

Preparation and characterization of phosphate and arsenate apatites of strontium and their solid solutions

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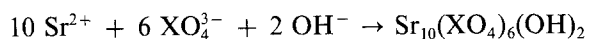
Samples of phosphate and arsenate apatites of strontium and six of their solid solutions, spread over the entire compositional range, were prepared by a wet method. They were characterized by chemical, X-ray, electron microscopic and infrared analyses. The validity of Vegard's law established the homogeneity of the solid solutions.

1. Introduction

Calcium hydroxylapatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$, the principal inorganic constituent [1] of animal bones and teeth, provides structural stability to skeletal and dental systems while storing calcium and phosphorus to maintain their biologically required levels in the body fluids. In addition, it acts as a detoxifying depository to store unwanted ions consequent upon its ability to undergo a series of cationic and anionic isomorphous substitutions [2]. Principal among such substitutions have been the replacement of Ca^{2+} by Sr^{2+} and of PO_4^{3-} by AsO_4^{3-} which constitute, respectively, the mechanisms of incorporation of strontium and arsenic in the human skeletal system, the former leading to radiation damage [3, 4] if β -active ^{90}Sr is involved, and the latter to toxicity [5, 6]. While $\text{Ca}^{2+} \rightleftharpoons \text{Sr}^{2+}$ exchange was investigated extensively [3, 7], studies on substitution of phosphate by arsenate on strontium hydroxylapatite were not undertaken earlier. In order to throw light on the influence of $\text{PO}_4^{3-} \rightleftharpoons \text{AsO}_4^{3-}$ exchange on the principal bone processes, a series of six solid solutions of phosphate and arsenate apatites of strontium, (SPA and SAA, respectively) spread over the entire compositional range, were prepared and characterized. The details of these investigations are reported in the present paper.

2. Experimental details

The experimental details for the preparation of the samples by precipitation were based on the following equation:



where X = phosphorus or arsenic for the end-members and (P + As) for the solid solutions. Stock solutions of Sr^{2+} , PO_4^{3-} and AsO_4^{3-} were prepared respectively from strontium nitrate, diammonium hydrogen phosphate and arsenic pentoxide, the latter being converted to AsO_4^{3-} by the addition of an appropriate amount of sodium hydroxide. From these solutions, preserved in polyethylene containers, the amounts of

Sr^{2+} , PO_4^{3-} and AsO_4^{3-} were determined by appropriate analytical methods [8].

For preparation of each sample, calculated volumes of solutions of the starting materials containing stoichiometric quantities required for a yield of ~ 30 g were used. An appropriate volume of strontium nitrate solution treated with a required volume of ethylene diamine [2, 3] to maintain a pH of ~ 12 on dilution to 1000 ml was taken in a 3 litre round-bottomed flask. Diammonium hydrogen phosphate and/or sodium orthoarsenate solutions, stoichiometric with that of the Sr^{2+} solution used, were likewise treated with ethylene diamine and diluted to 1000 ml such that the pH of the resulting solution was ~ 12 . This solution was added dropwise to that of Sr^{2+} , the precipitation being done at $37 \pm 0.5^\circ\text{C}$ to simulate biological conditions. Air free of CO_2 was bubbled through the precipitation medium to prevent the formation of carbonate apatite and also to keep the medium well stirred. The produce was refluxed for about 2 h in contact with the mother-liquor, left overnight, filtered through a G4 sintered glass crucible and washed with water until the washings were neutral. The samples were then washed with acetone and air-dried to 800°C for ~ 6 h and cooled in a desiccated atmosphere, for use in chemical, X-ray and infrared analyses, the experimental details of which are the same as those described elsewhere [8, 9]. The air-dried samples were used for electron microscopic analysis [10].

3. Results and discussion

3.1. Chemical analysis

The weight per cents of strontium, phosphorus and arsenic of the samples were determined by analytical procedures specially worked out for the purpose [8, 9]. These results are given in columns 3, 4 and 5 of Table I. The g atom ratios, Sr/P + As, and molecular formulae of the samples were calculated from these results and are given in column 6 of the table. The results indicated that these ratios vary between 1.63 and 1.69, the theoretical value being 1.67. A striking

TABLE I Chemical analysis of solid solutions of phosphate and arsenate apatites of strontium

Sample number	Sample	Sr (wt %)	P (wt %)	As (wt %)	g atom ratio, Sr/P + As	Molecular formula
1	2	3	4	5	6	7
1.	Strontium phosphate apatite	58.96	12.38	—	1.68	$\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$
2.	Solid solution: I	58.13	11.09	3.14	1.66	$\text{Sr}_{10}(\text{PO}_4)_{5.4}(\text{AsO}_4)_{0.6}(\text{OH})_2$
3.	Solid solution: II	56.47	8.83	8.11	1.64	$\text{Sr}_{10}(\text{PO}_4)_{4.4}(\text{AsO}_4)_{1.6}(\text{OH})_2$
4.	Solid solution: III	56.44	8.44	8.54	1.67	$\text{Sr}_{10}(\text{PO}_4)_{4.2}(\text{AsO}_4)_{1.8}(\text{OH})_2$
5.	Solid solution: IV	54.05	5.10	15.69	1.65	$\text{Sr}_{10}(\text{PO}_4)_{2.6}(\text{AsO}_4)_{3.4}(\text{OH})_2$
6.	Solid solution: V	58.55	4.37	16.58	1.69	$\text{Sr}_{10}(\text{PO}_4)_{2.3}(\text{AsO}_4)_{3.7}(\text{OH})_2$
7.	Solid solution: VI	51.59	1.85	21.97	1.66	$\text{Sr}_{10}(\text{PO}_4)_{1.0}(\text{AsO}_4)_{5.0}(\text{OH})_2$
8.	Strontium arsenate apatite	50.26	—	25.77	1.66	$\text{Sr}_{10}(\text{AsO}_4)_6(\text{OH})_2$

TABLE II X-ray and infrared analyses of solid solutions of phosphate and arsenate apatites of strontium

Sample number	Lattice parameters (nm)		Unit cell volume, V_{uc} , $\sqrt{3/2} a^2 c$ (nm ³)	Molar volume $V_{uc}N$ (ml mol ⁻¹)	Wave numbers of peaks (cm ⁻¹)		
	<i>a</i>	<i>c</i>			PO_4^{3-}	AsO_4^{3-}	OH^-
1	2	3	4	5	6	7	8
1.	0.976	0.726	0.598	360	1075 (s),* 1030 (s), 948 (m)	—	3572 (w)
2.	0.982	0.728	0.608	366	1072 (s), 1028 (s), 947 (m)	851 (s)	3564 (w)
3.	0.993	0.734	0.627	378	1068 (s), 1017 (s), 946 (m)	850 (s)	3564 (w)
4.	0.996	0.736	0.632	381	1018 (s), 945 (m),	852 (s)	3564 (w)
5.	1.013	0.744	0.662	399	1025 (s), 942 (m)	833 (s)	3562 (w)
6.	1.016	0.746	0.667	402	1028 (s), 941 (w)	830 (s)	3562 (w)
7.	1.031	0.754	0.694	418	1028 (s), 973 (m)	821 (s)	3556 (w)
8.	1.043	0.760	0.716	431	—	863 (s), 841 (s), 825 (s)	3556 (w)

*s = strong, m = medium, w = weak.

agreement between the experimental g atom ratios with the stoichiometric value justifies the suitability of the methods adopted for preparation and chemical analysis of the samples.

3.2. X-ray data

The lattice parameters *a* and *c* of the samples given in columns 2 and 3 of Table II were found to increase in

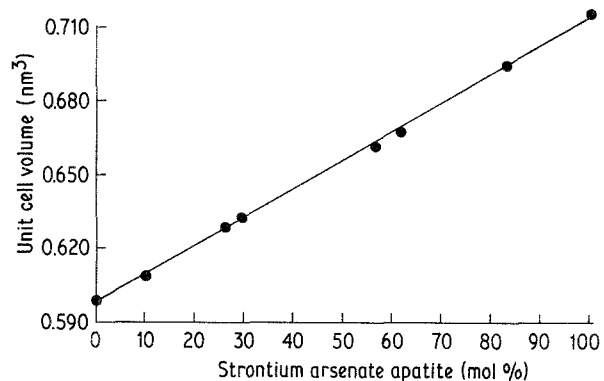


Figure 1 Dependence of unit cell volume of solid solutions of phosphate and arsenate apatites of strontium on the mol% strontium arsenate apatite.

the ranges 0.976 to 1.043 nm and 0.726 to 0.760 nm, respectively, with an increase in the proportion of arsenate. The unit cell and molar volumes of the samples given in columns 4 and 5, respectively, of Table II increase in the ranges, 0.598 to 0.716 nm³ and 360 to 431 ml, respectively. Such a systematic increase in the lattice parameters as well as in the unit cell volumes with an increase in the proportion of AsO_4^{3-} , as indicated in Figs 1 and 2, confirms the homogeneity of the solid solutions, since a dilation of the unit cell is expected by the replacement of phosphate by arsenate (covalent radii, 0.110 and 0.118 nm, respectively). In addition, Fig. 2 substantiates the validity of Vegard's law which states that the unit cell volume is a linear function of the composition in the case of homogeneous solid solutions.

3.3. Infrared data

The infrared absorption spectra of the samples [11, 12] exhibited characteristics OH-stretching mode of apatite in the vicinity of 3560 cm⁻¹. The characteristic phosphate peaks observed close to 1075, 1030 and 950 cm⁻¹ and those of arsenate observed in the vicinity

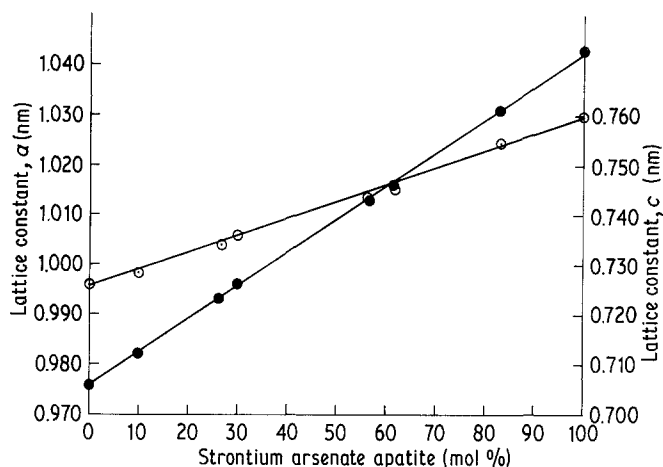


Figure 2 Dependence of lattice parameters of solid solutions of phosphate and arsenate apatites of strontium on the mol % strontium arsenate apatite. (●) Value of lattice parameter 'a'; (○) value of lattice parameter 'c'.



Figure 3 Electron micrograph of the solid solution of phosphate and arsenate apatite of strontium (sample 4 of Table I) $\times 35000$.

of 850 cm^{-1} also substantiate the homogeneity of the samples, the area under the phosphate peak being gradually suppressed and that under the arsenate peak increased as the proportion of the latter increased.

3.4. Electron microscopic studies

A representative electron micrograph of one of the samples (no. 4 of Table I) given in Fig. 3 shows the hexagonal shape of the crystals characteristic of apatites [13, 14].

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