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Review

A comprehensive guide to experimental and predicted thermodynamic properties of phosphate apatite minerals in view of applicative purposes

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A B S T R A C T

Apatite minerals represent a major class of ionic compounds of interest to many disciplines including medical sciences, geology, anthropology, cosmology, environmental and nuclear sciences. Yet, these compounds have not received great attention from a thermodynamic viewpoint, and some diverging data – often drawn from molecular modeling assays – were reported. In this contribution, an extensive literature overview of available experimental-based data on $M_{10}(PO_4)_6X_2$ apatites with M = Ca, Ba, Sr, Mg, Cd, Pb, Cu, Zn and X = OH, F, Cl or Br has first been made, on the basis of standard formation energetics (ΔH_f° and ΔG_f°) as well as entropy S° and molar heat capacity $C_{p,m}^\circ$. The case of oxyapatite was also included. From this overview, it was then possible to identify general tendencies, evidencing in particular the primary role of electronegativity and secondarily of ionic size. Using the experimental data as reference, several predictive thermodynamic methods were then evaluated, including the volume-based-thermodynamics (VBT) method and a more advanced additive contributional model. In particular, the latter allowed obtaining estimates of thermodynamic data of phosphate apatites within a maximum of 1% of relative error, generally within 0.5%. Fitted h_i, g_i and s_i contributive parameters are given for bivalent cations and monovalent anions, so as to derive, by simple summation, coherent estimates of ΔH_f°, ΔG_f° and S° for any apatite composition, at $T = 298$ K. The model was shown to also lead to consistent estimates in cases of solid-solutions or even non-stoichiometric or hydrated phosphates apatites. Ultimately, a *periodic table of recommended thermodynamic properties* of 33 phosphate apatites end-members (at $T = 298$ K and 1 bar) was established, with the view to serve as an easily readable reference database.

1. Introductive assessments

Phosphate-bearing apatites, for which stoichiometric end-members generally respond to the chemical formula $M_{10}(PO_4)_6X_2$ (M and X representing respectively a divalent cation and a monovalent anion) constitute an important group of mineral compounds. Either found in Nature (bones and teeth [1], rocks and sediments [2,3]) or obtained by synthesis, these minerals are in particular well-known in various scientific communities including medical and biomaterials sciences (bone tissue engineering, nanomedicine) [1,4–6], anthropology [7–9], geology/mineralogy [2,3,10], or else environmental sciences (immobilization of phosphates and metallic compounds, nuclear sciences) [11], among other domains. If hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and fluorapatite ($Ca_{10}(PO_4)_6F_2$) are probably the most illustrious examples in this series of compounds, chlorinated or bromated counterparts as well as apatites containing other cations than calcium (such as cadmium, lead, magnesium, strontium...) are also encountered [12,13] and questions relating to their relative stability, solubility, *etc.* regularly arise. Besides, stoichiometric end-members are not the only phases of interest, especially when aqueous precipitation at moderate temperature is involved [5,14]: non-stoichiometric apatite compositions are generally obtained in such conditions (unless perhaps for very long periods of time), and their thermochemical features are bound to depart from those of their stoichiometric parent phase, as we showed recently in the case of biomimetic apatites [15].

Whether for applied considerations (for answering questions like: which phase is the most stable in given experimental conditions? which of the present or expected phases is the most soluble? can we expect to prepare and stabilize a given substituted apatite phase in given conditions?...) or for more fundamental purposes, the need for reliable and readily usable thermodynamic data in terms of Gibbs free energies, enthalpies, entropies, or else heat capacities is obvious. Yet, regretfully, there is only a scarce literature addressing the thermodynamics of apatites.

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In this context, the goal of this paper is multiple. First, an overview of experimental-based reported thermochemical data for phosphate apatites will be listed, the idea being to gather the information dealing phosphate apatite minerals in a *single* document that could then serve as reference database in the future. Second, the use of various predictive methods for estimating thermodynamic data [16–19] – increasingly evoked in the literature for example for estimating data for not-yet synthesized materials or for cross-checking uncertain experimental data – will be investigated, with the final view to examine the case of solid-solutions or even non-stoichiometric compounds. Their application (for the first time with a specific focus on apatite minerals) will be evaluated and compared; and apatite-fitted parameters will then be determined. Finally, a comprehensive *periodic table of phosphate apatites recommended thermodynamic properties* will be established (in much the same way as was done for classifying not only chemical elements, but also other systems such as proteic structures [20] or also aminoacids [21]), so as to provide an easily-readable and portable chart, classified on the basis of apatite chemical composition.

This paper deals specifically with the wide family of phosphate apatites. Samples containing silicates, carbonates, arsenates or other molecular ions in place of phosphates are not addressed here; they will be the object of other dedicated studies. Throughout this contribution, formula units in the form $M_{10}(PO_4)_6X_2$ will be used (rather than $M_5(PO_4)_3X$) since it is more customary in nowadays studies. A total of 33 apatite end-member compositions involving various divalent M^{2+} ions and monovalent X^- anions will be examined in this work (including also the exceptional addition of calcium oxyapatite $Ca_{10}(PO_4)_6O$ where $2X^-$ are replaced by one O^{2-} ion).

2. Overview of experimental-based thermodynamic data on $M_{10}(PO_4)_6X_2$ apatites

Despite the vast scientific literature dealing with apatitic compounds (>15,800 entries in Web of Science® only for the last two decades) and the numerous multidisciplinary domains of research/applications where they may be involved, one can notice the relative scarcity of dedicated thermodynamic studies. In some instances, however, some data have been determined, and experimental-based evaluations were reported especially in terms of enthalpy measurements through calorimetry or dissolution experiments. Table 1 gathers the available thermodynamic data corresponding to the formation energetics of $M_{10}(PO_4)_6X_2$ apatite compounds (at $T = 298$ K and 1 bar). The case of oxyapatite $Ca_{10}(PO_4)_6O$ (where O^{2-} replaces $2X^-$) was also added since it represents another important apatitic compound. Some research groups such as Jemal *et al.* or Vieillard and Tardy have significantly contributed in this domain (see references for table 1). Published values for standard entropies S° have also been included in this table, although they often arise from estimations rather than on actual experimental measurements [2,22] (*e.g.* considering in a first approximation the system as energetically equivalent to the sum of its constituting binary compounds [22]). Nonetheless entropy values are generally used, in practice, in conjunction with enthalpy with the final goal to determine standard Gibbs free energies ΔG_f° (which represent the actual "driving force" of a chemical process). Since such thermodynamic properties are generally given for the reference temperature of 298 K, the entropy term $T\Delta S$ (in $kJ \cdot mol^{-1}$) therefore gets multiplied by a factor 0.298. This then drastically limits the effects of entropy imprecision on the final evaluation of ΔG_f° which, for such complex oxide materials, have a clearly dominant enthalpy contribution (see table 1).

Some heat capacity values ($C_{p,m}^\circ$), or their temperature coefficients in the function $C_{p,m}^\circ = f(T)$, have also been sporadically reported. Table 2 summarizes the published data for phosphate-bearing apatites $M_{10}(PO_4)_6X_2$ (as well as oxyapatite) along with the corresponding references. In the temperature ranges where the $C_{p,m}^\circ = f(T)$ temperature functions are reported (indicated in table 2), these values may then allow one to evaluate ΔH_f° and S° (and then ΔG_f°) at any final temperature $T_f > 298$ K thanks to the following equations:

$$\Delta H_f^\circ(T_f)/(kJ \cdot mol^{-1}) = \Delta H_f^\circ(298\ K)/(kJ \cdot mol^{-1}) + \int_{298}^{T_f} C_{p,m}^\circ/(J \cdot mol^{-1} \cdot K^{-1})dT, \quad (1)$$

and

$$S^\circ(T_f)/(J \cdot mol^{-1} \cdot K^{-1}) = S^\circ(298\ K)/(J \cdot mol^{-1} \cdot K^{-1}) + \int_{298}^{T_f} \frac{C_{p,m}^\circ/(J \cdot mol^{-1} \cdot K^{-1})}{T/K} dT. \quad (2)$$

Data for temperatures lower than 298 K were only occasionally made available, especially for fluorapatite and chlorapatite [50]. It may be noted from table 2 that, at least at $T = 298$ K, the $C_{p,m}^\circ$ values for the apatites listed are rather similar, roughly in the range (700 to 800) $J \cdot mol^{-1} \cdot K^{-1}$ and with an average value at $T = 298$ K close to 750 $J \cdot mol^{-1} \cdot K^{-1}$.

The literature data gathered in table 1 provide an overview of enthalpy, Gibbs free energy of formation and/or standard entropy of a variety of phosphate-bearing apatite compounds exhibiting different M^{2+} or X^- ionic contents (except in the case of oxyapatite where $2X^-$ are replaced by one O^{2-} ion). The discrepancies observable in some cases probably arise from variable crystallinity states, polymorphs (either hexagonal or monoclinic, those not being systematically identified in literature reports), nonstoichiometry, hydration state and/or the presence of undetected impurities. A lower degree of crystallinity, for example, may favor the obtainment of somewhat less negative values [68]. Concerning polymorphism, in the case of apatites the difference between the hexagonal ($P6_3/m$) and the monoclinic ($P2_1/b$) symmetries lies in fact only in the positioning of the X^- anions along the apatitic channels (giving rise or not to a mirror plane) and does not correspond to a large ion rearrangement; therefore the energetics of formation are expected to not differ very significantly (although not being identical), which allows considering both polymorphs.

With this recapitulated overview of available data, it is then possible to detect more clearly some trends in terms of ΔH_f°, ΔG_f° and/or S°. For instance, for a given X^- anion (taken among OH^-, F^-, Cl^- or Br^-), both ΔH_f° and ΔG_f° become significantly less negative (exothermic) when alkaline earth M^{2+} elements such as Ca^{2+}, Ba^{2+} or Sr^{2+} are replaced by heavy metal ions (Cd^{2+}, Pb^{2+}) or by transition metals (such as Cu^{2+} or Zn^{2+}). It illustrates the direct impact of apatites composition on their formation energetics. It is however difficult, by the sole inspection of table 1, to draw more "advanced" conclusions. To do so, the data from table 1 were compared by plotting ΔH_f° or ΔG_f° as a function of specific characteristics of the ions involved. For example, the complete substitution of Ca^{2+} ions (ionic radius [69] 1.00 Å in coordination VI) by smaller Cu^{2+} (0.73 Å) or larger Ba^{2+} (1.36 Å) may be expected to lead to diversely stable systems. Also, replacing OH^- ions from hydroxyapatite by various halides is anticipated to produce significant changes in thermodynamic properties.

If the relative ion sizes probably come into play for modifying thermodynamic features, other parameters such as the affinity of the cation for oxygen or else the strength of M–O bonds may also be appropriately investigated. In this contribution, the potential correlation with six different parameters has been checked. The ionic radius (extracted from reference [69]) and the derived ionic volume were two parameters considered for examining the effect

TABLE 1
Overview of experimental-based literature data available for phosphate-bearing apatite end-members, at T = 298 K and 1 bar.

Compound[a] (298 K, 1 bar)	ΔG_f°/(kJ · mol^{-1})	ΔH_f°/(kJ · mol^{-1})	S°/(J · mol^{-1} · K^{-1})
	OH-containing apatites (in cation-based alphabetical order)		
$Ba_{10}(PO_4)_6(OH)_2$	−12,553 [23]	−13,309 [23,24]	
$Ca_{10}(PO_4)_6(OH)_2$	−12,510 [23]	−13,305 [25]	780.7 ([26,27], HSC[c])
(=hydroxyapatite, HAP)	−12641.7 [28]	−13,399 ± 11 [29]	768 [30]
	−12,560 [22]	−13445.4 [31]	781.1 [32]
	−12507.8 [33]	−13431.0 ± 22.7 [15]	780.8 ± 3.4 [34]
	−12677.0 [26,27]	−13421.6 [35]	797.9 [2]
	−12674.2 ± 10.0 [34]	−13516.6 ± 20.9 [36]	785 [37]
	−12611.8 [27]	−13,525 [38]	
	−12533.4 [27]	−13,314 [30,39]	
	−12601.4 [2]	−13,508 [40]	
	−12655.1 [41]	−13292.0 [39]	
		−13443.2 (HSC)	
		−13395.8 [2]	
		−13,477 ± 10.0 [34,26,27]	
$Cd_{10}(PO_4)_6(OH)_2$	−7873 [23]	−8652 [24]	
		−8648 [25]	
$Cu_{10}(PO_4)_6(OH)_2$	−6523.6 [27,42]		
$Mg_{10}(PO_4)_6(OH)_2$	−11521.5 [43]		
$Pb_{10}(PO_4)_6(OH)_2$	−7482 [23]	−8261 [25]	
	−7548.2 [27]		
	−7551.5 [44]		
$Sr_{10}(PO_4)_6(OH)_2$	−12,587 [23]	−13,373 [25]	
$Zn_{10}(PO_4)_6(OH)_2$	−8623.2 [42]		
	F-containing apatites (in cation-based alphabetical order)		
$Ba_{10}(PO_4)_6F_2$	−12,834 [23]	−13,564 [23]	
$Ca_{10}(PO_4)_6F_2$	−12,781 [23]	−13,558 [30,39]	775.7 ([26,45,27]HSC)
(=fluorapatite, FAP)	−12899.5 [28]	−13,545 [25]	765 [30]
	−12,826 [22]	−13718.78 [46]	776.5 [47,48]
	−12758.9 [33]	−13654.7 [38]	775.8 ± 3.4 [34]
	−12990.62 [46]	−13,550 [49]	766.4 ± 3 [50]
	−12983.0 [26,45,27]	−13676.5 ± 1.7 [51]	771.8 [37]
	−12979.4 ± 10.0 [34]	−13797.1 ± 20.9 [36]	
	−12867.8 [28]	−13657.2 [35]	
	−12,886 [27]	−13,548 [24]	
	−12788.3 [27]	−13535.7 [39]	
	−12892.3 [2]	−13,684 [31]	
		−13744.4 (HSC)	
		−13,744 ± 10 [34,26,45,27]	
		−13653.4 [2]	
$Cd_{10}(PO_4)_6F_2$	−8045 [23]	−8795 [25]	
$Mg_{10}(PO_4)_6F_2$	−11714.1 [43]		
$Pb_{10}(PO_4)_6F_2$	−7782 [23]	−8529 [25]	
	−7735.7 [52]	−8466 [49] −7908 (see note[d])	
$Sr_{10}(PO_4)_6F_2$	−12,845 [23]	−13,604 [25]	
	Cl-containing apatites (in cation-based alphabetical order)		
$Ba_{10}(PO_4)_6Cl_2$	−12,519 [23]	−13,246 [30,53]	1044 [54]
	−12,539 [22]		
$Ca_{10}(PO_4)_6Cl_2$	−12,418 [23]	−13,180 [30,39]	914 [55]
(=chlorapatite, ClAP)	−12,514 [35,27]	−13,231 ± 82 [29]	795.8 [27,38]
	−12447.5 [27]	−13,119 [24]	800.2 [2]
	−12,462 [22]	−13,139 [56]	801.2 ± 3.2 [50]
	−12,403 [57,55]	−13096.1 ± 6.7 [55]	808 [54,58]
	−12440.8 [2]	−13,179 [23]	804.3 [37]
		−13200.8 [2]	796.2 [35]
		−13,278 [38]	
		−13160.7 [39]	
$Cd_{10}(PO_4)_6Cl_2$	−7719 [23]	−8463 [59,30]	
$Pb_{10}(PO_4)_6Cl_2$	−7458 [23]	−8220 [30]	
	−7586.7 [27,42,60]	−8204 [23] −7474 (see note[d])	
$Sr_{10}(PO_4)_6Cl_2$	−12,478 [23]	−13,233 [30,56]	904 [54]
	Br-containing apatites (in cation-based alphabetical order)		
$Ca_{10}(PO_4)_6Br_2$	−12382.7 [27]	−13,063 ± 81 [29]	827.3 [37]
$Pb_{10}(PO_4)_6Br_2$	−7460.3 [52]	−8180 [30]	
	O-containing apatite[b]		
$Ca_{10}(PO_4)_6O$	−12272.1 [57]		745.2 [37]
(oxyapatite)	−12307.8 [27]		

[a] For apatite formulas expressed as $M_{10}(PO_4)_6X_2$.
[b] The case of oxyapatite reported here differs somewhat from the general formula $M_{10}(PO_4)_6X_2$ in that the two monovalent X^- ions are substituted here by one oxygen O^{2-} divalent anion. It is still added here taking into account the importance of this phase in practical use.
[c] The term HSC refers to the HSC Chemistry® for Windows software (Outotec, Finland), version 5.11, and to the incorporated thermodynamic database.
[d] These values −(7908 and 7474) kJ/mol were reported respectively for Pb–F and Pb–Cl apatites from nitric acid dissolution tests [106,107]. It may however be noted that these values differ significantly from the previously evaluated ones. At this point, it is not possible to state which order of magnitude is the most accurate for these Pb-containing apatites (the variations may arise from either incomplete reactions or varying chemical compositions from either these works or the previous ones from other groups), therefore leading to some additional uncertainty in the case of Pb-apatites to this date.

TABLE 2
Literature data related to heat capacity ($C^{\circ}_{p,m}$ and its temperature coefficients) for phosphate apatites (under 1 bar).

Compound[a] (1 bar)	$C^{\circ}_{p,m}$ [b] (T = 298 K)/(J · mol^{-1} · K^{-1})	Temperature coefficients						T° interval /K	Reference
		A (cte)	B ([a]$10^{-3}T$)	C ([a]$10^{5}T^{-2}$)	D ($10^{-6}T^{2}$)	E ([a]$10^{3}T^{-0.5}$)	F ($10^{7}T^{-3}$)		
$Ca_{10}(PO_4)_6(OH)_2$	694 ± 68							298	[61]
	769.9							298	[26]
	calc. 769.9	1007.816	29.296	−226.12	90.124			298 to 800	([HSC][c])
	calc. 772.6	955.21	165.61	−206				298 to 1475	[62]
	calc. 765.8	977.04	126.26	−221				298 to 598	[63]
	calc. 770.2	956.13	165.77	−209.20				298 to 1500	[64]
	770.2							298 to 1500	[32]
	calc. 801.1	1518.35				−12.967	89.63	250 to 1470	[65]
	calc. 770.1	775.6	237.2	−254		3.622		298 to 1500	[34]
$Ca_{10}(PO_4)_6F_2$	646 ± 26							298	[61]
	751.9							298	[26]
	calc. 751.6	715.162	646.504	−114.616	−305.482			298 to 800	([HSC])
	calc. 751.0	944.85	120.72	−204.07				298 to 1580	[62]
	calc. 756.2	1338.18				−9.0727	−149.34	250 to 1580	[2]
	752.3	946.20	120.89	−204.36				298 to 1580	[48]
	calc. 750.9	907.56	195.91	−191				298 to 598	[63]
	calc. 751.9	948.85	113.77	−205.3				298 to 1600	[27]
	calc. 739.1	1362.48		−127.6268		−9.24346	147.6176	298 to 760	[50]
	740.9							298	[66]
	calc. 751.7	1508.6	−60.52	−18.168		−12.402		298 to 1600	[34]
$Ca_{10}(PO_4)_6Cl_2$	608 ± 14							298	(7)
	calc. 755.9	1610.2	−118.6	10.606	6.649	−14.27	−12.847	298 to 1000	[55]
	calc. 762.0	1328.38				−8.876	−138.11	298 to 1045	[2]
	calc. 746.6	1226.42		−375.928		−4.6278	559.85	298 to 760	[50]
	758	276.43	2079.9	−17.5939	−1300			298 to 800	[58]
	751							298	[54]
	calc. 752.6	914.87	188.58	−194				298 to 598	[63]
	758.3							298	[35]
$Ca_{10}(PO_4)_6Br_2$	811 ± 42							298	[61]
	calc. 728.7	806.94	296.77	−148				298 to 598	[63]
$Ca_{10}(PO_4)_6I_2$	877.8							298	[66]
$Ba_{10}(PO_4)_6Cl_2$	787	1110.96	−281.96	−231.1871	306.8329			298 to 800	[67]
	767							298	[54]
$Sr_{10}(PO_4)_6Cl_2$	868	[d]						298	[58]
	759							298	[54]
$Ca_{10}(PO_4)_6O$	*calc. 723.9*	788.83	314.91	−141				298 to 598	[63]

[a] For apatite formulas expressed as $M_{10}(PO_4)_6X_2$.
[b] The values noted "*calc.*" were calculated here, at T = 298 K, from the corresponding $C^{\circ}_{p,m}$ temperature coefficients.
[c] The term HSC refers to the HSC Chemistry® for Windows software (Outotec, Finland), version 5.11, and to the incorporated thermodynamic database.
[d] Temperature coefficients are also given in references [58] for $Sr_{10}(PO_4)_6Cl_2$, but calculation at T = 298 K indicates an error in this polynomial expression which is why it was not reported here.

of ionic size. The Pauling [45,70] electronegativity χ_M of the element M and the second ionization energy [45] E_M^{++} of M were considered to take into account the affinity of the metal ion for surrounding negative charges. In particular, E_M^{++} is the energy that accompanies the ionization process $M^+ \rightarrow M^{2+} + e^-$. Therefore, the opposite value "$-E_M^{++}$" gives an idea of the energy accompanying the capture of one electron by one M^{2+}, and thus of the affinity of the M^{2+} ion for one negative charge. Finally, two parameters involving the formation of theoretical M–O bonds were investigated: the typical M–O bond dissociation energy [45] (gas state data at $T = 298$ K) and the ionic character I of the M–O bond, as defined earlier [45] from a comparison of the electronegativity values of M and O ($I = 0.46\ |\chi_M - \chi_O| + 0.035\ (\chi_M - \chi_O)^2$). Indeed, although actual M–O bonds do not exist "as such" in such ionic crystals, the M^{2+} cations involved in the apatite lattice have oxygen atoms in their first coordination sphere, thus legitimating the use of such parameters as M–O dissociation bond or ionic character.

Figure 1 reports "correlation" lines obtained for ΔG_f° in the case of hydroxyapatites (the case of fluorapatites led to very similar trends), along with the corresponding R^2 correlation factors. As can be seen, and very interestingly, only a poor correlation ($R^2 < 0.16$) was found *versus* the ionic radius or volume, at least for ionic radii ranging from *ca.* 0.7 to 1.4 Å (corresponding to volumes between 1.6 and 10.5 Å^3). The same tendencies were found for either ΔG_f° or ΔH_f°, which is rather not surprising since the enthalpy term is preponderant in the Gibbs free energy value. This poor correlation with ionic size reveals that, contrarily to what could be presumed at first thought, the size of the M^{2+} cation does *not* appear to be the predominant factor dictating the thermodynamic stability of such apatite phases (for a given X^- anion). In

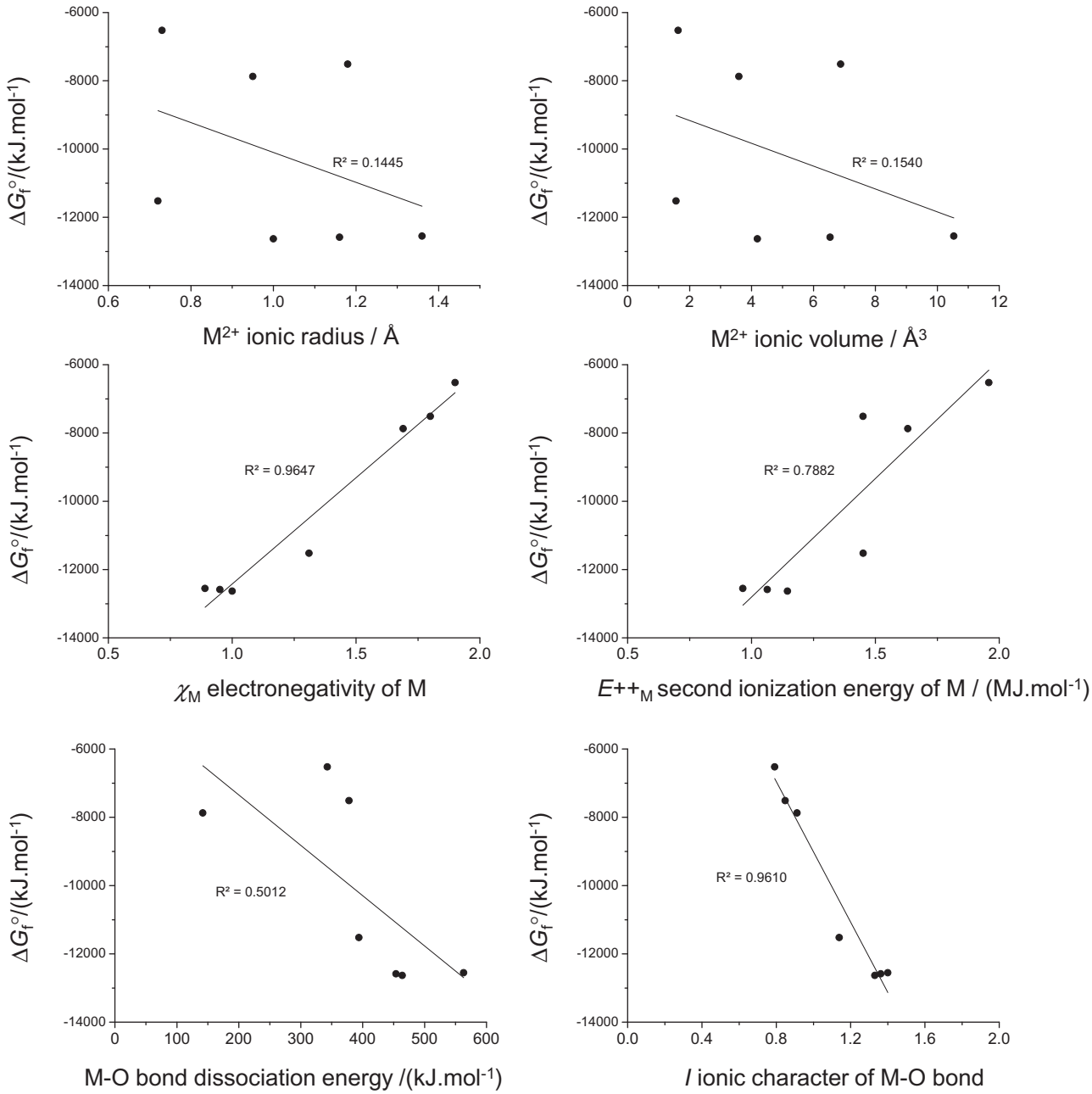


FIGURE 1. Effects of various parameters intrinsic to the M^{2+} cation on the thermodynamics of hydroxyapatites (X = OH).

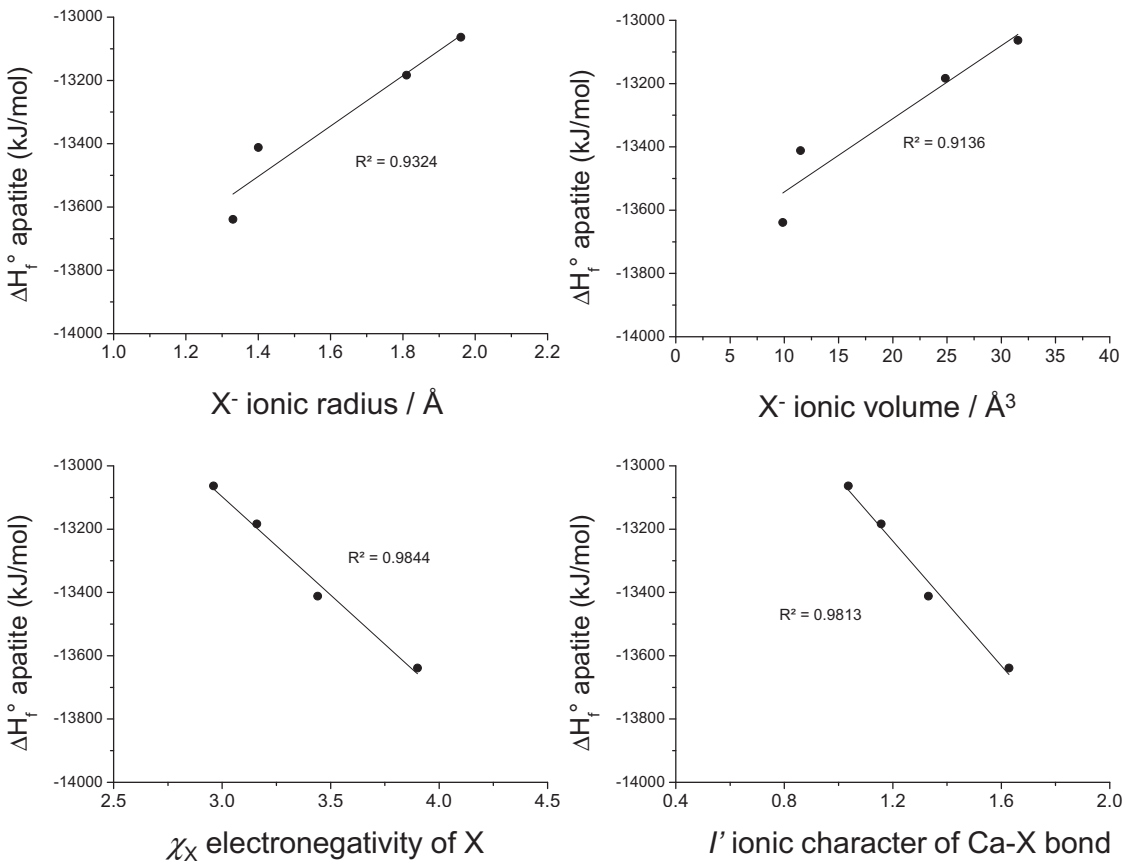


FIGURE 2. Effects of various parameters intrinsic to the X^- anion on the thermodynamics of calcium phosphate apatites.

contrast, a much better correlation was found for the other four parameters, and especially with the electronegativity χ_M of the element M ($R^2 \sim 0.965$) and the ionic character I of the M–O bond ($R^2 \sim 0.961$): for a given X, the apatite phase is found to be more stable for an M element exhibiting a lower electronegativity. The goodness of fit was found of the same order both for hydroxyapatites (X = OH) and for fluorapatites (X = F), allowing one to presumably consider the correlation with χ_M or I as generalizable to any given X anion from this study. For information, it may be noted that the use of Tardy *et al.* electronegativity scale (see for example reference [71]) led to lower correlations than Pauling's scale, and was thus not chosen here.

This correlation with χ_M or I strongly suggests that the thermodynamic stability of an apatite compound will be largely impacted by the affinity of the M^{2+} cation for surrounding oxygen atoms, with a more minor role played by the ionic size (at least in the range (0.7 to 1.4) Å for which thermodynamic data are available, see table 1). In such ionic compounds, anions and cations are attracted by each other so as to generate electrostatic interactions ensuring the 3D cohesion of the crystal. Although "true" chemical bonds – with the sense that is generally given to this term – are not literally formed between anions and cations in this type of ionic crystals, the presence around a given ion of a set of neighboring ions of opposite charge is manifestly likely to alter local electron densities (due to local electrical field contributions once the crystal is formed). Therefore, despite the pre-existence of charged anions and cations during the formation of such ionic crystals, the concept of element electronegativity still applies: a highly electropositive (=less electronegative) element M is expected to interact in a different way, with regard to its oxygen neighbors, as compared to a less electropositive one; by leaving a more negative charge q^- (denser electron density) around the oxygen neighbors and retaining a more positive charge q^+ on its side. Such an increased "segregation" of charges (electron density more significantly relayed on the oxygen anions) is then a factor of increased crystal stability, in relation with Coulomb law of electrostatics stating that the strength of attraction of opposite charges is proportional to the product of their charge values q^+ and q^-.

The previous paragraphs were relating to the case of apatite phases with a given X^- anion but varying M^{2+} cations. Let us now consider the inverse scenario. Unfortunately, the available experimental-based data (see table 1) do not allow one to check several systems since data for various X^- ions are only accessible in the case when M represents calcium. It is however interesting to investigate the case of such Ca^{2+}-containing apatites since they represent an important apatite subfamily found in practical applications (*e.g.* medicine, mineralogy, anthropology...).

Figure 2 reports the correlation plots drawn in this calcium case *versus* the ionic radius, ionic volume and electronegativity of X, as well as *versus* the ionic character of the Ca–X bond. On this figure, the ΔH_f° values were used instead of ΔG_f° because more datapoints were available (but similar trends were obtained for ΔG_f°). The OH^- ion was treated in a first approximation as a regular O^{2-} ion. In contrast to the previous case of M substitution, the thermodynamic properties of the apatite phase were found to be more significantly affected by the difference in ion size [69] in the "X" crystallographic site (*e.g.* from the smallest F^- ion: $V \sim 9.9$ Å^3 to the largest Br^- ion $V \sim 31.5$ Å^3). Indeed, a correlation factor of $R^2 = 0.9136$ was found on the influence of ionic volume. The anion size was however not the only factor to impact the thermodynamics of such apatites since even better correlations were found *versus* the electronegativity χ_X of the element X and *versus* the ionic character I'

of regular Ca–X bonds ($R^2 \sim 0.9844$ and $R^2 \sim 0.9813$ respectively). For the same reasons as previously, such good correlations with χ_X and I' indicate that the apatite thermodynamic stability is intimately linked to the difference in electronegativity between X and Ca (and probably also for any M).

To sum up, all of the above section was dedicated (1) to *summarize* in a single document the experimental-based thermodynamic data available in the literature for stoichiometric phosphate-bearing apatites $M_{10}(PO_4)_6X_2$ with varying M^{2+} and X^- contents, and (2) to *exploit* these data in a comparative manner so as to unveil thermodynamic stability trends relatable to parameters such as ionic size or relative electronegativity. The apatite stability for ionic substitutions in the "M" sites appears to be particularly sensitive to the difference in electronegativity between M and O ($\chi_O = 3.44$ after Pauling [45,70]): the greater the difference, the more stable the apatite phase. For substitutions in "X" site, not only the difference in electronegativity between M and X strongly influences the thermodynamic stability, but the impact of the size of the X^- anion also becomes clearly significant.

From the observation of table 1, it appears however that only a rather *limited* set of data is available on phosphate apatite compounds despite a large interest in several domains of application. These data are scarce and therefore do not allow thermodynamic calculations for compositions that are not in this table, nor for solid-solutions or non-stoichiometric samples. While waiting for additional thermochemistry experiments to be run on other compositions, the development of "predictive" thermodynamic methods is appealing. Based on experimental sets of experimental data, the idea lying behind such methods, that are increasingly considered in the scientific community for various types of compounds (see references in next section), is to extrapolate thermodynamic properties from known to unknown systems presenting some level of compositional or structural similarity [16–19]. In this contribution, the application (and corresponding parameter adjustment) of several estimative methods to phosphate apatites was thus considered, and this is the subject of the following section.

3. Use of predictive thermodynamic methods for application to $M_{10}(PO_4)_6X_2$ apatite stoichiometric end-members (at $T = 298$ K)

When experimental-based data are not available (or questionable), the so-called "prediction" of thermodynamic properties of solids becomes very relevant. For example, it may allow understanding some unsuccessful experiment aiming at obtaining a desired hypothetical composition, or it may fill the gap between reported and needed thermodynamic values for the evaluation of equilibria constants or for the establishment of phase diagrams. For these reasons, and also because the elaboration and realization of calorimetry experiments are often seen as time-consuming or complex, an increasing number of studies have emerged with examples of predictive methods and thermodynamic output values. Several groups of researchers have been especially active in this domain, such as Latimer [72], Nriagu *et al.* [27,73,74], Tardy/Vieillard *et al.* [71,75,76], Glasser/Jenkins *et al.* [16–18], Bogach *et al.* [37], or else La Iglesia [19], for example; and the related studies on several types of materials (silicates, clays, binary orthophosphates...) have illustrated the interest of such methods when experimental data are not accessible.

A classification of such methods has recently been set up by Glasser *et al.* [16]. Along this classification, methods range from rather simple ones (*e.g.* based on one evolving property of the system such as its formula unit volume: "volume-based method") to more advanced processes, adding in particular the thermodynamic contributions of each atom or group of atoms to determine the properties of the full system (="additive" or "contributional" methods). In the following, we will first check what type of outputs may be drawn from application of the volume-based thermodynamic method (VBT). We will then move toward more complex additive methods, keeping in mind as general goal to limit insofar as possible the relative errors by comparison to the experimental data reported in table 1.

3.1. Application of volume-based thermodynamic predictive method (VBT) to apatites

So-called "first order" methods have especially received much attention because they are rather easy to use and have been shown in some cases to lead to output data well related to experimental results [16–18]: in particular, the Volume-Based-Thermodynamic approach (VBT), particularly developed by the groups of Glasser/Jenkins, was exploited in several occasions for estimating thermodynamic values of solid phases (such as entropies, enthalpies, Gibbs free energies or heat capacities) [16,18,77,78], but also other properties such as isothermal compressibility [79]. The VBT method is based on the fact that, in a first approximation, many macroscopic properties of a solid are directly linked to the unit formula volume, V_m. Linear relationships between standard entropies and V_m were for example discussed in details [80], and the theoretical background explaining this first approximation correlative law (*e.g.* recalling Maxwell's equations) was also discussed in this literature [16,81]. For ionic solids, Coulombic forces are prevalent [81], and the identification of charges and of the "closeness of ion-packing" (thus related to the unit formula volume) were considered to be the main influential factors.

The application of the VBT method to *apatite* materials has however not received as yet a specific attention. So far, VBT considerations have otherwise been made on a *much larger scale* in the generic terms of "inorganic solids", "minerals", or "else condensed-phase organics" [16]. Yet, it would be interesting to check whether this approach would lead or not to satisfactory outputs when applying it specifically to phosphate apatite solids.

Taking into account the available data from table 1, ΔH_f° and ΔG_f° were plotted *versus* their unit formula volume V_m (figure 3). The latter was drawn from X-ray diffraction JCPDS crystallographic database (Match software, version 2.0.10, ICDD 2004 PDF-2 database) whenever possible, which is in the vast majority of cases. In the few instances when no diffraction information was found (*i.e.* for $Cu_{10}(PO_4)_6(OH)_2$, $Mg_{10}(PO_4)_6(OH)_2$, $Cd_{10}(PO_4)_6F_2$, $Mg_{10}(PO_4)_6F_2$ and $Zn_{10}(PO_4)_6(OH)_2$), the value of V_m was estimated by application of the additive ion volume determination method proposed by Glasser *et al.* [17]. The V_m values considered in this work are, for information, gathered in figure Suppl.1 (supporting information). For checking the validity of such V_m estimations in the case of apatites, they were also tentatively applied to apatites for which the experimental unit cell volume was known, and results indicated that the calculated V_m constantly fell within a maximum of 11% relative error which was judged reasonable in terms of volume uncertainty. Figure 3 shows only a mediocre overall correlation (R^2 of the order of 0.03 and 0.06 respectively) in terms of either ΔH_f° or ΔG_f° *versus* V_m. However, a closer look at the graphs indicates that *two subpopulations* of independently monotonous datapoints can be distinguished: one corresponding to a "higher" degree of thermodynamic stability (*i.e.* more negative ΔH_f° or ΔG_f°) for which M is found to be an alkaline earth metal (noted "AE", here Mg, Ca, Sr or Ba), and one corresponding to a lower stability state for which M is not an alkaline earth element (noted "NAE"), namely Cd, Pb, Cu or Zn in the present case. Indeed, despite the high similarity of V_m values between $Cd_{10}(PO_4)_6Cl_2$ (521.81 Å^3) and $Ca_{10}(PO_4)_6F_2$ (523.25 Å^3), for example, very distinct experimental enthalpies of Gibbs free energies of formation were observed for these two samples (*e.g.* $\Delta G_f^\circ \sim -7719$ kJ · mol^{-1} for

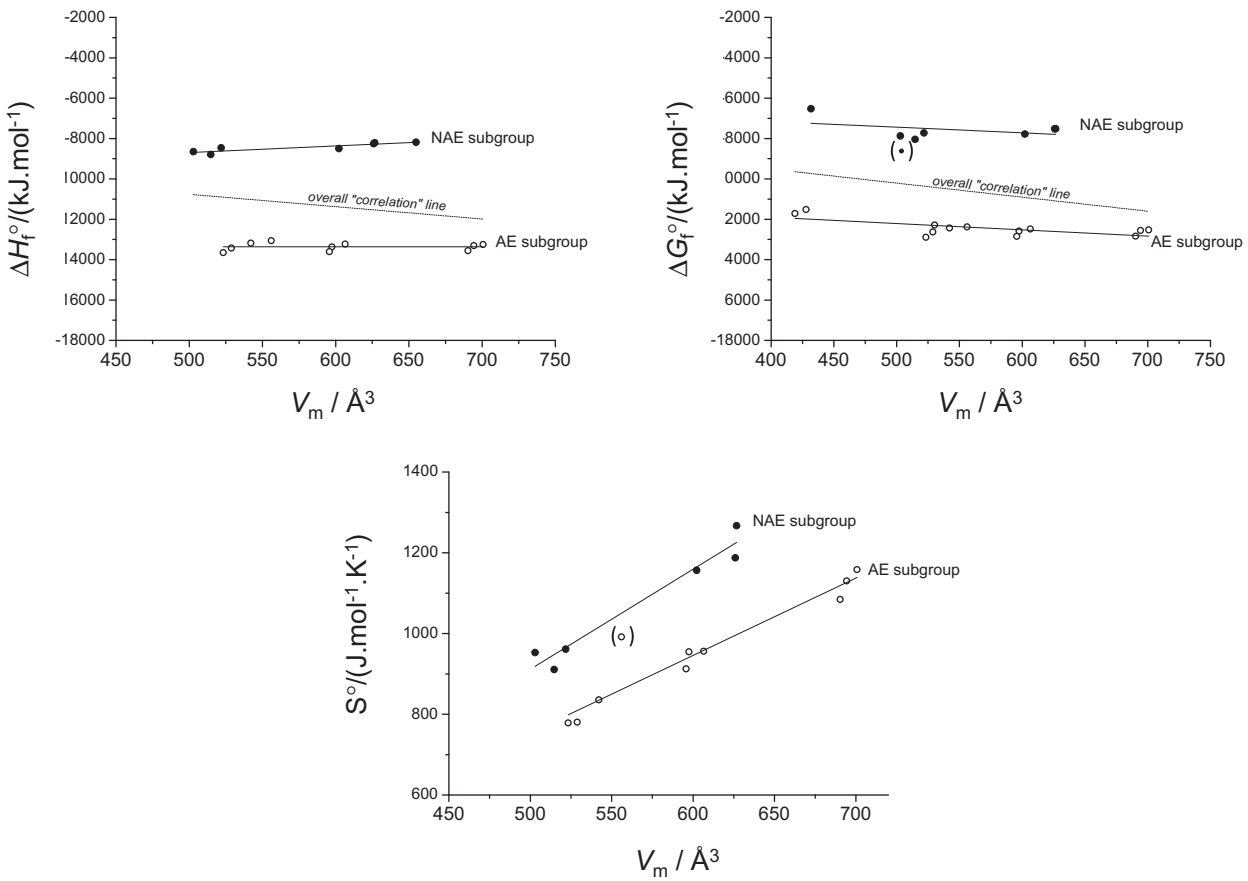


FIGURE 3. Evolution of ΔH_f°, ΔG_f° and S° (at $T = 298$ K) for several apatite phases, *versus* their unit formula volume V_m. Open circles (○) and plain circles (●) are respectively for alkaline-earth (AE) and non-alkaline-earth (NAE) subgroups of apatites.

the former to be compared to $\Delta G_f^\circ \sim -12{,}899$ kJ · mol^{-1} for the latter). It is therefore not possible to give one single VBT linear equation relating the ΔH_f° or ΔG_f° of apatite phases to their V_m. However, the present findings indicate that it *is* possible to identify a monotonous linear-like trend *for each of the two subpopulations* taken separately (*i.e.* either for apatites containing only alkaline earth (AE) cations, or for non-alkaline earth (NAE) cations), as noticeable on figure 3. This separation into two sub-categories may probably be related to the specific chemistry of alkaline-earth elements, exhibiting in particular strong electropositive characters (*i.e.* electronegativities [45] between 0.89 and 1.31 from Ba to Mg). Despite some scatter in each subpopulation, simple VBT linear equations of the form ΔH_f° or $\Delta G_f^\circ = a \cdot V_m + b$ can then be derived: these equations are summarized in table 3. As indicated in this table, mean relative errors in the range 1 to 5% were associated to these VBT-estimated ΔH_f° or ΔG_f° values.

A similar correlation was sought in terms of entropy, by plotting S° *versus* V_m (added in figure 3). S° values were calculated from the reported values of ΔH_f° or ΔG_f° in table 1 applying the relation $\Delta G_f^\circ = \Delta H_f^\circ - 0.298.\ \Delta S_f^\circ$, and using the entropies of the elements taken in their standard state (accessible in thermodynamic databases [45]). Although a better overall overall correlation was found for $S^\circ = f(V_m)$, with $R^2 = 0.52$, the points still appeared spread apart from a single linear fit. As previously, however, two subpopulations (AE and NAE) were distinguished and treated separately as before (see table 3), leading to S° estimates with mean relative errors S° reaching 1.7 and 2.5% respectively.

These VBT equations represent thus a first approach for estimating the values of ΔH_f°, ΔG_f° and/or S° for stoichiometric apatitic end-members $M_{10}(PO_4)_6X_2$ when no experimental data are available, or even to possibly extrapolate to $M_{10-x}M'_x(PO_4)_6X_{2-y}M'_y$ solid-solutions (making the hypothesis of negligible energetics of mixing), provided that the adequate equation is used (selecting either alkaline-earth (AE) or non-alkaline-earth (NAE) apatites). Note however that these equations cannot be used when considering "mixed" apatite solid solutions where M is an alkaline earth

TABLE 3
Linear VBT relationships linking estimates of ΔH_f°, ΔG_f°, or S° (at $T = 298$ K) of apatite phases $M_{10}(PO_4)_6X_2$ or $M_{10-x}M'_x(PO_4)_6X_{2-y}M'_y$ to their unit formula volume V_m (in Å^3), depending on the type of M/M′ cations (all alkaline earth: AE, or all non-alkaline earth: NAE). Numbers in parentheses represent the corresponding mean relative errors.

Thermodynamic property as estimated by VBT approximation ($T = 298$ K, 1 bar)	Type of cations	
	Alkaline earth cations (AE)	Non-alkaline earth cations (NAE)
ΔH_f°/(kJ · mol^{-1})	$=0.1111\ V_m/Å^3 - 13{,}434$ (±1.4%)	$=3.2460\ V_m/Å^3 - 10{,}315$ (±1%)
ΔG_f°/(kJ · mol^{-1})	$=-3.0893\ V_m/Å^3 - 10677$ (±2.0%)	$=-2.8125\ V_m/Å^3 - 6031$ (±4.9%)
S°/(J · mol^{-1} · K^{-1})	$=1.8455\ V_m/Å^3 - 155.68$ (±1.7%)	$=2.4776\ V_m/Å^3 - 329.14$ (±2.5%)

metal and M′ is not. Taking into account the large absolute values of ΔH_f° and ΔG_f° for such complex oxides and the non-negligible relative errors reached by these VBT equations (see table 3), they should be seen only as a way to draw first approximations for enthalpy and free energies (the end of this manuscript will identify more accurate estimative methods for ΔH_f° and ΔG_f° by way of additive contributional models).

The above findings pointed out some interests but also some limitations in the use of the VBT method applied to apatites: a generalization to all M/X chemical compositions was not found possible as two (at least) subpopulations with different behaviors were identified depending on the type of cation present in the structure. Also, the relative errors associated to the VBT estimates remain relatively large, above 1%. In this context, the search for more advanced/accurate predictive methods remains appealing; with the objective to derive a more generalizable equation. In this view, *additive contributional methods* appeared interesting to evaluate: this is the topic of the next subsection.

3.2. Application of additive estimation methods to the case of phosphate apatites

Probably the simplest "additive" or "contributive" method consists in considering that, from a thermodynamic viewpoint, the apatite phase may be treated in first approximation as the sum of contributions arising from the constituting binary oxides/compounds. For example, in the case of fluorapatite $Ca_{10}(PO_4)_6F_2$, a decomposition into contributions of $9CaO + 3P_2O_5 + 1CaF_2$ could be considered, and this may be generalized to any end-member in the form $9MO + 3P_2O_5 + 1MX_2$. In reality, this type of approximation is rather optimistic and does not generally represent the actual behavior of complex oxides: this is for example pointed out by the fact that the enthalpy of formation "from the oxides" is not zero, as we showed for example for nonstoichiometric apatites [15] or in other systems [82,83]. However, it was interesting at this point to check the values obtained for apatites by using this simple binary-compounds-additive method, and to compare relative errors to those previously reached by VBT.

Taking into account the thermodynamic data available in databases [34,45] for MO simple oxides and MX_2 binary compounds (see summary of data in figure Suppl.2, supporting information), the sums $\sum \nu_i.\ \Delta H_{f\,i}^\circ$, $\sum \nu_i.\ \Delta G_{f\,i}^\circ$ and $\sum \nu_i \cdot S_i^\circ$ (denoted in the following by the simplified terms $\sum_H$, $\sum_G$ and $\sum_S$), where ν_i represent stoichiometry coefficients, were calculated to draw estimates of ΔH_f°, ΔG_f° and S° for the corresponding apatites in this simple additive scenario. Values obtained this way were found to significantly derive from the reported experimental data cited in table 1, especially for ΔH_f° and ΔG_f° with mean relative errors of ~18% (a better fit was found for S°, with mean errors of 3.8 %). However, although the slope is not unity, the plotting (figure 4) of these calculated numbers *versus* experimental ones led to rather good linear tendencies that may be satisfactorily represented by equations of the type "$y = a \cdot x$" with $R^2 \sim 0.97$ for both ΔH_f° and ΔG_f°. In this simple additive approach, *all* apatite samples taken into account here (both AE- and NEA-type apatites) follow the same general trend.

This proportionality between calculated $\sum_H$, $\sum_G$ or $\sum_S$ and experimental values may then allow one to propose the application of "corrective" multiplicative factors $a_{corr,H}$, $a_{corr,G}$ and $a_{corr,S}$ (=slopes of the linear fits) so as to reach better estimates. The corrective factors found here were $a_{corr,H} = 1.2207$, $a_{corr,G} = 1.2221$ and $a_{corr,S} = 1.0428$. Applying these corrections then leads to the estimates $\Delta H_f^\circ = 1.2207 \cdot \sum_H$, $\Delta G_f^\circ = 1.2221 \cdot \sum_G$ and $S^\circ = 1.0428 \cdot \sum_S$ that are found closer from experimental values, with 2.8% (5.1% max.), 3.3% (7.2% max.) and 3.8% (15% max.) of mean relative errors

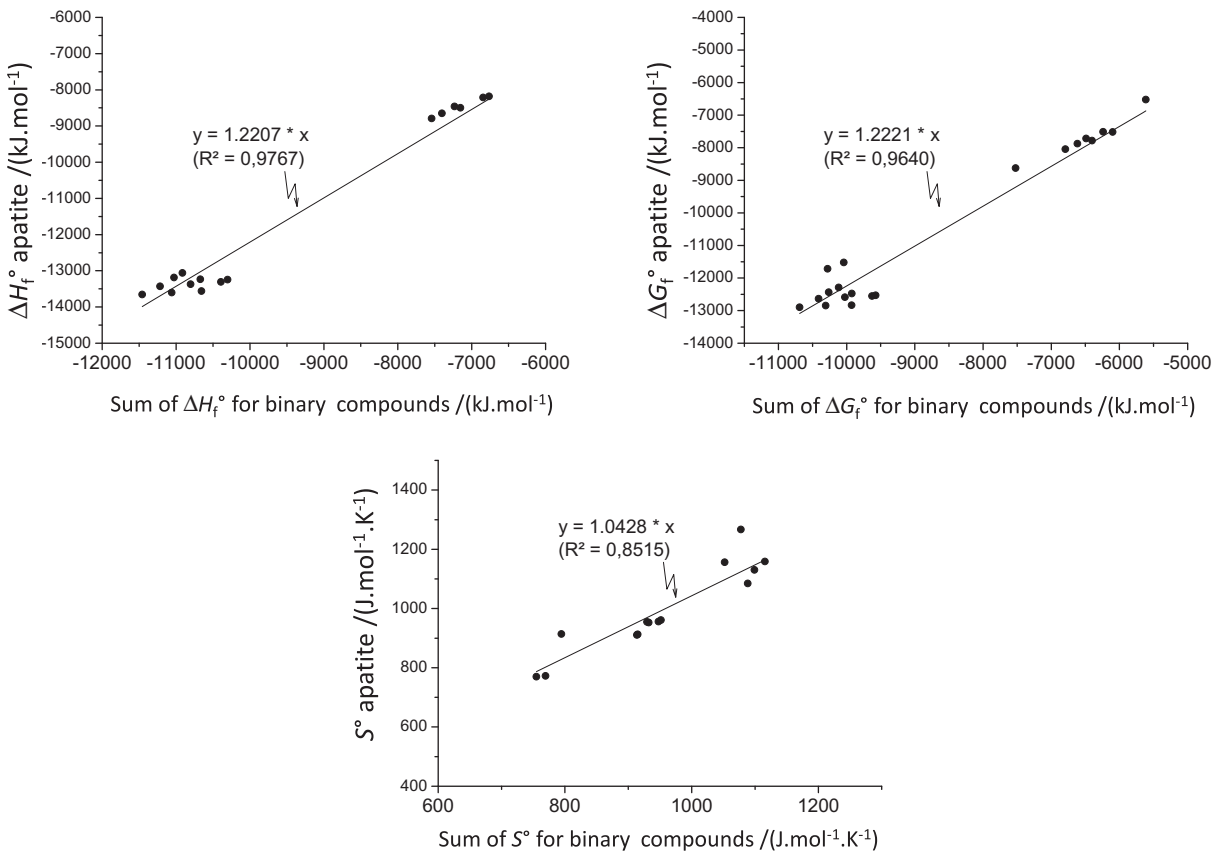


FIGURE 4. Comparison of experimental ΔH_f°, ΔG_f° and S° (at $T = 298$ K) for several apatite phases to the sums of contributions of their constitutive binary compounds.

respectively. These errors are however larger than those estimated by use of the VBT equations of table 3.

As an alternative to the above additive method, a different attempt to approximate the experimental values from the addition of binary compounds contributions was tested here by using unmodified sums $\sum_H$ and $\sum_G$ at the only exception of the values of ΔH_f° and ΔG_f° for P_2O_5. Since this phosphate entity is the only one that remains unchanged for all the apatitic compounds treated in this paper, the idea was here to check whether a modification of the P_2O_5 contribution *alone* could lead or not to satisfactory estimates. By least square refinement, "modified" hypothetical values for $\Delta H_f^\circ(P_2O_5)$ and $\Delta G_f^\circ(P_2O_5)$, in solid phase at $T = 298$ K, were evaluated (respectively leading to add 47.6% and 34.9% to their original values). However, the derived calculated values of ΔH_f° (apatites) and ΔG_f° (apatites) were then associated to greater mean relative errors of 5.4% (12% max.), and this method was then ruled out.

It was shown in the previous paragraphs that additive methods based on the summation of the thermodynamic properties of binary compounds, as tabulated in databases, could lead (with the application of corrective factors) to rough estimations of enthalpy, Gibbs free energy or entropy of apatites; however these calculations came with rather large relative errors pointing out the limits of this method.

The idea of adding the contributions of constitutive entities or atomic sub-groups nonetheless remains appealing. Several authors [19,71,73,76,84,85] have developed such methods for various types of minerals, including modified versions of the binary-compound additive method, by considering the addition of thermodynamic contributions of given ions in a more or less common environment (so-called polyhedral-based method). In particular, La Iglesia [19] reported a study focused on many phosphate compounds (only few apatites though) where he reports fitted enthalpy and Gibbs free energy contributive values "h_i" and "g_i" for ions "i" present in the sample composition (including in particular Ca^{2+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Zn^{2+}, OH^-, F^-, Cl^- and phosphate ions). Generally speaking, the objective of this method is to provide *contributive values* applied to phosphate minerals so as to directly estimate their ΔH_f° and/or ΔG_f° from the sole knowledge of their composition (regardless of their complexity, stoichiometry, *etc.*) and without any additional literature data such as values for binary compounds. This author pointed out, very interestingly, the existence of linear-like correlations with experimental values, out of which were drawn the fitted "h_i" and "g_i" values. The case of apatites was however not directly treated in a specific way by this authors, which was thus done in the present contribution.

Taking La Iglesia's parameters into account [19], the ΔH_f° and ΔG_f° for the Ca-, Pb-, Mg-, Cu- and Zn-apatites (with either X = OH, F or Cl) listed in table 1 were then calculated. Remarkably, the obtained estimates were found to be in good agreement with experimental data, typically with a mean relative error of 0.7% and a maximum of 1.7%, thus pointing out significantly better outcomes than those drawn from the other estimative methods discussed previously.

However, h_i and g_i parameters for other cationic species such as Sr^{2+}, Cd^{2+} or Ba^{2+} or for anions like Br^- were not available in La Iglesia's investigations. In order to also be able to evaluate the energetics of apatites containing these ions, the corresponding h_i and g_i parameters were evaluated in the present contribution from extrapolations of La Iglesia's data. This was made possible by remarking that La Iglesia's fitted parameters [19] for a cation M^{2+} corresponded in fact to the ΔH_f° (or ΔG_f° respectively) of the binary oxide MO to which a corrective multiplying factor a_{corr} was applied. While the energetics of MO are found to depend on both the electronegativity of M and the ionic radius r_{M2+} of M^{2+}, the corrective factors for La Iglesia's data were found here to depend rather exclusively on r_{M2+}, through the linear fitted equations $a_{corr.}(h_M) = 0.4305 \cdot r_{M2+} + 0.815$ and $a_{corr.}(g_M) = 0.4578 \cdot r_{M2+} + 0.7541$ (with correlation factors of $R^2 \sim 0.95$). This observation then allowed evaluating here the h_M and g_M contribution parameters for the ions Sr^{2+}, Cd^{2+} or Ba^{2+} which were not included in La Iglesia's report [19], but which are important ions in the field of apatite minerals. The estimation of the contribution of the Br^- anion was treated in a different way: in this case, the observation of a linear trend between all g_i contributions and their h_i counterparts ($R^2 \sim 0.99$) was used, so as to evaluate h_{Br} and g_{Br}.

Thanks to these new h_i and g_i determinations for Cd, Sr, Ba and Br, it then became possible to estimate the ΔH_f° and ΔG_f° for the corresponding apatites. Adding these estimates to those previously drawn for the Ca, Mg, Pb, Cu and Zn hydroxy-, fluor- and/or chlor-apatites from table 1 led to an overall mean relative error of 0.9% (maximum 2.6%) which is also very satisfying (the detailed results are not reported at this point since even better fits will be obtained in the following paragraphs, where all the h_i and g_i parameters will be further fitted).

At this point, it may however be pointed out that the energetic contribution of a given ion is probably bound to differ in function of the crystallographic structure it is included in. For example, it is rather improbable that a calcium ion Ca^{2+} should have exactly the same thermodynamic impact in brushite $CaHPO_4 \cdot 2H_2O$ (monoclinic, space group Ia), Ca_2ClPO_4 (orthorhombic, space group Pbcm) or else fluorapatite (hexagonal, $P6_3/m$) which represent three very different structural arrangements. Therefore, when a given type of structure is at the center of interest, as it is the case in the present contribution, the set of "h_i" and "g_i" parameters may probably be more finely tuned. This adjustment was performed here by modifying individually each of the h_i or g_i parameter using a least square refinement method (by comparison to data from table 1) leading to a minimization of the relative error. The corresponding fully adjusted h_i and g_i parameters are gathered in table 4 (expressed, for an easier use, per contributing ion in the apatite formula). These parameters are thus usable for estimating the Gibbs free energy or the enthalpy of formation of phosphate apatites $M_{10}(PO_4)_6X_2$ (containing any ion among Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, OH^-, F^-, Cl^- or Br) based on their sole chemical composition. The comparison with the available experimental data for end-members given in table 1 showed that the estimates were all obtained with less than 1% of relative error, with a mean error close to 0.5%, thus making of these tabulated values the *best estimative tools* to this date for evaluating the standard thermodynamic properties of such phosphate apatites.

The use of table 4 is simple. For example, based on a given $M_{10}(PO_4)_6X_2$ stoichiometry for which the contributive energetic parameters h_M, h_{PO4} and h_X are tabulated, the estimation of the enthalpy of formation can be made by simply summing $10 \cdot h_M + 6 \cdot h_{PO_4} + 2 \cdot h_X$. In this summation, each parameter has been pre-adjusted with regard to values found in table 1. These fitted h_i and g_i parameter can be seen as a corrected version of the enthalpies or free energies of formation of the corresponding binary compound. For instance, the parameter h_M corresponds to the "corrected" value of $\Delta H_f^\circ(MO)$ relative to the binary oxide MO; h_M thus gives an idea of the energetic contribution of the M^{2+} cations in an oxygen environment initially considered as identical to that in the MO oxide and then fitted to the apatitic structure. This summation is equivalent to the sum $10 \cdot h_M + 3 \cdot h_{P_2O_5} + 2 \cdot h_X$ since the values given to the parameters named "PO_4^{3-}" (created for simplification of the use of table 4) correspond in fact exactly to half of the P_2O_5 contribution.

At this point, it may be wondered if the "stoichiometry in oxygen" is conserved with such summations. Indeed, since h_M is in fact related the MO stoichiometry, the expression $10 \cdot h_M + 3 \cdot h_{P_2O_5} + 2 \cdot h_X$ would lead to $10 + 3 \cdot 5 = 25$ oxygens rather than the expected 24 oxygens for a "$M_{10}(PO_4)_6X_2$" unit. In fact, this "extra"

TABLE 4
g_i, h_i and s_i contributive values fitted for the estimation of ΔG_f°, ΔH_f° or S° of phosphate apatites (at $T = 298$ K, 1 bar) from their chemical composition.

Contributing sub-units in the apatite formula ($T = 298$ K, 1 bar)	g_i/(kJ · mol^{-1})	h_i/(kJ · mol^{-1})	s_i/(J · mol^{-1} · K^{-1})	Contribution to the oxygen stoichiometry
		Energetic contributions per divalent cation		
Ca^{2+}	−740	−790	38.8	+1
Sr^{2+}	−740.9	−796.1	53	+1
Mg^{2+}	−634.3	−666.4	23.1	+1
Ba^{2+}	−739.4	−791.9	71.1	+1
Cu^{2+}	−134.6	−171	34.6	+1
Cd^{2+}	−262.4	−317	53.6	+1
Pb^{2+}	−236.2	−282.2	81	+1
Zn^{2+}	−344.5	−394.8	52.4	+1
		Energetic contributions per anion		
PO_4^{3-}	−816.15	−861.6	41.05	+2.5
OH^-	−140.8	−121.5	80.65	−0.5
F^-	−269.5	−237.2	68	−0.5
Cl^-	−103.5	−70	95.7	−0.5
Br^-	−90.5	−58	118.3	−0.5
		Energetic contributions for other species		
H^+	−147.75	−187.85	66.2	
H_2O (hydration)	−234	−290	50.7	
P_2O_5	−1632.3	−1723.2	82.1	

oxygen is taken into account in the calculation of the parameters for X: the contribution h_X for the anion X^- was chosen so as to correspond to the (fitted) half-difference in enthalpies of formation between MX_2 and MO, *i.e.* $\frac{1}{2}[\Delta H_f^\circ(MX_2) - \Delta H_f^\circ(MO)]$. This trick is a way to determine an h_X parameter that is directly linked to the X contribution while allowing at the same time a simple use of table 4 by considering directly the stoichiometry coefficients in the formula unit $M_{10}(PO_4)_6X_2$. A calculation based on the parameters h_i and g_i as given by La Iglesia for phosphate minerals [19] shows in fact that the same half-difference rule already applied for their reported contributions of F^- and Cl^- ions, although the authors did not point this out. Therefore, the overall oxygen stoichiometry of the chemical formula $M_{10}(PO_4)_6X_2$ is conserved in all cases: each M^{2+} contribution relates in fact to the MO oxide and thus involves also 1 oxygen (hence the "+1" indication in the final column of table 4); each X^- ion relates in fact to $\frac{1}{2}[MX_2 - MO]$ and is thus associated to "−½" oxygen; and the notation "PO_4^{3-}" in fact corresponds to only +2.5 oxygens (indeed $3P_2O_5$ correspond to "$6PO_4^{3-} - 9O$", hence one PO_4^{3-} only implies a contribution of 2.5 oxygens in the oxygen stoichiometry). The notation "PO_4" is however interesting because it facilitates the use and reading of table 4 (but it has to be kept in mind that the oxygen stoichiometry is insured at all times when using the self-consistent fitted parameters of table 4). In the particular case of oxyapatite $Ca_{10}(PO_4)_6O$ where one ion O^{2-} replaced $2X^-$ anions, the term $\frac{1}{2}[MX_2 - MO]$ naturally cancels out. Therefore, the thermodynamic properties for oxyapatite (which has a $10CaO + 3P_2O_5$ stoichiometry) can be estimated by simply adding the contributions $10 \cdot h_{Ca} + 3 \cdot h_{P_2O_5} = 10 \cdot h_{Ca} + 6 \cdot h_{PO_4}$ (there is therefore no "O^{2-}" energetic contribution to add since this oxygen ion is in fact already counted in the overall oxygen stoichiometry).

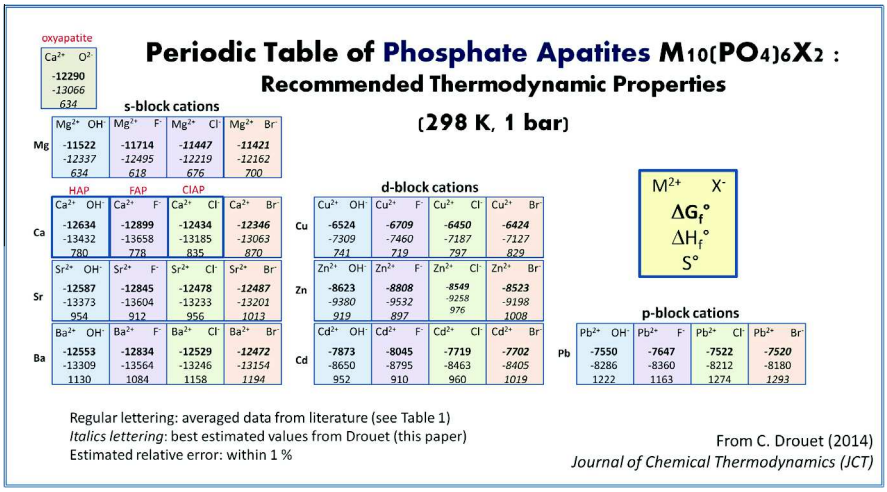
Interestingly, this table clearly points out the difference in energetic behavior between alkaline-earth and non-alkaline-earth elements. Indeed, while the former exhibit contributions of the order of 700 kJ · mol^{-1}, the latter have much less negative contributions (typically in the range 130 to 350 kJ · mol^{-1}). This can then be related to the preceding observations (see section dedicated to VBT estimations) where the behaviors of AE- and NAE-apatites had been found to be distinct when plotted against V_m.

In a similar way as was done for enthalpy and free energy contributions, it was attempted here to draw also, and for the first time by this method, entropy contributive parameters "s_i". Initial values were set to a $(h_i - g_i)/0.298$. Then, a previously for h_i and g_i, the parameters were adjusted one by one by least square refinement for an optimized fit with the experimental-based values. A good agreement was found between the S° values calculated here by combining the s_i contributions and the S° values derived from the reported ΔH_f° and ΔG_f° values (table 1), typically with mean relative errors close to 1% (maximum of 2%). Only the cases of Pb–F, Ca–Br and Pb–Br apatites led to surprisingly different entropies (7 to 15% difference) probably due to inaccurate ΔH_f° or ΔG_f° experimental values. The refined s_i values were thus added in table 4. Generally speaking, these entropy estimates were found to be more accurate, although of the same order of magnitude, than those drawn by VBT.

With the now available estimative parameters h_i, g_i and s_i, specifically fitted to phosphate apatites, it then becomes possible to evaluate the "missing" thermodynamic data (ΔG_f°, ΔH_f° or S°) for the apatites listed in table 1. This "correlation method" may appear empirical, but it leads to values in rather good accordance with experimental values as demonstrated above. This good accord then indicates that the thermodynamic properties of apatite compounds (enthalpy, free energy or entropy) are directly related to the sum of the enthalpy, free energy or entropy contributions of binary oxides composing the stoichiometry of the considered apatite system, provided that an appropriate correcting factor is applied for each constituting ion. The existence of a clear correlation therefore points out the "physical/chemical" basis of this additive model where the correcting factor for one type of ion (*e.g.* Ca^{2+}) is bound to be structure-specific (here apatite).

Based on (1) a rational compilation of data, either experimental-based or estimated in this work for "missing" data, (2) keeping in mind constrains like the $\Delta G_f^\circ = \Delta H_f^\circ - 0.298.\ \Delta S_f^\circ$ relationship, and (3) taking into account the nature of the M^{2+} and X^- ions, I propose herewith a *periodic table of* $M_{10}(PO_4)_6X_2$ *apatites* that summarizes their recommended thermodynamic properties at $T = 298$ K and 1 bar (table 5). This *periodic table* is intended to provide a concise tabulation of the main thermodynamic properties (ΔG_f°, ΔH_f° and S°) concerning these systems, to the best of the present knowledge, with entries that are easy to find thanks to the characteristic positioning of the elements M and X. This periodic table not only gathers information on apatites end-members for which experimental data were available, but also gives recommended estimates for "missing" data. For instance, estimates for the full series of

TABLE 5
Comprehensive periodic table of phosphate apatites recommended thermodynamic data to this date (at T = 298 K, 1 bar).



Periodic Table of Phosphate Apatites $M_{10}(PO_4)_6X_2$:
Recommended Thermodynamic Properties
(298 K, 1 bar)

oxyapatite

Ca^{2+}	O^{2-}
-12290	
-13066	
634	

s-block cations

	Mg^{2+} OH^-	Mg^{2+} F^-	Mg^{2+} Cl^-	Mg^{2+} Br^-
Mg	-11522	-11714	*-11447*	*-11421*
	-12337	*-12495*	*-12219*	*-12162*
	634	*618*	*676*	*700*

	HAP	FAP	ClAP	
	Ca^{2+} OH^-	Ca^{2+} F^-	Ca^{2+} Cl^-	Ca^{2+} Br^-
Ca	-12634	-12899	-12434	*-12346*
	-13432	-13658	-13185	*-13063*
	780	778	835	*870*
	Sr^{2+} OH^-	Sr^{2+} F^-	Sr^{2+} Cl^-	Sr^{2+} Br^-
Sr	-12587	-12845	-12478	*-12487*
	-13373	-13604	-13233	*-13201*
	954	912	956	*1013*
	Ba^{2+} OH^-	Ba^{2+} F^-	Ba^{2+} Cl^-	Ba^{2+} Br^-
Ba	-12553	-12834	-12529	*-12472*
	-13309	-13564	-13246	*-13154*
	1130	1084	1158	*1194*

d-block cations

	Cu^{2+} OH^-	Cu^{2+} F^-	Cu^{2+} Cl^-	Cu^{2+} Br^-
Cu	-6524	*-6709*	*-6450*	*-6424*
	-7309	*-7460*	*-7187*	*-7127*
	741	*719*	*797*	*829*
	Zn^{2+} OH^-	Zn^{2+} F^-	Zn^{2+} Cl^-	Zn^{2+} Br^-
Zn	-8623	*-8808*	*-8549*	*-8523*
	-9380	*-9532*	*-9258*	*-9198*
	919	*897*	*976*	*1008*
	Cd^{2+} OH^-	Cd^{2+} F^-	Cd^{2+} Cl^-	Cd^{2+} Br^-
Cd	-7873	-8045	-7719	*-7702*
	-8650	-8795	-8463	*-8405*
	952	910	960	*1019*

M^{2+} X^-
$\Delta G_f°$
$\Delta H_f°$
$S°$

p-block cations

	Pb^{2+} OH^-	Pb^{2+} F^-	Pb^{2+} Cl^-	Pb^{2+} Br^-
Pb	-7550	-7647	-7522	*-7520*
	-8286	-8360	-8212	-8180
	1222	1163	1274	*1293*

Regular lettering: averaged data from literature (see Table 1)
Italics lettering: best estimated values from Drouet (this paper)
Estimated relative error: within 1 %

From C. Drouet (2014)
Journal of Chemical Thermodynamics (JCT)

Cu-, Mg-, Zn- and Br-containing apatites (for which only few data were available) are also included. For these systems, VBT entropies $S°_{VBT}$ were selected (then allowing to refine the corresponding s_i parameters) and $\Delta G°_f$ values were calculated thanks to the additive model of table 4, and finally enthalpies could be derived from $\Delta G°_f$ and $S°_{VBT}$.

Cruz *et al.* [29] pointed out in their study on hydroxylated apatites that their enthalpy of formation followed a linear-like trend when plotted against the enthalpy of formation of the corresponding CaX_2 binary compound. Such linear trends had also previously been noticed by Bogach *et al.* [37] in some apatite compounds. Interestingly, the recommended $\Delta H°_f$ values reported in table 5 also follow such linear correlations, not only *versus* $\Delta H°_f(MX_2)$ but also *versus* $\Delta H°_f(MO)$; and similar linear tendencies were also found in terms of Gibbs free energies (see figure Suppl.3 (supporting information)). A minimal correlation factor R^2 of 0.95 and 0.90 was found for enthalpies and free energies, respectively. Additionally, as pointed out by Chermak and Rimstidt [85] who applied an additive model to the case of silicate minerals, the plot of h_i (or g_i) fitted parameters *versus* $\Delta H°_f$ (or $\Delta G°_f$) of the corresponding binary compounds also led to linear trends, which in the present work gave correlation factors $R^2 > 0.95$. The observation of all these linear correlations strongly supports the self-consistency of the recommended data tabulated in table 5, including for the Mg-, Zn-, Cu- and Br-apatites which are not commonly envisioned.

It may be noted at this point that some authors have attempted to estimate apatites thermodynamic properties based on lattice energy computational estimations and molecular modeling calculations [30,61,86]. However, the outcomes of these computed methods sometimes deserve to be debated as they do not always agree well with experimental facts. For example, Gibbs free energies of dissolution (denoted by the authors "ΔG_{diss}") for Mg- or Zn-apatites have been tentatively estimated via lattice energy assessments [30] (where the term "lattice energy" refers to the theoretical destruction of the lattice into constituting ions in a hypothetical gaseous state) and negative values were drawn, which the authors related to an expected high solubility and eventually to a low probability of formation in aqueous medium. However, the analysis at the computed ΔG_{diss} values reported by these authors shows that they correspond to $\Delta G°_f$ values for Pb-, Mg- and Zn-apatites that significantly depart from experimental reported data. For instance, their values of ΔG_{diss} computed for Zn–OH, Mg–OH and Mg–F apatites would correspond to $\Delta G°_f = -(4365, 8642$ and $9262)$ kJ · mol^{-1}, respectively; which fully disagree with reported values drawn by various research groups from experimental calorimetry and dissolution tests [42,43], measuring respectively $\Delta G°_f = -(8623.2, 11521.5$ and $11714.1)$ kJ · mol^{-1}. The value of −4365 kJ · mol^{-1} computed for the Zn–OH apatite would for example better correspond to a formula in Zn_5 than in Zn_{10}. A similar type of discrepancy was found [87] for a molecular modeling approach on Cl-containing apatites, where computed values calculated for enthalpies and Gibbs free energies of formation for Cd- and Zn-chlorapatites appear highly questionable: for example $\Delta G°_f$(Cd–Cl apatite) was estimated to −1544.32 kJ · mol^{-1} for $Cd_5(PO_4)_3Cl$, corresponding to −3088.64 kJ · mol^{-1} for $Cd_{10}(PO_4)_6Cl_2$, which clearly departs from the experimentally measured [24,59] order of magnitude close to −8460 kJ · mol^{-1}. In such modeling studies, care should probably be taken in precautious validations of computed outcomes with experimental data. In fact, as evidenced by the good fit obtained with the "additive" model developed here (table 4), the *order of magnitude to be expected* for the thermodynamic properties of formation of apatites is directly connected (via some correction factor) to the energetics of formation of the binary compounds MO and MX_2 corresponding to a given apatite composition. Since data for MO and MX_2 are generally available in databases (see for example references [26,45]), it is then possible to roughly check the expected order of magnitude. Any significant departure from the order of magnitude given by the sum of binary constituents, or more accurately by the presently determined additive model, should be questioned.

In fact, the non-easy detection of a given phase does *not systematically* infer its instability/inexistence. Reasons for explaining the apparent rareness in aqueous medium of some phases may sometimes be sought elsewhere. For example the precipitation of other insoluble compound may occur instead of the expected one (*e.g.* several zinc phosphates may form such as parascholzite $CaZn_2(PO_4)_2 \cdot 2H_2O$ or hopeite $Zn_3(PO_4)_2 \cdot 4H_2O$, among others, and in the co-presence of ammonium ions zinc may form the phase NH_4ZnPO_4). Another explanation may also be found in kinetics considerations. Indeed, the precipitation of apatite compounds (which are complex systems involving many ions per unit formula) takes time, especially at moderate temperature where ion diffusion processes remain slow. Therefore, the achievement of thermodynamic equilibrium may not have yet occurred when the experimentalist checks the reaction outcome. Plus, ions like Mg^{2+} and Zn^{2+} for example can act like growth inhibitors for the apatite structure,

thus influencing (unfavorably) the kinetics of crystallization. Finally, it may be noted that apatite formation through precipitation in aqueous medium is not the only way to presumably form such phases; for example solid state reactions might allow the preparation of selected apatites thanks to the absence of competitive precipitation schemes with other ionic species.

In addition to the low relative errors reached with this additive model, another potential advantage of this contributional method is to theoretically allow estimations not only for end-members but also for "mixed" apatites, *i.e.* solid-solutions between various end-members listed in table 1 (independently on the chemical nature, AE or NAE, of the cations). The case of such solid-solutions is thus also interesting to address, and it is treated in the dedicated next section.

4. Solid-solutions between apatite end-members of the type $M_{10}(PO_4)_6X_2$

In practical situations dealing with apatites (*e.g.* geological evaluations, fixation of heavy metals from waste waters, setup of biomaterials compositions, *etc.*), apatite end-members $M_{10}(PO_4)_6X_2$ are not expected to be the only phases of interest. "Mixed" compositions based on solid-solutions of two (or more!) end-members may in fact often be encountered taking into account the potential complexity of surrounding fluids, and this situation is thus worth analyzing.

The elaboration of table 4 should theoretically allow the evaluation of the thermodynamic properties of such solid-solutions due to its additive nature. However, assuming this additivity implies that we neglect the energetics of mixing (which corresponds to consider the solid-solution as thermodynamically ideal). This ideality does not always apply in real systems, where the existence of inhomogeneities of ionic distribution as well as associated geometrical distortions may lead to alterations of the energetics of the solid-solution. Since this ideal/non-ideal character (from a thermodynamic point of view) cannot be easily evaluated *a priori*, direct experimental measurements remain of course the best option to check this out. Nevertheless, from a practical viewpoint, although the non-ideal character of some apatitic solid-solutions has been reported [25] (*e.g.* for Ca–Cd substitutions in hydroxyapatites, fluorapatites or chlorapatites), the corresponding heats of mixing were found to remain limited, reaching only a few tens of $kJ \cdot mol^{-1}$ [23,25]. Therefore, taking into account the large numbers found for enthalpies and Gibbs free energies (calculated with reference to the elements taken in their standard states), the application of this additive method to determine the ranking in stability between various members of a solid-solution is expected to remain reasonably applicable. This is supported by the fact that, in practice, authors found that the plot of ΔH_f° (from the elements) *versus* the molar fraction of substituting ion was in fact very close to linearity [24,49,88].

As illustrative examples of thermodynamic estimates for apatite solid-solutions and comparison with existing literature data on such systems, let us consider the case of the mixing between Ca- and Cd-hydroxyapatites as was already considered experimentally by Ben Cherifa and Jemal [24]. Interestingly, applying the additive parameters of table 4 leads to a very good correlation (mean relative error: 0.45%) in comparison to the experimental data reported by these authors. The same conclusions were also drawn for Ca–Cd solid-solutions in fluorapatites and in chlorapatites (also available in the literature [24]), still allowing estimates of heats of formation with respectively mean relative errors of 0.17% and 0.61%. Although non-zero enthalpies of mixing ΔH_{mix} have been noticed from dissolution calorimetry by these authors for such solid-solutions [24], they only reached a maximum of $30\ kJ \cdot mol^{-1}$, which remains very limited in comparison to the enthalpies of formation (from the elements taken in their standard state) of the related apatites. Therefore, a very close-to-linearity behavior of the plot ΔH_f° = f(molar fraction of substituent) is found [24], which then justifies the possible use of an additive model.

The above findings therefore confirms the possibility to draw thermodynamic estimates not only for $M_{10}(PO_4)_6X_2$ apatite end-members, but also for their solid-solutions. Although experimental data should remain as always the "golden standard" for such determinations, the parameters given in table 4 (which were derived from direct comparison with experimental data) represent a pertinent tool for evaluating apatite solid-solutions energetics.

Besides the possibility to obtain solid-solutions, other types of chemical composition variations may also be encountered in real situations, including in particular *non-stoichiometry* and *hydration*. This will be addressed in the next section.

5. Non-stoichiometry and hydration aspects

Phosphate apatite minerals are present in various types of environments and may be obtained via many different ways [1,89] (*e.g.* coprecipitation, preparation by solid state reaction at high temperature, hydrothermal synthesis...). Consequently, variations in chemical composition and stoichiometry may be expected.

In high temperature systems or when long periods of time have been allowed (*e.g.* in the geological field for instance), samples exhibiting a high crystallinity and a composition close or equal to stoichiometry may be reached. In contrast, apatites obtained at rather "low" temperature (typically lower than 100 °C) often depart from stoichiometry [14], unless extended maturation times are used. This non-stoichiometry can probably be related to the high number of ions to accommodate in the structure which is a time-consuming process (kinetics limitations), especially if not thermally activated. Due to residual crystal defects (in particular ion vacancies), non-stoichiometric apatites are anticipated to be metastable and may be expected to evolve, whenever the external conditions allow it, towards stoichiometry. As an illustration, we recently pointed out and quantified experimentally [15] the existence of a thermodynamic "driving force" in the case of biomimetic calcium phosphate apatites, and the spontaneous tendency to evolve towards stoichiometry – when in humid conditions – has been evidenced [15].

Non-stoichiometry in phosphate apatites not only implies M^{2+} and X^- vacancies, but also the *protonation* of some trivalent PO_4^{3-} anions into bivalent HPO_4^{2-}, which contributes to keep the crystals neutral. For instance, the presence of HPO_4^{2-} ions in bone apatite or its synthetic biomimetic analogs is well-known [14,90–92]. Despite the frequent potential occurrence of non-stoichiometry in apatites, the impact on thermodynamics has almost never been investigated on an experimental basis. An exception is the above-mentioned case [15] of non-stoichiometric biomimetic calcium phosphate apatites where ΔH_f° calorimetry-based values were reported as well as the derived S° and ΔG_f°. In this context, the setup of estimative methods is again appealing approximating thermodynamic properties, while awaiting future experimental reports on non-stoichiometric specimens.

As previously discussed for solid-solutions, the additivity of the "apatite-fitted" parameters listed in table 4 is a precious advantage since it is intended to allow one to estimate thermodynamic values on the sole basis of chemical composition. In our previous paper [15], a rather good linearity was evidenced when plotting experimental-based ΔH_f° values (or ΔG_f°) *versus* the calcium or hydroxide content of $Ca_{10-x-Z}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x-2Z}$ apatites corresponding to an increasing degree of stoichiometry. This linearity is a good indication in favor of an additive predictive model, as it points out

the direct impact of the "chemical contents" of an apatite sample on its energetics. Therefore, these findings suggest that the additive parameters of table 4 may also presumably be used in the case of non-stoichiometric apatites (for which the chemical composition will have, as always, to be determined previously).

In non-carbonated apatites, as was the case in that work [15], the relative amounts of PO_4^{3-} and HPO_4^{2-} ions can be for example measured by visible spectrophotometry using the yellow phospho-vanado-molybdenum complex [93] (taking into account the condensation [94] of HPO_4^{2-} ions into pyrophosphate ions $P_2O_7^4$, not titrated by this method, after a typical heat treatment at 600 °C for 1 h). The thermodynamic contribution of HPO_4^{2-} ions is however expected to differ somewhat from that of PO_4^{3-} due to the presence of an associated proton. Fitted h_i and g_i values taking into account this protonation are thus needed at this point to evaluate the thermodynamic properties of HPO_4-containing specimens. La Iglesia [19] had considered the presence of HPO_4^{2-} ions in other phosphate compounds such as $(NH_4)_2HPO_4$ or K_2HPO_4, and he treated (with success) the additional proton as a separate sub-unit; which in other words consists in "considering" the HPO_4^{2-} ion as separated H^+ and PO_4^{3-} contributions.

Therefore, the determination of h_{H+} and g_{H+} parameters relative to such H^+ ions is required. To the best of the author's knowledge, experimental data on H-containing apatites (in the form of HPO_4^{2-} ions) are only available, to this date, in one single set of data relating to biomimetic calcium phosphate apatites [15]. This set of data was thus used here as a reference for comparison with estimated values. However, in these nanocrystalline apatites, precipitated at room temperature and freeze-dried, a residual amount of hydration water associated to the apatite phase was identified and quantified by the authors via thermal analyses [15]. Consequently, the presence of H_2O molecules in these samples has also to be taken into account when evaluating thermodynamic properties. It is thus also needed to evaluate concomitantly the h_{H_2O} and g_{H_2O} contributions. In his report on various phosphate minerals, La Iglesia [19] reported some h_i and g_i contributions for H^+ and for structural H_2O. As a starting point for the evaluation of these contributions, the H^+ and H_2O parameters were thus set to the values reported by this author. Then, the comparison with experimental data from Rollin-Martinet *et al.* [15] allowed refining these parameters, which could then be added in table 4. It may be remarked that the values for hydration water ($h_{H_2O} = -290\ \mathrm{kJ \cdot mol^{-1}}$ and $h_{H_2O} = -234\ \mathrm{kJ \cdot mol^{-1}}$) are less negative than those reported for other phosphate minerals by La Iglesia [19], where "structural" water molecules (and not simply hydration water) were involved. The numbers fitted here are closer to the values $\Delta H_f^\circ(H_2O,\mathrm{liq})$ and $\Delta G_f^\circ(H_2O,\mathrm{liq})$ relative to liquid water, reaching respectively $-(285.8$ and $237.1)\ \mathrm{kJ \cdot mol^{-1}}$. This confirms the hypothesis already guessed by Rollin-Martinet *et al.* [15], and suggests that these water molecules may globally be considered as rather loosely bound to the apatite surface (a distinction between physisorbed water and H_2O belonging to the hydrated layer present on the surface of some non-stoichiometric apatites cannot be made here due to insufficient data).

The application of the whole set of fitted parameters from the completed table 4 may then lead to estimate ΔH_f° and ΔG_f° for the apatite compositions $Ca_{10-x-Z}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x-2Z}$ investigated by Rollin-Martinet *et al.* [15]. These estimates were found to closely approach the reported experimental values, with a mean relative error of 0.4% (maximum of $\sim$ 0.7%), thus confirming the possible use of the additive model to non-stoichiometric and hydrated specimens. In turn, the contributive entropy parameters s_i for H^+ and H_2O were then also evaluated, by comparison with data from Martinet *et al.* [15], and added in table 4.

It should be reminded that in such non-stoichiometric nanocrystalline apatites, a vast literature [1,14,90–92,95–99] has pointed out the presence of a non-apatitic hydrated (and ionic) layer on the surface of the constituting nanocrystals. In addition to water, this surface layer was shown to contain cations and anions located in chemical environments differing from those found in conventional apatites. This matter of fact then evidences the co-existence of two types of ions in such "apatite" compounds: "apatitic" and "non-apatitic" ones (the latter being present on the surface of the crystals) [1,14,90,92,100–102]. Therefore, the identification of slightly different h_i and g_i energetic contributions should theoretically be envisioned in nanocrystalline non-stoichiometric specimens so as to take into account more accurately the contribution of the non-apatitic hydrated layer and of the apatitic core of the crystals. However, at this stage, there is not enough information on this surface layer nor enough calorimetry data to distinguish between apatitic and non-apatitic energetic contributions. Nonetheless, the goodness of the fits obtained here (within a maximum of $\sim$0.9% of relative error, generally within 0.4%) suggests that the parameters as gathered in table 4 allow reasonably accurate estimates to be drawn. This favorable situation might be in part related to the fitted values for H^+, since these species appear in HPO_4^{2-} ions which are known to be more extensively located within the non-apatitic surface layer on the nanocrystals [1,14,98,102,103].

6. Last considerations and important concluding statements

In a first part, this contribution gathered experimental-based literature data on phosphate apatites $M_{10}(PO_4)_6X_2$ (also extended to oxyapatite), which are encountered in many distinct fields such as biomaterials, biominerals, heavy metal waste treatments, geology, mineralogy, *etc.* permitting then to draw general principles and to discuss in particular the role of electronegativity and ion radius.

In a subsequent part, predictive methods for estimating the ΔG_f°, ΔH_f° and S° of such apatite end-members were investigated and compared. The most accurate, a "fourth-order" method based on the additivity of energetic contributions of constituting sub-units, was especially examined and the parameters were fitted specifically for phosphate apatites so as to decrease insofar as possible relative errors made in comparison to experimental data. In fact, the contributive enthalpy, free energy or entropy parameters (h_i, g_i and s_i respectively) of these sub-units correspond to a "corrected" value related to the energetics of the binary compounds MO and MX_2. Table 4 gathers all the fitted parameters that are proposed here. The fits obtained between values calculated by this additive method and experimentally-based data led to good correlations, with a mean relative error of the order to 0.4% and a maximum error of about 1%.

Interestingly, it was found in this paper that this additive model can also be applied (with similar estimation errors) to solid-solutions between $M_{10}(PO_4)_6X_2$ end-members, as well as for non-stoichiometric or even hydrated samples.

In cases when experimental data are available, they should be primarily considered in thermodynamic calculations (*e.g.* for the establishment of phase or stability diagrams). However, when none or only one of the three values ΔG_f°, ΔH_f° or S° is available, the need to evaluate the missing properties motivates the use of a predictive method such as the one established in the present paper. In order to consider internally-consistent ΔG_f°, ΔH_f° and S° values (*i.e.* which satisfy the equation $\Delta G_f^\circ = \Delta H_f^\circ - 0.298 \cdot \Delta S_f^\circ$), one of these three values can be drawn from the knowledge of the other two. Since ΔG_f° and ΔH_f° are large numbers, the evaluation of entropy (at $T = 298$ K) from ΔG_f° and ΔH_f° would lead to non-negligible propagated uncertainties; therefore it is advised to estimate *first* the entropy and then to determine the remaining unknown value(s) among ΔG_f° and ΔH_f°.

Another important point is that while the knowledge of ΔG_f°, ΔH_f° and S° is interesting *per se*, these values are generally used with a *final comparative objective*. For example, for evaluating if a process involving two types of apatite compositions will be spontaneous or not, the Gibbs free energy of the reaction will have to be estimated, which will involve the *difference* in ΔG_f° between the two apatite forms. This is not a trivial point. Indeed, although the ΔG_f° (as well as ΔH_f°) of apatites taken individually are large numbers, their *difference* could then lead to situations where it approaches the propagated estimation error. The relative error on each estimate (from which a standard deviation can easily be determined from the 1% maximal relative error) should therefore always be kept in mind in any calculation; and care should be taken whenever differences in ΔG or ΔH are close to the propagated standard deviation.

With this limitation in mind, such an additive fitted model should however prove helpful in view of predicting/following general tendencies. For example, figure 5 reports the evolution of the difference in ΔG° for biomimetic calcium phosphate apatites, relatively to the least matured specimen (maturation 20 min), *versus* their initial maturation time in solution (data published previously [15]). It is interesting to note that the same global evolution towards stoichiometric hydroxyapatite is seen both for the experimental datapoints and for the values calculated from the additive model. Therefore, in this example, the general variation in ΔG° could be adequately predicted by this additive model, which illustrates its potential interest, especially when experimental data are missing.

Considering both the existing experimental data and the "missing" values estimated in this work, a *periodic table* of recommended thermodynamic properties (ΔG_f°, ΔH_f° and S° at $T = 298$ K, 1 bar) of phosphate apatite end-members has then been proposed in table 5. Values given in this table have been shown to reasonably obey various linearity checks, thus supporting their consistency, at least until more experimental data become available. This table allows one to easily access to the values considered here as the most reliable to this day, for apatite end-members containing ions among Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, F^-, OH^-, Cl^- and Br^-. A total of 33 compositions are presented.

It may also be interesting to have access "at a glance" to the stability ranking of such apatite solid phases, which is the goal of figure 6 (plotted in terms of ΔG_f°). The general stability order F-apatites > OH-apatites > Cl-apatites > Br-apatites can be easily *visualized* on this graph, as well as the alkaline earth (AE) > non-alkaline-earth (NAE) stability tendency. Moreover, oxyapatite $Ca_{10}(PO_4)_6O$ remains the least stable phase within the calcium-containing samples considered in this study.

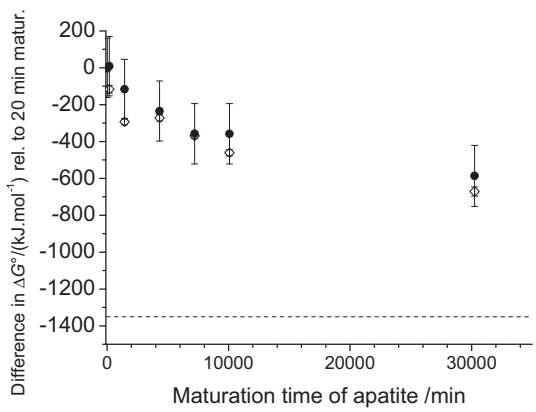


FIGURE 5. Experimental (◇) and estimated (●) evolution of the difference in ΔG° for biomimetic apatites relatively to the apatite matured 20 min, *versus* their initial maturation time in solution. The broken line (- - - -) indicates the level corresponding to stoichiometric HAP.

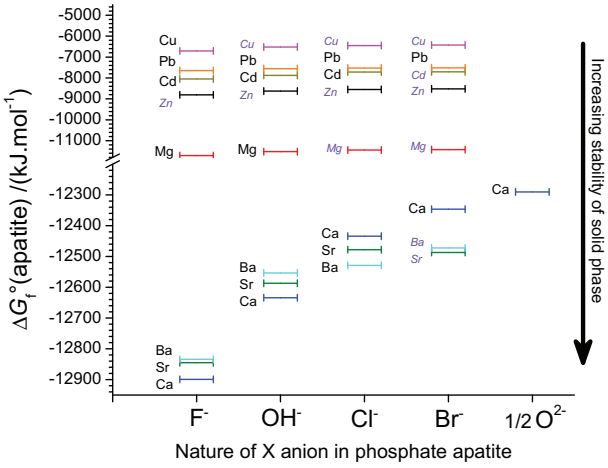


FIGURE 6. Stability energy diagram of ΔG_f° (apatites) as a function of their chemical composition of apatite $M_{10}(PO_4)_6X_2$. Lettering in *italics* refers to values estimated by the presently developed additive model (cases where experimental data were missing).

One important aspect deserves attention at this point. Indeed, although the relative stability of apatite phases is interesting to have at hand, the evaluation of the Gibbs free energy of a reaction that involved not only these phases but also other chemical species (such as aqueous ions for example) requires also to take into account the ΔG_f° of these species so as to get a full picture of the energetics of the process. In this context, the energetically-unfavorable transformation of a rather stable apatite phase into a less stable apatite composition (which could appear surprising at first) may sometimes occur because it is accompanied by a more energetically-favorable counter-effect linked to the disappearance of some unstable aqueous ions and the creation of more stable ones. For example, while aqueous calcium ions $Ca^{2+}_{(aq)}$ have a noticeably negative free energy of formation ($\Delta G_f^\circ = -553.6$ kJ · mol^{-1}), this is not the case for lead ions $Pb^{2+}_{(aq)}$ ($\Delta G_f^\circ = -24.2$ kJ · mol^{-1}) [34]. Therefore, if one considers (at $T = 298$ K) the replacement of calcium by lead in hydroxyapatite, in solution, represented by the scheme:

$$Ca_{10}(PO_4)_6(OH)_2 + 10Pb^{2+}_{(aq)} \rightarrow Pb_{10}(PO_4)_6(OH)_2 + 10Ca^{2+}_{(aq)} \quad (3)$$

the associated standard variation in free energy of this reaction, ΔG°_{react}, at equilibrium is notably negative (-210 kJ · mol^{-1}), which corresponds to an equilibrium constant estimated to $K_{eq} = 6.5 \cdot 10^{36}$, implying a clearly favorable transformation from left to right, despite the lower stability of lead-hydroxyapatite ($\Delta G_f^\circ = -7515$ kJ · mol^{-1}) as compared to calcium-hydroxyapatite ($\Delta G_f^\circ = -12634$ kJ·mol^{-1}). In other words, the substitution of calcium by lead turns out to be globally favorable thanks to the overall gain in energy linked to the disappearance of $Pb^{2+}_{(aq)}$ ions in favor of $Ca^{2+}_{(aq)}$. Such a lead incorporation into apatite has indeed been observed experimentally [13]. Consequently, as always in chemical thermodynamics, the full evolving system has to be taken into account for assessing reliable energetic considerations.

The knowledge of Gibbs free energies of formation ΔG_f° of apatite phases also allows one to estimate their solubility products, K_{sp}, at $T = 298$ K. This is made possible by considering a given dissolution equilibrium between the solid phase and its constituting ions and by evaluating the associated free energy of reaction, ΔG_{disso}. For a dissolution reaction written as:

$$M_{10}(PO_4)_6X_2 \rightarrow 10M^{2+}_{(aq)} + 6PO_4^{3-}{}_{(aq)} + 2X^-_{(aq)} \quad (4)$$

one can write, at equilibrium, $\Delta G_{disso}/(\text{kJ} \cdot \text{mol}^{-1}) = \Delta G^\circ_{disso}/(\text{kJ} \cdot \text{mol}^{-1}) + RT.\,\text{Ln}K_{sp} = 0$ where $K_{sp} = (M^{2+}_{(aq)})^{10}\,(PO_4^{3-}{}_{(aq)})^6(X^-_{(aq)})^2$ is the solubility product, parentheses denoting ionic activities,

and where $\Delta G^{\circ}_{disso} = 10\Delta G^{\circ}_{f}(M^{2+}_{(aq)}) + 6\Delta G^{\circ}_{f}(PO^{3-}_{4\,(aq)}) + 2\Delta G^{\circ}_{f}(X^{-}_{(\,aq)}) - \Delta G^{\circ}_{f}(\text{apatite})$. The values of K_{sp} for all the apatitic systems $M_{10}(PO_4)_6X_2$ discussed in this work were estimated from this equation, using the recommended values tabulated in the periodic table (table 5) and the NBS thermodynamic database [26] for aqueous species (using in particular the value $\Delta G^{\circ}_{f}(PO^{3-}_{4(\,aq)}) = -1018.8\ \text{kJ}\cdot\text{mol}^{-1}$). The values obtained are listed in terms of pK_{sp} in figure Suppl.4 (supporting information). They can serve as first estimates of K_{sp}, especially when no other experimental dissolution data are available. Note for example that the data relative to HAP, FAP, copper-HAP, lead-HAP or barium chlorapatite, respectively 10^{-118}, 10^{-121}, 10^{-131}, 10^{-154} and 10^{-105}, agree very well with experimentally-available values [42,52,104,105] (respectively $10^{-116.6}$, $10^{-121.2}$, $10^{-131.2}$, 10^{-154} and $10^{-102.8}$).

7. Concluding remark 1

With all these considerations in mind, the thermodynamics of phosphate apatites ultimately become accessible to end-users and researchers from various domains, which should allow more numerous energetic calculations in the future.

Thermodynamic properties may vary somewhat depending on the crystallinity state and grain size of the samples produced – in much the same way as was mentioned for example for silicate materials [75] – and, of course, will be impacted by non-stoichiometry or ionic substitutions. In some instances, however, some apatite systems happen to exhibit rather similar properties/stabilities: it may for example be noted from table 1 (and also from the deriving recommended values of the periodic table, table 5) that Ba-, Ca-, and Sr-apatite end-members have (for a given X^- anion) rather close levels of stability (in terms of ΔG°_{f}). This can also be visualized graphically from figure 6. Therefore, as may be expected, the contributive values of g_i for these ions are close from each other (namely −739.4 for Ba^{2+}, −740 for Ca^{2+}, and −740.9 for Sr^{2+}, see table 4). With these g_i values in mind, the stability ranking Sr-apatite > Ca-apatite > Ba-apatite would be expected. In "real" systems (as shown in table 1, some variability in this Sr/Ca/Ba ranking may however be evidenced upon changing X^-. As mentioned above, this may be due to different crystallinity states or grain sizes, and/or to the presence of vacancies not taken into account by the authors, and/or to the involvement of additional (de)stabilizing secondary effects that have not yet been identified for these systems.

8. Concluding remark 2

To summarize:

- When considering *stoichiometric end-members* or simple chemical equation between them, it is recommended (to the best of today knowledge) to use the thermodynamic data tabulated in the periodic table of table 5.
- When considering *non-stoichiometric* apatites or complex solid solutions, the use of the additive model of table 4 is bound to prove helpful to evaluate standard thermodynamic properties of such apatite systems, at least in a first approximation (estimated within 1% of relative error, and often within 0.5%). This table is made available, in the form of an easy-to-use free calculation sheet at the following address: www.christophedrouet.com/thermAP.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2014.09.012.

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