The prediction method for standard enthalpies of apatites using the molar volume, lattice energy, and linear correlations from existing experimental data

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Abstract
Experimental data of thermodynamic state functions and molar volume for phosphate, arsenate, and vanadate apatites containing Ca, Sr, Ba, Pb, and Cd at the cationic positions Me2+ and F, OH, Cl, Br, and I at the halide position X were collected. The apatite supergroup splits into distinct subgroups (populations) constituted by Me10(AO4)6X2 with the same Me2+ cations and tetrahedral AO43− anions but with different anions at the X position. Linear relationships between various parameters within apatite subgroups are observed. The prediction method for standard enthalpies of apatites (ΔH°f,el) is based on regression analysis of the linear correlations within the subgroups between ΔH°f,el of apatites and their molar volume Vm, lattice energy UPOT, and ΔH°f,el of their anions AO43− or X−. This allowed to predict 22 new ΔH°f,el values for apatites and materials with an apatite structure. The prediction precision is comparable to the experimental uncertainty obtained when reproducing experimental data using calorimetric measurements or dissolution experiments and can be applied to a wider range of apatites than other methods.

Keywords Iodoapatites · Thermodynamics of apatites · Thermodynamic stability · Volume-based Thermodynamics · Thermodynamic database

Introduction
Quantitative geochemical calculations are not possible without thermodynamic databases. Considerable advances in the quantity and quality of these databases have been made since the early days of Lewis and Randall (1923), Latimer (1952), and Rossini et al. (1952). According to Oelkers and Shott (2018), the emergence of thermodynamic databases can be considered one of the greatest advances in geochemistry of the last century. Thermodynamic data have been used in basic research and for countless applications in computational modelling, computer simulations, waste management, and policy-making. The challenges today are to evaluate thermodynamic data for internal consistency and to reach a most reliable properties. The present work focuses on the enthalpy of formation from elements (ΔH°f,el) of minerals and synthetic compounds belonging to the apatite supergroup.

The natural apatites and apatite-based materials are a class of compounds with the stoichiometry Me10(AO4)6X2, where the Me-site is occupied by larger monovalent (Na+, K+, etc.), divalent (Ca2+, Sr2+, Ba2+, Pb2+, Cd2+, etc.), or trivalent (La3+, Y3+, Ce3+, Sm3+, etc.) cations, the A-site is occupied by a smaller metal, metalloid or nonmetal (P5+, As5+, V5+, S4+, etc., often accompanied by carbonate anion CO32−), and the X-site is filled by halides, hydroxides, or oxides (F−, Cl−, Br−, I−, OH−, O2−, etc., also often accompanied by a carbonate anion CO32−) (e.g., Rakovan and Hughes 2000; Pan and Fleet 2002; Pasero et al. 2010; Tait et al. 2015; Ptáček 2016; Hughes and Rakovan 2018; Pieczka 2018; Rakovan and Scovil 2021). Due to the extremely rich array of possible substitutions in each of the highlighted positions, the possible end-members alone are over 200 types, indicating that this is currently the most numerous supergroup of minerals and compounds (Baker 1966; Oelkers and Valsami-Jones 2008; Rakovan...
Overview of experimental thermodynamic data of apatites

Table 1 provides a compilation of the thermodynamic data available in the literature (based on experiments and “ab initio” calculations) for stoichiometric $\text{Me}_{10}(\text{AO}_4)_6\text{X}_2$ apatites (phosphate, arsenate, and vanadate with different $\text{Me}^{2+}$ and $\text{X}^-$), such as the standard enthalpy of formation from elements $\Delta H^{o}_{f,\text{el}}$, the standard entropy $S^{o}_{298.15K}$, the specific heat capacity $C^{o}_{p,m}$, the molar volume $V_m$, and the solubility constant $K_{sp,298.15K}$. The Gibbs free energy of formation ($\Delta G^{o}_{f,\text{el}}$) is not included to maintain consistency in the thermodynamic data presented. $\Delta G^{o}_{f,\text{el}}$ values available in the literature are mostly calculated from approximations or using different, often mixed thermodynamic databases, which contributes significant scatter. Therefore, the compilation and variability analysis of the $\Delta G^{o}_{f,\text{el}}$ data for apatites should be discussed in a separate paper.

The observed discrepancies in the data are likely due to the varying crystallinity states, polymorphs (either hexagonal or monoclinic, mostly not identified in literature reports), nonstoichiometry, hydration state and/or the presence of undetected impurities. A lower degree of crystallinity, for example, may favor somewhat less negative values of $\Delta H^{o}_{f,\text{el}}$ (Craig and Rootare 1974). The difference between the hexagonal (P6$_3$/m) and monoclinic (P2$_1$/b) symmetries results in different positioning of the $\text{X}^-$ anions along the apatitic channels (giving rise or not to a mirror plane) but does not correspond to a large ion rearrangement. Therefore, the energetics of formation are not expected to be very different (although not identical), allowing both polymorphs to be considered equal.

Drouet (2015) and Puzio et al. (2022) previously reported that thermodynamic state functions for apatites vary in a regular, mostly linear manner, depending on various physicochemical parameters of their components, such as the ionic radius of $\text{X}^-$, the electronegativity of $\text{X}$, the ionization energy of $\text{X}$, and others. A current and complete review of the data presented in Table 1 allows such trends and relationships to be clearly observed. For example, for a given $\text{X}^-$ anion (from among OH$^-$, F$^-$, Cl$^-$, or Br$^-$), the formation of apatite is less exothermic (the enthalpy of formation $\Delta H^{o}_{f,\text{el}}$ is less negative) when apatite contains a heavier element, such as As or V instead of P and Cd or Pb instead of alkali metals (Fig. 1A). In contrast, this relationship is not observed when alkali metals ($\text{Ca}^{2+}$, $\text{Ba}^{2+}$ or $\text{Sr}^{2+}$) are substituted in the $\text{Me}^{2+}$ position. It is clearly apparent from the graph that apatites form distinctly separate subgroups (Fig. 1A). Here, a subgroup is defined as a population of apatites with the same substitution at position $\text{Me}$ and $\text{A}$ but with different substitutions at position $\text{X}$ (where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OH}$) e.g., subgroup of
Table 1  Experimental-based and “ab initio” literature data available for apatite end-members with the general chemical formula $\text{Me}_10(\text{AO}_4)_6\text{X}_2$ (where $\text{Me} = \text{Ca, Ba, Sr, Pb, Cd}$; $\text{A} = \text{P, As, V}$, and $\text{X} = \text{F, OH, Cl, Br, I}$), at $T = 298 \text{ K}$ and 1 bar

| Chemical formula | $\Delta H_{\text{f, el}}^{\circ}$ (kJ mol$^{-1}$) | Reference | $S^{\circ}$ (J mol$^{-1}$ K$^{-1}$) | Reference | $C_{\text{p, m}}^{\circ}$ (J mol$^{-1}$ K$^{-1}$) | Reference | log $K_{\text{sp}}$ | Reference | $V_{\text{m}}$ (nm$^3$) | Reference |
|------------------|-----------------------------------|-----------|---------------------------------|-----------|---------------------------------|-----------|-----------------|-----------|-----------------|-----------|
| Ca$_{10}$(PO$_4$)$_6$F$_2$ | $-13,449$ | Yan et al. 2020 | 766.4 | Dachs et al. 2010 | 739.2 | Dachs et al. 2010 | $-118.0$ | Stumm and Morgan 2012 | 0.5236 | Lim et al. 2011 |
|                  | $-13,548$ | Cherifa and Jemal 2004 | 765.0 | Flora et al. 2004a, b | 646.0 | Cruz et al. 2005a, b | $-114.4$ | Zhu et al. 2009 | 0.5237 | O’Donnell et al. 2009 |
|                  | $-13,558$ | Flora et al. 2004a, b | 771.8 | Bogach et al. 2001 | 740.9 | Fleche 2002 | $-58.8$ | Harouiya et al. 2007 | 0.5246 | Mercier et al. 2007 |
|                  | $-13,550$ | Niahomovukiyi et al. 1997 | 775.8 | Robie and Hemingway 1995 | 751.0 | Bogach et al. 2001 | $-61.9$ | Stefansson 2001 | 0.5231 | ICDD 1997 |
|                  | $-13,545$ | Jemal et al. 1995 | 775.7 | Wagman et al. 1982 | 751.8 | Robie and Hemingway 1995 | $-116.3$ | Jaynes et al. 1999 | 0.5233 | Sudarsanan et al. 1972 |
|                  | $-13,744$ | Robie and Hemingway 1995 | 776.5 | Egan et al. 1951 | 751.6 | Roine 1994 | $-65.9$ | Valsami-Jones et al. 1998 |
|                  | $-13,536$ | Cherifa et al. 1991 | 776.5 | Egan et al. 1951 | 751.6 | Roine 1994 | $-65.9$ | Valsami-Jones et al. 1998 |
|                  | $-13,653$ | Zhu and Sverjensky 1991 | 756.2 | Zhu and Sverjensky 1991 | 756.2 | Zhu and Sverjensky 1991 | $-50.9$ | Elliot 1994 |
|                  | $-13,657$ | Valyashko et al. 1968 | 751.9 | Wagman et al. 1982 | 751.0 | Mooney and Aia 1961 | $-121.2$ | Driessens 1982 |
|                  | $-13,677$ | Farr and Elmore 1962 | 751.0 | Mooney and Aia 1961 | 751.0 | Mooney and Aia 1961 | $-121.2$ | Driessens 1982 |
|                  | $-13,684$ | Smirnova et al. 1962 | 752.3 | Egan et al. 1951 | 752.3 | Egan et al. 1951 | $-120.3$ | Amjad et al. 1981 |
|                  | $-13,797$ | Jacques 1963 | 768.0 | Flora et al. 2004a, b | 694.0 | Cruz et al. 2005a, b | $-115.8$ | Puzio et al. 2018 | 0.5300 | Puzio et al. 2018 |
|                  | $-13,719$ | Kelley and King 1961 | 785.0 | Bogach et al. 2001 | 765.8 | Bogach et al. 2001 | $-116.8$ | Zhu et al. 2016 | 0.5243 | Chernorukov et al. 2011 |
|                  | $-13,655$ | Gottschall 1958 | 785.0 | Bogach et al. 2001 | 765.8 | Bogach et al. 2001 | $-116.8$ | Zhu et al. 2016 | 0.5243 | Chernorukov et al. 2011 |
### Table 1 (continued)

| Chemical formula          | $\Delta H^\circ_{\text{f,el}}$ (kJ mol$^{-1}$) | Reference      | $S^\circ$ (J mol$^{-1}$ K$^{-1}$) | Reference      | $C_p, m$ (J mol$^{-1}$ K$^{-1}$) | Reference | $\log K_{sp}$ | Reference | $V_m$ (nm$^3$) | Reference |
|----------------------------|-----------------------------------------------|----------------|---------------------------------|----------------|---------------------------------|-----------|--------------|-----------|----------------|-----------|
| $\text{Ca}_{10}\text{PO}_{4}\text{Cl}_2$ | $-13,231$                                     | Cruz et al. 2005a, b | 808.0                           | Babu et al. 2011 | 747.8                           | Dachs et al. 2010 | 747.8            | Narasaraju et al. 1979 | 0.5371               | Cruz et al. 2005a, b |
|                           | $-13,179$                                     | Jemal 2004       | 804.3                           | Bogach et al. 2001 | 756.0                           | Tacker and Stormer 1989 | 756.0            | Zhu and Sverjensky 1991 | 0.5561               | White and Dong 2003  |
|                           | $-13,179$                                     | Jemal 2004       | 804.3                           | Bogach et al. 2001 | 756.0                           | Tacker and Stormer 1989 | 756.0            | Zhu and Sverjensky 1991 | 0.5561               | White and Dong 2003  |
|                           | $-13,179$                                     | Jemal 2004       | 804.3                           | Bogach et al. 2001 | 756.0                           | Tacker and Stormer 1989 | 756.0            | Zhu and Sverjensky 1991 | 0.5561               | White and Dong 2003  |
|                           | $-13,231$                                     | Cruz et al. 2005a, b | 808.0                           | Babu et al. 2011 | 747.8                           | Dachs et al. 2010 | 747.8            | Narasaraju et al. 1979 | 0.5371               | Cruz et al. 2005a, b |
|                           | $-13,179$                                     | Jemal 2004       | 804.3                           | Bogach et al. 2001 | 756.0                           | Tacker and Stormer 1989 | 756.0            | Zhu and Sverjensky 1991 | 0.5561               | White and Dong 2003  |
| Chemical formula | \( \Delta H'_{\text{cal}} \) (kJ mol\(^{-1}\)) | Reference | \( S^0 \) (J mol\(^{-1}\) K\(^{-1}\)) | Reference | \( C_{p,m}^0 \) (J mol\(^{-1}\) K\(^{-1}\)) | Reference | log\( K_{sp} \) | Reference | \( V_m \) (nm\(^3\)) | Reference |
|------------------|---------------------------------|-----------|-----------------|-----------|-----------------|-----------|-----------------|-----------|-----------------|-----------|
| \( \text{Ca}_{10}(\text{PO}_4)_6\text{Br}_2 \) | -13,139 | Khattech and Jemal 1997 | 795.8 | Vieillard and Tardy 1984 | 758.0 | Krishnan et al. 2008 | 0.5389 | Kim et al. 2000 |
|                  | -13,161 | Cherifa et al. 1991 | 796.2 | Valyashko et al. 1968 | 751.0 | Babu et al. 2011 | 0.5450 | ICDD 1997 |
|                  | -13,201 | Zhu and Sverjensky 1991 | 752.6 | Bogach et al. 2001 | 0.5448 | Ben Cherifa et al. 1991 |
|                  | -13,096 | Tacker and Stormer 1989 | 758.3 | Valyashko et al. 1968 | 0.5450 | Mayer et al. 1979 |
|                  | -13,278 | Gottshall 1958 | 0.5445 | Sudarsanan and Young 1978 |
| \( \text{Ca}_{10}(\text{PO}_4)_6\text{I}_2 \) | -13,201 | Cruz et al. 2005a, b | 827.3 | Bogach et al. 2001 | 811.0 | Cruz et al. 2005a, b | 0.5430 | Mackie et al. 1972 |
|                  |          |                        |       |                        | 728.8 | Bogach et al. 2001 | 0.5486 | Cruz et al. 2005a, b |
| \( \text{Sr}_{10}(\text{PO}_4)_6\text{F}_2 \) | -13,063 | Cruz et al. 2005a, b | 873.8 | Cruz et al. 2005a, b | 0.5561 | White and Dong 2003 |
| \( \text{Ca}_{10}(\text{PO}_4)_6\text{I}_0.66 \) | -12,949 | Cruz et al. 2005a, b | - | - | 0.5561 | Elliot et al. 1981 |
| \( \text{Ca}_{10}(\text{PO}_4)_6\text{I}_0.92 \) |          |                        |       |                        | 873.8 | Cruz et al. 2005a, b | 0.5560 | Dykes 1974 |
| \( \text{Sr}_{10}(\text{PO}_4)_6\text{F}_2 \) | -13,604 | Jemal et al. 1995 | - | - | 0.5440 | Phebe and Narasaratju 1995 |
|                  | -13,982 | Jain et al. 2013 | - | - |                        | Not shown | Coulon et al. 2016 |
|                  | -13,201 | Yuan et al. 2017 | - | - | 0.5484 | Alberius Henning et al. 1999 |
| \( \text{Sr}_{10}(\text{PO}_4)_6\text{F}_2 \) | -13,604 | Jemal et al. 1995 | - | - | 0.6178 | Jain et al. 2013 |
|                  | -13,982 | Jain et al. 2013 | - | - | 0.5695 | Yuan et al. 2017 |
|                  | -13,201 | Yuan et al. 2017 | - | - | 0.6010 | Knyazev et al. 2015 |
| \( \text{Sr}_{10}(\text{PO}_4)_6\text{F}_2 \) | -13,604 | Jemal et al. 1995 | - | - | 0.6010 | Chernorukov et al. 2011 |
|                  | -13,982 | Jain et al. 2013 | - | - | 0.5961 | Lim et al. 2011 |
|                  | -13,201 | Yuan et al. 2017 | - | - | 0.5964 | Aissa et al. 2004 |
| \( \text{Sr}_{10}(\text{PO}_4)_6\text{F}_2 \) | -13,604 | Jemal et al. 1995 | - | - | 0.5958 | ICDD 2004 |
|                  | -13,982 | Jain et al. 2013 | - | - | 0.5901 | Swafford and Holt 2002 |
|                  | -13,201 | Yuan et al. 2017 | - | - | 0.5967 | ICDD 1997 |
| \( \text{Sr}_{10}(\text{PO}_4)_6\text{F}_2 \) | -13,604 | Jemal et al. 1995 | - | - | 0.5952 | Corker et al. 1995 |
|                  | -13,982 | Jain et al. 2013 | - | - | 0.5944 | McConnell 1974 |
## Table 1 (continued)

| Chemical formula | $\Delta H^o_{f,el}$ (kJ mol$^{-1}$) | Reference | $S^o$ (J mol$^{-1}$ K$^{-1}$) | Reference | $C^o_{p,m}$ (J mol$^{-1}$ K$^{-1}$) | Reference | log $K_{sp}$ | Reference | $V_m$ (nm$^3$) | Reference |
|------------------|----------------------------------|-----------|-----------------|-----------|----------------------------------|-----------|--------------|-----------|----------------|-----------|
| Sr$_{10}$(PO$_4$)$_6$OH$_2$ | $-13,373$ | Jemal et al. 1995 | – | – | – | – | 0.5955 | ICDD 2004 |
| Sr$_{10}$(PO$_4$)$_6$Cl$_2$ | $-13,570$ | Jain et al. 2013 | 904.0 | Babu et al. 2011 | 759.0 | Babu et al. 2011 | – | 0.6152 | ICDD 2004 |
| Sr$_{10}$(PO$_4$)$_6$Br$_2$ | $-13,322$ | Jain et al. 2013 | – | – | – | – | 0.6434 | Jain et al. 2013 |
| Ba$_{10}$(PO$_4$)$_6$F$_2$ | $-13,667$ | Junhui et al. 2016 | – | – | – | – | 0.6959 | Junhui et al. 2016 |

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**Notes:**
- $\Delta H^o_{f,el}$: Standard heat of formation.
- $S^o$: Standard entropy.
- $C^o_{p,m}$: Standard molar heat capacity.
- $K_{sp}$: Solubility product.
- $V_m$: Molar volume.

**References:**
- Jemal et al. 1995
- Mayer et al. 1979
- Verbeeck et al. 1977
- Jemal 2004
- Sudarsanan and Young 1974
- Knyazev et al. 2015
- Chernorukov et al. 2011
- Alberius–Henning et al. 2000
- Junhui et al. 2016
- Aissa et al. 2004
- ICDD 1997
- ICDD 2004
| Chemical formula | $\Delta H^\circ_{f,el}$ (kJ mol$^{-1}$) | Reference | $S^\circ$ (J mol$^{-1}$ K$^{-1}$) | Reference | $C^\circ_p, m$ (J mol$^{-1}$ K$^{-1}$) | Reference | $\log K_{sp}$ | Reference | $V_m$ (nm$^3$) | Reference |
|------------------|---------------------------------|-----------|-------------------------------|-----------|---------------------------------|-----------|----------------|-----------|----------------|-----------|
| Ba$_{10}$(PO$_4$)$_6$OH$_2$ | $-13,309$ | Ben Cherifa and Jemal 2004 | – | – | – | – | | | 0.6903 | Mathew et al. 1979 |
| Ba$_{10}$(PO$_4$)$_6$Cl$_2$ | $-13,348$ | Junhui et al. 2016 | 1044.0 | Babu et al. 2011 | 767.0 | Babu et al. 2011 | – | | 0.6943 | McConell 1974 |
| | $-13,246$ | Khattech et al. 1996 | 787.0 | Jena et al. 2011 | – | | | | 0.7056 | Junhui et al. 2016 |
| Ba$_{10}$(PO$_4$)$_6$Br$_2$ | $-13,047$ | Junhui et al. 2016 | – | – | – | – | | | 0.7051 | Junhui et al. 2016 |

**Table 1 (continued)**
| Chemical formula         | $\Delta H^\circ_{\text{f,el}}$ (kJ mol$^{-1}$) | Reference             | $S^\circ$ (J mol$^{-1}$ K$^{-1}$) | Reference | $C^\circ_{p,m}$ (J mol$^{-1}$ K$^{-1}$) | Reference | $\log K_{\text{sp}}$ | Reference | $V_m$ (nm$^3$) | Reference |
|--------------------------|-----------------------------------------------|------------------------|----------------------------------|-----------|----------------------------------------|-----------|---------------------|-----------|-------------|-----------|
| Ba$_{9.06}$(PO$_4$)$_6$I$_{0.08}$ | –                                         | –                      | –                               | –         | –                                      | –         | 0.6929              | Bulanov et al. 2021 |
| Cd$_{10}$(PO$_4$)$_6$F$_2$      | – 8817                                    | Lin et al. 2018        | –                               | –         | –                                      | –         | – 120.1             | Lin et al. 2018    |
|                             | – 8795                                    | Jemal et al. 1995      | –                               | –         | –                                      | –         | 0.4966              | McConell 1974     |
| Cd$_{10}$(PO$_4$)$_6$OH$_2$    | – 8652                                    | Ben Cherifa and Jemal 2004 | –                               | –         | –                                      | –         | – 129.2             | Zhu et al. 2015b  |
|                             | – 8648                                    | Jemal et al. 1995      | –                               | –         | –                                      | –         | Not shown           | Zhu et al. 2015b  |
|                             | – 8566                                    | Zhu et al. 2015b       | –                               | –         | –                                      | –         | Not shown           | Karbovsky and Soroka 2014 |
|                             | – 8678                                    | Mahapatra et al. 1982  | –                               | –         | –                                      | –         | 0.5029              | Hata et al. 1978  |
|                             |                                           |                        |                                  |           |                                        |           | 0.5006              | McConell 1974     |
|                             |                                           |                        |                                  |           |                                        |           | Not shown           | Hayek and Peter 1959 |
| Cd$_{10}$(PO$_4$)$_6$Cl$_2$    | – 8463                                    | Ben Cherifa et al. 2001| –                               | –         | –                                      | –         | – 131.2             | Wołowiec et al. 2019|
|                             |                                           |                        |                                  |           |                                        |           | 0.5105              | Wołowiec et al. 2019|
|                             |                                           |                        |                                  |           |                                        |           | – 99.3              | Veillard and Tardy 1984 |
|                             |                                           |                        |                                  |           |                                        |           | 0.5209              | Chernorukov et al. 2011|
|                             |                                           |                        |                                  |           |                                        |           | 0.5218              | ICDD 2004          |
|                             |                                           |                        |                                  |           |                                        |           | 0.5264              | McConell 1974     |
|                             |                                           |                        |                                  |           |                                        |           | 0.5211              | ICDD 1997          |
|                             |                                           |                        |                                  |           |                                        |           | 0.5282              | Sudarsanan and Young 1972 |
|                             |                                           |                        |                                  |           |                                        |           | 0.5306              | Sudarsanan et al. 1977|
|                             |                                           |                        |                                  |           |                                        |           | 0.5306              | Sudarsanan et al. 1977|
|                             |                                           |                        |                                  |           |                                        |           | 0.5282              | Sudarsanan et al. 1977|
| Pb$_{10}$(PO$_4$)$_6$F$_2$     | – 8529                                    | Jemal et al. 1995      | –                               | –         | –                                      | –         | – 156.6             | Yan et al. 2020   |
|                             | – 8466                                    | Nutahomvuksiye et al. 1997| –                               | –         | –                                      | –         | Not shown           | Dziura et al. 2012|
|                             | – 8523                                    | Yan et al. 2020        | –                               | –         | –                                      | –         | 0.6213              | Chernorukov et al. 2011|
|                             |                                           |                        |                                  |           |                                        |           | 0.6022              | ICDD 2004          |
|                             |                                           |                        |                                  |           |                                        |           | 0.6010              | ICDD 1997          |
|                             |                                           |                        |                                  |           |                                        |           | 0.6047              | McConell 1974     |
|                             |                                           |                        |                                  |           |                                        |           | 0.6014              | Merker and Wondratschek 1957 |
Table 1 (continued)

| Chemical formula | $\Delta H^\circ_{f,el}$ (kJ mol$^{-1}$) | Reference | $S^\circ$ (J mol$^{-1}$ K$^{-1}$) | Reference | $C^\circ_p, m$ (J mol$^{-1}$ K$^{-1}$) | Reference | $\log K_{sp}$ | Reference | $V_m$ (nm$^3$) | Reference |
|------------------|--------------------------------------|-----------|---------------------------------|-----------|-------------------------------------|-----------|----------------|-----------|----------------|-----------|
| Pb$_{10}$(PO$_4$)$_6$OH$_2$ | – 8261 | Jemal et al. 1995 | – | – | – 161.5 | Zhu et al. 2016 | 0.6062 | Olds et al. 2021 |
|                  | – 8220 | Zhu et al. 2015a | – | – | – 125.6 | Allison et al. 1991 | 0.6260 | ICDD 2004 |
| Pb$_{10}$(PO$_4$)$_6$Cl$_2$ | – 8216 | Puzio et al. 2021 | 1244.0 | Topolska et al. 2016 | 804.0 | Topolska et al. 2016 | – 159.1 | Puzio et al. 2021 | 0.6348 | Gu et al. 2020 |
|                  | – 8217 | Topolska et al. 2016 | 1170.6 | Bisengalieva et al. 2010 | 826.0 | Bisengalieva et al. 2010 | – 159.2 | Topolska et al. 2016 | 0.6297 | Antao and Dhaliwal 2018 |
|                  | – 8248 | Bisengalieva et al. 2010 | – | – | – 159.0 | Drouet et al. 2015 | **0.6350** | Antao and Dhaliwal 2018 |
|                  | – 7474 | Chernorukov et al. 2010 | – | – | – 159.3 | Flis et al. 2011 | 0.6321 | Solecka et al. 2018 |
|                  | – 8220 | Flora et al. 2004a, b | – | – | – 161.7 | Manecki and Maurice 2008 | 0.6336 | Okudera 2013 |
|                  | – 8204 | Jemal et al. 2004 | – | – | – 160.8 | Xie and Grammar 2007 | 0.6323 | Chernorukov et al. 2011 |
|                  | – 167.5 | Manecki et al. 2000 | – | – | – 167.5 | Manecki et al. 2000 | 0.6316 | Chernorukov et al. 2010 |
|                  | – 168.8 | Allison et al. 1992 | – | – | – 168.8 | Allison et al. 1992 | 0.6349 | Flis et al. 2010 |
|                  | – 168.0 | Nriagu 1973 | – | – | – 168.0 | Nriagu 1973 | 0.6268 | ICDD 2004 |
|                  | – 167.5 | Manecki et al. 2000 | – | – | – 167.5 | Manecki et al. 2000 | 0.6323 | Chernorukov et al. 2011 |
|                  | – 168.8 | Allison et al. 1992 | – | – | – 168.8 | Allison et al. 1992 | 0.6349 | Flis et al. 2010 |
|                  | – 168.0 | Nriagu 1973 | – | – | – 168.0 | Nriagu 1973 | 0.6268 | ICDD 2004 |
|                  | – 167.5 | Manecki et al. 2000 | – | – | – 167.5 | Manecki et al. 2000 | 0.6323 | Chernorukov et al. 2011 |
|                  | – 168.8 | Allison et al. 1992 | – | – | – 168.8 | Allison et al. 1992 | 0.6349 | Flis et al. 2010 |
|                  | – 168.0 | Nriagu 1973 | – | – | – 168.0 | Nriagu 1973 | 0.6268 | ICDD 2004 |
|                  | – 167.5 | Manecki et al. 2000 | – | – | – 167.5 | Manecki et al. 2000 | 0.6323 | Chernorukov et al. 2011 |
|                  | – 168.8 | Allison et al. 1992 | – | – | – 168.8 | Allison et al. 1992 | 0.6349 | Flis et al. 2010 |
|                  | – 168.0 | Nriagu 1973 | – | – | – 168.0 | Nriagu 1973 | 0.6268 | ICDD 2004 |
|                  | – 167.5 | Manecki et al. 2000 | – | – | – 167.5 | Manecki et al. 2000 | 0.6323 | Chernorukov et al. 2011 |
|                  | – 168.8 | Allison et al. 1992 | – | – | – 168.8 | Allison et al. 1992 | 0.6349 | Flis et al. 2010 |
|                  | – 168.0 | Nriagu 1973 | – | – | – 168.0 | Nriagu 1973 | 0.6268 | ICDD 2004 |
|                  | – 167.5 | Manecki et al. 2000 | – | – | – 167.5 | Manecki et al. 2000 | 0.6323 | Chernorukov et al. 2011 |
|                  | – 168.8 | Allison et al. 1992 | – | – | – 168.8 | Allison et al. 1992 | 0.6349 | Flis et al. 2010 |
|                  | – 168.0 | Nriagu 1973 | – | – | – 168.0 | Nriagu 1973 | 0.6268 | ICDD 2004 |
| Chemical formula       | $\Delta H^\circ_{f,el}$ (kJ mol$^{-1}$) | Reference             | $S^\circ$ (J mol$^{-1}$ K$^{-1}$) | Reference | $C^\circ_p, m$ (J mol$^{-1}$ K$^{-1}$) | Reference | log$K_{sp}$ | Reference | $V_m$ (nm$^3$) | Reference |
|------------------------|--------------------------------------|------------------------|----------------------------------|-----------|--------------------------------------|-----------|-------------|-----------|---------------|-----------|
| Pb$_{10}$(PO$_4$)$_2$I$_2$ | $-$8042                              | Puzio et al. 2022      | $-$                               | $-$       | $-$                                  | $-$       | $-$         | $-$       | $-$           | $-$       |
| Pb$_{14}$(PO$_4$)$_6$I$_{0.26}$ | $-$                                  | $-$                    | $-$                              | $-$       | $-$                                  | $-$       | $-$         | $-$       | $-$           | $-$       |
| Ca$_{10}$(AsO$_4$)$_6$F$_2$ | $-$11.259                            | Zhu et al. 2011        | $-$                              | $-$       | $-$                                  | $-$       | $-$9.42     | Li et al. 2012 | $-$         | $-$       |
|                        | $-$11.279                            | Li et al. 2012         | $-$                              | $-$       | $-$                                  | $-$       | $-$9.42     | Zhu et al. 2011 | $-$         | $-$       |
| Ca$_{10}$(AsO$_4$)$_6$OH$_2$ | $-$11.208                            | Puzio et al. 2018      | 937.7                            | Zheng et al. 2015 | $-$       | $-$6.74        | Puzio et al. 2018 | 0.5265     | $-$       |
|                        | $-$10.935                            | Puzio et al. 2018      | $-$                              | $-$       | $-$                                  | $-$       | 81.7        | Li et al. 2012  | $-$         | $-$       |
|                        | $-$11.156                            | Mahapatra et al. 1987  | $-$                              | $-$       | $-$                                  | $-$       | $-$83.2     | Zhu et al. 2006 | 0.5704     | $-$       |
| Ca$_{10}$(AsO$_4$)$_6$Cl$_2$ | $-$                                  | $-$                    | $-$                              | $-$       | $-$                                  | $-$       | $-$83.2     | Zhu et al. 2006 | 0.5708     | $-$       |
|                        | $-$                                  |                       |                                  |           |                                      |           | $-$80.2     | Zhu et al. 2006 | 0.5711     | $-$       |
|                        |                                      |                        |                                  |           |                                      |           | $-$76.1     | Bothe and Brown 1999 | 0.6705 | $-$       |
|                        |                                      |                        |                                  |           |                                      |           | $-$89.8     | Mahapatra et al. 1987 | 0.5647     | $-$       |
|                        |                                      |                        |                                  |           |                                      |           | $-$94.5     | Narasaraju et al. 1979 | 0.5681 | $-$       |
| Ca$_{10}$(AsO$_4$)$_6$Br$_2$ | $-$                                  | $-$                    | $-$                              | $-$       | $-$                                  | $-$       | $-$         | $-$       | $-$           | $-$       |

0.6472 Merker and Wondratschek 1957
0.5721 Biagioni and Pasero 2013
0.5652 Baikie et al. 2007
0.5265 Puzio et al. 2018
0.5704 Biagioni and Pasero 2013
0.5708 Henderson et al. 2009
0.5711 Lee et al. 2009
0.6705 Mahapatra et al. 1989
0.5647 Dunn et al. 1980
0.5681 Mayer et al. 1979
0.5852 Biagioni et al. 2017
0.5984 Wardojo and Hwu 1996
0.6460 Wardojo and Hwu 1996
0.5724 Dunn et al. 1985
Not shown Karbovsky and Soroka 2014
| Chemical formula      | $\Delta H^\circ_{el}$ (kJ mol$^{-1}$) | Reference          | $S^\circ$ (J mol$^{-1}$ K$^{-1}$) | Reference          | $C^\circ_{p,m}$ (J mol$^{-1}$ K$^{-1}$) | Reference          | $\log K^\circ_{sp}$ | Reference | $V_m$ (nm$^3$) | Reference          |
|----------------------|--------------------------------------|---------------------|----------------------------------|---------------------|---------------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Sr$_{10}$(AsO$_4$)$_6$F$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.6392              | Dordevic et al. 2008  |
| Sr$_{10}$(AsO$_4$)$_6$OH$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.6396              | Kreidler and Hummel 1970 |
| Sr$_{10}$(AsO$_4$)$_6$Cl$_2$  | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.6466              | Weil et al. 2009     |
| Sr$_{10}$(AsO$_4$)$_6$Br$_2$  | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.6439              | Mayer et al. 1979    |
| Sr$_{10}$(AsO$_4$)$_6$OH$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.6556              | Bell et al. 2009     |
| Sr$_{10}$(AsO$_4$)$_6$Cl$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.6554              | Weil et al. 2009     |
| Ba$_{10}$(AsO$_4$)$_6$F$_2$  | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.6533              | Kreidler and Hummel 1970 |
| Ba$_{10}$(AsO$_4$)$_6$OH$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.7348              | Kreidler and Hummel 1970 |
| Ba$_{10}$(AsO$_4$)$_6$Cl$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.7426              | Chance 2014          |
| Ba$_{10}$(AsO$_4$)$_6$Br$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.7470              | Manca et al. 1980    |
| Ba$_{10}$(AsO$_4$)$_6$Cl$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.6551              | Dunn and Rouse 1978  |
| Ba$_{10}$(AsO$_4$)$_6$Br$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.5589              | Johnston et al. 2004 |
| Ba$_{10}$(AsO$_4$)$_6$Cl$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.5689              | Kreidler and Hummel 1970 |
| Cd$_{10}$(AsO$_4$)$_6$F$_2$  | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.5689              | Kreidler and Hummel 1970 |
| Cd$_{10}$(AsO$_4$)$_6$OH$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.5609              | Dordević et al. 2008 |
| Cd$_{10}$(AsO$_4$)$_6$Cl$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.5759              | Sudarsanan et al. 1977 |
| Pb$_{10}$(AsO$_4$)$_6$F$_2$  | –6288                                | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.6536              | Sordyl et al. 2020   |
| Cd$_{10}$(AsO$_4$)$_6$Cl$_{1.16}$(OH)$_{0.84}$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.5689              | Kreidler and Hummel 1970 |
| Cd$_{10}$(AsO$_4$)$_6$Br$_2$ | –                                    | –                   | –                                | –                   | –                                     | –                   | –                   | –                   | 0.5689              | Kreidler and Hummel 1970 |
Table 1 (continued)

| Chemical formula | \( \Delta H_{f,el}^0 \) (kJ mol\(^{-1}\)) | Reference | \( S^0 \) (J mol\(^{-1}\) K\(^{-1}\)) | Reference | \( C_{p,m}^0 \) (J mol\(^{-1}\) K\(^{-1}\)) | Reference | \( \log K_{sp} \) | Reference | \( V_m \) (nm\(^3\)) | Reference |
|------------------|---------------------------------|-----------|---------------------------------|-----------|---------------------------------|-----------|----------------|-----------|----------------|-----------|
| \( \text{Pb}_{10}(\text{AsO}_4)_6\text{OH}_2 \) | – | | | | | | | | 0.6529 | Kreidler and Hummel 1970 |
| \( \text{Pb}_{10}(\text{AsO}_4)_6\text{OH}_{1.72}(\text{CO}_3)_{0.14} \) | –6060 | Puzio et al. 2022 | – | | | | | | 0.6516 | Merker and Wandratschek 1959 |
| \( \text{Pb}_{10}(\text{AsO}_4)_6\text{Cl}_2 \) | –5932 | Bajda 2010 | 1315.0 | Bajda 2010 | – | | | | 0.6690 | Kwaśniak–Komeinek et al. 2015 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{F}_2 \) | – | – | – | – | – | – | | | 0.6710 | Engel 1970 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{Cl} \) | – | | | | | | | | 0.6769 | ICDD 1997 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{Br}_2 \) | – | | | | | | | | 0.6710 | Not shown |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{Br}_{1.6}(\text{CO}_3)_{0.2} \) | –6053 | Puzio et al. 2022 | | | | | | | 0.6763 | Sordyl et al. 2020 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{I}_{0.9}\text{OH}_{0.7}(\text{CO}_3)_{0.2} \) | –5986 | Puzio et al. 2022 | | | | | | | 0.6779 | Antao and Dhalidwal 2018 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{I}_2 \) | –6876 | | | | | | | | –152.6 | Flis et al. 2011 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{Br}_2 \) | –6883 | Sordyl et al. 2020 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{I}_{1.6}(\text{CO}_3)_{0.2} \) | –6991 | Sordyl et al. 2020 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{I}_2 \) | –7022 | Merker and Wandratschek 1959 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{I}_{0.9}\text{OH}_{0.7}(\text{CO}_3)_{0.2} \) | –5986 | Puzio et al. 2022 | | | | | | | 0.5534 | Pekov et al. 2021 |
| \( \text{Ca}_{10}(\text{VO}_4)_6\text{I}_2 \) | –5725 | Dong and White 2004 |
Table 1 (continued)

| Chemical formula | $\Delta H^\circ_{f,el}$ (kJ mol$^{-1}$) | Reference | $S^\circ$ (J mol$^{-1}$ K$^{-1}$) | Reference | $C^\circ_{p, m}$ (J mol$^{-1}$ K$^{-1}$) | Reference | log $K_{sp}$ | Reference | $V_m$ (nm$^3$) | Reference |
|------------------|--------------------------------------|-----------|---------------------------------|-----------|-------------------------------------|-----------|------------|-----------|-------------|-----------|
| Ca$_{10}$(VO$_4$)$_6$OH$_2$ | – | – | – | – | – | Not shown | – | – | Not shown | Kreidler and Hummel 1970 |
| Ca$_{10}$(VO$_4$)$_6$Cl$_2$ | – | – | – | – | – | – | – | – | – | Karbovsky and Soroka 2014 |
| Ca$_{10}$(VO$_4$)$_6$Br$_2$ | – | – | – | – | – | – | 0.5778 | – | – | – | Getman et al. 2001 |
| Sr$_{10}$(VO$_4$)$_6$F$_2$ | – | – | – | – | – | – | 0.6062 | – | – | – | Beck et al. 2006 |
| Sr$_{10}$(VO$_4$)$_6$OH$_2$ | – | – | – | – | – | – | 0.6076 | – | – | – | Kreidler and Hummel 1970 |
| Sr$_{10}$(VO$_4$)$_6$Cl$_2$ | – | – | – | – | – | – | 0.6076 | – | – | – | Baran 1972 |
| Sr$_{10}$(VO$_4$)$_6$Br$_2$ | – | – | – | – | – | – | 0.6461 | – | – | – | Knyazev et al. 2015 |
| Ba$_{10}$(VO$_4$)$_6$F$_2$ | – | – | – | – | – | – | 0.6408 | – | – | – | Zhang et al. 2015 |
| Ba$_{10}$(VO$_4$)$_6$OH$_2$ | – | – | – | – | – | – | 0.6426 | – | – | – | ICDD 2004 |
| Ba$_{10}$(VO$_4$)$_6$Cl$_2$ | – | – | – | – | – | – | 0.6442 | – | – | – | ICDD 2004 |
| Ba$_{10}$(VO$_4$)$_6$Br$_2$ | – | – | – | – | – | – | 0.6478 | – | – | – | ICDD 2004 |
| Ba$_{10}$(VO$_4$)$_6$OH$_2$ | – | – | – | – | – | – | 0.6487 | – | – | – | ICDD 2004 |
| Ba$_{10}$(VO$_4$)$_6$Cl$_2$ | – | – | – | – | – | – | 0.6590 | – | – | – | ICDD 2004 |
| Ba$_{10}$(VO$_4$)$_6$Br$_2$ | – | – | – | – | – | – | 0.6699 | – | – | – | ICDD 2004 |
| Ba$_{10}$(VO$_4$)$_6$OH$_2$ | – | – | – | – | – | – | 0.7118 | – | – | – | ICDD 2004 |
| Ba$_{10}$(VO$_4$)$_6$Cl$_2$ | – | – | – | – | – | – | 0.7320 | – | – | – | ICDD 2004 |
| Ba$_{10}$(VO$_4$)$_6$Br$_2$ | – | – | Not shown | – | – | – | 0.7385 | – | – | – | ICDD 2004 |
Table 1 (continued)

| Chemical formula | $\Delta H^o_{f,el}$ (kJ mol$^{-1}$) | Reference | $S^o$ (J mol$^{-1}$ K$^{-1}$) | Reference | $C^o_{p, m}$ (J mol$^{-1}$ K$^{-1}$) | Reference | $\log K_{sp}$ | Reference | $V_m$ (nm$^3$) | Reference |
|------------------|--------------------------------|-----------|----------------------------|-----------|--------------------------------|-----------|----------------|-----------|---------------|-----------|
| Ba$_{10}$ (VO$_4$)$_6$Br$_2$ | – | – | – | – | – | – | 0.7555 | Baran 1972 |
| Cd$_{10}$ (VO$_4$)$_6$F$_2$ | – | – | – | – | – | – | 0.5381 | Karbovsky et al. 2014 |
| Cd$_{10}$ (VO$_4$)$_6$OH$_2$ | – | – | – | – | 0.5596 | Karbovsky et al. 2014 |
| Cd$_{10}$ (VO$_4$)$_6$Cl$_2$ | – | – | – | – | 0.5798 | Chernorukov et al. 2011 |
| Cd$_{10}$ (VO$_4$)$_6$I$_2$ | – | – | – | – | 0.5698 | Karbovsky et al. 2014 |
| Pb$_{10}$ (VO$_4$)$_6$F$_2$ | – | – | – | – | 0.6510 | Oka et al. 2022 |
| Pb$_{10}$ (VO$_4$)$_6$OH$_2$ | – | 7592 | Puzio et al. 2021 | 1334.0 | Puzio et al. 2021 | 867.4 | 0.6677 | Engel 1970 |
| Pb$_{10}$ (VO$_4$)$_6$Cl$_2$ | – | – | – | – | 0.5976 | Sudarsanan et al. 1977 |
| Pb$_{10}$ (VO$_4$)$_6$Br$_2$ | – | – | – | – | 0.5854 | Sudarsanan et al. 1977 |
| Pb$_{10}$ (VO$_4$)$_6$Cl$_2$ | – | – | – | – | 0.6497 | Kreidler and Hummel 1970 |
| Pb$_{10}$ (VO$_4$)$_6$I$_2$ | – | – | – | – | 0.6532 | Grisafe and Hummel 1970 |
| Pb$_{10}$ (VO$_4$)$_6$Br$_2$ | – | – | – | – | 0.6484 | Merker and Wondratschek 1957 |

References:
- Baran 1972
- Karbovsky et al. 2014
- Chernorukov et al. 2011
- Karbovsky et al. 2014
- Puzio et al. 2021
- Chernorukov et al. 2010
- Puzio et al. 2021
- Nakamura et al. 2020
- Kreidler and Hummel 1970
- Grisafe and Hummel 1970
- Engel 1970
- Oka et al. 2022
- Not shown
- Puzio et al. 2021
- Antao and Dhaliwal 2018
- Solecka et al. 2018
- Okudera 2013
- Chernoquok et al. 2011
- Chernoquok et al. 2010
- Trotter and Barnes 1958
- Merker and Wondratschek 1957
The correlation of $\Delta H^\circ_{f,el}$ of apatites with molar volume of apatite ($V_m$) is also apparent (Fig. 1B). So far, such relationships can be found within P-apatites. Gaps in experimental data do not allow a complete picture of these relationships for As- or V-apatites.

**Correlation of $V_m$ with ionic radius of halogen anion X**

The molar volume $V_m$ is not yet known for all apatites e.g., $\text{Ca}_{10}(\text{VO}_4)_6\text{X}_2$, $\text{Cd}_{10}(\text{AsO}_4)_6\text{I}_2$ or $\text{Ba}_{10}(\text{AsO}_4)_6\text{Br}_2$ (Table 1). Glasser and Jenkins have proposed a method to calculate missing $V_m$ values based on the sum of contributions of internally consistent single-ion volumes (Jenkins and Glasser 2003; Glasser and Jenkins 2008). The use of their method gives promising and accurate results with the uncertainty not exceeding $\pm 11\%$ compare to experimental $V_m$ (Glasser and Jenkins 2008). Over the last 15 years, many of the experimental diffraction data have been published for not only phosphate but also arsenate and vanadate apatites. This allows the calculation of more experimental $V_m$ values and verification of this approach.

In this work, we propose a different procedure for predicting $V_m$ values for apatites whose structure has not yet been determined or for potential apatite-based structures predicted by Wang (2015) and Hartnett et al. (2019). The method is based on the linear correlation of the $V_m$ value with the ionic radius ($R_i$) of the halides present at the X position (Fig. 2). In this procedure, all available experimental data of apatites and their synthetic analogs ($\text{exptl}V_m$) are divided into apatite subgroups based on the same substitution at $\text{Me}^{2+}$ and $\text{AO}_4^{3−}$ positions but different X. The subgroups should be considered separately within the X substitutions excluding OH (X = F, Cl, Br, I), e.g., $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, $\text{Pb}_{10}(\text{PO}_4)_6\text{X}_2$, $\text{Ca}_{10}(\text{AsO}_4)_6\text{X}_2$, $\text{Pb}_{10}(\text{AsO}_4)_6\text{X}_2$, $\text{Ca}_{10}(\text{VO}_4)_6\text{X}_2$, $\text{Pb}_{10}(\text{VO}_4)_6\text{X}_2$, etc. A complete dataset within apatite subgroups exists for the $\text{Pb}_{10}(\text{AsO}_4)_6\text{X}_2$, $\text{Pb}_{10}(\text{VO}_4)_6\text{X}_2$ and $\text{Cd}_{10}(\text{VO}_4)_6\text{X}_2$ (Fig. 2). Both visual inspection and Pearson correlation coefficient along with $R^2$ values greater than 0.99 indicate positive linear correlations. This positive correlation of $V_m$ vs. $R_i$ allows for interpolation and extrapolation within other apatite subgroups. Linear correlation was assumed for all apatite subgroups based on linearity within subgroups with the most available experimental data. If there are at least two known values of $\text{exptl}V_m$ within a subgroup, the parameters a and b of the linear regression between $\text{exptl}V_m$ and $R_i$ of the halides can be calculated. The unknown values of $V_m$ are predicted from the relationship (determined separately for each subgroup of apatites):

$$\text{pred}V_m = a \times R_i + b$$ (1)

**Table 1 (continued)**

| Chemical formula | $V_m$ (nm$^3$) | Reference | $S°$ (J mol$^{-1}$ K$^{-1}$) | Reference | $C°p, m$ (J mol$^{-1}$ K$^{-1}$) | Reference | $\log K_{sp}$ Reference |
|------------------|-------------|----------|-----------------|-----------|-------------------|-----------|------------------|
| $\text{Pb}_{10}(\text{VO}_4)_6\text{Br}_2$ | – | – | – | – | – | – | Not shown Nakamura et al. 2020 |
| $\text{Pb}_{9.85}(\text{VO}_4)_6\text{I}_1.7$ | – | – | – | – | – | – | Audubert et al. 1999 |
| $\text{Pb}_{10}(\text{VO}_4)_6\text{I}_2$ | 877.8 | Fieche 2002 | | | | | |
where \( \text{pred}V_m \) is predicted molar volume of apatite and \( R_i \) is the ionic radius of element \( X \) \((X = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-; \) Table SI 1). Linear regression coefficients \( a \) and \( b \) are listed in Table SI 2. The results of calculations are presented in Fig. 2 as empty marks. Predicted molar volumes \( (\text{pred}V_m) \) are summarized in Table 2. These volumes will be used in calculations below as data equal to the experimental ones.

A comparison of the values obtained using the approach presented here \( (\text{pred}V_m) \) with those obtained using the Glasser–Jenkins (2008) method \( (\text{calc}V_m) \) and with the experimental values is presented in Table 2. Precision of prediction was estimated by the relative percentage difference. The difference between \( \text{exptl}V_m \) and the same values calculated from the regression does not exceed 0.5% for any apatite considered. In contrast, the differences determined for the values calculated by the Glasser–Jenkins method are up to 10% for calcium phosphate apatites, 30% for lead phosphate apatites, or 20% for cadmium phosphate apatites. This large difference is partly because the volumes used by Glasser and Jenkins (2008) for \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) cations were not corrected (calibrated) but taken directly from Marcus (1987). This indicates that greater precision in predicting \( V_m \) values was achieved using the approach presented in this work.

### Correlation of lattice energy \( U_{\text{POT}} \) with \( V_m \)

\( U_{\text{POT}} \) is the energy change upon the formation of one mole of an ionic compound from its constituent ions in the gaseous state. Experimental lattice energy \( (\text{exptl}U_{\text{POT}}) \) can be determined using Born–Haber thermochemical cycles described in detail by Flora et al. (2004b). For those apatites for which experimentally determined \( \Delta H^0_{\text{f,el}} \) is available, the \( \text{exptl}U_{\text{POT}} \) values are summarized in Table 3. The thermochemical data necessary to determine \( \text{exptl}U_{\text{POT}} \) are given in Table SI 3.

The lattice energies listed as \( \text{exptl}U_{\text{POT}} \) in Table 3 were obtained from the lattice enthalpy \( \Delta H_{\text{latt}} \) by correcting for the difference between enthalpy and lattice energy \( U_{\text{POT}} \) (Jenkins 2005). \( \Delta H_{\text{latt}} \) involves correction of the \( U_{\text{POT}} \) term by an appropriate RT (where \( R \) is the gas constant and \( T \) is the temperature in K; Jenkins and Liebman 2005). For \( U_{\text{POT}} \) extraction from the Born–Fajans–Haber cycle (which is essentially an enthalpy-based thermochemical cycle) the \( \Delta H_{\text{latt}} \) must be transformed using an extension discussed by Jenkins et al. 1999. Finally, for \( \text{F}^- \), \( \text{Cl}^- \), \( \text{Br}^- \) and \( \text{I}^- \) apatites, \( \Delta H_{\text{latt}} = U_{\text{POT}} \), so we do not present \( \Delta H_{\text{latt}} \) values separately (Jenkins et al. 1999).

Lattice energy can be calculated also as \( \text{calc}U_{\text{POT}} \) using the improved Kapustinskii equation, a generalized version of which was given by Glasser and Jenkins (2000). This equation for an isostructural family of minerals requires no parameters other than the molar volume \( V_m \) (in \( \text{nm}^3 \)) and is reduced to the form:

\[
\text{calc}U_{\text{POT}} \left( \frac{\text{kJ}}{\text{mol}} \right) = \frac{26680}{\sqrt{V_m}} \quad (2)
\]

Flora et al. (2004b) used this equation to calculate \( \text{calc}U_{\text{POT}} \) values for phosphate apatites. We have extended these calculations to \( \text{As}^- \) and \( \text{V}^- \)apatites using both experimental and predicted \( V_m \) (Table 3). The results are presented in Table 3 \( (\text{calc}U_{\text{POT}}) \) and in Fig. 3. The values calculated based on Eq. (2) differ both from \( \text{exptl}U_{\text{POT}} \) and from intuitively expected numbers. The \( U_{\text{POT}} \) value depends not only on the morphology and distribution of the individual atoms.
Fig. 2  Correlation of $V_m$ with the ionic radius of halogen $X^-$ for selected apatite subgroups. Experimental data used for regression are plotted as solid marks. Values predicted based on the Eq. 1 are plotted as open symbols.
Glasser and Jenkins (2008) and values calculated based on experimental molar volumes.

| Apatite | $exptV_m$ or $predV_m$ (nm$^3$) | calc$V_m$ (nm$^3$) | % diff | $predV_m$ (nm$^3$) | % diff |
|---------|-------------------------------|------------------|--------|-------------------|--------|
| Ca$_{10}$(PO$_4$)$_6$F$_2$ | 0.5246 | 0.5710 | -9 | 0.5246 | -0.0023 |
| Ca$_{10}$(PO$_4$)$_6$Cl$_2$ | 0.5430 | 0.6026 | -11 | 0.5429 | 0.0095 |
| Ca$_{10}$(PO$_4$)$_6$Br$_2$ | 0.5486 | 0.6156 | -12 | 0.5487 | 0.0072 |
| Ca$_{10}$(PO$_4$)$_6$I$_2$ | 0.5578 | 0.6406 | -15 | 0.5578 | 0.0000 |
| Sr$_{10}$(PO$_4$)$_6$F$_2$ | 0.5967 | 0.5830 | 2 | 0.5967 | 0.0052 |
| Sr$_{10}$(PO$_4$)$_6$Cl$_2$ | 0.6152 | 0.6146 | 0 | 0.6153 | -0.0211 |
| Sr$_{10}$(PO$_4$)$_6$Br$_2$ | 0.6213 | 0.6276 | -1 | 0.6212 | 0.0159 |
| Sr$_{10}$(PO$_4$)$_6$I$_2$ | 0.6305 | 0.6526 | -4 | 0.6305 | 0.0000 |
| Ba$_{10}$(PO$_4$)$_6$F$_2$ | 0.6874 | 0.6400 | 7 | 0.6868 | 0.0933 |
| Ba$_{10}$(PO$_4$)$_6$Cl$_2$ | 0.7008 | 0.6716 | 4 | 0.7035 | -0.3843 |
| Ba$_{10}$(PO$_4$)$_6$Br$_2$ | 0.7107 | 0.6846 | 4 | 0.7087 | 0.2887 |
| Ba$_{10}$(PO$_4$)$_6$I$_2$ | 0.7170 | 0.7096 | 1 | 0.7170 | 0.0000 |
| Cd$_{10}$(PO$_4$)$_6$F$_2$ | 0.4970 | 0.4160 | 16 | 0.4970 | -0.0096 |
| Cd$_{10}$(PO$_4$)$_6$Cl$_2$ | 0.5211 | 0.4476 | 14 | 0.5209 | 0.0385 |
| Cd$_{10}$(PO$_4$)$_6$Br$_2$ | 0.5282 | 0.4606 | 13 | 0.5284 | -0.0289 |
| Cd$_{10}$(PO$_4$)$_6$I$_2$ | 0.5403 | 0.4856 | 10 | 0.5403 | 0.0000 |
| Pb$_{10}$(PO$_4$)$_6$F$_2$ | 0.6010 | 0.4660 | 22 | 0.6008 | 0.0286 |
| Pb$_{10}$(PO$_4$)$_6$Cl$_2$ | 0.6350 | 0.4976 | 22 | 0.6357 | -0.1136 |
| Pb$_{10}$(PO$_4$)$_6$Br$_2$ | 0.6472 | 0.5106 | 21 | 0.6467 | 0.0849 |
| Pb$_{10}$(PO$_4$)$_6$I$_2$ | 0.6641 | 0.5356 | 19 | 0.6641 | 0.0000 |
| Ca$_{10}$(AsO$_4$)$_6$F$_2$ | 0.5721 | 0.6238 | -9 | 0.5721 | 0.0000 |
| Ca$_{10}$(AsO$_4$)$_6$Cl$_2$ | 0.5984 | 0.6554 | -10 | 0.5984 | 0.0000 |
| Ca$_{10}$(AsO$_4$)$_6$Br$_2$ | 0.6066 | 0.6684 | -10 | 0.6066 | 0.0000 |
| Ca$_{10}$(AsO$_4$)$_6$I$_2$ | 0.6198 | 0.6934 | -12 | 0.6198 | 0.0000 |
| Sr$_{10}$(AsO$_4$)$_6$F$_2$ | 0.6392 | 0.6358 | 1 | 0.6392 | 0.0000 |
| Sr$_{10}$(AsO$_4$)$_6$Cl$_2$ | 0.6556 | 0.6674 | -2 | 0.6556 | 0.0000 |
| Sr$_{10}$(AsO$_4$)$_6$Br$_2$ | 0.6607 | 0.6804 | -3 | 0.6607 | 0.0000 |
| Sr$_{10}$(AsO$_4$)$_6$I$_2$ | 0.6690 | 0.7054 | -5 | 0.6690 | 0.0000 |
| Ba$_{10}$(AsO$_4$)$_6$F$_2$ | 0.7348 | 0.6928 | 6 | 0.7348 | 0.0000 |
| Ba$_{10}$(AsO$_4$)$_6$Cl$_2$ | 0.7470 | 0.7244 | 3 | 0.7470 | 0.0000 |
| Ba$_{10}$(AsO$_4$)$_6$Br$_2$ | 0.7508 | 0.7374 | 2 | 0.7508 | 0.0000 |
| Ba$_{10}$(AsO$_4$)$_6$I$_2$ | 0.7569 | 0.7624 | -1 | 0.7569 | 0.0000 |
| Cd$_{10}$(AsO$_4$)$_6$F$_2$ | 0.5465 | 0.4688 | 14 | 0.5465 | 0.0000 |
| Cd$_{10}$(AsO$_4$)$_6$Cl$_2$ | 0.5689 | 0.5004 | 12 | 0.5689 | 0.0000 |
| Cd$_{10}$(AsO$_4$)$_6$Br$_2$ | 0.5759 | 0.5134 | 11 | 0.5759 | 0.0000 |
| Cd$_{10}$(AsO$_4$)$_6$I$_2$ | 0.5871 | 0.5384 | 8 | 0.5871 | 0.0000 |
| Pb$_{10}$(AsO$_4$)$_6$F$_2$ | 0.6516 | 0.5188 | 20 | 0.6515 | 0.0214 |
| Pb$_{10}$(AsO$_4$)$_6$Cl$_2$ | 0.6792 | 0.5504 | 19 | 0.6793 | -0.0119 |
| Pb$_{10}$(AsO$_4$)$_6$Br$_2$ | 0.6876 | 0.5634 | 18 | 0.6880 | -0.0544 |
| Pb$_{10}$(AsO$_4$)$_6$I$_2$ | 0.7022 | 0.5884 | 16 | 0.7019 | 0.0449 |
| Ca$_{10}$(VO$_4$)$_6$F$_2$ | 0.5725 | 0.6268 | -9 | 0.5725 | 0.0000 |
| Ca$_{10}$(VO$_4$)$_6$Cl$_2$ | 0.6062 | 0.6584 | -9 | 0.6062 | 0.0000 |
| Ca$_{10}$(VO$_4$)$_6$Br$_2$ | 0.6167 | 0.6714 | -9 | 0.6167 | 0.0000 |
| Ca$_{10}$(VO$_4$)$_6$I$_2$ | 0.6335 | 0.6964 | -10 | 0.6335 | 0.0000 |
| Sr$_{10}$(VO$_4$)$_6$F$_2$ | 0.6408 | 0.6388 | 0 | 0.6403 | 0.0000 |
| Sr$_{10}$(VO$_4$)$_6$Cl$_2$ | 0.6593 | 0.6704 | -2 | 0.6614 | -0.3134 |
| Sr$_{10}$(VO$_4$)$_6$Br$_2$ | 0.6695 | 0.6834 | -2 | 0.6679 | 0.2351 |
| Sr$_{10}$(VO$_4$)$_6$I$_2$ | 0.6785 | 0.7084 | -4 | 0.6785 | 0.0000 |
| Ba$_{10}$(VO$_4$)$_6$F$_2$ | 0.7118 | 0.6958 | 2 | 0.7119 | -0.0181 |
| Ba$_{10}$(VO$_4$)$_6$Cl$_2$ | 0.7460 | 0.7274 | 2 | 0.7455 | 0.0726 |
in the structure but also to a large extent on the chemical nature of these atoms, which is not included in the calculations. For example, for the apatite pair Ca10(PO4)6F2 and Cd10(PO4)6Cl2, the experimentally determined $\text{exptl}U_{\text{POT}}$ values are 17,124 and 18,063 kJ mol$^{-1}$, respectively. However, since the difference in $\text{exptl}V_m$ for these end-members is small (on the order of 0.4%), the $\text{calc}U_{\text{POT}}$ values determined for these apatites from Eq. (2) are 16,554 and 16,577 kJ mol$^{-1}$, respectively. Not only do these values deviate significantly from experimental determinations, but they are also almost indistinguishable from one another. This is, among other things, an artifact of using the molar volume $V_m$ as the only variable in Eq. (2).

In contrast, the plot of $\text{exptl}U_{\text{POT}}$ against $V_m$ shows that there is a linear relationship between them within the distinct apatite subgroups (Fig. 3). The different slopes of the trend lines show the varying effect of the halogen on the thermochemical behavior for apatite subgroups. Some apatites have

Table 2 (continued)

| Apatite          | $\text{exptl}V_m$ or $\text{calc}V_m$ (nm$^3$) | $\% \text{diff}^1$ | $\text{pred}V_m$ (nm$^3$) | $\% \text{diff}^2$ |
|------------------|-----------------------------------------------|---------------------|---------------------------|---------------------|
| Ba$_{10}$(VO$_4$)$_6$Br$_2$ | 0.7555                                       | 0.7404              | 2                         | 0.7559              | -0.0546 |
| Ba$_{10}$(VO$_4$)$_6$I$_2$  | 0.7727                                       | 0.7654              | 1                         | 0.7727              | 0.0000  |
| Cd$_{10}$(VO$_4$)$_6$F$_2$  | 0.5381                                       | 0.4718              | 12                        | 0.5379              | 0.0348  |
| Cd$_{10}$(VO$_4$)$_6$Cl$_2$ | 0.5689                                       | 0.5034              | 12                        | 0.5715              | -0.4589 |
| Cd$_{10}$(VO$_4$)$_6$Br$_2$ | 0.5854                                       | 0.5164              | 12                        | 0.5820              | 0.5966  |
| Cd$_{10}$(VO$_4$)$_6$I$_2$  | 0.5976                                       | 0.5414              | 9                         | 0.5987              | -0.1823 |
| Pb$_{10}$(VO$_4$)$_6$F$_2$  | 0.6484                                       | 0.5218              | 20                        | 0.6482              | 0.0370  |
| Pb$_{10}$(VO$_4$)$_6$Cl$_2$ | 0.6771                                       | 0.5534              | 18                        | 0.6781              | -0.1415 |
| Pb$_{10}$(VO$_4$)$_6$Br$_2$ | 0.6881                                       | 0.5664              | 18                        | 0.6874              | 0.0997  |
| Pb$_{10}$(VO$_4$)$_6$I$_2$  | 0.7024                                       | 0.5914              | 16                        | 0.7024              | 0.0045  |

Note: $\% \text{diff}^1 = 100 \cdot (\text{exptl}V_m - \text{calc}V_m) / \text{exptl}V_m$; $\% \text{diff}^2 = 100 \cdot (\text{exptl}V_m - \text{pred}V_m) / \text{exptl}V_m$; the data in the first column will be used in further calculations

Table 3 Comparison of the experimental lattice energies with values calculated using the improved Kapustinskii equation (Flora et al. 2004b) and values predicted in this work

| Apatite          | $\text{exptl}U_{\text{POT}}$ or $\text{pred}U_{\text{POT}}$ (kJ mol$^{-1}$) | $\text{calc}U_{\text{POT}}$ (kJ mol$^{-1}$) | $\% \text{diff}^1$ | $\text{pred}U_{\text{POT}}$ (kJ mol$^{-1}$) | $\% \text{diff}^2$ |
|------------------|---------------------------------------------------------------|---------------------------------------------|---------------------|---------------------------------------------|---------------------|
| Ca$_{10}$(PO$_4$)$_6$F$_2$ | 34,158                                                       | 33,080                                       | 3                   | 34,160                                       | -0.01               |
| Ca$_{10}$(PO$_4$)$_6$Cl$_2$ | 33,865                                                       | 32,703                                       | 4                   | 33,856                                       | 0.03                |
| Ca$_{10}$(PO$_4$)$_6$Br$_2$ | 33,756                                                       | 32,591                                       | 4                   | 33,763                                       | -0.02               |
| Ca$_{10}$(PO$_4$)$_6$I$_2$  | 33,611                                                       | 32,411                                       | 4                   | 33,611                                       | 0.00                |
| Sr$_{10}$(PO$_4$)$_6$F$_2$  | 32,837                                                       | 31,691                                       | 3                   | 32,837                                       | 0.00                |
| Sr$_{10}$(PO$_4$)$_6$Cl$_2$ | 32,516                                                       | 31,370                                       | 4                   | 32,516                                       | 0.00                |
| Sr$_{10}$(PO$_4$)$_6$Br$_2$ | 32,411                                                       | 31,268                                       | 4                   | 32,411                                       | 0.00                |
| Sr$_{10}$(PO$_4$)$_6$I$_2$  | 32,251                                                       | 31,114                                       | 4                   | 32,251                                       | 0.00                |
| Ba$_{10}$(PO$_4$)$_6$F$_2$  | 31,372                                                       | 30,231                                       | 4                   | 31,372                                       | 0.00                |
| Ba$_{10}$(PO$_4$)$_6$Cl$_2$ | 31,104                                                       | 30,037                                       | 4                   | 31,104                                       | 0.00                |
| Ba$_{10}$(PO$_4$)$_6$Br$_2$ | 30,905                                                       | 29,896                                       | 4                   | 30,905                                       | 0.00                |
| Ba$_{10}$(PO$_4$)$_6$I$_2$  | 30,779                                                       | 29,809                                       | 3                   | 30,779                                       | 0.00                |
| Cd$_{10}$(PO$_4$)$_6$F$_2$  | 36,408                                                       | 33,682                                       | 7                   | 36,408                                       | 0.00                |
| Cd$_{10}$(PO$_4$)$_6$Cl$_2$ | 36,126                                                       | 33,155                                       | 8                   | 36,126                                       | 0.00                |
| Cd$_{10}$(PO$_4$)$_6$Br$_2$ | 36,043                                                       | 33,006                                       | 8                   | 36,043                                       | 0.00                |
| Cd$_{10}$(PO$_4$)$_6$I$_2$  | 35,902                                                       | 32,758                                       | 9                   | 35,902                                       | 0.00                |
| Pb$_{10}$(PO$_4$)$_6$F$_2$  | 33,603                                                       | 31,615                                       | 6                   | 33,600                                       | 0.01                |
| Pb$_{10}$(PO$_4$)$_6$Cl$_2$ | 33,435                                                       | 31,040                                       | 7                   | 33,445                                       | -0.03               |
| Pb$_{10}$(PO$_4$)$_6$Br$_2$ | 33,397                                                       | 30,844                                       | 8                   | 33,389                                       | 0.02                |
| Pb$_{10}$(PO$_4$)$_6$I$_2$  | 33,312                                                       | 30,580                                       | 8                   | 33,312                                       | 0.00                |

Note: $\% \text{diff}^1 = 100 \cdot (\text{exptl}U_{\text{POT}} - \text{calc}U_{\text{POT}}) / \text{exptl}U_{\text{POT}}$; $\% \text{diff}^2 = 100 \cdot (\text{exptl}U_{\text{POT}} - \text{pred}U_{\text{POT}}) / \text{exptl}U_{\text{POT}}$; the data from the first column will be used in further calculations
very similar molar volumes but completely different chemical compositions. The linear correlations shown in Fig. 3 can be used for interpolation and extrapolation to predict missing \( U_{\text{POT}} \) values. The steps in determining \( U_{\text{POT}} \) and the prediction process are similar to the prediction of \( V_m \). The exptl\( U_{\text{POT}} \) data of apatites and their synthetic analogs should be divided into apatite subgroups. The subgroups should be considered separately within the X substitutions excluding OH (X = F, Cl, Br, I), e.g., \( \text{Ca}_{10}(\text{PO}_4)_6X_2 \), \( \text{Pb}_{10}(\text{PO}_4)_6X_2 \), \( \text{Ca}_{10}(\text{AsO}_4)_6X_2 \), \( \text{Pb}_{10}(\text{AsO}_4)_6X_2 \), \( \text{Ca}_{10}(\text{VO}_4)_6X_2 \), \( \text{Pb}_{10}(\text{VO}_4)_6X_2 \), etc. If there are at least two known values of exptl\( U_{\text{POT}} \) within a subgroup, the parameters a and b of the linear regression between exptl\( U_{\text{POT}} \) and the molar volume \( V_m \) are calculated. Lattice energy pred\( U_{\text{POT}} \) is predicted from the equation:

\[
\text{pred}U_{\text{POT}} = a \times V_m + b
\]  

The pred\( U_{\text{POT}} \) values obtained by this method are plotted in Fig. 3 as empty marks. Linear regression coefficients a and b along with Pearson coefficient \( R \) and \( R^2 \) are listed in Table SI 4. A comparison of the pred\( U_{\text{POT}} \) values and calc\( U_{\text{POT}} \) obtained using Eq. (2) with the experimental values shows that greater precision in predicting \( U_{\text{POT}} \) values was achieved (as assessed by the relative percentage deviation from experimental data). The difference between exptl\( U_{\text{POT}} \) and the values calculated from the regression does not exceed 0.05% for any apatite considered. In contrast, the differences calculated using the values computed by the Glasser–Jenkins (2000) method are up to 4% for calcium phosphate apatites, 8% for lead phosphate apatites, or 9% for cadmium phosphate apatites. All the pred\( U_{\text{POT}} \) values summarized in Table 3 will be used in further calculations below on par with the experimental data.

**Prediction of \( \Delta H^\circ_{\text{f,el}} \) of apatites using \( \Delta H^\circ_{\text{f,el}} \) of \( X^- \)**

Figure 4 shows examples of the linear correlation of \( \Delta H^\circ_{\text{f,el}} \) of apatites as a function of \( U_{\text{POT}} \) for selected phosphate apatites. The linearity of these correlations is enforced by the Born–Haber cycle. Phosphate apatites were chosen to present these correlations. This is currently impossible for As- and V-apatites due to the lack of data. Using all the exptl\( U_{\text{POT}} \) and the pred\( U_{\text{POT}} \) calculated from Eq. 3, the pred\( \Delta H^\circ_{\text{f,el}} \) can be determined by extrapolating the linear relationships shown in Fig. 4:

\[
\text{pred}\Delta H^\circ_{\text{f,el}} = a \times U_{\text{POT}} + b
\]  

The linear regression coefficients given in Table SI 5 were used for the calculations according to Eq. 4. The values obtained by this method are plotted in Fig. 4 as empty marks. A comparison of the pred\( \Delta H^\circ_{\text{f,el}} \) with the experimental ones is shown in Table 4. The discrepancies do not exceed 0.1% relative error. This correlation allowed the prediction of eight, so far unknown, \( \Delta H^\circ_{\text{f,el}} \) values for the following end-members: \( \text{Ca}_{10}(\text{PO}_4)_6I_2 \), \( \text{Sr}_{10}(\text{PO}_4)_6Br_2 \), \( \text{Sr}_{10}(\text{PO}_4)_6I_2 \), \( \text{Ba}_{10}(\text{PO}_4)_6Br_2 \), \( \text{Ba}_{10}(\text{PO}_4)_6I_2 \), \( \text{Cd}_{10}(\text{PO}_4)_6Br_2 \), \( \text{Cd}_{10}(\text{PO}_4)_6I_2 \), and \( \text{Pb}_{10}(\text{PO}_4)_6I_2 \).
for Ba\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}X\textsubscript{2} where \(R^2 = 0.97\); Table SI 6). The extrapolation of the regression lines allowed to obtain a prediction of \(\Delta H^\circ_{\text{f,el}}\) for calcium and lead As-apatites. For calculation of predicted \(\Delta H^{\circ}_{\text{f,el}}\) from the equation:

\[
pred\Delta H^\circ_{\text{f,el}} = a \times \Delta H^\circ_{\text{f,el} \text{of } X^-} + b \tag{5}
\]

The \(\Delta H^{\circ}_{\text{f,el}}\) of \(X^-\) from Table SI 1 and linear correlation coefficients from Table SI 6 were used. The existing and predicted \(\Delta H^{\circ}_{\text{f,el}}\) data are compared in Table 5. The difference between \(\text{exptl}\Delta H^{\circ}_{\text{f,el}}\) and the values calculated from the regression does not exceed 0.27\% for anyapatite considered. The \(\Delta H^{\circ}_{\text{f,el}}\) values were predicted for the followingapatites: Ca\textsubscript{10}(AsO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2}, Ca\textsubscript{10}(AsO\textsubscript{4})\textsubscript{6}Br\textsubscript{2}, Ca\textsubscript{10}(AsO\textsubscript{4})\textsubscript{6}I\textsubscript{2}, Pb\textsubscript{10}(AsO\textsubscript{4})\textsubscript{6}Br\textsubscript{2}, and Pb\textsubscript{10}(AsO\textsubscript{4})\textsubscript{6}I\textsubscript{2}. Linear extrapolation from only two points was used for Ca\textsubscript{10}(AsO\textsubscript{4})\textsubscript{6}X\textsubscript{2}. The linear correlation was assumed based on the linearity within otherapatite subgroups.

**Prediction of \(\Delta H^\circ_{\text{f,el}}\) of apatites using \(\Delta H^\circ_{\text{f,el}}\) of AO\textsubscript{4}\textsuperscript{3−}**

Due to lack of data, the prediction methods presented above do not allow estimation of \(\Delta H^\circ_{\text{f,el}}\) for V-apatites. Only two experimental \(\Delta H^\circ_{\text{f,el}}\) for the synthetic vanadinite analog Pb\textsubscript{10}(VO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2} are known. Therefore, an attempt was made to use the relationship between \(\Delta H^\circ_{\text{f,el}}\) ofapatite and \(\Delta H^\circ_{\text{f,el}}\) of the AO\textsubscript{4}\textsuperscript{3−} anion. The availability of experimental data allows to plot such a dependence only for leadapatites Pb\textsubscript{10}(AO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2}, where A = P, V, or As (Fig. 6). Since ideal linear fit is apparent (\(R^2 = 1.00\)), we hypothesize that linear correlation also exists for other apatite subgroups, with the same Me and X but different A. The lines drawn for the various P- and As-apatites (Fig. 7) allow to

![Fig. 4 Correlation of \(\Delta H^\circ_{\text{f,el}}\) with \(U_{\text{pot}}\) (from the first column in Table 3) within apatite subgroups used for prediction of missing \(\Delta H^\circ_{\text{f,el}}\). Values predicted using the Eq. 4 are plotted as open symbols. Error bars from literature where available.](image)

![Fig. 5 Correlation of the \(\Delta H^\circ_{\text{f,el}}\) of apatites vs. the \(\Delta H^\circ_{\text{f,el}}\) of anions \(X^-\). Experimental data and values predicted using Eq. 4 (Table 4) were used to plot regression lines (full symbols). Empty marks indicate values calculated from Eq. 5.](image)

**Table 4** Comparison of the experimental enthalpies of formation with values predicted using \(U_{\text{pot}}\)

| Apatite       | exptl\(\Delta H^\circ_{\text{f,el}}\) (kJ mol\(^{-1}\)) | \(\text{pred}\Delta H^\circ_{\text{f,el}}\) (kJ mol\(^{-1}\)) | % diff |
|--------------|---------------------|---------------------|--------|
| Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2} | -13,545 | -13,546 | -0.01 |
| Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2} | -13,201 | -13,196 | 0.04 |
| Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Br\textsubscript{2} | -13,063 | -13,067 | -0.03 |
| Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}I\textsubscript{2} | -12,893 | -12,893 | - |
| Sr\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2} | -13,604 | -13,604 | 0.00 |
| Sr\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Br\textsubscript{2} | -13,233 | -13,233 | 0.00 |
| Sr\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}I\textsubscript{2} | -13,111 | -13,111 | - |
| Ba\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2} | -13,564 | -13,564 | 0.00 |
| Ba\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2} | -13,246 | -13,246 | 0.00 |
| Ba\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Br\textsubscript{2} | -13,009 | -13,009 | - |
| Ba\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}I\textsubscript{2} | -12,859 | -12,859 | - |
| Cd\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2} | -8795 | -8795 | 0.00 |
| Cd\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2} | -8463 | -8463 | 0.00 |
| Cd\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Br\textsubscript{2} | -8365 | -8365 | - |
| Cd\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}I\textsubscript{2} | -8199 | -8199 | - |
| Pb\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2} | -8466 | -8468 | -0.02 |
| Pb\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2} | -8248 | -8240 | 0.10 |
| Pb\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Br\textsubscript{2} | -8180 | -8187 | -0.08 |
| Pb\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}I\textsubscript{2} | -8072 | - |

Note: exptl\(\Delta H^\circ_{\text{f,el}}\) – experimental data extracted from Table 1; \(\text{pred}\Delta H^\circ_{\text{f,el}}\) – calculated based on Eq. 4; %diff = 100 - \((\text{exptl}\Delta H^\circ_{\text{f,el}} - \text{pred}\Delta H^\circ_{\text{f,el}}) / \text{exptl}\Delta H^\circ_{\text{f,el}}\)
**Table 5** Comparison of the experimental enthalpies of formation and selected \( \Delta H^o_{\text{f,el}} \) from Table 4 with values predicted using \( \Delta H^o_{\text{f,el}} \) of monovalent anion \( X^- \)

| Apatite                  | \( \text{exptl} \Delta H^o_{\text{f,el}} \) (kJ mol\(^{-1}\)) | \( \text{pred} \Delta H^o_{\text{f,el}} \) (kJ mol\(^{-1}\)) | \% diff |
|--------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------|
| \( \text{Ca}_{10}(PO_4)_6F_2 \) | -13,545.0                                                     | -13,550.1                                                     | 0.0     |
| \( \text{Ca}_{10}(PO_4)_6OH_2 \) | -13,292.0                                                     | -13,308.5                                                     | -0.1    |
| \( \text{Ca}_{10}(PO_4)_6Cl_2 \) | -13,200.8                                                     | -13,164.2                                                     | 0.3     |
| \( \text{Ca}_{10}(PO_4)_6Br_2 \) | -13,063.0                                                     | -13,059.5                                                     | 0.0     |
| \( \text{Ca}_{10}(PO_4)_6I_2 \) | -12,892.7                                                     | -12,911.4                                                     | -0.1    |
| \( \text{Sr}_{10}(PO_4)_6F_2 \) | -13,604.0                                                     | -13,618.7                                                     | -0.1    |
| \( \text{Sr}_{10}(PO_4)_6OH_2 \) | -13,373.0                                                     | -13,364.9                                                     | 0.1     |
| \( \text{Sr}_{10}(PO_4)_6Cl_2 \) | -13,233.0                                                     | -13,213.3                                                     | 0.1     |
| \( \text{Sr}_{10}(PO_4)_6Br_2 \) | -13,111.5                                                     | -13,103.2                                                     | 0.1     |
| \( \text{Sr}_{10}(PO_4)_6I_2 \) | -12,926.3                                                     | -12,947.6                                                     | -0.2    |
| \( \text{Ba}_{10}(PO_4)_6F_2 \) | -13,564.0                                                     | -13,584.4                                                     | -0.2    |
| \( \text{Ba}_{10}(PO_4)_6OH_2 \) | -13,309.0                                                     | -13,318.3                                                     | -0.1    |
| \( \text{Ba}_{10}(PO_4)_6Cl_2 \) | -13,246.0                                                     | -13,159.4                                                     | 0.7     |
| \( \text{Ba}_{10}(PO_4)_6Br_2 \) | -13,008.9                                                     | -13,044.0                                                     | -0.3    |
| \( \text{Ba}_{10}(PO_4)_6I_2 \) | -12,859.1                                                     | -12,880.9                                                     | -0.2    |
| \( \text{Cd}_{10}(PO_4)_6F_2 \) | -8795.0                                                       | -8797.7                                                      | 0.0     |
| \( \text{Cd}_{10}(PO_4)_6OH_2 \) | -8565.8                                                       | -8577.6                                                      | -0.2    |
| \( \text{Cd}_{10}(PO_4)_6Cl_2 \) | -8463.0                                                       | -8446.1                                                      | 0.2     |
| \( \text{Cd}_{10}(PO_4)_6Br_2 \) | -8365.2                                                       | -8350.7                                                      | 0.2     |
| \( \text{Cd}_{10}(PO_4)_6I_2 \) | -8198.8                                                       | -8215.7                                                      | -0.2    |
| \( \text{Pb}_{10}(PO_4)_6F_2 \) | -8466.0                                                       | -8471.9                                                      | -0.1    |
| \( \text{Pb}_{10}(PO_4)_6OH_2 \) | -8325.2                                                       | -8325.0                                                      | 0.0     |
| \( \text{Pb}_{10}(PO_4)_6Cl_2 \) | -8248.0                                                       | -8237.3                                                      | 0.1     |
| \( \text{Pb}_{10}(PO_4)_6Br_2 \) | -8180.0                                                       | -8173.6                                                      | 0.1     |
| \( \text{Pb}_{10}(PO_4)_6I_2 \) | -8072.1                                                       | -8083.6                                                      | -0.1    |
| \( \text{Ca}_{10}(AsO_4)_6F_2 \) | -11,258.8                                                     | -11,258.8                                                    | 0.0     |
| \( \text{Ca}_{10}(AsO_4)_6OH_2 \) | -10,934.7                                                     | -10,934.7                                                    | 0.0     |
| \( \text{Ca}_{10}(AsO_4)_6Cl_2 \) | -10,741.1                                                     | -10,741.1                                                    | -0.1    |
| \( \text{Ca}_{10}(AsO_4)_6Br_2 \) | -10,600.6                                                     | -10,600.6                                                    | -0.1    |
| \( \text{Ca}_{10}(AsO_4)_6I_2 \) | -10,401.9                                                     | -10,401.9                                                    | -0.1    |
| \( \text{Pb}_{10}(AsO_4)_6F_2 \) | -6288.0                                                       | -6286.8                                                      | 0.0     |
| \( \text{Pb}_{10}(AsO_4)_6OH_2 \) | -6060.0                                                       | -6063.3                                                      | -0.1    |
| \( \text{Pb}_{10}(AsO_4)_6Cl_2 \) | -5931.8                                                       | -5929.8                                                      | 0.0     |
| \( \text{Pb}_{10}(AsO_4)_6Br_2 \) | -5832.2                                                       | -5832.2                                                      | -0.1    |
| \( \text{Pb}_{10}(AsO_4)_6I_2 \) | -5695.8                                                       | -5695.8                                                      | -0.1    |

Note: \( \text{exptl} \Delta H^o_{\text{f,el}} \) – experimental data extracted from Table 1; \( \text{pred} \Delta H^o_{\text{f,el}} \) – calculated based on Eq. 4; \( \% \text{diff} = 100 \cdot \frac{\text{exptl} \Delta H^o_{\text{f,el}} - \text{pred} \Delta H^o_{\text{f,el}}}{\text{exptl} \Delta H^o_{\text{f,el}}} \)

The \( \Delta H^o_{\text{f,el}} \) of \( \text{AO}_4^{3-} \) were extracted from Table SI 3. The results are summarized in Table 6. It is important to note that prediction of \( \Delta H^o_{\text{f,el}} \) for V-apatites would not have been possible without firstly estimating the values of \( \Delta H^o_{\text{f,el}} \) by the predictive methods described above.

**Discussion**

Experimental data selected from Table 1 and predicted values recommended in this work (Table 7) allow for comparison of \( \Delta H^o_{\text{f,el}} \) and presentation of the linear relationships observed within apatite subgroups (Fig. 8). The dependence of \( \Delta H^o_{\text{f,el}} \) on the molecular weight is apparent. The heavier halide substituted within any of the apatite subgroups the less negative \( \Delta H^o_{\text{f,el}} \) (apatite is less stable). This relationship is identical within all apatite subgroups studied but the intensity of this effect varies as evidenced by different slope coefficients of the trends lines. This observation also applies to the molecular weight of whole apatite. The lightest phosphate apatites have the most negative \( \Delta H^o_{\text{f,el}} \) and the heaviest lead arsenate apatites have the least negative \( \Delta H^o_{\text{f,el}} \). Therefore, \( \text{Sr}_{10}(PO_4)_6F_2 \) is enthalpically the most stable of all the apatites studied while \( \text{Pb}_{10}(AsO_4)_6I_2 \) is the least stable one.

The mass of the tetrahedral anion \( \text{AO}_4^{3-} \) and the mass of the anion at the X position strongly and equally affect the \( \Delta H^o_{\text{f,el}} \) but the mass of the metal cation \( \text{Me}^{2+} \) does not influence \( \Delta H^o_{\text{f,el}} \) unambiguously. Apatites containing alkaline earth metal cations (\( \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+} \)) are more enthalpically stable than apatites of other metals, e.g., \( \text{Pb} \) and \( \text{Cd} \) (but also \( \text{Zn}, \text{Cu}, \text{Fe}, \text{see Drouet 2015, 2019} \)), regardless of...
Fig. 7 Plot of $\Delta H_{\text{f,el}}^\circ$ of apatites with $\Delta H_{\text{f,el}}^\circ$ of tetrahedral anion $\text{AO}_4^{3-}$ for Pb- and Ca-apatites. Empty marks indicate values calculated from Eq. 6.

Table 6 Compilation of the experimental and predicted enthalpies of formation for phosphate, arsenate and vanadate Ca- and Pb-apatites

| Apatite | exptl$\Delta H_{\text{f,el}}^\circ$ A=P (kJ mol$^{-1}$) | exptl$\Delta H_{\text{f,el}}^\circ$ A=As (kJ mol$^{-1}$) | exptl$\Delta H_{\text{f,el}}^\circ$ A=V (kJ mol$^{-1}$) |
|---------|--------------------------------------------------|--------------------------------------------------|--------------------------------------------------|
| Ca$_{10}$(AO$_4$)$_6$F$_2$ | $-13,545$ | $-11,259$ | $-12,761$ |
| Ca$_{10}$(AO$_4$)$_6$OH$_2$ | $-13,292$ | $-10,935$ | $-12,484$ |
| Ca$_{10}$(AO$_4$)$_6$Cl$_2$ | $-13,201$ | $-10,741$ | $-12,357$ |
| Ca$_{10}$(AO$_4$)$_6$Br$_2$ | $-13,063$ | $-10,601$ | $-12,218$ |
| Ca$_{10}$(AO$_4$)$_6$I$_2$ | $-12,893$ | $-10,402$ | $-12,038$ |
| Pb$_{10}$(AO$_4$)$_6$F$_2$ | $-8466$ | $-6288$ | $-7719$ |
| Pb$_{10}$(AO$_4$)$_6$OH$_2$ | $-8325$ | $-6060$ | $-7548$ |
| Pb$_{10}$(AO$_4$)$_6$Cl$_2$ | $-8248$ | $-5932$ | $-7465$ |
| Pb$_{10}$(AO$_4$)$_6$Br$_2$ | $-8180$ | $-5833$ | $-7375$ |
| Pb$_{10}$(AO$_4$)$_6$I$_2$ | $-8072$ | $-5696$ | $-7257$ |

Note: exptl$\Delta H_{\text{f,el}}^\circ$ A=P - experimental data extracted from Table 1; $^a$exptl$\Delta H_{\text{f,el}}^\circ$ A=As - calculated based on Eq. 4; $^b$exptl$\Delta H_{\text{f,el}}^\circ$ A=V - calculated based on Eq. 5; $^{a'}$pred$\Delta H_{\text{f,el}}^\circ$ A=P - calculated based on Eq. 6; $^{b'}$pred$\Delta H_{\text{f,el}}^\circ$ A=As - calculated based on Eq. 5; $^{a''}$pred$\Delta H_{\text{f,el}}^\circ$ A=V - calculated based on Eq. 6.
Table 7  Enthalpy of formation from elements $\Delta H^\circ$\textsubscript{f,el} for apatites recommended for use in thermodynamic calculations (recom$\Delta H^\circ$\textsubscript{f,el}) in comparison with data obtained by two other prediction methods: ThermAP (Drouet 2015) and SSA (Glasser 2019)

| Apatite       | recom$\Delta H^\circ$\textsubscript{f,el} (kJ mol$^{-1}$) | ThermAP$\Delta H^\circ$\textsubscript{f,el} (kJ mol$^{-1}$) | % diff$^1$ | SSA $\Delta H^\circ$\textsubscript{f,el} (kJ mol$^{-1}$) | % diff$^2$ |
|---------------|--------------------------------------------------------|-------------------------------------------------------------|------------|-------------------------------------------------------|------------|
| Ca$_{10}$(PO$_4$)$_6$F$_2$ | $-13,545.0$ | $-13,598.0$ | $-0.39$ | $-13,590.4$ | $-0.34$ |
| Ca$_{10}$(PO$_4$)$_6$OH$_2$ | $-13,392.8$ | $-13,373.0$ | $-0.61$ | $-13,348.5$ | $-0.43$ |
| Ca$_{10}$(PO$_4$)$_6$Cl$_2$ | $-13,200.8$ | $-13,258.0$ | $-0.43$ | $-13,157.8$ | $0.33$ |
| Ca$_{10}$(PO$_4$)$_6$Br$_2$ | $-13,063.0$ | $-12,833.0$ | $1.76$ | $-13,046.2$ | $0.13$ |
| Ca$_{10}$(PO$_4$)$_6$I$_2$ | $-12,592.7$ | $-12,895.9$ | $-0.20$ | $-12,890.4$ | $-0.02$ |
| Sr$_{10}$(PO$_4$)$_6$F$_2$ | $-13,040.0$ | $-13,098.0$ | $-0.41$ | $-13,053.0$ | $0.14$ |
| Sr$_{10}$(PO$_4$)$_6$OH$_2$ | $-13,373.0$ | $-13,379.0$ | $0.04$ | $-13,327.7$ | $0.27$ |
| Sr$_{10}$(PO$_4$)$_6$Cl$_2$ | $-13,233.0$ | $-13,265.0$ | $-0.24$ | $-13,220.7$ | $0.27$ |
| Sr$_{10}$(PO$_4$)$_6$Br$_2$ | $-13,111.5$ | $-12,839.0$ | $2.08$ | $-13,086.3$ | $0.19$ |
| Sr$_{10}$(PO$_4$)$_6$I$_2$ | $-12,926.3$ | $-12,926.3$ | $0.00$ | $-12,926.8$ | $0.00$ |
| Ba$_{10}$(PO$_4$)$_6$F$_2$ | $-13,564.0$ | $-13,558.0$ | $-0.04$ | $-13,483.1$ | $0.60$ |
| Ba$_{10}$(PO$_4$)$_6$OH$_2$ | $-13,309.0$ | $-13,333.0$ | $-0.18$ | $-13,220.7$ | $0.27$ |
| Ba$_{10}$(PO$_4$)$_6$Cl$_2$ | $-13,246.0$ | $-13,265.0$ | $-0.24$ | $-13,197.6$ | $0.27$ |
| Ba$_{10}$(PO$_4$)$_6$Br$_2$ | $-13,008.9$ | $-12,793.0$ | $1.66$ | $-13,033.3$ | $0.14$ |
| Ba$_{10}$(PO$_4$)$_6$I$_2$ | $-12,859.1$ | $-12,895.9$ | $-0.20$ | $-12,890.4$ | $-0.02$ |
| Cd$_{10}$(PO$_4$)$_6$F$_2$ | $-8795.0$ | $-8808.0$ | $-0.15$ | $-8546.7$ | $1.23$ |
| Cd$_{10}$(PO$_4$)$_6$OH$_2$ | $-8565.8$ | $-8583.0$ | $-0.20$ | $-8546.7$ | $0.22$ |
| Cd$_{10}$(PO$_4$)$_6$Cl$_2$ | $-8463.0$ | $-8469.0$ | $0.07$ | $-8377.5$ | $1.01$ |
| Cd$_{10}$(PO$_4$)$_6$Br$_2$ | $-8365.2$ | $-8043.0$ | $3.85$ | $-8302.2$ | $0.75$ |
| Cd$_{10}$(PO$_4$)$_6$I$_2$ | $-8198.8$ | $-8189.0$ | $0.12$ | $-8189.0$ | $1.20$ |
| Pb$_{10}$(PO$_4$)$_6$F$_2$ | $-5288.0$ | $-5288.0$ | $0.00$ | $-8004.6$ | $4.51$ |
| Pb$_{10}$(PO$_4$)$_6$OH$_2$ | $-5060.0$ | $-5060.0$ | $0.00$ | $-5856.6$ | $3.36$ |
| Pb$_{10}$(PO$_4$)$_6$Cl$_2$ | $-4931.8$ | $-4931.8$ | $0.00$ | $-5700.0$ | $3.91$ |
| Pb$_{10}$(PO$_4$)$_6$Br$_2$ | $-4825.2$ | $-4825.2$ | $0.00$ | $-5619.3$ | $3.66$ |
| Pb$_{10}$(PO$_4$)$_6$I$_2$ | $-4718.9$ | $-4718.9$ | $0.00$ | $-5516.1$ | $3.16$ |

Note: bold – experimental data extracted from Tab. 1; italics – values predicted in this work; %diff$^1$ = 100 · (ThermAP$\Delta H^\circ$\textsubscript{f,el}−recom$\Delta H^\circ$\textsubscript{f,el}) / recom$\Delta H^\circ$\textsubscript{f,el}; %diff$^2$ = 100 · (SSA $\Delta H^\circ$\textsubscript{f,el}−recom$\Delta H^\circ$\textsubscript{f,el}) / recom$\Delta H^\circ$\textsubscript{f,el}
substitution at the A or X position. However, the difference between \( \Delta H^\circ_{\text{f,el}} \) of phosphate apatites containing Ca\(^{2+}\), Sr\(^{2+}\) or Ba\(^{2+}\) is minimal compared to the differences with other apatites (even though the difference in the molecular mass of these cations is very pronounced, and the contribution of the cation to the formula is the largest). This may indicate that it is the chemical character of the Me\(^{2+}\) bond in the apatite structure that has also a strong effect on the \( \Delta H^\circ_{\text{f,el}} \).

The chemical character of the bonds is similar within alkali earth elements (Ca\(^{2+}\), Sr\(^{2+}\), and Ba\(^{2+}\)) and different for heavy metals (Pb\(^{2+}\), Cd\(^{2+}\), etc.).

Hydroxylapatites fit well into linear regression line in the relationship between \( \Delta H^\circ_{\text{f,el}} \) of apatite and \( \Delta H^\circ_{\text{f,el}} \) of \( X^- \) seen within apatite subgroups. Empty marks indicate values for OH-apatites not included in regression. Error bars from literature where available.

The recommended \( \Delta H^\circ_{\text{f,el}} \) (Table 8) show linear correlation also with the electronegativity of the halide \( X^- \), the ionization energy of the halide \( X^- \) and \( \Delta H^\circ_{\text{f,el}} \) of \( \text{MeX}_2 \) (Figs. SI 1, 2, 3). All relationships give a very good or good linear fit. These correlations have been reported before but referred only to experimental data (Cruz et al. 2005b; Drouet 2015; Puzio et al. 2022). The fact that the experimental and predicted values match these lines equally well can be taken as evidence of their reliability.

Linear relationships between selected parameters within apatite subgroups are used to predict missing thermodynamic data by regression analysis. The proposed complete procedure consists of 5 steps and is shown in Table 9.
order in which the calculations are performed is crucial because only by supplementing the database with the values obtained from one prediction could the calculations for obtaining subsequent prediction values be performed. This procedure allowed for the prediction of 22 thus far experimentally unknown ΔH°f,el values for apatite end-members. This includes 9 values for iodoapatites which are the least characterized apatites. The percentage relative difference which is a measure of precision is in most cases less than 1%. The prediction precision is due to the high regression coefficients (above R² = 0.98). Such precision is comparable to the experimental uncertainty obtained when reproducing experimental data using calorimetric measurements or dissolution experiments. It is also higher than in other prediction methods proposed so far.

Using the ΔH°f,el recommended in this work the solubility constants Ksp,298.15K can be calculated and compared where available with experimental data. It is based on dissolution reaction:

\[
Me_{10}(AO_4)_6X_2 \rightleftharpoons 10Me^{2+} + 6AO_4^{3-} + 2X^- \tag{7}
\]

LogKsp,298.15K is calculated from the equation:

\[
logKsp,298.15K = \log e^{-\frac{\Delta G°f,el}{RT}} \tag{8}
\]

where ΔG°f,el is the free Gibbs energy of the dissolution reaction (7), T is temperature (in K), R is the gas constant (8.31447 J mol⁻¹K⁻¹) and superscript “°” denotes normal conditions. The thermodynamic data used in calculations are provided in Tables SI 3 and SI 9. Comparison of the calculated Ksp,298.15K with previously reported values indicates very good or good agreement within the experimental error (Tab. SI 9). This confirms the usefulness and reliability of the ΔH°f,el predicted here for thermodynamic calculations.

### Conclusions

A method for predicting the ΔH°f,el of apatites using molar volume, lattice energy, and ΔH°f,el of anions AO₄³⁻ or X⁻ was proposed and demonstrated on phosphate, arsenate, and vanadate apatites containing Ca, Sr, Ba, Pb, and Cd at the cationic positions and F, OH, Cl, Br, and I at the halide position. The approach is based on regression analysis of the correlations occurring within apatite subgroups. These subgroups are formed by Me₁₀(AO₄)₆X₂ apatites with the same Me²⁺ cations and tetrahedral AO₄³⁻ anions and with different halides in the X position (or a complex monovalent OH⁻ anion). This approach not only leads to more accurate predictions (with precision comparable with the experimental uncertainty) but also to see important relationships between apatites and should also be used when analyzing other properties of apatite end-members. The proposed prediction procedure allowed for the prediction of 22 so far unknown ΔH°f,el and can be applied to a wider range of apatites than other methods. Due to lack of experimental data, it is still not possible to predict the ΔH°f,el for Sr₁₀(VO₄)₆X₂, Ba₁₀(VO₄)₆X₂, Cd₁₀(AsO₄)₆X₂, Sr₁₀(AsO₄)₆X₂, or Ba₁₀(AsO₄)₆X₂. The new prediction method for ΔH°f,el of apatites could provide important insights, e.g., allowing optimization of the chemical composition and properties of apatite-based materials for their suitability to various forms of nuclear waste deposited in geological repositories.

### Supplementary Information

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### Authors contributions

Conceptualization; Methodology; Formal analysis; Investigation resources; Data curation; Writing—original draft
preparation; Visualization; Project administration; Funding acquisition: Bartosz Puzio; Writing—review and editing; supervision: Maciej Manecki. All authors have read and agreed to the published version of the manuscript.

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**References**

Aissa A, Badraoui B, Thouenot R, Debbabi M (2004) (2004) Synthesis, x-ray structural analysis and spectroscopic investigations (IR and 31P MAS NMR) of mixed barium/strontium fluoroapatites. Eur J Inorg Chem 19:3828–3836. https://doi.org/10.1002/ejc.200400224

Alberius HP, Lidin S, Petříček V (1999) Iodo-oxyapatite, the first example from a new class of modulated apatites. Acta Crystall B-Stru 55(2):165–169. https://doi.org/10.1107/S0108768198012312

Alberius-Henning P, Mattsson C, Lidin S (2000) Crystal structure of pentastriontium triis (phosphate) bromide, Sr5(PO4)3Br and of pentabarium triis (phosphate) bromide Ba5(PO4)3Br, two bro-mooapatites. Z Krist-New Crys St 215(3):345–346. https://doi.org/10.1107/S0108270199800319

Allison ID, Brown DS, Novo-Gradac KJ (1991) MINEQA2/PRO-DEFA2, a geochemical assessment model for environmental systems: version 3.0 user’s manual. Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Athens, Georgia

Amjad Z, Koutsoukos PG, Nancollas GH (1981) The mineralization of enamel surfaces. A constant composition kinetics study. J Dent Res 60(10):1783–1792. https://doi.org/10.1177/00220345810601000901

Antao SM, Dhalivel I (2018) Lead apatites: structural variations among Pb5(BO3)Cl2 with B=P (pyrophosphate), As (mimetite) and V (vanadate). J Synchrotron Radiat 25(1):214–221. https://doi.org/10.1107/S1600577517014217

Audubert F, Savariault JM, Lacout JL (1999) Pentalead tris (vanadate) iodide, a defect vanadinite-type compound. Acta Crystall c 55(3):271–273. https://doi.org/10.1107/S0108727199800534

Avnimelech Y, Moreno EC, Brown WE (1973) Solubility and surface properties of finely divided hydroxyapatite. J Res NBS a Phys Ch 77(1):149. https://doi.org/10.6028/jres.077A.008

Babu R, Jena H, Kutty KG, Nagarajan K (2011) Thermodynamic functions of Ba5(PO4)3Cl2, Sr5(PO4)3Cl2 and Ca5(PO4)3Cl2. Thermoch Acta 526(1–2):78–82. https://doi.org/10.1016/j.thermaling.2011.08.027

Baikie T, Mercier PH, Elcombe MM, Kim JY, Le Page Y, Mitchell LD, White TJ, Whitfield PS (2007) Triclinic apatites. Acta Crystall B-Stru 63(2):251–256. https://doi.org/10.1107/S0108788107065316

Bajda T, Szmit E, Manecki M (2007) Removal of As(V) from solutions by precipitation of mimetite Pb3(AsO4)2Cl. Environ. Eng. 1:119–124

Bajda T (2010) Solubility of mimetite Pb3(AsO4)2Cl at 5–55 °C. Environ Chem 7:268–278. https://doi.org/10.1071/EN10021

Baker WE (1966) An X-ray diffraction study of synthetic members of the pyromorphite series. Am Mineral J Earth Planet Mater 11(11–12):1712–1721

Ball JW, Nordstorm DK, Jenne EA (1980) Additional and revised thermochemical data and computer code for WATEQ2: A computerized chemical model for trace and major element speciation and mineral equilibria of natural waters (Vol. 78). US Geological Survey, Menlo Park, California

Baran EJ (1972) Kristallographische Daten einiger Vanadin-Bromapatite. Monatsh Chem 103(6):1684–1690. https://doi.org/10.1007/BF00904623

Beck HP, Douiheche M, Haberkorn R, Kohlmann H (2006) Synthesis and characterisation of chloro-vanadato-apatites M2(VO4)3Cl (M=Ca, Sr, Ba). Solid State Sci 8(1):64–70. https://doi.org/10.1016/j.solidstatesciences.2005.08.014

Bell LC, Mika H, Kruger BJ (1978) Synthetic hydroxyapatite-solubility product and stoichiometry of dissolution. Arch Oral Biol 23(5):329–336. https://doi.org/10.1016/0003-9969(78)90008-4

Bell AM, Henderson CMB, Wendlandt RF, Harrison WJ (2009) Rietveld refinement of Ba5(AsO4)3Cl from high-resolution synchrotron data. Acta Crystalllogr e 64(9):i63–i64. https://doi.org/10.1107/S1600536809026901

Bell AM, Henderson CMB, Wendlandt RF, Harrison WJ (2009) Rietveld refinement of Sr5(AsO4)3Cl from high-resolution synchrotron data. Acta Crystalllogr e 65(3):i16–i17. https://doi.org/10.1107/S1600536809005054

Ben Cherifa A, Nounah A, Lacot JL, Jemal M (2001) Synthèse et thermochimie de phosphates au cadmium. Thermochim Acta 366(1):7–13. https://doi.org/10.1016/S0040-6031(00)00713-9

Bhatnagar VM (1970) Preparation, lattice parameters and X-ray powder patterns of lead fluoroapatite and lead chlorapatite. Inorg Nucl Chem Lett 6(12):913–917. https://doi.org/10.1007/BF00650874

Biagnoni C, Pasero M (2013) The crystal structure of johnbaumite, Ca5(AsO4)3OH, the arsenate analogue of hydroxyapatite. Am Mineral 98(8–9):1580–1584. https://doi.org/10.2138/am.2013.4443

Biagnoni C, Bosi F, Hålenius U, Pasero M (2017) The crystal structure of turneaureite, Ca5(AsO4)3Cl, the arsenate analog of hydroxyapatite, and its relationships with the arsenate apatites johnbaumite and svabite. Am Mineral 1016(10):1981–1986. https://doi.org/10.2138/am-2017-6041

Bigi A, Foresti E, Marchetti F, Ripamonti A, Roveri N (1984) Barium calcium hydroxyapatite solid solutions. J Chem Soc Dalton 80123 12

Bisengalieva MR, Ogorodova LP, Vigasina MF, Melchakova LV (2004) (2004) Synthesis, x-ray structural analysis and spectroscopic investigations (IR and 3P MAS NMR) of mixed barium/strontium fluoroapatites. Eur J Inorg Chem 19:3828–3836. https://doi.org/10.1002/ejc.200400224

Bothe JV Jr, Brown PW (1999) The stabilities of calcium arsenates of the pyromorphite series. Am Mineral J Earth Planet Mater 11(11–12):1712–1721

Bondareva OS, Malinovskii YA (1986) Crystal structure of synthetic johnbaumite and svabite. Am Mineral 98(8–9):1580–1584. https://doi.org/10.2138/am.2013.4443

Bogach VV, Dobrydnev SV, Beskov VS (2001) Calculation of the thermodynamic properties of apatites. Russ J Phys Chem A 84(7):1011–1014

Bondareva OS, Malinovskii YA (1986) Crystal structure of synthetic Ba hydroxyapatite. Kristallografiya 31:233–236

Boje JV Jr, Brown PW (1999) The stabilities of calcium arsenates at 23±1 °C. J Hazard Mater 69(2):197–207. https://doi.org/10.1016/S0304-3894(99)00105-3
61(32):12552–12558. https://doi.org/10.1021/acs.inorgchem.2c01300

Okudera H (2013) Relationships among channel topology and atomic displacements in the structures of Pb5(BO4)3Cl with B=P (pyromorphite), V (vanadinite), and As (mimetite). Am Mineral 98(8-9):1573–1579. https://doi.org/10.2138/am.2013.4417

Olds TA, Kampf AR, Rakovan JF, Burns PC, Mills OP, Laughlin-Yurs C (2021) Hydroxyapatite, a mineral important to lead remediation: Modern description and characterization. Am Mineral 106(6):922–929. https://doi.org/10.2138/am-2021-7516

Pan Y, Fleet ME (2002) Compositions of the apatite-group minerals: substitution mechanisms and controlling factors. Rev Mineral Geochem 48(2):13–49. https://doi.org/10.2138/rmg.2002.48.2

Pasero M, Kampf AR, Ferraris C, Pekoiv J, Rakovan J, White TJ (2010) Nomenclature of the apatite supergroup minerals. Eur J Mineral 22(2):163–179. https://doi.org/10.1127/0935-1221/2010/0022-2022

Pekov IV, Koshlyakova NN, Zubkova NV, Krzątala A, Galuskina IO, Puzio B, Manecki M, Kwaśniak-Kominek M (2018) Transition from endothermic to exothermic dissolution of hydroxyapatite and the novel natural ternary solid-solution system pliniusite–svabite–fluorapatite. Am Mineral (In Press). https://doi.org/10.2138/am-2022-8100

Phebe DE, Narasaraju TSB (1995) Preparation and characterization of hydroxyl and iodide apatites of calcium and their solid solutions. J Mater Sci Lett 14(4):229–231. https://doi.org/10.1007/ BF00275066

Pieczka A, Biagioni C, Gołębiowska B, Jeleń P, Pasero M, Sitarz M (2018) Parafiniukite, Ca2Mn3(PO4)3Cl, a new apatite-group mineral and the novel natural ternary solid-solution system pliniusite–svabite–fluorapatite. Am Mineral (In Press). https://doi.org/10.2138/am-2022-8100

Posner AS, Perloff A, Diorio AF (1958) Refinement of the hydroxyapatite structure. Acta Crystallogr 11:308–309. https://doi.org/10.1107/S0365110X58000815

Ptáček P (2016) Synthetic phase with the structure of apatite. In Chemistry: Apatites and their synthetic analogues-synthesis, structure, properties and applications (pp. 177–244). INTECH

Puzzio B, Manecki M, Kwaśniak-Kominek M (2018) Transition from endothermic to exothermic dissolution of hydroxyapatite Ca5(PO4)3OH–johnbaumite Ca5(AsO4)3OH solid solution series at temperatures ranging from 5 to 65°C. Geosci 8:281. https://doi.org/10.3390/s8050281

Puzzio B, Solecu U, Polopska J, Manecki M, Bajda T (2021) Solubility and dissolution mechanisms of vanadinite Pb5(VO4)3Cl: effects of temperature and PO4 substitutions. Appl Geochem 131:105015. https://doi.org/10.1016/j.apgeochem.2021.105015

Puzzio B, Zhang L, Szymanowski JES, Burns PC, Manecki M (2022) Thermodynamic characterization of synthetic lead-arsenate apatites with different halogen substitutions. Am Mineral. https://doi.org/10.2138/am-2020-7452

Rakovan JF, Hughes JM (2000) Strontium in the apatite structure: strontian fluorapatite and belovite-(Ce). Can Mineral 38(4):839–845. https://doi.org/10.2138/gscamin.38.4.839

Rakovan JF, Pasteris JD (2015) A technological gem: Materials, medical, and environmental mineralogy of apatite. Elements 11(3):195–200. https://doi.org/10.2138/egelements.11.3.195

Rakovan J, Scovil JA (2021) Apatite and the apatite supergroup. Rocks Miner 96(1):13–19. https://doi.org/10.1080/00357529.2021.1827906

Robie RA, Hemingway BS, Fischer JR (1979) Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures. Geol Survey Bull 1452: 456

Robie RA, Hemingway BS (1995) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 Pascals) pressure and at higher temperatures, 2131, 461 p. US Government Printing Office, Washington

Roh YH, Hong ST (2005) Apatite-type Ba5(VO4)3Cl. Acta Crystallogrr e 61(8):i40–i42. https://doi.org/10.1107/S160053605018854

Roine A (1994) Outokumpu HSC chemistry for windows. Chemical Reaction and Equilibrium Software with Extensive Thermochemical Database

Rollin-Martinet S, Navrotsky A, Champion E, Grossin D, Drouet C (2013) Thermodynamic basis for evolution of apatite in calcified tissues. Am Mineral 98:2037–2045. https://doi.org/10.2138/am.2013.4537

Rossini FD, Gucker FT Jr, Johnston HL, Pauling L, Vinal GW (1952) Status of the values of the fundamental constants for physical chemistry as of July 1, 1951. J Am Chem Soc 74(11):2699–2701

Santillan-Medrano J, Jurinak JJ (1975) The chemistry of lead and cadmium in soil: solid phase formation. Soil Sci Soc Am J 39(5):851–856. https://doi.org/10.2136/sssaj1975.03615995003900050020x

Sassani DC, Shock EL (1992) Estimation of standard partial molal entropies of aqueous ions at 25 C and 1 bar. Geochim Cosmochim Acta 56(11):3895–3908. https://doi.org/10.1016/0016-7037(92)90004-3

Shellis RP, Wahab FK, Heywood BR (1993) The hydroxyapatite ion activity product in acid solutions equilibrated with human enamel at 37 C. Caries Res 27(5):365–372. https://doi.org/10.1111/j.1050-1849.1993.tb00256.x

Shock EL, Sassani DC, Willis M, Sverjensky DA (1997) Inorganic species in geologic fluids: correlations among standard molar thermodynamic properties of aqueous ions and hydrogen complexes. Geochim Cosmochim Acta 61(5):907–950. https://doi.org/10.1016/S0016-7037(96)00339-0

Smirnova ZG, Illarionov VV, Volkovich SI (1962) Heats of formation of fluorapatite and hydroxyl apatite and the α and β modifications of tricalcium phosphate. Zhr Neorg Khim 7:1779–1782

Solecka U, Bajda T, Topolska J, Zlek-Pogudz S, Manecki M (2018) Raman and Fourier transform infrared spectroscopic study of pyromorphite-vanadinite solid solutions. Spectrochim Acta 190:99–106. https://doi.org/10.1016/j.saa.2017.08.061

Sordyl J, Puzzio B, Manecki M, Borkiewicz O, Topolska J, Zlek-Pogudz S (2020) Structural assessment of fluorine, chlorine, bromine, iodine, and hydroxide substitutions in lead arsenate apatites (Mimetites–Pb5(AsO4)3X). Minerals 10(6):494. https://doi.org/10.3390/min10060494

Stefánsson A (2001) Dissolution of primary minerals of basalt in natural waters: I. Calculation of mineral solubilities from 0 C to 350 C. Chem Geol 172(3–4):225–250. https://doi.org/10.1016/S0009-2541(00)00263-1

Stennett MC, Pinnock JJ, Hyatt NC (2011) Rapid synthesis of Pb5(VO4)3I, for the immobilisation of iodine radioisotopes, by microwave dielectric heating. J Nucl Mater 414(3):252–256. https://doi.org/10.1016/j.jnucmat.2011.04.041

Stumm W, Morgan JJ (2012) Aquatic chemistry: chemical equilibria and rates in natural waters. John Wiley & Sons, New York

Sudarsanan KT, Young RA (1969) Significant precision in crystal structural details Holly Springs Hydroxyapatite. Acta Crystall B-Stru 25(8):1534–1543. https://doi.org/10.1107/S0002617769008478

Sudarsanan K, Mackie PE, Young RA (1972) Comparison of synthetic and mineral fluorapatite, Ca5(PO4)3F, in crystallographic detail. Mater Res Bull 7(11):1331–1337. https://doi.org/10.1016/0025-5408(72)90113-4

Sudarsanan K, Young RA (1974) Structure refinement and random error analysis for strontiumchlorapatite, Sr5(PO4)3Cl. Acta
Zhu Y, Zhu Z, Zhao X, Liang Y, Huang Y (2015a) Characterization, dissolution, and solubility of lead hydroxyapatite [Pb$_x$(PO$_4$)$_3$OH] at 25–45 °C. J Chem-NY. https://doi.org/10.1155/2015/29387

Zhu Y, Zhu Z, Zhao X, Liang Y, Dai L, Huang Y (2015b) Characterization, dissolution and solubility of synthetic cadmium hydroxyapatite [Cd$_5$(PO$_4$)$_3$OH] at 25–45° C. Geochem Trans 16(1):1–11. https://doi.org/10.1186/s12932-015-0025-1

Zhu Y, Huang B, Zhu Z, Liu H, Huang Y, Zhao X, Liang M (2016) Characterization, dissolution and solubility of the hydroxyapatite–hydroxyapatite solid solution [(Pb$_{1-x}$Ca$_x$)$_5$(PO$_4$)$_3$OH] at 25 °C and pH 2–9. Geochem Trans 17(1):1–18. https://doi.org/10.1186/s12932-016-0034-8

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