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Thermochemistry of phosphate products.
Part II: Standard enthalpies of formation and mixing of calcium and strontium fluorapatites

I. Khattech, M. Jemal*

Chemistry Department, Faculty of Sciences, Tunis-1060, Tunisia

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Abstract

Calcium–strontium fluorapatites solid solutions, having the general formula $Ca_{10-x}Sr_x(PO_4)_6F_2$, were prepared and characterized by X-ray diffraction, infrared spectroscopy and chemical analysis. Using an isoperibol calorimeter, enthalpies of solution of these products in 9% nitric acid solution were measured. The standard enthalpy of formation of these apatites and the enthalpy of mixing of end-member products were deduced. The variation of all these quantities vs. composition showed a clear change at $Sr/(Sr+Ca)$ close to 0.6. This result has been related to the preferential occupation of the sixfold metal position by strontium in the lattice. © 1997 Elsevier Science B.V.

Keywords: Enthalpy of formation; Heat of mixing; Heat of solution; Strontium fluorapatite

1. Introduction

Apatites make up a family of phosphate compounds. One of its well-known representative is phosphocalcium fluorapatite $Ca_{10}(PO_4)_6F_2$; which crystallizes in the hexagonal system $P6_3/m$. This compound presents various substitution possibilities and, in particular, the substitution of Ca^{2+} ions with bivalent, trivalent or even monovalent ions.

In their calcic form, apatites constitute the major part of phosphate sedimentary minerals and the mineral phase of calcified tissues (bones, teeth). In the latter case, traces of strontium (0.01 to 0.08%) [1–3] are frequently found. Many studies have focused on the effects of this element on the quality of these tissues. Their conclusions raise some controversies. Thus, the role of this element in the mineralization of the bone tissues and dental caries is not yet completely understood [1,4]. Many investigations on synthetic apatites containing this element, and with various substitutions, have been carried out in order to explain the effects of strontium on the apatitic structure and the physico-chemical properties of the material. These works agree on the existence of continuous solid solutions between calcium and strontium hydroxyapatites, fluorapatites and chlorapatites [5–9]. In these solids, strontium occupies preferentially the sixfold metal position in the lattice [5–7].

In previous works, we have determined the standard enthalpy of formation of strontium apatites: $Sr_{10}(PO)_4)_6Y_2$ where $Y = F(F_{ap}Sr)$, $OH(H_{ap}Sr)$ and

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*Corresponding author. Tel.: 216 1 885008; fax: 216 1 500 666.

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Cl(Cl$_{ap}$Sr) [10,11]. These studies allowed us to show that $\Delta_f H^\circ$ (298 K) increases when one moves from F$_{ap}$Sr to H$_{ap}$Sr, and then to Cl$_{ap}$Sr [12]. A similar pattern of evolution is also observed for the corresponding calcium apatites.

In the present work, we have synthesized and determined the dissolution and formation enthalpies of calcium–strontium fluorapatites solid solutions: $Ca_{10-x}Sr_x(PO_4)_6F_2$ with $0 \leq x \leq 10$. The mixing enthalpy of the limiting products has also been deduced over the entire composition range.

2. Synthesis and characterization of the samples

2.1. Samples preparation

Calcium–strontium fluorapatites have been prepared by double decomposition in an aqueous medium. The method consists in dropping calcium nitrate and strontium nitrate solution (1 l; 0.2 M) for 3 h into a boiling solution (0.6 l) of diammonium phosphate (0.2 M) and ammonium fluoride (0.1 M). The pH of the two solutions was adjusted to ≈10 by addition of ammonia solution ($d = 0.92$). The nitrates solution was prepared in various ratios depending on the composition of the solid to be synthesized. The solid was filtered, then dried at 70°C for 12 h. Finally, samples were ignited at 450°C for 6 h under pure nitrogen flow atmosphere.

The reagents are products used for analysis (99% purity). These products are manufactured by Merck and Fluka.

2.2. Characterization and control

The control of purity of the synthesized products was achieved by chemical analysis of the different components, X-ray diffraction and infrared spectroscopy.

2.2.1. X-ray diffraction

X-ray diffraction was carried out by a CPS 120 INEL diffractometer. X-ray diffraction diagrams show that all the samples were pure apatitic phases and crystallize in the hexagonal system. Diffractogram indexing allowed to calculate the lattice parameters. As mentioned by Akhavan-Niaki [8], these quantities vary linearly with the ratio Sr/(Sr + Ca). In the present case, they justify the following equations:

$$a = (0.9372 + 0.0338X)\,\text{nm} \quad r = 0.9995$$

$$c = (0.6883 + 0.0405X)\,\text{nm} \quad r = 0.9997$$

$$V = (52.33 + 7.20X)\,\text{nm}^3 \quad r = 0.9995$$

with $X = \text{Sr}/(\text{Sr} + \text{Ca})$ and r the regression coefficient.

2.2.2. IR spectroscopy

IR spectroscopy has been carried out between 4000 and 400 cm^{-1}, using a Perkin–Elmer 7700FT-IR spectrometer. Spectra of precipitated phosphate show absorption band characteristic of apatites and do not indicate any impurities which may exist in the solid such as HPO_4^{2-}(1180 – 1200, 875 cm^{-1}), CO_3^{2-} (1410 – 1450, 860 – 885 cm^{-1}) and $P_2O_7^{4-}$(1200–1250 cm^{-1}).

Table 1
Chemical titration and formulas for the calcium–strontium fluorapatites

Atomic ratio Sr/(Sr + Ca) experimental	(Sr + Ca)/P	F/g% experimental	F/g% from the formula	Formula
0	1.663	3.73	3.77	$Ca_{10}(PO_4)_6F_2$
0.103	1.657	3.60	3.59	$Ca_{8.97}Sr_{1.03}(PO_4)_6F_2$
0.203	1.662	3.49	3.44	$Ca_{7.97}Sr_{2.03}(PO_4)_6F_2$
0.300	1.674	3.24	3.30	$Ca_7Sr_3(PO_4)_6F_2$
0.405	1.659	3.10	3.16	$Ca_{5.95}Sr_{4.05}(PO_4)_6F_2$
0.504	1.661	2.98	3.05	$Ca_{4.96}SR_{5.04}(PO_4)_6F_2$
0.606	1.660	2.98	2.93	$Ca_{3.94}Sr_{6.06}(PO_4)_6F_2$
0.702	1.677	2.85	2.83	$Ca_{2.98}SR_{7.02}(PO_4)_6F_2$
0.809	1.662	2.75	2.73	$Ca_{1.91}Sr_{8.09}(PO_4)_6F_2$
0.898	1.665	2.67	2.65	$Ca_{1.02}Sr_{8.98}(PO_4)_6F_2$
1	1.666	2.61	2.56	$Sr_{10}(PO_4)_6F_2$

2.2.3. Chemical analysis

The strontium and calcium contents were determined by atomic absorption spectroscopy. Phosphorus was determined by colorimetry using the method of Gee and Deitz [13]. Experimental (Ca + Sr)/P atomic ratios of the samples were close to the stoichiometric value of 1.667 (Table 1, Column 2)

The fluorine titration was carried out potentiometrically, using a fluorine specific electrode. This titration was achieved at a pH = 5.9, obtained by adding a buffer solution of sodium citrate [14] Table 1.

If one assumes, as almost all the authors do, that cation substitution does not introduce any defects in the structural frame built up with the PO_4^{3-} anions, the number of which is six per lattice, it is possible to propose a formula for the different synthesized materials based on the results of the titration. Assuming the full occupation of fluoride-ion sites, the difference between theoretical amounts of fluorine, determined from these formulas and the experimental ones is in the (0.7–2.3)% range (Table 1, columns 2 and 3). The latter value is observed only in the case of two products.

3. Calorimetric study

3.1. The calorimeter

The apparatus was an isoperibol calorimeter. It was, previously described in detail [15,16]. Experimental procedure and results processing are detailed in the previous paper [11].

3.2. Enthalpy of dissolution

Measurements of the enthalpy of dissolution of calcium–strontium fluorapatites in 9% by weight nitric acid (HNO_3, $35.35H_2O$) were carried out in the same volume of acid ($350\ cm^3$) by successively dissolving variable amounts of the solids at 298 K. The results are reported in Table 2. Fig. 1 shows the variation of standard molar enthalpy of dissolution ($\Delta_{sol}H°(298\ K)$) vs. the atomic ration Sr/(Ca + Sr).

3.3. Standard enthalpies of formation

Standard enthalpies of formation of calcium–strontium fluorapatites are determined by arranging for each of them a succession of reactions, the final balance of which represents the formation reaction of the particular product. For the apatite with general formula $Ca_{10-x}Sr_x(PO_4)_6F_2$, one can propose the following sequence:

$$\{6H_3PO_4 + (10-x)Ca(NO_3)_2 + xSr(NO_3)_2 + 2HF\}_{(sln)} \rightarrow Ca_{10-x}Sr_x(PO_4)_6F_{2(s)_{20}}\{HNO_3\}_{(sln)} \quad (I)$$

$$20(HNO_3 \cdot 35.35H_2O)_{(l)} \rightarrow 10H_{2(g)} + 10N_{2(g)} + 30O_{2(g)} + 707H_2O_{(l)} \quad (II)$$

$$9H_{2(g)} + 6P_{(s)} + 12O_{2(g)} + 4.536H_2O_{(l)} \rightarrow 6(H_3PO_4; 0.756H_2O)_{(l)} \quad (III)$$

$$6(H_3PO_4; 0.756H_2O)_{(l)} + \{sln\} \rightarrow 6(H_3PO_4; 0.756H_2O)_{(sln)} \quad (IV)$$

$$(10-x)Ca + (10-x)N_2 + 5(10-x)O_2 + 4(10-x)H_2 \rightarrow (10-x)(Ca(NO_3)_2 + 4(10-x)H_2O)_{(s)} \quad (V)$$

$$(10-x)Ca(NO_3)_2 \cdot 4H_2O)_{(s)} + \{sln\} \rightarrow \{(10-x)(Ca(NO_3)_2 + 4(10-x)H_2O)\}_{(sln)} \quad (VI)$$

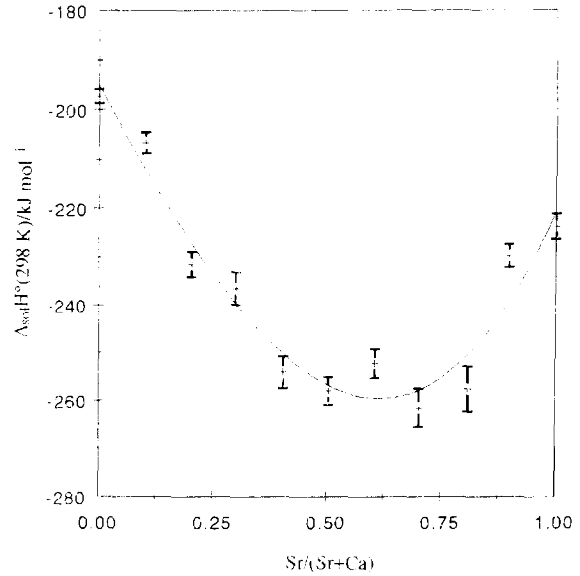

Fig. 1. Standard enthalpy of dissolution of calcium–strontium fluorapatites in the nitric acid 9% vs. the atomic ratio Sr/(Sr + Ca).

Table 2
Enthalpies of solution at 298 K of calcium–strontium fluorapatites in HNO_3, $35.35H_2O$

Experiment No.	m/g	$\varepsilon/(\mathrm{J\ mm^{-1}})$ [a]	D/mm [b]	$-\Delta_{sol}H/\mathrm{J}$	Error/J
1	0.10384	0.31550	65.5	20.665	0.203
2	0.11130	0.31406	69.0	21.670	0.346
3	0.14501	0.30549	90.5	27.647	0.343
4	0.15239	0.33288	87.5	29.127	0.488
5	0.19138	0.32924	110.5	36.381	0.461
6	0.25563	0.33289	147.0	48.935	0.581
7	0.16140	0.32649	98.5	32.159	0.228
$\langle\Delta_{sol}H^\circ(Ca_{8.97}Sr_{1.03}(PO_4)_6F_2)\rangle = (-206.6 \pm 1.2)\,\mathrm{kJ\,mol^{-1}}$					
1	0.11080	0.32947	69.0	22.733	0.199
2	0.12465	0.31124	89.0	27.700	0.302
3	0.15964	0.3074	112.0	34.429	0.478
4	0.15547	0.30855	111.0	34.429	0.652
5	0.09340	0.30977	67.0	34.249	0.244
6	0.09964	0.31436	64.0	20.755	0.222
7	0.09760	0.31263	60.0	18.758	0.257
$\langle\Delta_{sol}H^\circ(Ca_{7.97}Sr_{2.03}(PO_4)_6F_2)\rangle = (-231.5 \pm 2.6)\mathrm{kJ\,mol^{-1}}$					
2	0.11339	0.31999	68.0	21.759	0.483
4	0.10130	0.32939	62.0	20.422	0.496
5	0.13838	0.32311	84.0	27.141	0.347
6	0.16479	0.32085	104.5	33.528	0.297
7	0.14417	0.32964	98.5	32.470	0.361
8	0.10130	0.32939	62.0	20.422	0.496
$\langle\Delta_{sol}\mathrm{H}^\circ(Ca_{7.00}Sr_{3.00}(PO_4)_6F_2)\rangle = (-236.5 \pm 3.4)\,\mathrm{kJ\,mol^{-1}}$					
1	0.05702	0.30250	39.5	11.949	0.138
3	0.6889	0.29743	51.0	15.169	0.272
4	0.09642	0.30380	66.0	20.051	0.158
5	0.13059	0.31225	92.5	28.883	1.124
6	0.14900	0.28623	111.5	31.915	0.989
7	0.12208	0.30295	87.0	26.357	0.387
8	0.18600	0.29695	138.5	41.128	0.838
$\langle\Delta_{sol}H^\circ(Ca_{5.95}Sr_{4.05}(PO_4)_6F_2)\rangle = (-254.1 \pm 3.3)\,\mathrm{kJ\,mol^{-1}}$					
1	0.12713	0.31739	82.5	26.185	0.232
2	0.11874	0.31420	79.0	24.821	0.471
4	0.18466	0.31364	122.0	38.264	0.303
5	0.19167	0.31979	127.5	40.773	0.507
6	0.17349	0.30982	113.0	35.009	0.639
7	0.11084	0.31454	71.0	22.332	0.388
8	0.15159	0.31411	98.0	30.782	0.593
$\langle\Delta_{sol}H^\circ(Ca_{4.96}Sr_{5.04}(PO_4)_6F_2)\rangle = (-258.1 \pm 2.9)\,\mathrm{kJ\,mol^{-1}}$					
1	0.07248	0.31239	43.5	13.589	0.125
2	0.12727	0.32031	78.5	25.144	0.516
5	0.10828	0.30214	68.0	20.545	0.528
6	0.13916	0.30181	89.0	26.861	0.621
7	0.09876	0.31132	60.5	18.835	0.340
8	0.15726	0.31725	98.5	31.249	0.192

Table 2
(Continued)

$\langle \Delta_{sol}H^\circ(\mathrm{Ca_{3.94}Sr_{6.06}(PO_4)_6F_2})\rangle = (-252.3 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}$					
1	0.21908	0.31073	143.0	44.434	0.769
2	0.17785	0.32194	113.5	36.540	0.689
3	0.1909	0.31762	115.5	36.685	0.344
4	0.19305	0.31744	121.5	38.569	0.516
6	0.20164	0.30987	129.0	39.973	0.539
$\langle \Delta_{sol}H^\circ(\mathrm{Ca_{2.98}Sr_{7.02}(PO_4)_6F_2})\rangle = (-261.5 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}$					
2	0.13762	0.30755	82.5	25.37	0.491
3	0.16154	0.30805	96.0	29.573	0.523
4	0.14995	0.30935	90.0	27.842	0.761
5	0.19521	0.30800	119.5	36.806	0.884
6	0.21066	0.31225	125.0	39.031	1.231
7	0.21379	0.31340	126.0	39.488	0.895
$\langle \Delta_{sol}H^\circ(\mathrm{Ca_{1.91}Sr_{8.09}(PO_4)_6F_2})\rangle = (-257.6 \pm 4.7)\,\mathrm{kJ\,mol^{-1}}$					
1	0.12576	0.31957	63.0	20.133	0.150
2	0.13845	0.31903	70.0	22.332	0.210
5	0.15047	0.26896	80.0	21.517	1.150
6	0.18992	0.32075	96.5	30.952	0.569
7	0.19967	0.31157	99.0	30.845	0.388
8	0.20634	0.31797	108.0	34.341	1.062
9	0.14978	0.31839	75.5	24.038	0.196
$\langle \Delta_{sol}H^\circ(\mathrm{Ca_{1.02}Sr_{8.98}(PO_4)_6F_2})\rangle = (-229.7 \pm 2.4)\,\mathrm{kJ\,mol^{-1}}$					
1	0.11762	0.30364	60.0	18.218	0.426
2	0.15263	0.30267	75.0	22.700	0.397
3	0.20153	0.30576	98.0	29.965	0.444
4	0.17508	0.31183	80.0	24.947	0.224
7	0.2620.	0.29941	137.0	41.019	0.302
8	0.23058	0.30717	116.5	35.785	0.437
$\langle \Delta_{sol}H^\circ\mathrm{Sr_{10}(PO_4)_6F_2})\rangle = (-223.7 \pm 2.6)\,\mathrm{kJ\,mol^{-1}}$					

[a] ε is the mean calibration constant.
[b] D is the shift recorded between the base lines.

$$x\mathrm{Sr_{(s)}} + x\mathrm{N_{2(g)}} + 3x\mathrm{O_{2(g)}} \rightarrow x\mathrm{Sr(NO_3)_{2(s)}} \qquad \text{(VII)}$$

$$x\mathrm{Sr(NO_3)_{2(s)}} + \{\mathrm{sln}\} \rightarrow x\{\mathrm{Sr(NO_3)_2}\}_{(\mathrm{sln})} \qquad \text{(VIII)}$$

$$4(10-x)\mathrm{H_2O(l)} \rightarrow 4(10-x)\mathrm{H_{2(g)}} + 2(10-x)\mathrm{O_{2(g)}} \qquad \text{(IX)}$$

$$\mathrm{H_{2(g)}} + \mathrm{F_{2(g)}} + 3.416\mathrm{H_2O_{(l)}} \rightarrow 2(\mathrm{HF};1.708\mathrm{H_2O})_{(l)} \qquad \text{(X)}$$

$$2(\mathrm{HF}\cdot 1.708\mathrm{H_2O})_{(l)} + \{\mathrm{sln}\} \rightarrow \{2\mathrm{HF} + 3.416\mathrm{H_2O}\}_{(\mathrm{sln})} \qquad \text{(XI)}$$

$$\{(4(10-x)+7.952)\mathrm{H_2O}\}_{(\mathrm{sln})} \rightarrow (4(10-x)+7.952)\mathrm{H_2O_{(l)}} + \{\mathrm{sln}\} \qquad \text{(XII)}$$

$$(10-x)\mathrm{Ca_{(s)}} + x\mathrm{Sr_{(s)}} + 6\mathrm{P_{(s)}} + 12\mathrm{O_{2(g)}} + \mathrm{F_{2(g)}} \rightarrow \mathrm{Ca_{10-x}Sr_x(PO_4)_6F_{2(s)}}$$

In addition to the dissolution reaction mentioned (step I), it can be noted that this succession of reactions consists in various steps; some of them are dissolution or dilution reactions (steps IV, VI, VIII, XI, XII). Their corresponding enthalpies were measured according to the experimental procedure previously described and the results are shown in Table 3. The other steps are the formation reactions of well-known compounds.

Their corresponding enthalpies are picked from literature (Table 3).

Standard enthalpies for calcium–strontium fluorapatites are shown in Table 4. Those corresponding to the limiting apatites, $Ca_{10}(PO_4)_6F_2$ and $Sr_{10}(PO_4)_6F_2$, have been taken from Ref. [10]. Fig. 2 shows the variation of standard enthalpy of formation $\Delta_f H^\circ(298\ K)$ vs. the strontium content Sr/Ca + Sr).

3.4. *Enthalpy of mixing*

Enthalpy of mixing of the limit products was determined by combining the solution enthalpies of solid solutions and those of the limiting products, according to the expression:

$$\Delta_m H^\circ = (1-X)\Delta_{sol}H^\circ(F_{ap}Ca) + X\Delta_{sol}H^\circ(F_{ap}Sr) - \Delta_{sol}H^\circ(F_{ap}Ca_{10-x}Sr_x)$$

where $X = S_x/(Sr + Ca)$

The values obtained are reported in Table 4, whereas Fig. 3 shows the variation of the mixing enthalpy $\Delta_m H$ vs. the strontium content X.

4. Discussion

One can notice that all of the curves do not show a monotonous variation in the entire composition range. A change in the pattern is observed at a composition close to 0.6 for the curves in Figs. 1 and 3 and between 0.5 and 0.6 in Fig. 2. This change is probably related to the occupancy of the nonequivalent cation position in the apatitic structure. There are two different kinds of sites in that structure: the first one Me(I), containing six sites, is located in the tunnels, the diameter of which is ca. 0.2 nm, and the second Me(II) generated by other tunnels having a diameter greater than the previous one (0.30 to 0.35 nm). They contain six sites per lattice.

Table 3
Enthalpies of the complementary reactions at 298 K

	$\Delta_{sol}H^\circ(298\,K)$/ kJ mol^{-1}	Ref.	$\Delta_f H^\circ(298\,K)$/ kJ mol^{-1}	Ref.
$HNO_3 \cdot 35.35H_2O$	0	—	−206.8	[17]
$H_3PO_4 \cdot 0.756H_2O$	−7.87±0.04	[20]	−1271.8	[17]
H_2O	0	[20]	−258.8	[18,19]
$Ca(NO_3)_2 \cdot 4H_2O$	33.3±0.2	[20]	−2132.3	[18,19]
$Sr(NO_3)_2$	13.9±0.2	[10,11]	−978.2	[18,19]
$HF \cdot 1.708H_2O$	−4.52±0.04	[20]	−316.9	[17]

Table 4
Solution, formation and mixing enthalpies of Ca–Sr fluorapatites at 298 K

	$\Delta_{sol}H^\circ(298\,K)$/ kJ mol^{-1}	$\Delta_f H^\circ(298\,K)$/ kJ mol^{-1}	$\Delta_m H^\circ(298\,K)$/ kJ mol^{-1}
$Ca_{10}(PO_4)_6F_2$	−197.3 ± 1.2	−13545	0
$Ca_{8.97}Sr_{1.03}(PO_4)_6F_2$	−206.6 ± 2.1	−13545	6.6 ± 2.4
$Ca_{7.97}Sr_{2.03}(PO_4)_6F_2$	−231.5 ± 2.6	−13529	28.9 ± 2.8
$Ca_7Sr_3(PO_4)_6F_2$	−236.5 ± 3.4	−13532	31.3 ± 3.5
$Ca_{5.95}Sr_{4.05}(PO_4)_6F_2$	−254.1 ± 3.3	−13523	46.1 ± 3.5
$Ca_{4.96}Sr_{5.04}(PO_4)_6F_2$	−258.0 ± 2.9	−13528	47.4 ± 32
$Ca_{3.94}Sr_{6.06}(PO_4)_6F_2$	−252.3 ± 3.0	−13542	39.0 ± 3.3
$Ca_{2.98}Sr_{7.02}(PO_4)_6F_2$	−261.5 ± 4.0	−13541	45.7 ± 4.3
$Ca_{1.91}Sr_{8.09}(PO_4)_6F_2$	−257.6 ± 4.7	−13554	38.9 ± 5.0
$Ca_{1.02}Sr_{8.98}(PO_4)_6F_2$	−229.7 ± 2.4	−13590	8.7 ± 3.1
$Ca_{10}(PO_4)_6F_2$	−223.7 ± 2.6	−13604	0

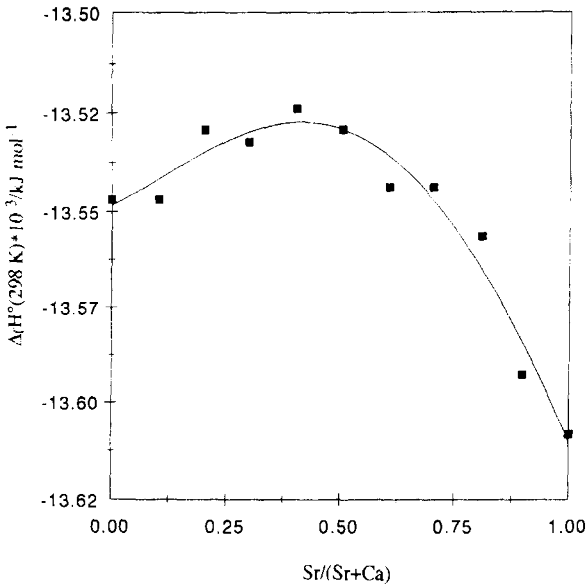

Fig. 2. Standard enthalpy of formation of calcium–strontium fluorapatites vs. the atomic ratios Sr/(Sr + Ca).

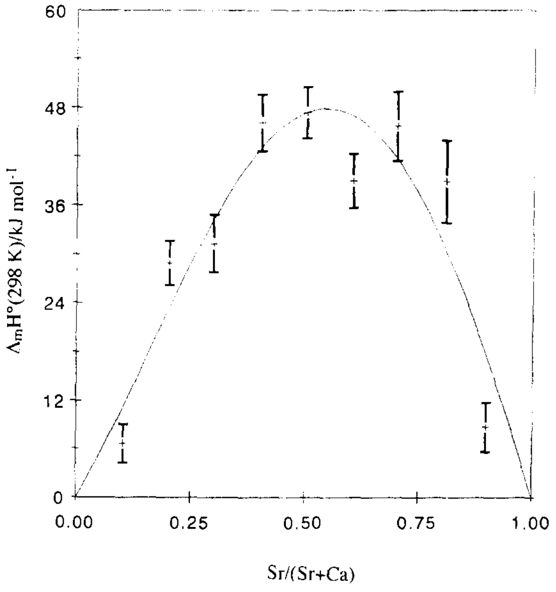

Fig. 3. Enthalpy of mixing vs. the atomic ratio Sr/(Sr + Ca).

Considering the ionic radii of the metals, 0.099 nm for Ca and 0.116 nm for Sr, and the average diameters of the two cation sites, it is likely that the substitution of Ca by Sr is oriented, preferably taking into account the steric effect. Heijligers [5] and Khudolozhkin [6] works on hydroxyapatites showed that strontium substitutes for calcium, preferably in the larger sites.

On the other hand, powder X-ray diffraction shows that substitution of Ca by Sr results in a linear variation of the lattice parameters. That technique does not seem to show the difference between occupancy of metallic sites, whereas thermochemical results do. It seems that substitution of calcium by strontium and, in particular, the selective occupation by Sr affects enthalpy bonds much more than the geometry of the lattice.

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