seen in tables 1 and 2, and in fig. 1. curve B, and fig. 2. Fig. 1, curve A, illustrates the relations if there are no discriminations of strontium in the precipitates. In curve B it will be seen that the discrimination of strontium in the solid solutions of calcium strontium hydroxyapatite is considerable smaller than was revealed by previous investigations - fig. 1, curve C (1).

The discrimination of strontium in the precipitation of calcium strontium apatites may be due to irregular dislocations of the lattice planes in the solid solutions, which in turn may have been caused by unideal conditions during the precipitation. Lattice interferences which result in inhomogeneous solid solutions can be neutralized by supplying energy (heating to 950 °C for four hours).

In fig. 2 the lattice constants a_o and c_o are plotted against atom % strontium in each sample of the solid solutions.

With increasing atom % strontium in solid solution the length of the c-axis will increase more than the length of the a-axis. As the ionic radii for calcium and strontium are 1.06 Å and 1.27 Å, this means that more strontium ions will be built into the lattice above each other in the direction of the c-axis than beside each other in the direction of the a-axis.

The unit cell, which contains 10 metal ions, 6 phosphate ions and 2 hydroxyl ions, will be of greater extent in the direction of the c-axis than in the direction of the a-axis.

4. Conclusions

By means of homogeneous precipitation it was possible to synthetize crystalline solid solutions of calcium strontium hydrozyapatite.

The results of the chemical (fig. 1) and the X-ray spectrometrical (fig. 2) investigations demonstrate that an isomorphic substitution of calcium by strontium in the unit cell of calcium hydroxyapatite can take place in the range $Ca_9Sr(PO_4)_6(OH)_2$ to $CaSr_9(PO_4)_6(OH)_2$.

In view to these results it does not seem to be preposterous that solid solutions of calcium and strontium hydroxyapatite may be formed in bone tissue, the most important mineral of which is calcium hydroxyapatite.

Acknowledgement

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Table 1

Discrimination of strontium in solid solutions of calcium strontium hydroxyapatite.

Sample no.	Atom % Sr initial solution	Atom % Sr solid solution
115	0.0	0.0
116	10.0	8.2
117	20.0	16.9
118	30.0	27.4
119	40.0	35.0
120	50.0	45.5
121	60.0	56.9
122	70.0	66.2
123	80.0	76.9
124	90.0	87.9
125	100.0	100.0

Table 2

Lattice constants and the ratio Ca/P for calcium and strontium hydroxyapatite.

	a_o	c_o	Ca/P
CaHA	9.42 ± 0.01 Å	6.87 ± 0.01 Å	1:0.600
SrHA	9.77 ± 0.01 Å	7.28 ± 0.01 Å	1:0.600

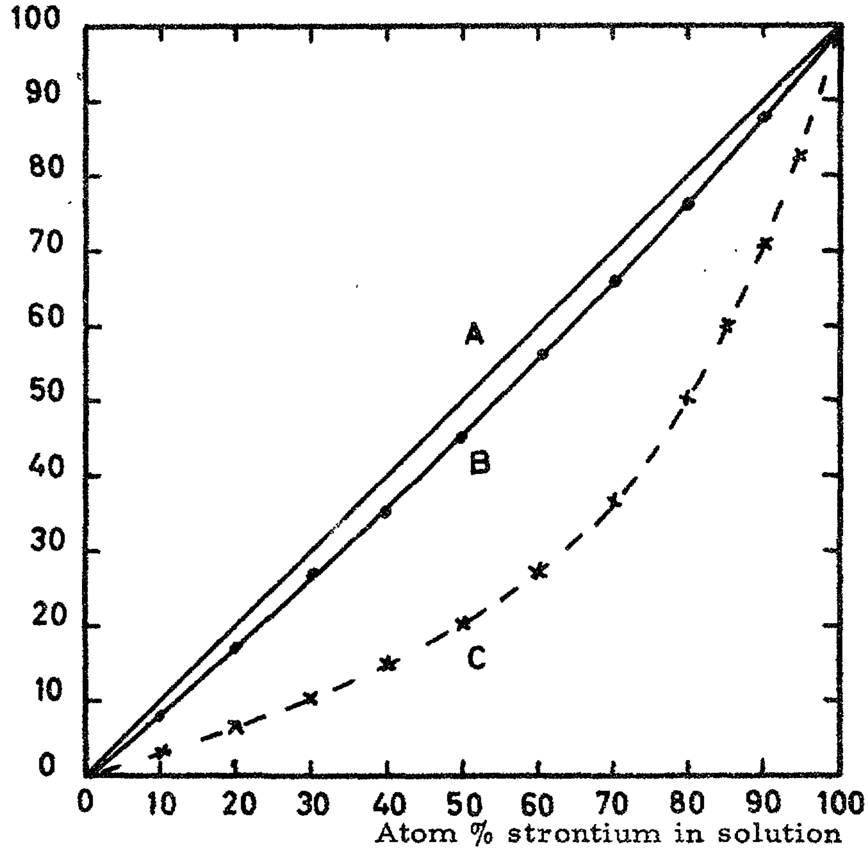

Fig. 1. Atom % strontium in the solid solution vs. atom % strontium in the intial solution

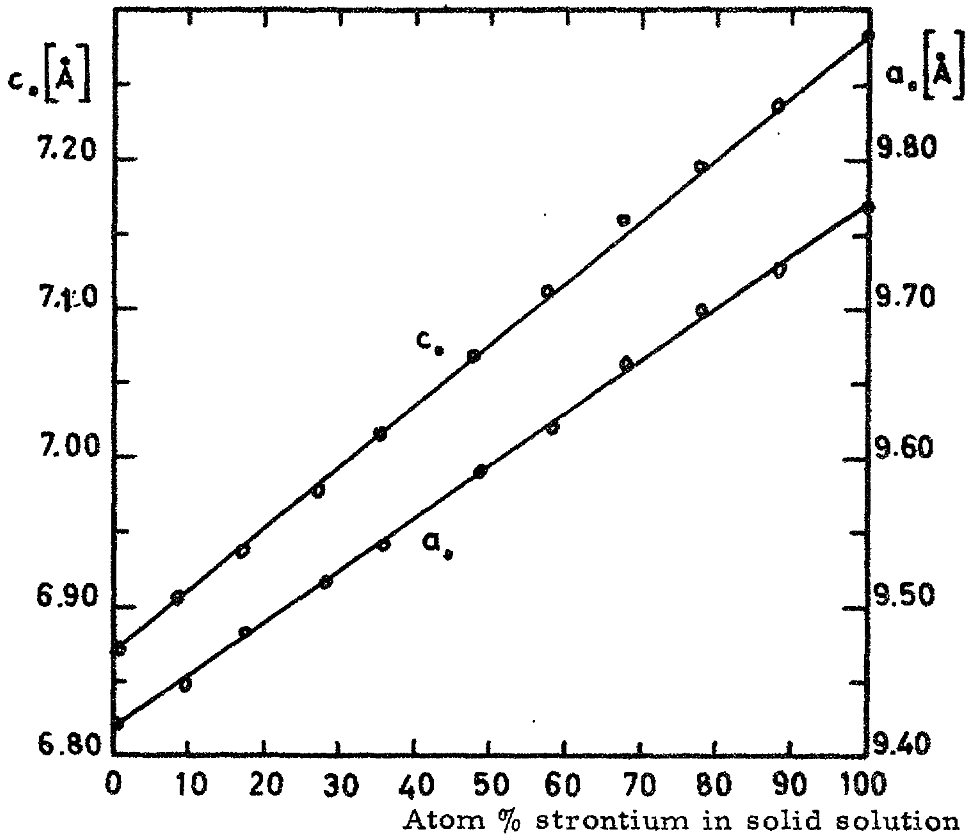

Fig. 2. Lattice constants of solid solution vs. atom % strontium in the solid solutions.

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