



Synthesis, structural analysis and thermochemistry of B-type carbonate apatites

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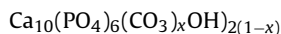
ABSTRACT

A series of B-type carbonate apatites have been prepared by the “direct” method and their structural properties investigated. The standard molar enthalpy of formation have been determined from enthalpy of solution measured by calorimetric technique. Statistical treatment of thermochemical results shows that the most probable substitutions in this kind of products are couple substitutions (CO_3 , OH) for PO_4 and (2CO_3 , V^{Ca}) for 2PO_4 .

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Apatites constitute a family of compounds having similar structure and different compositions. Apatite structure allows various substitutions without significant changes in symmetry. Generally the substitutions are accompanied by changes in the lattice parameters and chemical properties [1–5]. The presence of carbonate in the lattice affects the size and shape of the apatite crystal and causes a weakening of the bonds in the apatite structure. This leads to an increase of chemical reactivity particularly by increasing the solubility product and the rate of dissolution in acids and by reducing the thermal stability [5]. Chemical analysis, X-ray diffraction, Raman and IR-absorption performed on biological apatite and carbonate mineral apatites [6–8,10] showed two kinds of carbonate bearing apatites:

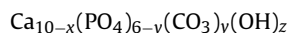
a/- “A” type carbonate apatites in which OH^- or F^- are replaced by CO_3^{2-} . Carbonate ions are centred on the helicoidal senary axis of the network along the tunnels. This substitution was obtained by a solid gas reaction at high temperature, 900°C , under CO_2 flow gas in very dry conditions [8–9]. The IR spectrum shows bands around 1542 , 1465 and 867 cm^{-1} assigned to CO_3^{2-} in OH^- sites. On the basis of these results, the solid composition fitted the general formula:



with $0 < x < 1$

b/- “B” type carbonate apatites in which the carbonate ions are substituting the PO_4^{3-} . These compounds are easily prepared by precipitating the solids in the presence of CO_3^{2-} or HCO_3^- ions. B-type carbonate apatites can be obtained by pouring a calcium solution in an ammonium phosphate and carbonate solution. This method is called the “direct” one, in opposition to the “reverse” one in which precipitation of the solid occurs in the calcium medium [8,11]. Both “direct” and “reverse” B- CO_3 apatites have ν_3 and ν_2 absorption bands usually interpreted as showing the presence of CO_3^{2-} ions in two environments, without bands attributable to A-type substitution. Table 1 summarizes the different νCO_3^{2-} positions around which IR bands have been observed in B-type carbonate apatites and in enamel [3].

The XRD patterns show that the structure of “B” type hydroxyphosphocalcium carbonate apatites is isomorphous of the hydroxyapatite. The normal apatite structure is hexagonal, with space group $P6_3/m$. The unit cell contents of “direct” and “reverse” B-type CO_3 apatites dried at approximately 400°C were determined experimentally from density measurements, lattice parameters and chemical analysis [9,10,12]. The study of the physico-chemical properties of the carbonate apatites, as well as quantitative analysis has allowed Labarthe et al. [12] to suggest a structural model, assuming all the PO_4^{3-} sites are filled. This first structural formula was:



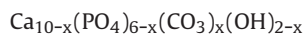
where x and y are independent variables and $0 \leq z \leq 2$. The electroneutrality requires for $z = 2 + y - 2x$, and so $0 \leq 2 + y - 2x \leq 2$.

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Table 1
Assignments of IR ν_3 and ν_2 CO_3 bands in precipitated CO_3 apatites [3].

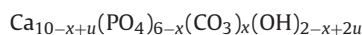
Frequency cm^{-1}	Assignment
1470	$\nu_3(\text{CO}_3^{2-} + \square)$
1460	$\nu_3(\text{CO}_3^{2-}, \text{X}^-)\text{X}^- = \text{F}^- \text{ or } \text{OH}^-$
1420	$\nu_3(\text{CO}_3^{2-} + \square)$ and $(\text{CO}_3^{2-} + \text{X}^-)$
873	$\nu_2\text{CO}_3$ to a labile environment

Then, these authors have shown that for every negative charge lost when a CO_3^{2-} ion replaces a PO_4^{3-} one, another negative charge is lost by the departure of an OH^- ion. The loss of supplementary two negative charges is compensated by the loss of two positive charges through the formation of a calcium site vacancy. This gave the following formula:



With $0 \leq x \leq 2$

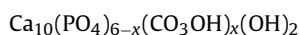
However, to explain the often found excess of Ca^{2+} and OH^- determined by chemical analyses, it has been admitted that some of the OH^- and Ca^{2+} ions vacancies are filled by adding “ u ” $\text{Ca}(\text{OH})_2$ per unit cell. The resulting composition fitted the general formula:



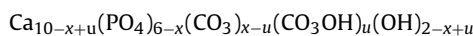
With $0 \leq x \leq 2$ and $0 \leq u \leq x/2$

Consequently, physicochemical studies, especially by E.S.R. [10,13] and thermogravimetric with simultaneous gas chromatography analyses [14,15] suggested two modes for CO_3^{2-} ions replacing PO_4^{3-} ones. These are:

- (i) $(\text{CO}_3^{2-}, \text{X}^-)$ ion pairs replacing PO_4^{3-} . In accordance with this type of substitution, Vignoles et al. [13] proposed the structural formula as:

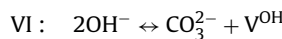
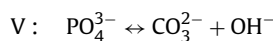
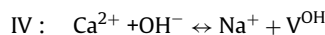
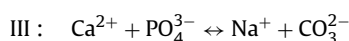
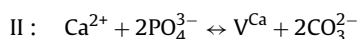
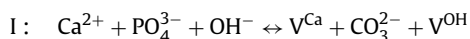


- (ii) CO_3^{2-} ions replacing PO_4^{3-} with the formation of adjacent OH^- and Ca^{2+} ion vacancies ($\text{CO}_3 + \square$). This mechanism is analogous to the earlier proposal suggested by Labarthe et al. [12]. One or the other mechanism of substitution is preponderant depending on the ion concentration in precipitation medium, “direct” or “reverse” method [13–15] and so the general formula suggested for “B” type carbonate apatites [13] is:



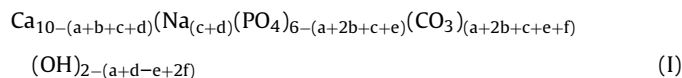
In which there are u ($\text{CO}_3^{2-}, \text{OH}^-$) ion pairs per unit cell. “ u ” value varies according to the nature and the concentration of the ions present in the precipitation solution.

In 1993 De Maeyer and Verbeeck [16] suggested that the substitution of the lattice ions will be restricted to mechanisms which are energetically acceptable and so substitutions which destabilize considerably the hexagonal crystal lattice can be rejected. For electrostatic reasons, it is obvious that each lattice cation (or anion) can only be substituted by other cations (or anions). These authors showed that in the Na bearing carbonate apatites, CO_3^{2-} can be incorporated into the lattice by combining the six fundamental substitution mechanisms, which are as follows:

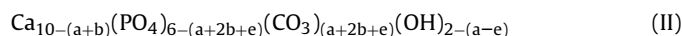


The latter one corresponding to substitution of hydroxyl for carbonate (A-type apatite).

Let a, b, c, d, e and f the contributions of mechanisms I–VI in the composition of the unit cell respectively, the carbonate apatite can be described by the general formula as:



Contribution of each of these mechanisms could be estimated taking into account the chemical as well as the physical analysis of the samples. These authors showed that the various formulas proposed in the literature [12–13] derive from the general one. In Na-free B-type carbonate apatites, only mechanisms I, II, V have to be considered and the general formula is:



The present work deals with the calorimetric aspect of dissolution of Na free B-type carbonate hydroxyapatites leading to their enthalpies of formation. The results are processed statistically in order to determine the most probable general formula for these compounds.

1. Synthesis

A series of “B” type carbonate hydroxyapatites were prepared by the “direct” method [10,14] which consists in adding drop by drop, during 3 hours, 900 cm^3 of a solution of calcium nitrate 0.03 mol L^{-1} into 2250 cm^3 of a hot solution containing diammonium phosphate 0.008 mol L^{-1} and variable quantities of ammonium carbonate so as the ionic ratio in the initial solutions $[\text{CO}_3^{2-}]/[\text{PO}_4^{3-}]$ lies in the range 1–40. It was shown that outside this interval the apatite is poorly crystallized and mixed with calcite [10,11]. The temperature is maintained at 80°C and the pH near 9.5 by addition of ammonia concentrated solution (28% weight) during the precipitation. The precipitate obtained is washed and filtered then oven-dried at 70°C during one night. Samples are subjected to dehydration at 400°C before analysis.

2. Characterisation

2.1. Infrared spectroscopy and X-ray diffraction

Infrared absorption spectra were made on a Shimadzu IR spectrometer in the range $4000\text{--}400 \text{ cm}^{-1}$. Absorption pellets were prepared using the usual KBr disk technique. Infra-Red profiles, Fig. 1, showed bands at 872, 1415 and 1450 cm^{-1} characterizing carbonate substituting the phosphate. A weak band at 2340 cm^{-1} was assigned to CO_2 accumulated on the crystals [3,11]. However discrepancies in bands frequencies from values in Table 1 are observed. They could be attributed to differences in precipitation medium or thermal evolution.

The samples were identified by X-ray diffraction using X-ray diffractometer MRD with a generator (40 kV and 40 mA). The scanning speed is $0.04^\circ 2\theta/\text{s}$. The calculated patterns have been scaled so that the intensity of the maximum peak is 100%. X-ray diffraction patterns of substituted apatites, Fig. 2, show well-crystallized one-phase apatite specimens.

The structure was refined by a cell parameter refinement program “ERACEL”, Table 2. “ a ” values as a function of wt% carbonate

- 1- 0.53 CO₃ ion per unit cell.
- 2- 1.06 CO₃ ion per unit cell.
- 3- 1.58 CO₃ ion per unit cell.

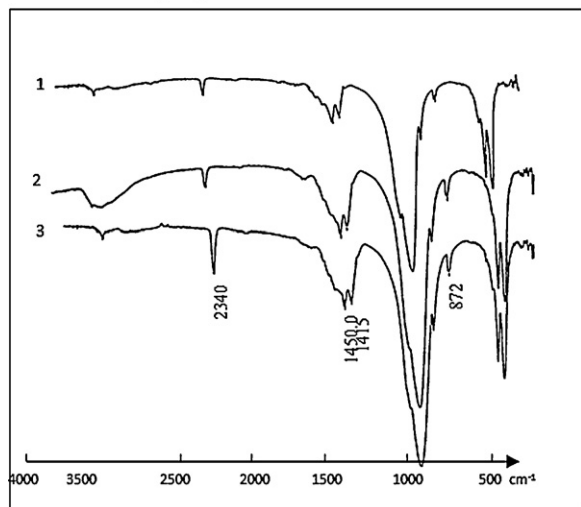


Fig. 1. Infrared spectrum of three samples B-type CO₃ apatites.

- 1- 0.53 CO₃ ion per unit cell.
- 2- 1.06 CO₃ ion per unit cell
- 3- 1.58 CO₃ ion per unit cell

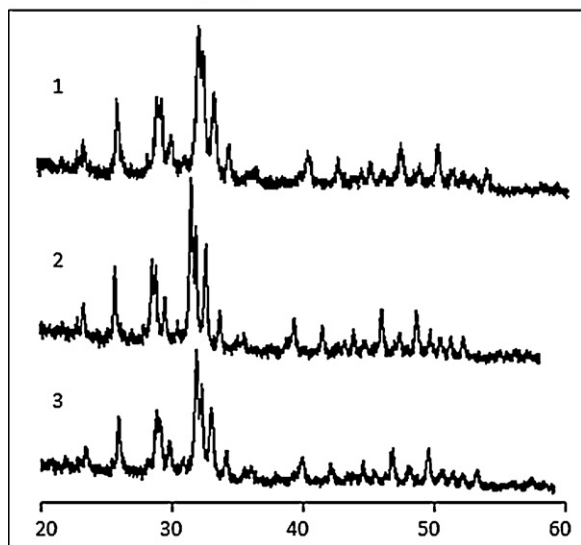


Fig. 2. X-ray diffractin patterns of three samples of B-type CO₃ apatites.

Table 2
Lattice parameters “a” and “c” and volume of unit cell.

Sample	(a ± 0.0070)/Å	c ± 0.005/Å	v/Å ³
1	9.4264	6.8963	530.69
2	9.4197	6.9004	530.24
3	9.4215	6.9001	530.43
4	9.4150	6.8794	528.46
5	9.3995	6.8830	526.64
6	9.3975	6.8856	529.07
7	9.4038	6.8891	527.67
8	9.3812	6.8770	524.20
9	9.3601	6.8780	526.03
10	9.3590	6.879	523.83

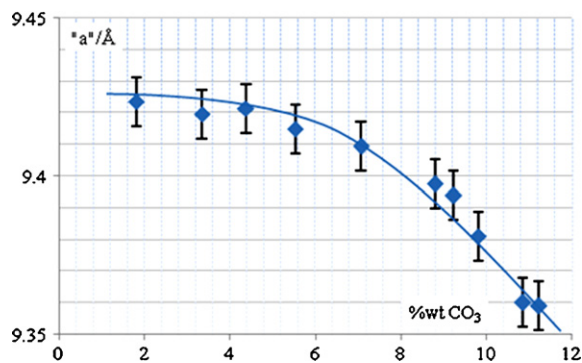


Fig. 3. Effect of CO₃ content on the crystallographic.

content, Fig. 3, showed that at lower CO₃²⁻ concentration (<4% weight), the a axis is almost independent on CO₃²⁻ content, then increasing the CO₃²⁻ content leads to a contraction of the a-axis.

These results are in agreement with that obtained on samples prepared in the same conditions [8,10]. These authors suggested that at low CO₃²⁻ concentration, NH₄⁺ ions contribute to the crystallographic parameters in B carbonate apatite structure. The presence of a few amount of ammonium ion has been confirmed by Khattech and Jemal. [14] by simultaneous thermogravimetry and escaping gas analysis

2.2. Chemical analysis and density measurements

The dehydrated samples were subjected to a chemical analysis. CO₃²⁻ ions are titrated by coulometry, PO₄³⁻ ions by colorimetry [18], Ca²⁺ ions by compleximetry [17]. Density of the solids was determined by pycnometric measurements on liquid having the same density as the solid [19]. The results of densities and chemical composition of products in wt% are given in Table 3.

2.3. Stoichiometry and structure

Lattice volume calculated from X-Ray analysis allows to determine the molar weight (Mw) taking into account pycnometric density measurements, and so considering the percentage of calcium, carbonate and phosphate determined by chemical analysis, one can deduce the number of Ca, CO₃ and PO₄ ions in the unit cell of the apatite. The amount of OH ions was calculated taking into account the electroneutrality of each compound. Table 4 gathers the calculation results.

3. Determination of the enthalpy of formation

Dissolution calorimetry leads to the standard enthalpy of dissolution of the apatites. In order to get the enthalpy of formation of any compound, it was necessary to imagine a succession of processes, the combination of which leads to the reaction of formation

Table 3
wt% Ca, wt% CO₃, wt% PO₄ and density of B-type carbonate apatites.

Sample	%Ca ± 0.09	%CO ₃ ± 0.02	%PO ₄ ± 0.05	ρ ± 0.02/g cm ⁻³
1	40.00	1.81	56.26	3.07
2	40.46	3.35	55.60	2.97
3	40.55	4.38	55.04	2.89
4	40.12	5.53	52.13	2.84
5	39.78	7.07	51.03	2.83
6	39.50	8.80	50.42	2.80
7	39.06	9.23	49.79	2.79
8	40.31	9.81	49.65	2.78
9	39.85	10.86	49.28	2.75
10	39.13	11.23	48.11	2.76

Table 4

Unit cell contents in mol and molar weight of the series of B-type carbonate apatites.

Sample	n_{Ca}	n_{CO_3}	n_{PO_4}	n_{OH}	Mw
1	9.83	0.28	5.82	1.64	982.8
2	9.60	0.53	5.55	1.49	949.1
3	9.35	0.67	5.34	1.34	922.5
4	9.06	0.83	4.95	1.61	903.0
5	8.93	1.06	4.83	1.25	898.4
6	8.82	1.31	4.74	0.80	893.5
7	8.86	1.37	4.65	1.03	888.0
8	8.76	1.44	4.59	0.87	879.0
9	8.68	1.58	4.52	0.64	871.3
10	8.51	1.63	4.41	0.53	870.2

of the product in concern. As indicated further on, some of these processes are dilution or dissolution steps and the others involve the formation of entities or compounds.

3.1. Preliminary experiment

It was previously necessary to check the performance and accuracy of the device by dissolving a well-known product in the same conditions as for the apatites. Calcium carbonate has been considered and its standard molar enthalpy of formation is deduced then compared to that of literature [21].

As for the apatites, dissolution of $CaCO_3$ was carried out in an isoperibol calorimeter which was previously described in detail [22–24]. In this device, the heat affect results in a variation of the temperature of the reactional medium, which is detected by a thermistance probe acting as one of the four arms of a Wheatstone bridge connected to a recorder through a “177 Keitley” current amplifier. Experiments consist in dissolving a variable amount of solid, m (mg) in 350 ml of a 9% weight nitric acid solution corresponding to $(HNO_3, 35.35H_2O)$, in which CO_2 gas was continuously bubbled in order to avoid the retention of CO_2 produced by the reaction. Before and after each dissolution, the calibration was carried out by joule effect using a stabilized “DC” current supplier connected to a $14\ \Omega$ electrical resistance. The magnitude of current power was measured by an A.C. power meter “GPM-8212” and the heating duration was accurately measured using a digital electronic timer with a 0.01 s resolution.

Experiment started by searching a quasi-steady state in which the electrical current is practically null and the baseline deviates slightly from the horizontal line. Injection of electrical energy in the medium results in a deviation of the signal, which then becomes parallel to the previous baseline. Calibration coefficient E is calculated by dividing the calibration energy (J) over the resulting shift d (mm) on the recorder paper. Three calibration experiments were performed, the energy resulting from the reaction was calculated from the product of the corresponding shift “ d ” by the mean calibration coefficient and the error on $\Delta_{sol}H^\circ$ was determined considering the scatter between the extreme values of E .

Various amounts of each product were dissolved in the same volume of solution and the molar dissolution enthalpy is determined using a mathematical treatment in which the statistical weight of an experimental result depends on the corresponding variance. This procedure leads to express the dissolution enthalpy as: $\Delta_{sol}H = \frac{\sum w_i m_i \Delta H_i}{\sum w_i m_i^2}$ where w_i is the reciprocal of the variance.

The theoretical basis of this calculation is detailed in references [25,26]. However, application of this formula has been preceded by a statistical treatment on results obtained by the same device [27] which has shown that the enthalpy measurements are proportional to the corresponding solid mass “ m ”.

Table 5 gathers the mean calibration coefficient E in joule per mm of the recording paper (column 2), the “ d ” shift resulting from the dissolution of an m (mg) amount of calcite (column 3) and the

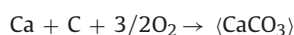
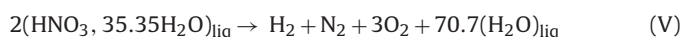
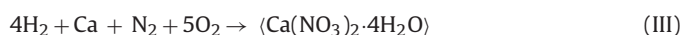
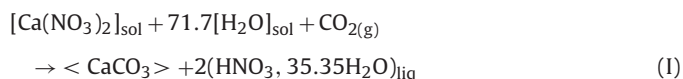
Table 5Mean calibration coefficient E , “ d ” shift, m mass and the corresponding enthalpy of dissolution and deviation for $CaCO_3$ in $(HNO_3; 35.35H_2O)$ at 298 K.

N°	$E/J\ mm^{-1}$	d/mm	m/mg	$\Delta_{sol}H^\circ/J$	$\sigma(\Delta_{sol}H)/J$
1	0.3132	22.5	29.27	-7.046	0.106
2	0.3379	32.5	32.50	-10.983	0.510
3	0.3193	35.5	48.49	-11.336	-0.142
4	0.3382	34.0	33.28	-11.499	-0.225
5	0.3412	37.5	46.50	-12.795	0.663
6	0.3411	48.0	41.82	-16.374	-0.655
7	0.3210	59.5	66.24	-19.101	-0.544
8	0.3205	73.0	81.01	-23.394	-2.256
9	0.3263	86.5	97.57	-28.223	-0.765
10	0.2988	146	155.57	-43.623	4.418

$$(\Delta_{sol}H)/(J\ g^{-1}) = -257.05 \pm 4.63.$$

corresponding dissolution enthalpies (column 5). The last column contains the error on $\Delta_{sol}H^\circ$. Considering the statistical weight of a particular $\Delta_{sol}H^\circ$ as proportional to the reverse of the square of the corresponding error led to: $(-257.05 \pm 4.63)/J\ g^{-1}$ as the dissolution enthalpy of calcite in 9% weight nitric acid solution.

Dissolution process was combined with other dissolution, dilution and formation processes in order to get the formation reaction of calcite. The following succession has been selected because of the availability of the data of the involved compounds and entities:



The subscript “sol” means “in solution”.

In this succession, step I is the reverse of the dissolution. Steps II and VI correspond to dissolution of $< Ca(NO_3)_2 \cdot 4H_2O >$ and dilution of H_2O respectively, the corresponding enthalpies were determined in the same conditions as for calcite. Steps III, IV, V and VII correspond to the formation reactions. Their enthalpies were picked from the literature [20–21]. Table 6 gathers the enthalpies of formation and dissolution of the compounds and chemical entities appearing in the reaction pathway. Combining these values leads to: $-1195.7\ kJ/mol$ for the standard formation enthalpy of calcite at 25 °C. This value differs from that of literature ($-1207.6\ kJ/mol$) [21] by about 0.8%.

3.2. Dissolution of the apatites

Measurements of the enthalpy of dissolution of the carbonated apatites in a 9% weight nitric acid solution $(HNO_3, 35.35H_2O)$ were

Table 6

Enthalpies of dissolution and formation of the chemical products and entities.

Compound	$\Delta_{sol}H^\circ/kJ\ mol^{-1}$	Ref	$\Delta fH^\circ/kJ\ mol^{-1}$	Ref
$Ca(NO_3)_2 \cdot 4H_2O$	33.3	20	-2132.3	20
$CO_{2(g)}$	-	-	-393.51	21
H_2O_{liq}	0	20	-285.83	21
$HNO_3; 35.35H_2O$	-	-	-206.8	20

Table 7
Mean calibration coefficient E , “ d ” shift, m mass and the corresponding enthalpy of dissolution and deviation for hydroxyl carbonate apatites in (HNO_3 ; $35.35\text{H}_2\text{O}$) at 298 K.

	$E/\text{J mm}^{-1}$	d/mm	m/mg	$\langle_{\text{sol}}H/\text{J}\rangle$	$\sigma_{\langle_{\text{sol}}H/\text{J}\rangle}$
$\text{Ca}_{9.83}(\text{PO}_4)_{5.82}(\text{CO}_3)_{0.28}(\text{OH})_{1.64}$					
1	0.443	40.5	50.9	-17.941	-0.567
2	0.361	60.0	57.9	-21.700	-0.390
3	0.432	54.5	60.7	-23.544	-1.471
4	0.438	60.0	66.4	-26.360	0.060
5	0.369	91.0	83.90	-33.579	0.273
6	0.368	100.0	92.7	-36.800	-0.350
7	0.360	104.0	95.0	-37.475	-0.988
8	0.368	112.0	102.0	-41.179	0.840
$\langle_{\text{sol}}H/\text{J g}^{-1}\rangle = -394.5 \pm 4.99$					
$\text{Ca}_{9.60}(\text{PO}_4)_{5.55}(\text{CO}_3)_{0.53}(\text{OH})_{1.49}$					
1	0.347	41.0	23.36	-14.246	1.896
2	0.331	48.5	26.45	-16.060	-0.337
3	0.318	56.5	40.78	-17.972	0.979
4	0.324	58.0	45.26	-18.823	0.519
5	0.342	62.0	49.36	-21.219	-0.393
6	0.307	73.5	56.97	-22.571	0.361
7	0.338	73.0	60.92	-24.696	-0.396
8	0.345	86.0	69.44	-29.675	-0.889
9	0.326	99.0	79.34	-32.318	0.267
10	0.342	130.0	107.12	-44.451	0.757
$\langle_{\text{sol}}H/\text{J g}^{-1}\rangle = -416.1 \pm 5.8$					
$\text{Ca}_{9.35}(\text{PO}_4)_{5.34}(\text{CO}_3)_{0.67}(\text{OH})_{1.34}$					
1	0.315	29.5	21.24	-9.299	-0.671
2	0.337	36.5	28.35	-12.313	0.085
3	0.335	46.0	31.60	-15.436	-0.631
4	0.331	58.0	46.00	-19.205	-0.252
5	0.328	77.0	61.00	-25.289	0.734
6	0.334	80.0	62.96	-26.745	0.907
7	0.334	92.5	74.04	-30.878	0.495
8	0.331	139.5	104.7	-46.222	0.495
$\langle_{\text{sol}}H/\text{J g}^{-1}\rangle = -429.3 \pm 5.5$					
$\text{Ca}_{9.06}(\text{PO}_4)_{4.95}(\text{CO}_3)_{0.83}(\text{OH})_{1.61}$					
1	0.321	21.0	13.63	-6.75	-0.013
2	0.323	31.0	24.95	-10.00	0.141
3	0.321	38.0	28.31	-12.18	-0.089
4	0.319	44.5	34.36	-14.19	0.229
5	0.324	46.5	39.09	-15.07	0.371
6	0.325	62.0	44.77	-20.13	0.223
7	0.306	64.5	53.29	-19.74	-1.260
$\langle_{\text{sol}}H/\text{J g}^{-1}\rangle = -483.30 \pm 2.15$					
$\text{Ca}_{8.93}(\text{PO}_4)_{4.83}(\text{CO}_3)_{1.06}(\text{OH})_{1.25}$					
1	0.324	25.5	15.74	-8.257	0.104
2	0.325	31.5	22.20	-10.231	-0.102
3	0.327	36	25.44	-11.776	0.095
4	0.327	43.5	30.38	-14.236	0.141
5	0.327	51.5	35.70	-16.839	0.281
6	0.328	57.5	39.65	-18.864	0.178
7	0.327	64.5	45.80	-21.110	0.423
8	0.331	68.5	49.06	-22.685	-0.133
9	0.346	79.5	55.96	-27.547	-0.457
$\langle_{\text{sol}}H/\text{J g}^{-1}\rangle = -469.4 \pm 3.7$					
$\text{Ca}_{8.82}(\text{PO}_4)_{4.74}(\text{CO}_3)_{1.31}(\text{OH})_{0.80}$					
1	0.323	31.5	24.59	-10.17	0.247
2	0.323	43.0	32.07	-13.91	0.865
3	0.320	51.0	34.67	-16.34	-0.199
4	0.306	56.0	44.82	-17.13	-1.761
5	0.317	54.5	40.09	-17.25	-0.199
6	0.323	68.5	51.25	-22.12	-0.142
7	0.322	78	56.27	-25.13	-0.116
8	0.328	82.0	61.88	-26.87	0.267
9	0.325	83.5	60.51	-27.16	-0.111
10	0.318	98	72.06	-31.14	-0.376
$\langle_{\text{sol}}H/\text{J g}^{-1}\rangle = -436.0 \pm 3.7$					
$\text{Ca}_{8.86}(\text{PO}_4)_{4.65}(\text{CO}_3)_{1.37}(\text{OH})_{1.03}$					
1	0.326	21.5	14.20	-7.014	0.202
2	0.335	30.5	20.36	-10.212	-0.133
3	0.335	34.5	23.54	-11.544	0.093
4	0.338	42.0	29.03	-14.214	0.254
5	0.339	45.0	32.48	-15.274	-0.569
6	0.340	52.5	37.61	-17.840	-0.155

Table 7 (Continued)

	$E/\text{J mm}^{-1}$	d/mm	m/mg	$(\text{sol}H)/\text{J}$	$\sigma(\text{sol}H)/\text{J}$
7	0.332	54.0	42.52	-17.926	-0.283
8	0.328	64.5	48.85	-21.160	-0.313
$((\text{sol}H)/(\text{J g}^{-1})) = -473.2 \pm 5.1$					
$\text{Ca}_{8.76}(\text{PO}_4)_{4.59}(\text{CO}_3)_{1.44}(\text{OH})_{0.87}$					
1	0.324	19.5	13.79	-6.33	0.128
2	0.321	32.5	20.34	-10.43	-0.444
3	0.318	37.5	25.07	-11.93	0.588
4	0.316	46.5	32.90	-14.69	0.516
5	0.322	48.5	34.83	-15.61	-0.507
6	0.317	57.5	39.65	-18.25	0.520
7	0.325	61.0	44.42	-19.86	-0.614
8	0.320	72.0	52.90	-22.53	-0.972
$((\text{sol}H)/(\text{J g}^{-1})) = -456.1 \pm 12.1$					
$\text{Ca}_{8.68}(\text{PO}_4)_{4.52}(\text{CO}_3)_{1.58}(\text{OH})_{0.64}$					
1	0.325	25.0	17.55	-8.12	-0.260
2	0.335	28.0	21.08	-9.38	-0.056
3	0.329	35.5	27.32	-11.67	-0.374
4	0.325	41.0	30.95	-13.35	0.312
5	0.328	48.5	35.45	-15.91	-0.335
6	0.338	49.0	37.78	-16.54	-0.884
7	0.328	55.5	41.43	-18.21	0.068
8	0.335	59.5	44.72	-19.92	-0.335
9	0.329	63.5	51.12	-20.91	-1.032
$((\text{sol}H)/(\text{J g}^{-1})) = -(-444.7 \pm 3.0)$					
$\text{Ca}_{8.51}(\text{PO}_4)_{4.41}(\text{CO}_3)_{1.63}(\text{OH})_{0.53}$					
1	0.308	33.5	22.41	-10.33	-0.100
2	0.310	55.0	37.84	-17.07	-0.303
3	0.311	56.5	38.46	-17.60	0.763
4	0.319	60.0	41.48	-19.16	-0.03
5	0.308	68.0	47.16	-20.98	-0.374
6	0.323	81.0	58.21	-26.19	0.324
7	0.306	96.0	64.07	-29.38	0.144
8	0.315	127.5	87.85	-40.20	0.382
$((\text{sol}H)/(\text{J g}^{-1})) = -461.1 \pm 1.6$					

performed in the same conditions as for calcite and the results are gathered in Table 7.

The variation of the standard enthalpy of dissolution of the apatites as a function of the number of moles of CO_3 ions, $n \text{ CO}_3$, Fig. 4, shows two domains with a shift at about 0.9 carbonate per unit cell, confirming the occurrence of two carbonate incorporation processes.

4. Standard enthalpies of formation

Let us consider the general formula of the B-type carbonate compounds as: $\text{Ca}_{10-a-b}(\text{PO}_4)_{6-a-2b-e}(\text{CO}_3)_{a+2b+e}(\text{OH})_{2-a+e}$ (II)

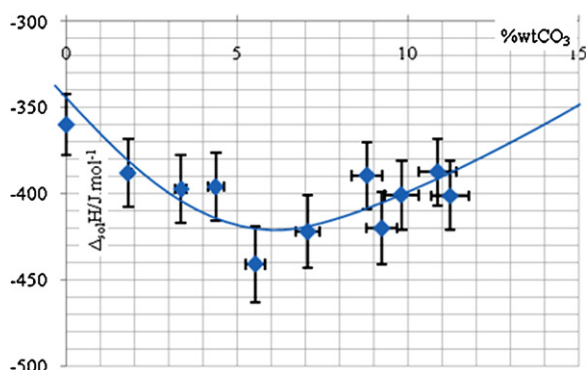


Fig. 4. Standard enthalpy of dissolution of carbonate apatites versus the number of carbonate in the lattice. ⁴Value for non-carbonated apatite in taken from Ref. [28].

The standard enthalpies of formation of these compounds can be determined considering the following succession of reactions.

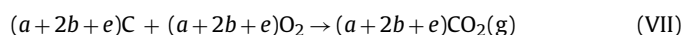
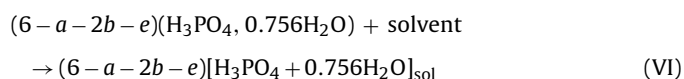
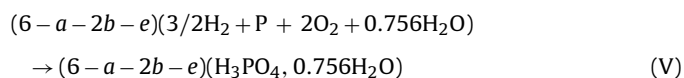
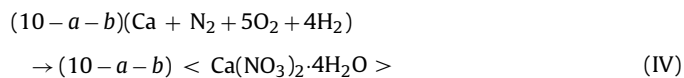
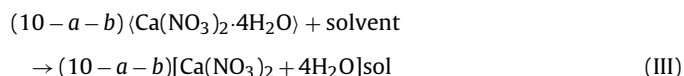
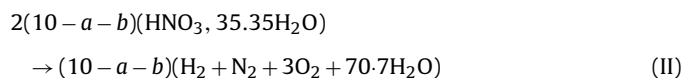
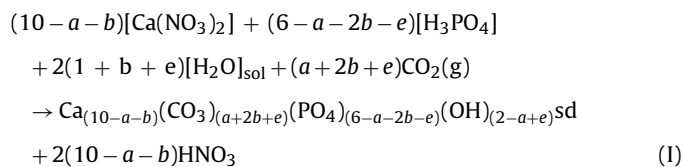
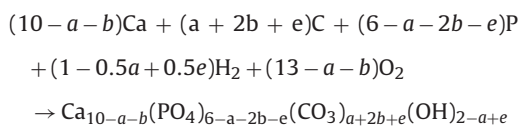
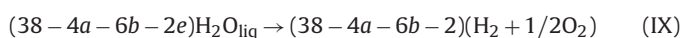
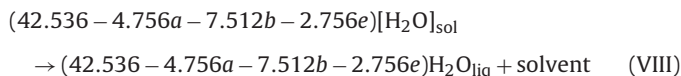


Table 8
Molar enthalpies of solution and formation for the apatites.

Sample	$\Delta_{\text{sol}}H$ (kJ/mol)	$\Delta_f H$ in kJ/mol
Ca _{9.83} (PO ₄) _{5.82} (CO ₃) _{0.28} (OH) _{1.64}	-387.76	-13133.3
Ca _{9.60} (PO ₄) _{5.55} (CO ₃) _{0.53} (OH) _{1.49}	-397.44	-12763.3
Ca _{9.35} (PO ₄) _{5.34} (CO ₃) _{0.67} (OH) _{1.34}	-396.05	-12352.6
Ca _{9.06} (PO ₄) _{4.95} (CO ₃) _{0.83} (OH) _{1.61}	-440.99	-11640.0
Ca _{8.93} (PO ₄) _{4.83} (CO ₃) _{1.06} (OH) _{1.25}	-421.71	-11583.0
Ca _{8.82} (PO ₄) _{4.74} (CO ₃) _{1.31} (OH) _{0.80}	-389.58	-11618.7
Ca _{8.86} (PO ₄) _{4.65} (CO ₃) _{1.37} (OH) _{1.03}	-420.20	-11575.4
Ca _{8.76} (PO ₄) _{4.59} (CO ₃) _{1.44} (OH) _{0.87}	-400.91	-11474.1
Ca _{8.68} (PO ₄) _{4.52} (CO ₃) _{1.58} (OH) _{0.64}	-387.48	-11443.9
Ca _{8.51} (PO ₄) _{4.41} (CO ₃) _{1.63} (OH) _{0.53}	-401.27	-11148.3



The first step is the reverse of the dissolution of the apatite and the others are dissolution (step III), dilution, (VI, VIII) or formation (II, IV, V, VII, IX) phenomena. Taking into account the literature data and the experimental dilution results, the enthalpy of formation of the general formula compound can be derived as:

$$\Delta_f H^\circ(\text{apatite}) = -\Delta_{\text{sol}}H^\circ(\text{apatite}) - 5144.9 - 1113.74(10 - a - b) - 1279.7(6 - a - 2b - e) - 965.16(a + 2b + e)$$

In which $(10 - a - b) = n_{\text{Ca}}$, $(6 - a - 2b - e) = n_{\text{PO}_4}$ and $(a + 2b + e) = n_{\text{CO}_3}$

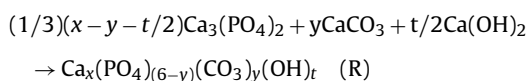
n_{Ca} , n_{PO_4} and n_{CO_3} are determined experimentally from chemical analysis (Table 4). Table 8 gathers values of standard enthalpies of solution and formation of the apatite unit cell, for the group of samples.

For steps II, III, IV, V, VII and IX the enthalpy of formation and dissolution are listed in Table 6. For H_3PO_4 , $0.756\text{H}_2\text{O}$:

$$\Delta_{\text{sol}}H^\circ = -7.87 \text{ kJ/mol and } \Delta_f H^\circ = -1271.8 \text{ kJ/mol [20].}$$

As indicated previously, the sum of CO_3 and PO_4 ion amounts equals 6 in the lattice cell, and so taking into account the electroneutrality of the lattice, the molar enthalpy of formation depends on two independent composition variables

It was interesting to determine the influence of carbonate introduction on the lattice enthalpy. This can be made by comparing the formation enthalpy of the apatite to that of the mixture of solids containing the same entities as in the apatite. Let $\text{Ca}_x(\text{PO}_4)_{(6-y)}(\text{CO}_3)_y(\text{OH})_t$ ($2x = 18 - y + t$), the general formula of the CO_3 -apatites, the effect of carbonate is tightly related to the enthalpy variation of the following reaction



Enthalpy of that reaction ($\Delta_R H$) has been determined from literature for the reactants [21,28] and from Table 8 for the apatites. Fig. 5 shows the variation of $\Delta_R H$ over both CO_3 and OH ion amounts in the apatite lattice. One can notice a maximum around 0.8CO_3 and 1.7OH , suggesting the presence in these compounds of two kinds of carbonate and of hydroxyl.

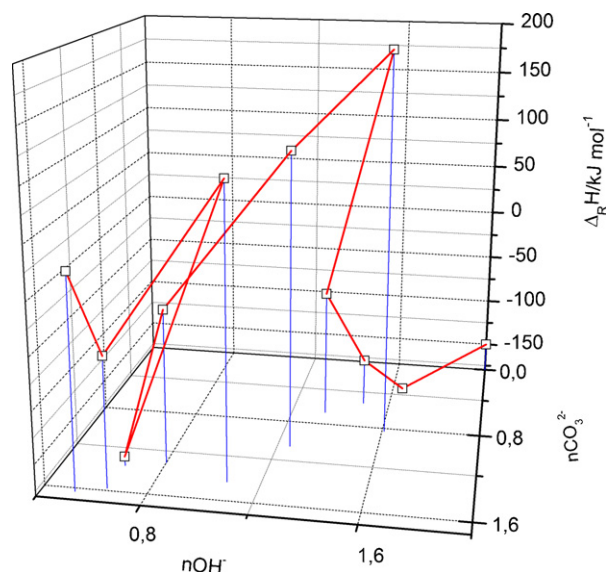


Fig. 5. Heat of reaction (R) in kJ mol^{-1} as a function of CO_3^{2-} and OH^+ amounts in the CO_3 apatite cell.

5. Statistical treatment

The presence of two kinds of carbonate Na free B type carbonate apatites has been previously affirmed by other authors, and so among a, b and e parameters, one has to be equal to zero. Experimental results have been treated statistically in order to find which couple of parameters has to be considered in the chemical formula of apatites in agreement with results. The mathematical model is based on the linear regression on two independent variables. The general formula is expressed as

$$Y_i = \beta_0 + \beta_1 X_{1,i} + \beta_2 X_{2,i} + \varepsilon.$$

In which $X_{1,i}$ and $X_{2,i}$ were (a_i, b_i) , (b_i, e_i) or (a_i, e_i) $Y_i = \Delta_f H^\circ$, ε is a random variable drawn from $N(0, \sigma^2)$ and $\beta_0, \beta_1, \beta_2$ are the regression coefficients. The model assumes that their deviations ε from the line are normally distributed with means 0 and constant variances σ^2 .

5.1. Calculation of regression and correlation coefficients

Least square method allows calculating the regression and correlation coefficients. The sample regression (prediction equation) is $\hat{Y}_i = \beta_0^* + \beta_1^* X_{1,i} + \beta_2^* X_{2,i}$ where $\hat{Y}_i, \beta_0^*, \beta_1^*$ and β_2^* are the estimated values of Y_i, β_0, β_1 and β_2

5.1.1. Calculation of β_0^*, β_1^* and β_2^*

The estimated values of β_0, β_1 and β_2 have been calculated by the following relationships:

$$\beta_0^* = \bar{Y} - \beta_1^* \bar{X}_1 - \beta_2^* \bar{X}_2,$$

$$\beta_1^* = \frac{\left[\sum_{i=1}^{i=10} x_{1,i} y_i \cdot \sum_{i=1}^{i=10} x_{2,i}^2 - \sum_{i=1}^{i=10} x_{1,i} x_{2,i} \cdot \sum_{i=1}^{i=10} x_{2,i} y_i \right]}{D} \text{ and}$$

$$\beta_2^* = \frac{\left[\sum_{i=1}^{i=10} x_{2,i} y_i \cdot \sum_{i=1}^{i=10} x_{1,i}^2 - \sum_{i=1}^{i=10} x_{1,i} x_{2,i} \cdot \sum_{i=1}^{i=10} x_{1,i} y_i \right]}{D}$$

Table 9

Calculation of regression and correlation coefficients.

Formula III: $\text{Ca}_{10-(a+b)}(\text{PO}_4)_{6-(a+2b)}(\text{CO}_3)_{(a+2b)}(\text{OH})_{(2-a)}$								
Sample	$Y_i = \Delta_f H^\circ$	$X_{1,i} = a$	$X_{2,i} = b$	$x_{1,i}$	$x_{2,i}$	y_i	\hat{Y}_i	d_i
1	-13133.3	0.16	0.01	-0.70	-0.09	-1260.06	-13061.3	-72.02
2	-12763.3	0.35	0.05	-0.51	-0.05	-890.01	-12708.8	-54.44
3	-12352.6	0.64	0.01	-0.22	-0.09	-479.36	-12365.3	12.70
4	-11640.0	0.83	0.11	-0.03	0.01	233.23	-11897.5	257.49
5	-11582.9	0.97	0.10	0.11	$-3.6 \cdot 10^{-16}$	290.30	-11713.7	130.83
6	-11618.7	1.10	0.08	0.24	-0.02	254.56	-11563.7	-54.99
7	-11575.4	0.93	0.21	0.07	0.11	297.89	-11560.2	-15.22
8	-11474.1	1.07	0.17	0.21	0.07	399.19	-11434.1	-39.98
9	-11443.9	1.16	0.16	0.30	0.06	429.32	-11322.8	-121.05
10	-11148.3	1.39	0.10	0.53	$-3.6 \cdot 10^{-16}$	724.94	-11104.8	-43.55
Total	118732.6	8.60	1.00					
Mean	-11873.3	0.86	0.10					

$\sum_{i=1}^{i=10} x_{1,i}^2 = 1.289$ $\sum_{i=1}^{i=10} x_{2,i}^2 = 0.040$ $\sum_{i=1}^{i=10} y_i^2 = 3771070.9$ $\sum_{i=1}^{i=10} x_{1,i}y_i = 2145.13$ $\sum_{i=1}^{i=10} x_{2,i}y_i = 284.76$ $\sum_{i=1}^{i=10} x_{1,i}x_{2,i} = 0.144\beta_0^* = -13312.5 \text{ kJ mol}^{-1}$, $D = 0.031$, $\beta_1^* = 1449.9$ and $\beta_2^* = 1923.5$ $r_{X_1Y} = 0.973$, $r_{X_2Y} = 0.735$ and $r_{X_1X_2} = 0.634$
 $\sum_{i=1}^{i=10} (d_i)^2 = \sum_{i=1}^{i=10} (Y_i - \hat{Y}_i)^2 = 113112.62$; $\sum_{i=1}^{i=10} \hat{Y}_i^2 = 3657958.3$ $R^2 = 0.97$
 Model I: $\Delta_f H^\circ / \text{kJ mol}^{-1} = (-13312.5 + 1449.9a + 1923.5b)$.

Formula IV: $\text{Ca}_{10-a}(\text{PO}_4)_{6-(a+e)}(\text{CO}_3)_{(a+e)}(\text{OH})_{(2-a+e)}$								
Sample	$Y_i = \Delta_f H^\circ$	$X_{1,i} = b$	$X_{2,i} = e$	$x_{1,i}$	$x_{2,i}$	y_i	\hat{Y}_i	d_i
1	-13133.4	0.17	0.01	-0.79	-0.09	-1260.10	-13061.28	-72.02
2	-12763.3	0.40	0.05	-0.56	-0.05	-890.00	-12708.86	-54.44
3	-12352.6	0.65	0.01	-0.31	-0.09	-479.35	-12365.30	12.70
4	-11640.0	0.94	0.11	-0.02	0.01	233.24	-11897.49	257.49
5	-11582.9	1.07	0.10	0.11	0	290.31	-11713.73	130.84
6	-11618.7	1.18	0.08	0.22	-0.02	254.57	-11563.71	-54.99
7	-11575.4	1.14	0.21	0.18	0.11	297.90	-11560.18	-15.21
8	-11474.1	1.24	0.17	0.28	0.07	399.20	-11434.12	-39.98
9	-11443.9	1.32	0.16	0.36	0.06	429.33	-11322.86	-121.04
10	-11148.3	1.49	0.10	0.53	0	724.95	-11104.76	-43.54
Total	-118732.7	9.60	1.00					
Mean	-11873.3	0.96	0.10					

$\sum_{i=1}^{i=10} x_{1,i}^2 = 1.616$ $\sum_{i=1}^{i=10} x_{2,i}^2 = 0.04$ $\sum_{i=1}^{i=10} y_i^2 = 3771070.9$ $\sum_{i=1}^{i=10} x_{1,i}y_i = 2429.9$ $\sum_{i=1}^{i=10} x_{2,i}y_i = 284.76$ $\sum_{i=1}^{i=10} x_{1,i}x_{2,i} = 0.183\beta_0^* = -13312.5 \text{ kJ mol}^{-1}$ $D = 0.031$, $\beta_1^* = 1449.9$ and $\beta_2^* = 473.6$ $r_{X_1Y} = 0.984$ $r_{X_2Y} = 0.735$ and $r_{X_1X_2} = 0.723$
 $\sum_{i=1}^{i=10} (d_i)^2 = \sum_{i=1}^{i=10} (Y_i - \hat{Y}_i)^2 = 113112.62$ $\sum_{i=1}^{i=10} \hat{Y}_i^2 = 3657958.3$ $R^2 = 0.97$
 Model II: $\Delta_f H^\circ / \text{kJ mol}^{-1} = (-13312.5 + 1449.9a + 473.6e)$

Formula V: $\text{Ca}_{10-b}(\text{PO}_4)_{6-(2b+e)}(\text{CO}_3)_{(2b+e)}(\text{OH})_{(2+e)}$								
Sample	$Y_i = \Delta_f H^\circ$	$X_{1,i} = b$	$X_{2,i} = e$	$x_{1,i} = b$	$x_{2,i} = e$	y_i	\hat{Y}_i	d_i
1	-13133.4	0.17	-0.16	-0.79	0.70	-1260.10	-13061.28	-72.02
2	-12763.3	0.40	-0.35	-0.56	0.51	-890.00	-12708.86	-54.44
3	-12352.6	0.65	-0.64	-0.31	0.22	-479.35	-12365.30	12.70
4	-11640.0	0.94	-0.83	-0.02	0.03	233.24	-11897.49	257.49
5	-11582.9	1.07	-0.97	0.11	-0.11	290.31	-11713.73	130.84
6	-11618.7	1.18	-1.10	0.22	-0.24	254.57	-11563.71	-54.99
7	-11575.4	1.14	-0.93	0.18	-0.07	297.90	-11560.18	-15.21
8	-11474.1	1.24	-1.07	0.28	-0.21	399.20	-11434.12	-39.98
9	-11443.9	1.32	-1.16	0.36	-0.30	429.33	-11322.86	-121.04
10	-11148.3	1.49	-1.39	0.53	-0.53	724.95	-11104.76	-43.54
Total	-118732.7	9.60	-8.60					
Mean	-11873.3	0.96	-0.86					

$\sum_{i=1}^{i=10} x_{1,i}^2 = 1.616$ $\sum_{i=1}^{i=10} x_{2,i}^2 = 1.289$ $\sum_{i=1}^{i=10} y_i^2 = 3771070.9$ $\sum_{i=1}^{i=10} x_{1,i}y_i = 2429.9$ $\sum_{i=1}^{i=10} x_{2,i}y_i = -2145.17$ $\sum_{i=1}^{i=10} x_{1,i}x_{2,i} = -1.43$
 $\beta_0^* = -13312.5 \text{ kJ mol}^{-1}$ $D = 0.031$ $\beta_1^* = 1923.5$ and $\beta_2^* = 473.6$
 $r_{X_1Y} = 0.988$ $r_{X_2Y} = -0.978$ and $r_{X_1X_2} = -0.993$
 $\sum_{i=1}^{i=10} (d_i)^2 = \sum_{i=1}^{i=10} (Y_i - \hat{Y}_i)^2 = 113112.62$ $\sum_{i=1}^{i=10} \hat{Y}_i^2 = 3657958.3$ $R^2 = 0.97$
 Model III: $\Delta_f H^\circ / \text{kJ mol}^{-1} = (-13312.5 + 1923.5b + 473.6e)$

$$\text{with } D = \left[\sum_{i=1}^{i=10} x_{1,i}^2 \sum_{i=1}^{i=10} x_{2,i}^2 - \left(\sum_{i=1}^{i=10} x_{1,i} x_{2,i} \right)^2 \right],$$

$x_{1,i}, x_{2,i}$ and y_i are the deviation from the mean values \bar{X}_1, \bar{X}_2 and \bar{Y} respectively.

$$x_{1,i} = X_{1,i} - \bar{X}_1, x_{2,i} = X_{2,i} - \bar{X}_2 \text{ and } y_i = Y_i - \bar{Y}$$

5.1.2. Calculation of correlation coefficients

The correlation coefficient is a measure of the closeness of relationship between two variables ($X_{1,i} Y_i$), ($X_{2,i} Y_i$) or ($X_{1,i} X_{2,i}$). For a couple (X, Y) variables, it is given by the relation of Person and Lee's:

$$r_{XY} = \frac{\sum x.y}{\sqrt{\sum x^2 \cdot \sum y^2}}$$

This coefficient has been calculated in different cases for the couples ($X_{1,i} Y_i$), ($X_{2,i} Y_i$) or ($X_{1,i} X_{2,i}$) where X_1 and X_2 could be a, b or e and $Y = \Delta_f H^\circ(T_0)$

5.1.3. Calculation of the multiple correlation coefficient

The multiple correlation coefficient is:

$$R^2 = \frac{\sum \hat{y}_i^2}{\sum y_i^2}$$

where $\sum_{i=1}^{i=10} \Sigma i = 1i = 10\hat{y}_i^2 = \sum_{i=1}^{i=10} \Sigma i = 1i = 10(\hat{Y}_i - \bar{Y})^2 = \sum_{i=1}^{i=10} \Sigma i = 1i = 10$ ($y_i - \beta_1^* x_{1,i} - \beta_2^* x_{2,i}$)² is the sum of squares of deviations of the fitted values from their means. It is often called the sum of squares due to the regression. $\sum_{i=1}^{i=10} \Sigma i = 1i = 10\hat{y}_i^2$ can be obtained from

$$\text{the equation } \sum_{i=1}^{i=10} \Sigma i = 1i = 10d_i^2 = \sum_{i=1}^{i=10} \Sigma i = 1i = 10y_i^2 + \sum_{i=1}^{i=10} \Sigma i = 1i = 10\hat{y}_i^2$$

Where $\sum_{i=1}^{i=10} \Sigma i = 1i = 10d_i^2 = \sum_{i=1}^{i=10} \Sigma i = 1i = 10(Y_i - \hat{Y}_i)^2$ d_i is the deviation or residual of the point Y_i from the fitted line. Calculation results are gathered in Table 9 considering the couples of parameters as (a, b), (a, e) or (b, e) respectively

Table 9 allows deriving the different expressions of the formation enthalpy as follows:

$$\text{Model I: } \Delta_f H^\circ / \text{kJ mol}^{-1} = (-13312.5 + 1449.9 a + 1923.5 b)$$

$$\text{Model II: } \Delta_f H^\circ / \text{kJ mol}^{-1} = (-13312.5 + 1449.9 a + 473.6 e)$$

$$\text{Model III: } \Delta_f H^\circ / \text{kJ mol}^{-1} = (-13312.5 + 1923.5 b + 473.6 e)$$

For non-carbonated apatite, these expressions lead to the same value ($-13312.5 \text{ kJ mol}^{-1}$) which is very close to the one determined in a previous work: $-13305 \text{ kJ mol}^{-1}$ [29].

The results of correlation coefficients showed that intercorrelations between variables are high. The negative value of $r_{X_1 X_2} = -0,993$ for $X_1 = b$ and $X_2 = e$, indicates large values of b are associated with small values of e .

5.2. Tests of the mathematical model

To be confident that X_1, X_2 and Y are related, several tests have to be performed. In the multiple regression, these tests are:

- the t -test or test of significance of regression coefficients
- the F -test in analysis of variance and
- the extension in analysis of variance.

Table 10
Values of variances and t -test on each β 's model.

$(j = 1, 2)$	$v(\beta_j)$	$t_j = \beta_j^* / s_{\beta_j}$	$c^2 = t_{v,0.95}^2 / t^2$
Model I	20961.54 678880.0	10.01 2.33	0.05 1.03
Model II	20961.54 851101.7	10.01 0.51	0.05 21.50
Model III	678880.0 851101.7	2.33 0.51	1.03 21.50

5.2.1. t -Test on each of the β 's model

To test the significance coefficient β_1 and β_2 we have to conduct t -test on each β 's model. For that we have to calculate the following quantities:

5.2.1.1. The variances of β_1 and β_2 .

$$v(\beta_1) = \frac{\sigma^2 \left(\sum_{i=1}^{i=10} \Sigma i = 1i = 10x_{2,i}^2 \right)}{D} \text{ and } v(\beta_2) = \frac{\sigma^2 \left(\sum_{i=1}^{i=10} \Sigma i = 1i = 10x_{1,i}^2 \right)}{D}$$

For the estimated variances σ^2 is replaced by the residual mean square: $s_{XY}^2 = \sum_{i=1}^{i=10} \Sigma i = 1i = 10 \frac{(Y_i - \hat{Y}_i)^2}{(n-k-1)} = \sum_{i=1}^{i=10} \Sigma i = 1i = 10 \frac{d_i^2}{(n-k-1)}$ ($n - k - 1 = v$) is degree of freedom. In this case k is the number of β_1^*, β_2^* parameters estimated in fitting the regression and n the sample size.

5.2.1.2. The quantities: $t_1 = \beta_1^* / s_{\beta_1}$ and $t_2 = \beta_2^* / s_{\beta_2}$, where $s_{\beta_1} = \sqrt{v(\beta_1)}$ and $s_{\beta_2} = \sqrt{v(\beta_2)}$. In this test of significance of β_1 and β_2 , t has to be calculated, and t^2 must be compared to $t_{v,p}^2$ picked from Student table. Alternatively we can calculate the quantity c^2 defined as: $c^2 = t_{v,p}^2 / t^2$. If β_1 or β_2 is significant at 5% level, $t > t_{v,95\%}$, hence ($c < 1$) and so $c^2 < 1$. Table 10 summarizes results of the tests of significance of β_j , where $j = 1$ then 2.

The lowest values of c^2 correspond to the regression coefficients β_1 and β_2 related to the parameters a and b (model I). So a and b parameters seem to be more significant in the expression of standard enthalpy of formation of the compounds.

5.2.2. F -test in analysis of variance

To testing the utility of the models, we conduct the F -test. It is a global statistic test that encompasses all β 's for each model and test null hypothesis: $H_0 : \beta_1^* = \beta_2^* = 0$. The F statistical is the ratio of (regression mean square) over (residual mean square). It is called a variance ratio

$$F_{obs} = \frac{\text{variance due to regression}}{\text{variance residual}}$$

$$\text{Variance due to regression is noted } r_{reg} = \sum_{i=1}^{i=10} \Sigma i = 1i = 10(\hat{Y}_i - \bar{Y})^2 / k$$

Table 11
Values of F -test: analysis of variance.

Source of variation	DF	Sum of squares	Mean square	F_{obs}
Regression	2	$R_2 = \sum_{i=1}^{i=10} \hat{y}_i^2 = 3657958.3$	1828979.1	113.2
Residual	7	$\sum_{i=1}^{i=10} d_i^2 = 113112.6$	$s^2 = 161589$	
Total	9	$\sum_{i=1}^{i=10} y_i^2 = 3771070.9$	419007.9	

Table 12
Extended analysis of variance.

Model I: $\Delta_f H^\circ / \text{kJ mol}^{-1} = (-13312.5 + 1449.9a + 1923.5b)$				
Source of variation	DF	Sum of squares	Mean square	F
Regression on $X_1 = a$	1	$R_1 = (\sum i = 1i = 10x_{1,i}y_i) / \sum i = 1i = 10x_{1,i}^2 = 3569896.4$	3569896.4	
$X_2 = b$ after $X_1 = a$	1	$R_2 - R_1 = 88061.9$	88061.9	5.45
Residuals	7	$\sum i = 1i = 10y^2 - R_2 = 113112.6$	$s^2 = 16158.9$	
Regression on $X_2 = b$	1	$R'_1 = (\sum i = 1i = 10x_{2,i}y) / \sum i = 1i = 10x_{2,i}^2 = 2037390.5$	2037390.5	
$X_1 = a$ after $X_2 = b$	1	$R_2 - R'_1 = 1620567.7$	1620567.7	100.3
Residuals	7	$\sum i = 1i = 10d^2 = 113112.6$	$s^2 = 16158.9$	
Model III: $\Delta_f H^\circ / \text{kJ mol}^{-1} = (-13312.5 + 1923.5b + 473.6e)$				
Source of variation	DF	Sum of squares	Mean square	F
Regression on $X_1 = b$	1	$R_1 = 3653700.5$	3653700.5	
$X_2 = e$ after $X_1 = b$	1	$R_2 - R_1 = 4257.8$	4257.8	0.26
Residuals	7	$\sum d^2 = 113112.6$	$s^2 = 16158.9$	
Regression on $X_2 = e$	1	$R_1 = 3569896.4$	3569896.4	
$X_1 = b$ after $X_2 = e$	1	$R_2 - R'_1 = 88061.9$	88061.9	5.45
Residuals	7	113112.6	16158.9	
Source of variation	DF	Sum of squares	Mean square	F
Regression on $X_1 = a$	1	$R_1 = 3653700.5$	3653700.5	
$X_2 = e$ after $X_1 = a$	1	$R_2 - R_1 = 4257.8$	4257.8	0.26
Residual	7	$\sum d^2 = 113112.6$	$s^2 = 16158.9$	
Regression on $X_2 = e$	1	$R_1 = 2037390.5$	2037390.5	
$X_1 = a$ after $X_2 = e$	1	$R_2 - R'_1 = 1620567.7$	1620567.7	100.3
Residual	7	113112.62	$s^2 = 16158.9$	

Model II: $\Delta_f H^\circ / \text{kJ mol}^{-1} = (-13312.5 + 1449.9a + 473.6e)$

Residual variance is $r_{res} = \sum i = 1i = 10(Y_i - \hat{Y}_i)^2 / (n - k - 1)$.

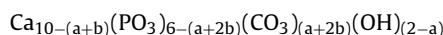
The results corresponding to the analysis of the variance are summarized in Table 11. They are the same for the three models.

The F value should be a good criterion for testing the significance level of values of coefficients of the regression. It is used to test null hypothesis: $H_0 : \beta_1^* = \beta_2^* = 0$. Critical value for the test is given in tables A 14 Ref. [30]. In our case F_{obs} (113.2) is higher than F -value (4.74), thus the null hypothesis has to be rejected.

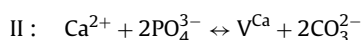
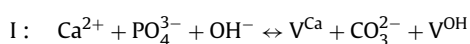
5.2.3. Extension of the analysis of variance

One can wonder if only one variable (a or b), (a or e), (b or e), is enough for the regression. So, separate F tests of β_1 and β_2 are performed. Table 12 summarizes the calculation results.

The F value for testing (e) after including (a) or (b) is 0.26, so this type of substitution seems unrelated to Y ($\Delta_f H$). Thus we can conclude that the most probable formula is:



In which the following fundamental substitutions are:



(with “ a ” and “ b ” contributions respectively)

As a concluding remark, the presence of two types of carbonate in B-type carbonate apatites has been confirmed by several methods. Statistical treatment of thermochemical results shows that the most probable substitutions in this kind of products are couple substitutions (CO_3 , OH) for PO_4 and (2CO_3 , V^{Ca}) for 2PO_4 .

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