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Prediction of Gibbs free energies of formation of minerals of the alunite supergroup

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Abstract—A method for the prediction of Gibbs free energies of formation for minerals belonging to the alunite family is proposed, based on an empirical parameter $\Delta_G O^= M^{z+}(c)$ characterizing the oxygen affinity of the cation M^{z+} . The Gibbs free energy of formation from constituent oxides is considered as the sum of the products of the molar fraction of an oxygen atom bound to any two cations, multiplied by the difference of oxygen affinity $\Delta_G O^= M^{z+}(c)$ between any two consecutive cations. The $\Delta_G O^= M^{z+}(c)$ value, using a weighing scheme involving the electronegativity of a cation in a specific site (12-fold coordination site, octahedral and tetrahedral) is assumed to be constant. It can be calculated by minimizing the difference between experimental Gibbs free energies (determined from solubility measurements) and calculated Gibbs free energies of formation from constituent oxides. Results indicate that this prediction method gives values within 0.5% of the experimentally measured values. The relationships between $\Delta_G O^= M^{z+}(\text{alunite})$ corresponding to the electronegativity of a cation in either dodecahedral sites, octahedral sites or tetrahedral sites and known as $\Delta_G O^= M^{z+}(\text{aq})$ were determined, thereby allowing the prediction of the electronegativity of rare earth metal ions and trivalent ions in dodecahedral sites and highly charged ions in tetrahedral sites. This allows the prediction of Gibbs free energies of formation of any minerals of the alunite supergroup (bearing various ions located in the dodecahedral and tetrahedral sites). Examples are given for hydronium jarosite and hindsalite, and the results appear excellent when compared to experimental values. Copyright © 2004 Elsevier Ltd

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1. INTRODUCTION

Experimental methods to determine Gibbs free energies of formation of minerals belonging to the alunite supergroup by calorimetry or solubility measurements are both complex and time consuming.

Minerals of the alunite supergroup (more than 40 species), having variable compositions (Scott, 1987; Jambor, 1999), present even greater difficulties since the Gibbs free energy of formation must be determined for each individual composition. The difficulties in the experimental processes, therefore, limits the availability of free energy data to a few selected minerals species such as jarosite and alunite minerals *sensu stricto* (Stoffregen et al., 2000), thereby reducing the general applicability of thermodynamics to a relatively small number of alunite supergroup mineral systems.

There are numerous empirical methods to evaluate Gibbs free energies of formation for minerals in general but their presentation would exceed the scope of this introduction. However, at present, there is no empirical method to predict thermodynamic data of minerals belonging to the alunite supergroup. That is why this paper describes an empirical method to predict the Gibbs free energies of these minerals. This method is based on the difference of electronegativity of cations located in two sites having a common oxygen.

This method has been already tested for hydrated clay minerals (Vieillard, 2000) and for micas and chlorites (Vieillard,

2002) and gave acceptable errors of prediction. It has two advantages: first, the technique is simple to implement because the chemical formula and the nature of cations in different sites are known; and secondly, this method allows to predict Gibbs free energies of thallium, bismuth, vanadium and chromium bearing minerals of the alunite supergroup thanks to some linear relationships between calculated and theoretical electronegativities of cations in the involved sites.

2. METHODOLOGY

The details concerning the prediction method of Gibbs free energies of formation of minerals have been explained by Vieillard (2000) and are based on parameters $\Delta_G O^= M^{z+}(\text{aq})$ and Gibbs free energies of formation from constituent oxides, $\Delta G_{f,ox}^\circ$.

2.1. Definitions of Parameters $\Delta G O^= M^{z+}(\text{aq})$ and $\Delta G_{f,ox}^\circ$

The parameter $\Delta G O^= M^{z+}(\text{aq})$ characterizes a given cation M^{z+} and is defined as the difference between the Gibbs free energy of formation of the corresponding oxides [$\Delta G_f^\circ \text{MO}_x(c)$] and the Gibbs free energy of formation of the corresponding aqueous cation [$\Delta G_f^\circ M^{z+}(\text{aq})$]:

$$\Delta_G O^= M^{z+}(\text{aq}) = (1/x) [\Delta G_f^\circ \text{MO}_x(c) - \Delta G_f^\circ M^{z+}(\text{aq})] \text{ (kJ} \cdot \text{mol}^{-1}) \quad (1)$$

where z is the charge of the cation M^{z+} and x is the number of oxygen atoms combined with one atom of M in the oxide ($x =$

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z/2), so the difference in Eqn. 1 refers to one oxygen atom. A set of values of $\Delta_{\text{G}}^{\circ} \text{M}^{\text{z}+}(\text{aq})$ is proposed here (Table 1) and comes mostly from Robie and Hemingway (1995) for oxides and from Shock and Helgeson (1988) for aqueous cations. Vieillard (2000) showed the dependence of a cation with the oxygen affinity by a relationships between the parameter $\Delta_{\text{G}}^{\circ} \text{M}^{\text{z}+}(\text{aq})$ with the difference of electronegativity between cation and oxygen.

The second parameter $\Delta \text{G}_{\text{f,ox}}^{\circ}$, designating Gibbs free energy of formation of a mineral from constituent oxides, is the difference between the Gibbs free energy of formation of a mineral of the alunite supergroup, $\Delta \text{G}_{\text{f}}^{\circ}(\text{mineral})$, and the sum of the Gibbs free energies of formation of the different constituent oxides in the alunite-like minerals. It is given by:

$$\Delta \text{G}_{\text{f,ox}}^{\circ} = \Delta \text{G}_{\text{f}}^{\circ}(\text{Mineral}) - \sum_{i=1}^{i=n_{\text{O}_i}} (n_i) \Delta \text{G}_{\text{f}}^{\circ}(\text{M}_i \text{O}_{x_i}) \quad (2)$$

where n_i is the number of moles of oxides. The Gibbs free energies of formation of oxides are given in Table 1.

Table 1. Gibbs free energies of formation of oxides and ions, and calculated parameters $\Delta_{\text{G}}^{\circ} \text{M}^{\text{z}+}(\text{aq})$ of selected cations.^a

Oxides	$\Delta \text{G}_{\text{f}}^{\circ}$ (kJ · mol ⁻¹)	Ions	$\Delta \text{G}_{\text{f}}^{\circ}$ (kJ · mol ⁻¹)	$\Delta_{\text{G}}^{\circ} \text{M}^{\text{z}+}(\text{aq})$ (kJ · mol ⁻¹)
Ag ₂ O	-11.20 ¹	Ag ⁺	77.11 ¹	-165.41
Na ₂ O	-376.00 ²	Na ⁺	-261.88 ⁷	147.76
K ₂ O	-322.10 ²	K ⁺	-282.46 ⁷	242.82
(NH ₄) ₂ O	-234.30 ³	NH ₄ ⁺	-79.41 ²	-75.47
Tl ₂ O	-147.30 ¹	Tl ⁺	-32.40 ¹	-82.50
PbO (red)	-188.90 ²	Pb ²⁺	-24.20 ²	-164.70
BaO	-520.40 ²	Ba ²⁺	-563.80 ⁷	43.40
SrO	-560.70 ²	Sr ²⁺	-555.40 ⁷	-5.30
CaO	-603.10 ²	Ca ²⁺	-552.79 ⁷	-50.31
Fe ₂ O ₃	-744.40 ²	Fe ³⁺	-16.28 ⁷	-237.28
Al ₂ O ₃	-1582.30 ²	Al ³⁺	-487.62 ⁷	-202.36
Ga ₂ O ₃	-998.30 ¹	Ga ³⁺	-159.00 ¹	-226.77
V ₂ O ₃	-1138.87 ⁴	V ³⁺	-241.71 ⁴	-218.48
La ₂ O ₃	-1705.98 ⁵	La ³⁺	-683.70 ¹	-112.86
Ce ₂ O ₃	-1706.20 ¹	Ce ³⁺	-672.00 ¹	-120.73
Pr ₂ O ₃ (hex)	-1720.24 ⁵	Pr ³⁺	-679.10 ¹	-120.68
Nd ₂ O ₃ (hex)	-1721.05 ⁵	Nd ³⁺	-671.60 ¹	-125.95
Sm ₂ O ₃ (cub)	-1737.38 ⁵	Sm ³⁺	-666.60 ¹	-134.73
Eu ₂ O ₃ (cub)	-1566.36 ⁵	Eu ³⁺	-574.10 ¹	-139.39
Gd ₂ O ₃ (cub)	-1739.55 ⁵	Gd ³⁺	-661.00 ¹	-139.18
Bi ₂ O ₃	-493.70 ¹	Bi ³⁺	82.80 ¹	-219.77
P ₂ O ₅	-1348.85 ¹	P ⁵⁺		-325.72 ⁸
SO ₃	-374.21 ¹	PO ₄ ³⁻	-1018.70 ¹	
		S ⁶⁺		-385.58 ⁹
As ₂ O ₅	-782.30 ¹	SO ₄ ²⁻	-744.53 ¹	
		As ⁵⁺		-228.98 ¹⁰
		AsO ₄ ³⁻	-648.41 ¹	
CrO ₃	-504.50 ⁶	Cr ⁶⁺		-264.39 ¹⁰
		CrO ₄ ²⁻	-727.75 ¹	
H ₂ O liq.	-237.18 ²			

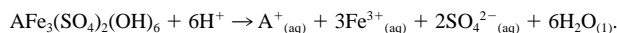
^a Numbers refer to literature, as follows: ¹ Wagman et al. (1982); ² Robie and Hemingway (1995); ³ Wilcox and Bromley (1963); ⁴ Naumov et al. (1971); ⁵ Barin (1985); ⁶ Ball and Nordstrom (1998); ⁷ Shock and Helgeson (1988); ⁸ Tardy and Vieillard (1977); ⁹ Tardy and Gartner (1977); ¹⁰ Gartner (1979).

Table 2. Values of solubility products and Gibbs free energy of formation of minerals (K⁺, Na⁺, NH₄⁺, Ag⁺, H₃O⁺, Pb²⁺, Sr²⁺) analog to jarosite.

Mineral	Log K ^a (298K)	Log K ^b (298 K)	$\Delta \text{G}_{\text{f}}^{\circ}$ (kJ · mol ⁻¹)
Jarosite	-29.51	-12.50	-3313.73
Natrojarosite	-25.57	-8.56	-3270.66
Ammoniojarosite	-26.77	-9.76	-3095.01
Argentojarosite	-28.55	-11.55	-2948.71
Hydroniumjarosite	-25.68	-8.67	-3246.59
Plumbojarosite	-28.43	-11.42	-3037.19
Strontiumjarosite	-27.46	-10.45	-3297.24

^a Mineral solubility product including Fe(OH)₂⁺ terms (Kashkai et al., 1975).

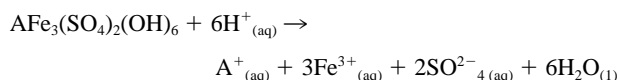
^b Mineral solubility product calculated according to the following reaction:



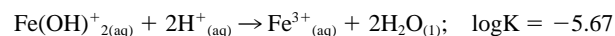
2.2. Inventory and Selection of $\Delta \text{G}_{\text{f}}^{\circ}$ of Minerals Belonging to the Alunite Supergroup

The $\Delta \text{G}_{\text{f}}^{\circ}$ of alunite-like minerals (alunite and natroalunite) recommended by Stoffregen et al. (2000) are used here. A detailed compilation of $\Delta \text{G}_{\text{f}}^{\circ}$ of jarosite has been performed by Baron and Palmer (1996a) and the recommended solubility product is $\log K = -11$ giving a $\Delta \text{G}_{\text{f}}^{\circ} = -3309.8$ kJ · mol⁻¹. This value is retained because of good concordance of $\Delta \text{G}_{\text{f}}^{\circ}$ of ions given by Baron and Palmer (1996a) and those given in Table 1. Baron and Palmer (1996b) measured the solubility product of a chromate analog to jarosite giving a $\Delta \text{G}_{\text{f}}^{\circ} = -3305.5$ kJ · mol⁻¹, this value is selected in this study.

Kashkai et al. (1975) provided solubility measurements of different cations bearing jarosites (K⁺, Na⁺, NH₄⁺, Ag⁺, H₃O⁺, Pb²⁺ and Sr²⁺) that are given in Table 2. The Gibbs free energies of formation of minerals analog to jarosite given by Kashkai et al. (1975) are not used here because of differences of Gibbs free energies of formation for ions from Kashkai et al. (1975) and those given in Table 1. Thus, the solubility products of the minerals analog to jarosite are calculated according to the following reaction:



using the following equation:



(Baes and Mesmer, 1976). From the calculated solubility products, the free energies of formation of different minerals analog to jarosite are computed using the Gibbs free energies of formation for the ions (Table 1) and are given in Table 2.

The $\Delta \text{G}_{\text{f}}^{\circ}$ values of minerals of the crandallite group were reported by Schwab et al. (1989) who determined the equilibrium constants for dissolution reactions at 298 K in aqueous solution after equilibration for at least 1 yr. These measurements were reconducted at 333 K for the determination of equilibrium constants of REE bearing florencite and minerals of the arseno-crandallite and arseno-florencite series (Schwab et al., 1993). Only $\Delta \text{G}_{\text{f}}^{\circ}$ of crandallite, goyazite, and plum-

Table 3. Values of solubility products and Gibbs free energy of formation of phosphates and arsenates minerals.^a

Mineral	ΔG°_f (kJ · mol ⁻¹)	LogK ^b	ΔG°_f (kJ · mol ⁻¹)	LogK ^c	LogK ^d	ΔG°_f calc. ^e (kJ · mol ⁻¹)
	T = 298K	T = 298K	T = 333K	T = 333K	T = 298K	T = 298K
Phosphates						
Crandallite	-5604.89 ¹	-23.57	-5608.65 ¹	-27.53	-23.57	-5610.69
Goyazite	-5625.39 ¹	-26.13	-5629.15 ¹	-29.71	-26.13	-5627.90
Plumbogummite	-5122.89 ¹	-31.83	-5153.43 ²	-38.79	-31.83	-5129.25
Gorceixite			-5632.50 ¹	-29.80	-25.40	-5632.11
			-5646.31 ²	-31.97	-27.24	-5642.65
Florencite Ce			-5737.52 ²	-27.56	-23.49	-5741.10
Florencite La			-5737.52 ²	-30.05	-25.61	-5742.53
Arsenates						
Arseno-crandallite			-4851.77 ²	-31.13	-26.53	-4887.01
Arseno-gorceixite			-4879.80 ²	-34.07	-29.03	-4912.29
Arseno-goyazite			-4871.01 ²	-33.12	-28.23	-4899.29
Phillipsbornite			-4333.79 ²	-32.55	-27.74	-4365.31
Arseno-florencite Ce			-4976.45 ²	-30.51	-26.00	-5014.88
Arseno-florencite La			-4985.65 ²	-34.45	-29.36	-5023.34

^a Numbers refer to literature, as follows: ¹ Schwab et al. (1989); ² Schwab et al. (1993).

^b Calculated from $\Delta G^\circ_{f,298}$ ions given in Schwab et al. (1993).

^c Calculated from $\Delta G^\circ_{f,333}$ ions given in Schwab et al. (1993).

^d Calculated from Log K at 333 K with a correction factor (0.852).

^e ΔG°_f calculated from Log Kcalc. at 298 K and ΔG°_f ions given in Table 1.

bogummite are given at 298 K, the ΔG°_f values for all other minerals are given at 333 K. The ΔG°_f at 298 K and 333 K for ions given by Schwab et al. (1993) allow the calculation of equilibrium constants for minerals of the crandallite-arseno-crandallite group (Table 3). It appears that the crandallite-like minerals are more stable at 333 K than at 298 K. Thus solubility products at 298 K of minerals of florencite, arseno-crandallite and arseno-florencite series are assumed to be equal to the product of dissociation constants at 333 K by a correction factor which is the average of the ratio $\log K(298 \text{ K})/\log K(333 \text{ K}) = 0.852$ for crandallite, goyazite and plumbogummite. From these calculated equilibrium constants, the ΔG°_f of minerals of the crandallite are calculated with ΔG°_f of ions from Table 1 and are given in Table 3.

All these selected values are gathered in Table 4. Their Gibbs free energies of formation from oxides were calculated from the ΔG°_f of oxides (Table 1).

2.3. Relationships between $\Delta G^\circ_{f,ox}$ and $\Delta_G O^\circ = M^{z+}(aq)$

By plotting calculated Gibbs free energies of formation from oxides, $\Delta G^\circ_{f,ox}$ vs. $\Delta_G O^\circ = M^{z+}(aq)$ of the cations located in the A site (Fig. 1), several relationships are observed for six different groups of minerals: the jarosite group for which seven different cations occupy the 12 fold coordination A site. In the alunite group, there are three different linear relations depending on the nature of the ions in the tetrahedral site: the alunite series (K and Na), the crandallite, and florencite series (six data), the arseno-crandallite and arseno-florencite series (six data) corresponding to divalent and trivalent cations of the A site. The REE bearing florencite and arseno-florencite significantly depart from the linear relationships with divalent ions. This is due to the absence of H in the charge compensation between the florencite and crandallite series on the one hand, and between the arseno-florencite and the arseno-crandallite series on the other hand. It appears that within a same family, the greater the parameter $\Delta_G O^\circ = M^{z+}(aq)$ (more electroposi-

tive), the lower the Gibbs free energy of formation from oxides. The electronegativity scale for these cations is $K^+ > Na^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > NH_4^+ > La^{3+} > Ce^{3+} > Pb^{2+}$, where K^+ is the most electropositive. This relationships is also true for compounds having the same cations in 12 fold coordination and fourfold sites (alunite and jarosite series); thus, $\Delta_G O^\circ = Al^{3+}(aq)$ appears to be more electropositive than $\Delta_G O^\circ = Fe^{3+}(aq)$.

There is a strong analogy with previous works on phosphates (Tardy and Vieillard, 1977; Vieillard, 1978), sulfates (Tardy and Gartner, 1977; Gartner, 1979), and arsenates (Gartner, 1979). By considering phosphates, sulfates, and arsenates as double oxide compounds, $(M_i)_{n_i}(M_j)_{n_j}O_N$, these previous authors showed an empirical relationships between $\Delta G^\circ_{f,ox}$ and $\Delta_G O^\circ = M^{z+}(aq)$ by the following equation:

$$\Delta G^\circ_{f,ox}(M_i)_{n_i}(M_j)_{n_j}O_N = -\alpha N(X_i X_j)[\Delta_G O^\circ = M_i^{z_i+}(aq) - \Delta_G O^\circ = M_j^{z_j+}(aq)] \quad (3)$$

where

—N is the total number of oxygen atoms in the compound and is equal to the sum of the number of oxygens n_i and n_j , respectively related to the cations M_i and M_j in each oxide $(M_i O_{x_i}$ and $M_j O_{x_j})$ i.e.:

$$N = n_i x_i + n_j x_j \quad (4)$$

— X_i and X_j are the molar fractions of oxygen atoms respectively related to cations $M_i^{z_i+}$ and $M_j^{z_j+}$ in the individual oxides $M_i O_{x_i}$ and $M_j O_{x_j}$;

— $\Delta_G O^\circ = M_i^{z_i+}(aq)$ and $\Delta_G O^\circ = M_j^{z_j+}(aq)$ are, respectively, the $\Delta_G O^\circ$ parameters as calculated for cations $M_i^{z_i+}$ and $M_j^{z_j+}$ in the aqueous states according to Eqn. (1).

— α is an empirical coefficient characterizing a given family of compounds.

Thus, for families such as sulfates, phosphates and arsenates, $\Delta_G O^\circ = M_j^{z_j+}(aq)$ and α are respectively evaluated to $\Delta_G O^\circ =$

Table 4. Chemical composition and selected, calculated and predicted Gibbs free energies of formation at 298 K of some minerals of the alunite supergroup.^a

Mineral	Formula	ΔG_f° select. (kJ · mol ⁻¹)	$\Delta G_{f,ox}^\circ$ calc. (kJ · mol ⁻¹)	ΔG_f° pred. (kJ · mol ⁻¹)	Residuals (kJ · mol ⁻¹)	% Residual
Alunite group						
Alunite ¹	K Al ₃ (SO ₄) ₂ (OH) ₆	-4659.30	-664.84	-4659.32	0.02	0.00
Natroalunite ¹	Na Al ₃ (SO ₄) ₂ (OH) ₆	-4622.40	-600.99	-4622.17	-0.23	0.00
Plumbogummite group						
Crandallite ²	Ca Al ₃ (PO ₄) ₂ (OH) ₅ H ₂ O	-5610.69	-455.16	-5612.55	1.86	0.03
Gorceixite ²	Ba Al ₃ (PO ₄) ₂ (OH) ₅ H ₂	-5642.65	-569.82	-5642.18	-0.47	0.00
Goyazite ²	Sr Al ₃ (PO ₄) ₂ (OH) ₅ H ₂ O	-5627.90	-514.77	-5627.84	-0.06	0.00
Plumbogummite ²	Pb Al ₃ (PO ₄) ₂ (OH) ₅ H ₂ O	-5129.25	-387.92	-5118.69	-10.56	0.21
Philipsbornite ³	Pb Al ₃ (AsO ₄) ₂ (OH) ₅ H ₂ O	-4365.31	-190.53	-4390.30	24.99	0.57
Arseno-crandallite ³	Ca Al ₃ (AsO ₄) ₂ (OH) ₅ H ₂ O	-4887.01	-298.03	-4884.16	-2.85	0.06
Arseno-gorceixite ³	Ba Al ₃ (AsO ₄) ₂ (OH) ₅ H ₂ O	-4912.29	-406.01	-4913.79	1.50	0.03
Arseno-goyazite ³	Sr Al ₃ (AsO ₄) ₂ (OH) ₅ H ₂ O	-4899.29	-352.71	-4899.45	0.16	0.00
Florencite group						
Florencite La ³	La Al ₃ (PO ₄) ₂ (OH) ₆	-5742.53	-455.70	-5749.94	7.41	0.13
Florencite Ce ³	Ce Al ₃ (PO ₄) ₂ (OH) ₆	-5741.10	-454.16	-5741.68	0.58	0.01
Arseno-florencite La ³	La Al ₃ (AsO ₄) ₂ (OH) ₆	-5023.34	-303.06	-5021.56	-1.78	0.03
Arseno-florencite Ce ³	Ce Al ₃ (AsO ₄) ₂ (OH) ₆	-5014.88	-294.49	-5013.29	-1.59	0.03
Jarosite group						
Jarosite ⁴	K Fe ₃ (SO ₄) ₂ (OH) ₆	-3309.80	-572.19	-3307.94	-1.86	0.06
Natrojarosite ⁵	Na Fe ₃ (SO ₄) ₂ (OH) ₆	-3270.66	-506.10	-3270.79	0.13	0.00
Ammoniojarosite ⁵	NH ₄ Fe ₃ (SO ₄) ₂ (OH) ₆	-3095.01	-401.30	-3095.01	0.00	0.00
Argentojarosite ⁵	Ag Fe ₃ (SO ₄) ₂ (OH) ₆	-2948.71	-377.75	-2948.71	0.00	0.00
Plumbojarosite ⁵	Pb _{0.5} Fe ₃ (SO ₄) ₂ (OH) ₆	-3037.19	-366.18	-3037.17	-0.02	0.00
Strontiumjarosite ⁵	Sr _{0.5} Fe ₃ (SO ₄) ₂ (OH) ₆	-3297.24	-440.33	-3297.24	0.00	0.00
Hydroniumjarosite ⁵	(H ₃ O) Fe ₃ (SO ₄) ₂ (OH) ₆	-3246.59	-314.26	-3246.59	0.00	0.00
Chromate analog jarosite ⁶	K Fe ₃ (CrO ₄) ₂ (OH) ₆	-3305.50	-307.31	-3305.50	0.00	0.00
						Average = 0.06

^a Numbers refer to literature, as follows: ¹ Stoffregen et al. (2000); ² Schwab et al. (1989); ³ Schwab et al. (1993); ⁴ Baron and Palmer (1996a); ⁵ Kashkai et al. (1975); ⁶ Baron and Palmer (1996b).

$S^{6+}(aq) = -385.68 \text{ kJ} \cdot \text{mol}^{-1}$ and $\alpha_{\text{sulfate}} = 1.332$ (Tardy and Gartner, 1977; Gartner, 1979); $\Delta_G O = P^{5+}(aq) = 325.72 \text{ kJ} \cdot \text{mol}^{-1}$ and $\alpha_{\text{phosphate}} = 1.37$ (Tardy and Vieillard, 1977; Vieillard, 1978); $\Delta_G O = As^{5+}(aq) = -228.984 \text{ kJ} \cdot \text{mol}^{-1}$ and

$\alpha_{\text{arsenate}} = 1.474$ (Gartner, 1979). The Gibbs free energy of formation of minerals, derived from their constituent oxides, appears to be proportional to three parameters: (1) coefficient α , which relates to the nature of the family, (2) the stoichio-

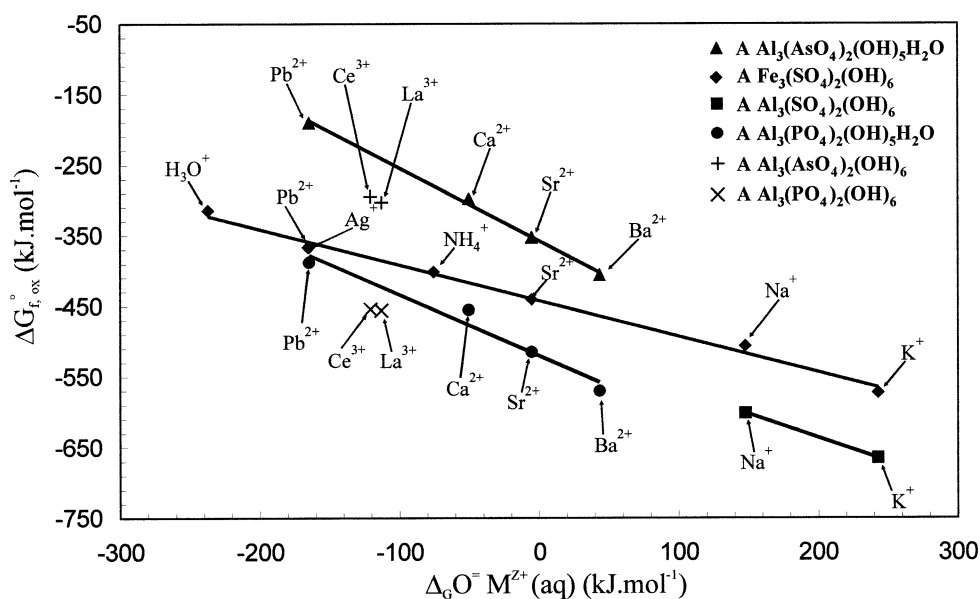


Fig. 1. Relationship between $\Delta G_{f,ox}^\circ$ vs. $\Delta_G O = M^{z+}(aq)$ for minerals from different groups of the alunite supergroup.

metric coefficient $N(X_i X_j)$, and (3) the difference $[\Delta_G O^\ominus M_i^{z_i+}(\text{aq}) - \Delta_G O^\ominus M_j^{z_j+}(\text{aq})]$. When two cations have the same oxygen affinity, the Gibbs free energy of formation of a compound from the two oxides must be equal or close to zero. The lowest Gibbs free energies of formation from oxides are obtained for electropositive cations, which show a $\Delta_G O^\ominus M_i^{z_i+}(\text{aq})$ value very different from $\Delta_G O^\ominus M_j^{z_j+}(\text{aq})$. Compared to their constituent oxides, the corresponding compounds are the most stable.

In minerals of the alunite supergroup, cations are uniformly surrounded by oxygens, whereas oxygens have several different cations as nearest neighbors. In developing empirical models of thermodynamic predictions, it is logical to concentrate on those aspects of bonds between oxygens and different cations and protons to explain these different linear relationships in Figure 1.

To generalize the technique and to increase its accuracy, a new set of parameters $\Delta_G O^\ominus M^{z+}(c)$ of different cations in the three different sites A (12 fold coordination), B octahedral, and T tetrahedral is proposed and can be obtained from the knowledge of the crystal structure. The concept of the parameter $\Delta_G O^\ominus M^{z+}(c)$ has been initially proposed to predict enthalpies of formation of different compounds (Vieillard, 1982; Vieillard and Tardy, 1988a). It has been tested on numerous silicates (Vieillard, 1994a,b). Vieillard (2000) proposed a method to predict Gibbs free energies of formation of hydrated clay minerals based on a new electronegativity scale for different ions located in interlayer, octahedral and tetrahedral sites. This method has been successfully applied to micas and chlorites (Vieillard, 2002).

2.4. Relationships between $\Delta G^\circ_{f,\text{ox}}$ and $\Delta G O^\ominus M^{z+}(c)$

The Gibbs free energy of formation from the oxides, $\Delta G^\circ_{f,\text{ox}}$ defined in Eqn. 2, is calculated by the following equation, which is analogous to that for the enthalpy of formation (Vieillard, 1994a):

$$\Delta G^\circ_{f,\text{ox}} = -14 \left[\sum_{i=1}^{i=n_b-1} \sum_{j=i+1}^{j=n_b} X_i X_j (\Delta_G O^\ominus M_i^{z_i+}(c) - \Delta_G O^\ominus M_j^{z_j+}(c)) \right] \quad (5)$$

where X_i and X_j are the molar fractions of oxygen bound to the cations $M_i^{z_i+}$ and $M_j^{z_j+}$ in the individual oxides $M_i O_{x_i}$ and $M_j O_{x_j}$, respectively, in the mineral formula:

$$X_i = (1/14)(n_i x_i) \quad (6)$$

$$X_j = (1/14)(n_j x_j) \quad (7)$$

The total number of oxygen atoms of the compound must be equal to 14:

$$\sum_{i=1}^{i=n_b} n_i x_i = 14 \quad (8)$$

The parameters $\Delta_G O^\ominus M_i^{z_i+}(c)$ and $\Delta_G O^\ominus M_j^{z_j+}(c)$ characterize the electronegativity of cations $M_i^{z_i+}$ and $M_j^{z_j+}$, respectively, in a specific site. These terms depend on structural parameters such as shortest bond length, average bond length,

and polarizability (Vieillard, 1982, 1994a) and they are assumed to be constant here.

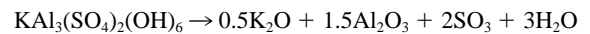
In Eqn. 5, the interaction energy between two cations $M_i^{z_i+}$ and $M_j^{z_j+}$ is defined by the difference $\Delta_G O^\ominus M_i^{z_i+}(c) - \Delta_G O^\ominus M_j^{z_j+}(c)$. This term characterizes short-range and long-range interactions between the different sites. Vieillard and Tardy (1988b, 1989) showed that the difference between the two $\Delta_G O^\ominus$ parameters is positive and can be assumed to be equal:

$$[\Delta_G O^\ominus M_i^{z_i+}(c) - \Delta_G O^\ominus M_j^{z_j+}(c)] = 96.483(\chi_{M_i} - \chi_{M_j})^2 \quad (9)$$

in which χ_M designates the Pauling's electronegativity of the cation M^{z+} (Pauling, 1960) in the considered crystal structure. When two cations sharing the same oxygen are identical, i.e., the same oxygen affinity, the interaction energy is equal to zero. The greater the difference of oxygen affinity between two cations is, the stronger is the interaction energy.

The development of Eqn. 5 can be illustrated by a short description of the crystal structure of minerals belonging to the alunite supergroup. The crystal structures of alunite, jarosite and plumbojarosite were first determined by Hendricks (1937). The crystal structures of numerous minerals in this supergroup have been determined and condensed by Jambor (1999). Most of these studies showed that the minerals have trigonal symmetry, space group $R\bar{3}m$. Even among the exceptions where a monoclinic or triclinic system was established, the basic topology of the structure remains strongly pseudotrigonal regardless of the chemical composition (Jambor, 1999). The basic structure is built from sheets of distorted B octahedra. Each of these octahedra shares four corners (labeled O_3 or OH) with other octahedra (Fig. 2). Thus, large hexagonal and small trigonal rings perpendicular to the c-axis are formed. Each tetrahedron shares three corners (labeled O_2) with three B octahedra of a trigonal ring. The remaining unshared oxygens (labeled O_1) point towards one another through a hexagonal hole built by an overlying sheet and in case of divalent cation in A site, they are linked by a hydrogen bond which disappears if the divalent cation is substituted by a trivalent cation.

Taking the example of $KAl_3(SO_4)_2(OH)_6$, four types of sites can be defined as follows: K in the 1twofold coordinated A site, Al in the octahedral B site, S in the tetrahedral T site and a hydrogen in the hydroxyl site (O_3 or OH). If we consider this compound as a sum of oxides:



with the molar fraction of oxygen bound to the following oxides K_2O , Al_2O_3 , SO_3 and H_2O being respectively, 0.5/14, 4.5/14, 6/14, and 3/14. The equation for $\Delta G^\circ_{f,\text{ox}}$ is given in Table 5.

The equation for the Gibbs free energies of formation from constituent oxides of alunite contains five interaction terms between any two different cations located within and between consecutive different sites: K^+ and Al^{3+} (oxygens O_3 and O_2), K^+ and S^{6+} (oxygens O_2), K^+ and $H^+_{O_3}$ (oxygens O_3), Al^{3+} and S^{6+} (oxygens O_2), and Al^{3+} and $H^+_{O_3}$ (oxygens O_2). The missing interaction term $H^+_{O_3}$ and S^{6+} is justified because there is no common oxygen between these two sites. The principles of Pauling (1960) regarding the predominance of nearest-neighbor interactions (short-range interactions) ob-

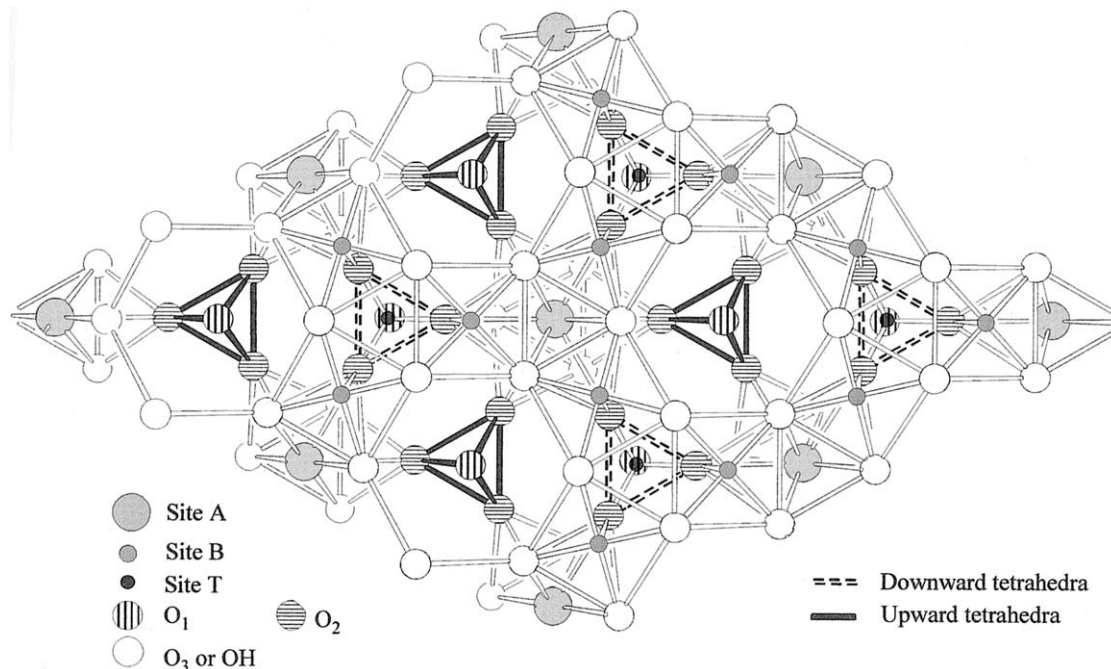


Fig. 2. Crystal structure of the minerals belonging to the alunite supergroup viewed perpendicular to the *c*-axis.

served in a crystal structure were applied here and had been successfully applied in silicates (Vieillard 1994a,b), hydrated clay minerals (Vieillard, 2000), and phyllosilicates (Vieillard, 2002). Thus, the presence of a nonbridging oxygen between any two adjacent sites in any mineral implies that long-range interaction energy terms between two sites are not required, and consequently:

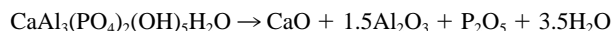
$$[\Delta_{\text{G}}\text{O}=\text{M}_i^{z_1+}(\text{c}) - \Delta_{\text{G}}\text{O}=\text{M}_j^{z_2+}(\text{c})] = 0 \quad (10)$$

In this case,

$$[\Delta_{\text{G}}\text{O}=\text{H}_{\text{O}_3}^+(\text{c}) - \Delta_{\text{G}}\text{O}=\text{S}_\text{T}^{6+}(\text{c})] = 0 \quad (11)$$

In crandallite, whose chemical formula can be expressed as $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_6\text{H}$ or $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5\text{H}_2\text{O}$ or $\text{CaAl}_3[\text{PO}_3(\text{O}_{1/2}(\text{OH})_{1/2})_2(\text{OH})_6]$ in which Blount (1974) considered the hydroxyl $\text{H}^+_{\text{O}_1}$ bound to the tetrahedra, five sites are defined as follows: Ca in Itwofold coordinated A site, Al in octahedral B site, P in tetrahedral T site, a hydrogen $\text{H}^+_{\text{O}_3}$ of the hydroxyl site, and another hydrogen $\text{H}^+_{\text{O}_1}$ bound to the

oxygen of the tetrahedra. If we consider this compound as a sum of oxides:



with the molar fraction of oxygen bound to the following oxides CaO , Al_2O_3 , P_2O_5 , $\text{H}_2\text{O}_{(\text{O}_3)}$ and $\text{H}_2\text{O}_{(\text{O}_1)}$ being respectively, 1/14, 4.5/14, 5/14, 3/14 and 0.5/14. The calculated equation of $\Delta G^\circ_{\text{f,ox}}$ is given in Table 6.

The equation for the Gibbs free energies of formation from constituent oxides of crandallite contains six interaction terms between any two different sites. The four missing interaction terms between $\text{H}^+_{\text{O}_3}$ and P^{5+} , $\text{H}^+_{\text{O}_3}$ and $\text{H}^+_{\text{O}_1}$, Al^{3+} and $\text{H}^+_{\text{O}_1}$, Ca^{+2} and $\text{H}^+_{\text{O}_1}$ do not appear in the general equation of Gibbs free energies of formation from constituent oxides because they are considered as long-range interactions energies due to the absence of common oxygens between each of these two sites. For crandallite, the following four interaction terms are given by:

Table 5. General equation of Gibbs free energy of formation from the oxides of alunite $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$.

$$\Delta G^\circ_{\text{f,ox}} = -14 \left\{ \begin{aligned} & \frac{0.5}{14} \times \frac{4.5}{14} [\Delta_{\text{G}}\text{O}=\text{K}^+(\text{c}) - \Delta_{\text{G}}\text{O}=\text{Al}^{3+}(\text{c})] + \frac{0.5}{14} \times \frac{6}{14} [\Delta_{\text{G}}\text{O}=\text{K}^+(\text{c}) - \Delta_{\text{G}}\text{O}=\text{S}^{6+}(\text{c})] \\ & + \frac{0.5}{14} \times \frac{3}{14} [\Delta_{\text{G}}\text{O}=\text{K}^+(\text{c}) - \Delta_{\text{G}}\text{O}=\text{H}_{\text{O}_3}^+(\text{c})] + \frac{4.5}{14} \times \frac{6}{14} [\Delta_{\text{G}}\text{O}=\text{Al}^{3+}(\text{c}) - \Delta_{\text{G}}\text{O}=\text{S}^{6+}(\text{c})] \\ & + \frac{4.5}{14} \times \frac{3}{14} [\Delta_{\text{G}}\text{O}=\text{Al}^{3+}(\text{c}) - \Delta_{\text{G}}\text{O}=\text{H}_{\text{O}_3}^+(\text{c})] \end{aligned} \right\}$$

Table 6. General equation of Gibbs free energy of formation from the oxides of crandallite $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5\text{H}_2\text{O}$.

$$\Delta G^\circ_{f,\text{ox}} = -14 \left\{ \begin{array}{l} \frac{1}{14} \times \frac{4.5}{14} [\Delta_{\text{G}}\text{O}^{\ominus}\text{Ca}^{2+}(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{Al}^{3+}(\text{c})] + \frac{1}{14} \times \frac{5}{14} [\Delta_{\text{G}}\text{O}^{\ominus}\text{Ca}^{2+}(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{P}^{5+}(\text{c})] \\ + \frac{1}{14} \times \frac{3}{14} [\Delta_{\text{G}}\text{O}^{\ominus}\text{Ca}^{2+}(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{H}_{\text{O}_3}^+(\text{c})] + \frac{4.5}{14} \times \frac{5}{14} [\Delta_{\text{G}}\text{O}^{\ominus}\text{Al}^{3+}(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{P}^{5+}(\text{c})] \\ + \frac{4.5}{14} \times \frac{3}{14} [\Delta_{\text{G}}\text{O}^{\ominus}\text{Al}^{3+}(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{H}_{\text{O}_3}^+(\text{c})] + \frac{5}{14} \times \frac{0.5}{14} [\Delta_{\text{G}}\text{O}^{\ominus}\text{P}^{5+}(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{H}_{\text{O}_1}^+(\text{c})] \end{array} \right\}$$

$$\begin{aligned} & [\Delta_{\text{G}}\text{O}^{\ominus}\text{H}_{\text{O}_3}^+(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{P}_{\text{T}}^{5+}(\text{c})] \\ &= [\Delta_{\text{G}}\text{O}^{\ominus}\text{H}_{\text{O}_3}^+(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{H}_{\text{O}_1}^+(\text{c})] \\ &= [\Delta_{\text{G}}\text{O}^{\ominus}\text{Al}^{3+}(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{H}_{\text{O}_1}^+(\text{c})] \\ &= [\Delta_{\text{G}}\text{O}^{\ominus}\text{Ca}^{2+}(\text{c}) - \Delta_{\text{G}}\text{O}^{\ominus}\text{H}_{\text{O}_1}^+(\text{c})] = 0 \end{aligned} \quad (12)$$

3. RESULTS

We considered the following cations Ag^+ , NH_4^+ , Na^+ , K^+ , Pb^{2+} , Ba^{2+} , Ca^{2+} , Sr^{2+} , La^{3+} , Ce^{3+} in the 12-fold coordination, Al^{3+} and Fe^{3+} in octahedral sites, S^{6+} , P^{5+} , As^{5+} and Cr^{6+} in tetrahedral sites. By assuming that $\Delta G^\circ_f \text{H}^+(\text{c}) = 0$, the parameters $\Delta_{\text{G}}\text{O}^{\ominus} \text{H}^+_{\text{O}_3}$, $\Delta_{\text{G}}\text{O}^{\ominus} \text{H}^+_{\text{O}_1}$ and $\Delta_{\text{G}}\text{O}^{\ominus} \text{H}_3\text{O}^+$ are all together equal to $-237.18 \text{ kJ} \cdot \text{mol}^{-1}$, which represents the reference value for the setting of an electronegativity scale for different cations located in different sites of a alunite mineral. Using a short-range approach, the parameters $\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{c})$ of 16 cations characterizing the electronegativity of ions located in different sites were determined by minimizing the difference between calculated Gibbs free energies of formation from oxides and those computed by Eqns. 5 and 9.

These values obtained by minimization are given in Table 7 and contribute to the determination of Gibbs free energy of formation from constituent oxides. Consequently, the determined Gibbs free energies of formation of the alunite minerals may be compared with experimental (or calculated) values (Table 4). The average difference between the predicted and the measured values is 0.1% with a maximum value (0.57%) for philipsbornite. This mineral has an abnormal ΔG°_f that has already been pointed out by Schwab et al. (1993) which are unable to explain the strange behavior of lead in comparison with the solubility products of Ba, Sr, Ca and Pb bearing crandallite and arseno-crandallite series (Table 3).

4. DISCUSSION

4.1. Accuracy of the Model

Values $\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{c})$, obtained from minimization (Table 7) are different from $\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{aq})$ given in Table 1. Among the values for $\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{c})$ corresponding to different sites in the mineral of the alunite supergroup, three sets of values are observed, corresponding to the interlayer, octahedral, and tetrahedral sites (Fig. 3).

12-fold coordination site (11 data)

$$\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{c}) = 26.848 + 1.051[\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{aq})] \quad (13)$$

with a regression coefficient $r = 0.9919$ and a standard deviation $\sigma = 13.65 \text{ kJ} \cdot \text{mol}^{-1}$

Octahedral sites (2 data)

$$\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{c}) = -1.9888 + 0.9913[\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{aq})] \quad (14)$$

Tetrahedral sites (4 data)

$$\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{c}) = -46.447 + 0.8698[\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{aq})] \quad (15)$$

with a regression coefficient $r = 0.9674$ and a standard deviation $\sigma = 11.02 \text{ kJ} \cdot \text{mol}^{-1}$.

The accuracy of the model was tested by predicting the thermodynamic properties of minerals not used to develop the model. Experimental measurements of equilibrium constants of Pr^{3+} , Nd^{3+} , Gd^{3+} , Sm^{3+} and Eu^{3+} bearing florencite and arseno-florencite are available only at 333 K (Schwab et al., 1993). By using the same correction factor ($\log K(298 \text{ K}) / \log K(333 \text{ K}) = 0.852$) as for crandallite minerals, solubility

 Table 7. Values of parameter $\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{c})$ obtained by minimization.

Ions	$\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{c})$ ($\text{kJ} \cdot \text{mol}^{-1}$)	Ions	$\Delta_{\text{G}}\text{O}^{\ominus} \text{M}^{z+}(\text{c})$ ($\text{kJ} \cdot \text{mol}^{-1}$)
12 fold coordination A site		12 fold coordination A site	
Ag^+	-128.71 ^a	Ca^{2+}	-40.29 ^a
Ti^+	-59.89 ^b	Bi^{-3+}	-204.22 ^b
Na^+	-161.00 ^a	La^{3+}	-97.22 ^a
K^+	293.94 ^a	Ce^{3+}	-103.47 ^a
NH_4^+	-56.63 ^a	Pr^{3+}	-100.03 ^b
H_3O^+	-237.18 ^a	Nd^{3+}	-105.58 ^b
Pb^{2+}	-129.51 ^a	Sm^{3+}	-114.81 ^b
Ba^{2+}	85.81 ^a	Eu^{3+}	-119.71 ^b
Sr^{2+}	24.32 ^a	Gd^{3+}	-119.49 ^b
Tetrahedral T site		Octahedral B site	
P^{5+}	-332.10 ^a	Fe^{3+}	-237.20 ^a
S^{6+}	-383.84 ^a	Al^{3+}	-202.59 ^a
As^{5+}	-256.57 ^a	V^{3+}	-218.57 ^c
Cr^{6+}	-261.10 ^a	Ga^{3+}	-226.79 ^c

^a Obtained by minimization.

^b A site value calculated from Eqn. 12.

^c B site values calculated from Eqn. 13.

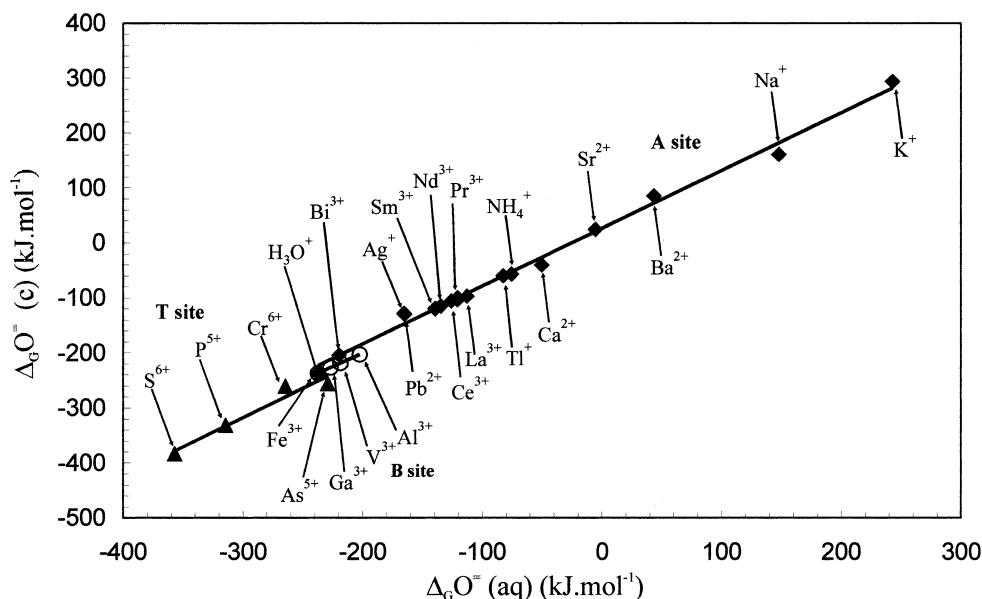


Fig. 3. Relationship between $\Delta_{\text{G}}^{\circ} \text{M}^{z+}(\text{c})$ and $\Delta_{\text{G}}^{\circ} \text{M}^{z+}(\text{aq})$ for cations from different sites in the alunite supergroup.

products are predicted at 298 K and Gibbs free energies of formation for Pr^{3+} , Nd^{3+} , Gd^{3+} , Sm^{3+} and Eu^{3+} bearing florencite and arseno-florencite are calculated with $\Delta G_{\text{f}}^{\circ}$ for ions (Table 1). The evaluations of $\Delta_{\text{G}}^{\circ} \text{M}^{z+}(\text{c})$ for rare earth ions (Pr^{3+} , Nd^{3+} , Gd^{3+} , Sm^{3+} and Eu^{3+}) given in Table 7 contribute to the prediction of Gibbs free energies of formation of some REE bearing florencite and arseno-florencite. Table 8 compares the results of the model with experimental data for 11 different minerals and gives associated differences. Average residuals for these minerals are 0.25% for 11 data.

4.2. Prediction of Gibbs Free Energies of Uncommon Minerals of the Alunite Supergroup

Eqns. 13, 14, and 15 are useful relationships to predict the affinity of oxygen, $\Delta_{\text{G}}^{\circ} \text{M}^{z+}(\text{c})$ of cations such as Ti^{+} and Bi^{3+} located in the A sites, V^{3+} and Ga^{3+} located in octahedral

sites. Table 9 introduces the predicted Gibbs free energies of different minerals in their ideal formula of the alunite supergroup for which thermodynamic data are unknown.

Two minerals hindsalite and hydronium jarosite were chosen to describe the protocol for estimating their Gibbs free energy of formation, using the model described above. Hindsalite, $[\text{PbAl}_3(\text{PO}_4, \text{SO}_4)(\text{OH})_6]$ has two different ions P^{5+} and S^{6+} in tetrahedral site. The detail of the expression of the Gibbs free energy of formation from constituent oxides is given in Table 10. $\Delta G_{\text{f,ox}}^{\circ}$ contains 7 interaction terms corresponding to the difference between oxygen affinity of different ions around a common oxygen. The calculated Gibbs free energy of formation from oxides is $-449.44 \text{ kJ} \cdot \text{mol}^{-1}$. The predicted Gibbs free energy of formation from elements is $-4774.9 \pm 11.9 \text{ kJ} \cdot \text{mol}^{-1}$. Our predicted value is not in good agreement with the value $\Delta G_{\text{f}}^{\circ} = -4672.69 \text{ kJ} \cdot \text{mol}^{-1}$ reported by Baker (1964).

Table 8. Selected and predicted Gibbs free energies of formation of some minerals of the alunite supergroup.^a

Mineral	Formula	$\Delta G_{\text{f}}^{\circ}$ select. ($\text{kJ} \cdot \text{mol}^{-1}$)	$\Delta G_{\text{f}}^{\circ}$ pred. ($\text{kJ} \cdot \text{mol}^{-1}$)	Residuals ($\text{kJ} \cdot \text{mol}^{-1}$)	% Residual
Arseno-florencite Pr	$\text{PrAl}_3(\text{AsO}_4)_2(\text{OH})_6$	-5010.92^1	-5024.91	-13.99	0.28
Arseno-florencite Nd	$\text{NdAl}_3(\text{AsO}_4)_2(\text{OH})_6$	-5009.17^1	-5017.88	-8.71	0.18
Arseno-florencite Sm	$\text{SmAl}_3(\text{AsO}_4)_2(\text{OH})_6$	-4994.91^1	-5013.69	-18.78	0.38
Arseno-florencite Eu	$\text{EuAl}_3(\text{AsO}_4)_2(\text{OH})_6$	-4907.52	-4921.61	-14.09	0.29
Florencite Pr	$\text{PrAl}_3(\text{PO}_4)_2(\text{OH})_6$	-5740.01^1	-5753.31	-13.30	0.23
Florencite Nd	$\text{NdAl}_3(\text{PO}_4)_2(\text{OH})_6$	-5744.96^1	-5734.86	10.10	0.18
Florencite Sm	$\text{SmAl}_3(\text{PO}_4)_2(\text{OH})_6$	-5748.90^1	-5742.09	6.81	0.12
Florencite Eu	$\text{EuAl}_3(\text{PO}_4)_2(\text{OH})_6$	-5633.73^1	-5650.01	-16.28	0.29
Florencite Gd	$\text{GdAl}_3(\text{PO}_4)_2(\text{OH})_6$	-5715.84^1	-5736.90	-21.06	0.37
Hydronium jarosite	$\text{K}_{0.77}\text{Na}_{0.03}(\text{H}_3\text{O})_{0.20}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$	-3293.50^2	-3289.90	3.60	0.11
Corkite	$\text{PbFe}_3(\text{PO}_4, \text{SO}_4)(\text{OH})_6$	-3421.13^3	-3431.72	-10.59	0.31
					Average = 0.25

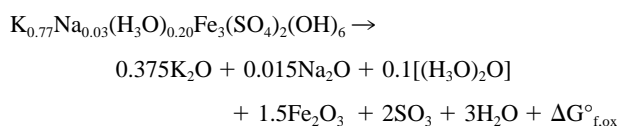
^a Numbers refer to literature, as follows: ¹ Schwab et al. (1993); ² Alpers et al. (1989); ³ Nriagu (1974).

Table 9. Predicted Gibbs free energies of formation of some minerals of the alunite supergroup.

Mineral	Formula	ΔG°_f pred. (kJ · mol ⁻¹)
Hindsalite	PbAl ₃ (PO ₄ ,SO ₄)(OH) ₆	-4771.9
Svanbergite	SrAl ₃ (PO ₄ ,SO ₄)(OH) ₆	-5286.6
Beudantite	PbFe ₃ (AsO ₄) ₂ (OH) ₅ H ₂ O	-3055.6
Hidalgoite	PbAl ₃ (AsO ₄ ,SO ₄)(OH) ₆	-4414.5
Woodhouseite	CaAl ₃ (PO ₄ ,SO ₄)(OH) ₆	-5269.0
Gallobaudantite	PbGa ₃ (AsO ₄ ,SO ₄)(OH) ₆	-5853.6
Waylandite	BiAl ₃ (PO ₄) ₂ (OH) ₆	-5002.0
Arseno-waylandite	BiAl ₃ (AsO ₄) ₂ (OH) ₆	-4273.6
Springcreekite	BaV ₃ (PO ₄) ₂ (OH) ₅ H ₂ O	-4941.3
Zairite	BiFe ₃ (PO ₄) ₂ (OH) ₆	-3671.3
Dorallcharite	TlFe ₃ (SO ₄) ₂ (OH) ₆	-3049.9
Waltherite	Ba _{0.5} Al ₃ (SO ₄) ₂ (OH) ₆	-4658.1
Huangite	Ca _{0.5} Al ₃ (SO ₄) ₂ (OH) ₆	-4638.6
Kintoreite	PbFe ₃ (PO ₄) ₂ (OH) ₅ H ₂ O	-3784.0
Benauite	SrFe ₃ (PO ₄) ₂ (OH) ₅ H ₂ O	-4293.1
Dusserite	BaFe ₃ (AsO ₄) ₂ (OH) ₅ H ₂ O	-3579.3
Segnitite	PbFe ₃ (AsO ₄) ₂ (OH) ₅ H ₂ O	-3576.0

This disparity can be explained by the fact that Baker (1964) did not consider the formation of ion-pairs in his calculation. This precision of calculation, can be improved by considering the formation of ion-pairs in the measurement of solubility data of pyromorphite, Pb₅(PO₄)₃Cl (Nriagu, 1973), which lead to a more negative value than this of Baker (1964). Other data for hindsalite from Nriagu (1974) are $\Delta G^\circ_f = -4759.0$ kJ · mol⁻¹, but the origin and nature of this measurement are unknown.

A solid solution of composition K_{0.77}Na_{0.03}(H₃O)_{0.20}Fe₃(SO₄)₂(OH)₆ was analyzed by Alpers et al. (1989). This mineral exhibits three different ions K⁺, Na⁺ and H₃O⁺ in the alkali site (site A). The Gibbs free energy of formation from constituent oxides contains 11 effective interaction terms and is developed in Table 11. The calculated Gibbs free energy of formation from constituent oxides is -512.50 kJ · mol⁻¹. By considering the following reaction:


 Table 10. Detailed computation of $\Delta G^\circ_{f,\text{ox}}$ of hindsalite.

Nature of interactions terms ^a	-14 X _i X _j	$[\Delta_G\text{O}^\ominus\text{M}_i^{\text{Z}^+}(\text{c}) - \Delta_G\text{O}^\ominus\text{M}_j^{\text{Z}^+}(\text{c})]$ (kJ · mol ⁻¹)	Interaction energy ^b (kJ · mol ⁻¹)
Pb _(A) ²⁺ - Al _(B) ³⁺	-0.321	73.08	-23.49
Pb _(A) ²⁺ - P _(T) ⁵⁺	-0.179	202.59	-36.18
Pb _(A) ²⁺ - S _(T) ⁶⁺	-0.214	254.33	-54.50
Pb _(A) ²⁺ - H _(O3) ⁺	-0.214	107.67	-23.07
Al _(B) ³⁺ - P _(T) ⁵⁺	-0.804	129.51	-104.07
Al _(B) ³⁺ - S _(T) ⁶⁺	-0.964	181.25	-174.78
Al _(B) ³⁺ - H _(O3) ⁺	-0.964	34.59	-33.35
		$\Delta G^\circ_{f,\text{ox}}$ (kJ · mol ⁻¹) =	-449.44

^a A, B, T denote 12-fold coordination, octahedral and tetrahedral sites, respectively.

^b Product of the two first columns, i.e., equal to -14X_iX_j[$\Delta_G\text{O}^\ominus\text{M}_i^{\text{Z}^+}(\text{c}) - \Delta_G\text{O}^\ominus\text{M}_j^{\text{Z}^+}(\text{c})$].

 Table 11. Detailed computation of $\Delta G^\circ_{f,\text{ox}}$ of hydronium jarosite.

Nature of interactions terms ^a	-14 X _i X _j	$[\Delta_G\text{O}^\ominus\text{M}_i^{\text{Z}^+}(\text{c}) - \Delta_G\text{O}^\ominus\text{M}_j^{\text{Z}^+}(\text{c})]$ (kJ · mol ⁻¹)	Interaction energy ^b (kJ · mol ⁻¹)
K _(A) ⁺ - Fe _(B) ³⁺	-0.124	531.14	-65.72
Na _(A) ⁺ - Fe _(B) ³⁺	-0.005	76.20	-0.36
H ₃ O _(A) ⁺ - Fe _(B) ³⁺	-0.032	0.02	-0.00
K _(A) ⁺ - S _(T) ⁶⁺	-0.165	677.78	-111.82
Na _(A) ⁺ - S _(T) ⁶⁺	-0.006	222.84	-1.42
H ₃ O _(A) ⁺ - S _(T) ⁶⁺	-0.043	146.66	-6.28
Fe _(B) ³⁺ - S _(T) ⁶⁺	-1.928	146.64	-282.81
Fe _(B) ³⁺ - H _(O3) ⁺	-0.964	0.02	-0.02
K _(A) ⁺ - H _(O3) ⁺	-0.082	531.12	-43.82
Na _(A) ⁺ - H _(O3) ⁺	-0.003	76.18	-0.24
H ₃ O _(A) ⁺ - H _(O3) ⁺	-0.021	0.00	-0.00
		$\Delta G^\circ_{f,\text{ox}}$ (kJ · mol ⁻¹) =	-512.50

^a A, B, T denote 12-fold coordination, octahedral and tetrahedral sites, respectively.

^b Product of the two first columns, i.e., equal to -14X_iX_j[$\Delta_G\text{O}^\ominus\text{M}_i^{\text{Z}^+}(\text{c}) - \Delta_G\text{O}^\ominus\text{M}_j^{\text{Z}^+}(\text{c})$].

The Gibbs free energies of formation from elements is $\Delta G^\circ_f = -3289.9 \pm 8.22$ kJ · mol⁻¹. This value is very close to the experimental value of -3293.50 ± 2.1 kJ · mol⁻¹ calculated from the experimental solubility product (Alpers et al., 1989).

5. CONCLUSIONS

The model of prediction of Gibbs free energies of formation based on $\Delta_G\text{O}^\ominus\text{M}^{\text{Z}^+}(\text{c})$, a parameter assumed to be constant within three sites of an alunite mineral, give very good results if the formalism of the Gibbs free energies of formation from constituent oxides uses an approach from short-range interactions. The only data needed for the estimation technique is the chemical composition. The advantages of this model are its simplicity, its widespread application to all minerals of the alunite supergroup thanks to the large diversity of ions and its suitability to any solid solutions.

The success of this model based on the difference of oxygen affinity of two cations around a common oxygen has already been demonstrated for smectites (Vieillard, 2000) and in well crystallized phyllosilicates (Vieillard, 2002), and is fully justified in the alunite supergroup. This supports the concept that the properties of minerals belonging to a "cristallographic" family are more determined by nearest-neighbor interactions than by the long-range interactions. In addition, it is likely that this technique could successfully model the thermodynamic properties of some families of minerals such as amphiboles, pyroxenes, garnets, and pyrochlores.

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