

A NEW METHOD FOR THE PREDICTION OF GIBBS FREE ENERGIES OF FORMATION OF HYDRATED CLAY MINERALS BASED ON THE ELECTRONEGATIVITY SCALE

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Abstract—A new method for the prediction of Gibbs free energies of formation for hydrated clay minerals is proposed based on the parameter $\Delta_G O^- M^{z+}(\text{clay})$ 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 electronegativity difference defined by the $\Delta_G O^- M^{z+}(\text{clay})$ between any two consecutive cations. The $\Delta_G O^- M^{z+}(\text{clay})$ value, using a weighting scheme involving the electronegativity of a cation in a specific site (interlayer, octahedral, or tetrahedral) is assumed to be constant and can be calculated by minimization of 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 compared to other determinations, gives values within 0.5% of the experimentally estimated values. The relationships between $\Delta_G O^- M^{z+}(\text{clay})$ corresponding to the electronegativity of a cation in either interlayer or octahedral sites and known $\Delta_G O^- M^{z+}(\text{aq})$ were determined, thereby allowing the prediction of the electronegativity of transition metal ions and trivalent ions in hydrated interlayer sites and octahedral sites. Prediction of Gibbs free energies of formation of any clay mineral with various ions located in the interlayer and with different cations in octahedral sites is possible. Examples are given for Al-rich montmorillonite from Aberdeen, transition element-exchanged montmorillonite, and Ni-rich stevensite, and the results appear excellent when compared to experimental values.

Key Words—Beidellite, Exchangeable Cations, Gibbs Free Energies of Formation, Hectorite, Hydration, Illite, Montmorillonite, Nontronite, Saponite, Sauconite, Stevensite, Vermiculite.

INTRODUCTION

Clay minerals such as smectite, vermiculite, illite, celadonite, montmorillonite, and beidellite are commonly considered to be of poor crystalline quality and of small grain size. Clay minerals have variable compositions and interlayer sites may be occupied by cations, such as Li^+ , Rb^+ , Cs^+ , Ba^{2+} , Sr^{2+} , transition metal ions, Al^{3+} , or NH_4^+ . Clay minerals whose Gibbs free energies of formation are derived directly or indirectly from solubility measurements are fully hydrated even if H_2O is not considered when equilibrium reactions are written (Tardy *et al.*, 1987). In hydrated clay minerals, H_2O molecules occur in two different positions: interlayer (strongly bonded to interlayer cations) and interparticles (relating to physical properties, such as porosity or surface tension).

A recent method of prediction of Gibbs free energies of formation was made for hydrated compounds (Tardy and Duplay, 1992). The principle is based on the following: assume that the poorly crystallized clay minerals are fully hydrated and are all of the same particle size (but not the same volume because of variable amounts of water in the interlayer of swelling clays). In a series of clay minerals of identical layer charge and with the same tetrahedral charge, hydration energies increase or decrease together with the parameter $\Delta_G O^- M^{z+}(\text{aq})$ (defined in detail below) charac-

terizing the cation in the octahedral site. For one given exchangeable cation, a clay mineral of a complex composition is considered as an ideal solid solution of 12 end-members (four uncharged minerals in the series talc-minnesotaite-pyrophyllite- Fe^{3+} -rich pyrophyllite, four micas, and four celadonites). The contribution of each end-member was recalculated by Tardy and Duplay (1992) according to the model of Tardy and Fritz (1981) and Tardy *et al.* (1987).

By comparing this method to natural clay minerals, some Fe-enriched clays (Clay Spur, Cheto from Huang and Keller, 1973; and idealized nontronite from Wolery and Daveler, 1992) show predicted Gibbs free energies of formation that are very different from experimental values. These differences are related to the poor choice of ΔG_f° of Fe^{2+} and Fe^{3+} for the prediction of solubility products of end-members (Fe^{2+} : -78.9 kJ/mole, Fe^{3+} : -4.7 kJ/mole). Values of ΔG_f° for aqueous ferrous and ferric iron from Parker and Khodakovskii (1995) are used here. These values enable a new scale of $\Delta_G O^- M^{z+}(\text{aq})$ values in octahedral coordination to be determined. This will allow the determination of Gibbs free energies of formation of some clays minerals containing Li and transition metals in octahedral coordination.

Mattigod and Sposito (1978) proposed a method of determining the Gibbs free energies of formation of smectites and clay minerals for nine exchangeable cat-

Table 1. Gibbs free energies of formation of oxides and ions, and calculated parameter $\Delta_G O^= M^{z+}(aq)$ of select cations.

Oxides	ΔG_f° (kJ/mole)	Ions	ΔG_f° (kJ/mole)	$\Delta_G O^=$ $M^{z+}(aq)$ (kJ/mole)
Li ₂ O	-561.2 ¹	Li ⁺	-292.6 ⁶	24.00
Na ₂ O	-376.0 ¹	Na ⁺	-261.881 ⁶	147.76
K ₂ O	-322.1 ¹	K ⁺	-282.462 ⁶	242.82
Rb ₂ O	-300.06 ²	Rb ⁺	-284.01 ⁴	267.96
Cs ₂ O	-308.4 ¹	Cs ⁺	-291.46 ⁴	274.52
(NH ₄) ₂ O	-234.3 ³	NH ₄ ⁺	-79.414 ⁴	-75.47
BaO	-520.4 ¹	Ba ²⁺	-563.8 ⁶	43.40
SrO	-560.7 ¹	Sr ²⁺	-555.4 ⁶	-5.30
CaO	-603.1 ¹	Ca ²⁺	-552.79 ⁶	-50.31
MgO	-569.3 ¹	Mg ²⁺	-453.985 ⁶	-115.32
FeO	-251.4 ¹	Fe ²⁺	-90.53 ⁷	-160.87
MnO	-362.9 ¹	Mn ²⁺	-228.1 ¹	-134.80
CuO	-128.3 ¹	Cu ²⁺	65.1 ¹	-193.40
CoO	-214.1 ¹	Co ²⁺	-54.392 ⁶	-159.71
NiO	-211.1 ¹	Ni ²⁺	-45.6 ⁶	-165.50
CdO	-258.35 ⁴	Cd ²⁺	-77.6 ¹	-151.1
ZnO	-320.4 ¹	Zn ²⁺	-147.3 ¹	-173.10
Fe ₂ O ₃	-744.4 ¹	Fe ³⁺	-16.28 ⁷	-237.28
Cr ₂ O ₃	-1053.1 ¹	Cr ³⁺	-206.27 ⁸	-213.52
Al ₂ O ₃	-1582.3 ¹	Al ³⁺	-487.616 ⁶	-202.36
La ₂ O ₃	-1705.982 ²	La ³⁺	-686.176 ⁶	-111.21
SiO ₂	-856.3 ⁴	SiO ₂ ^o aq	-833.411 ⁶	
H ₂ O(c)	-220.0 ⁵	H ₂ O liq.	-237.183 ⁶	-237.18

¹ Robie and Hemingway (1995).
² Barin (1985).
³ Wilcox and Bromley (1963).
⁴ *Codata Key Values for Thermodynamics* (1989).
⁵ This work.
⁶ Shock and Helgeson (1988).
⁷ Parker and Khodakovskii (1995).
⁸ Sverjensky *et al.* (1997).

ions (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺). No method of prediction is available for clay minerals with other exchangeable cations, such as some transition metals and rare-earth metals. These compounds frequently occur where environmental and waste-management problems exist.

The aim of this paper is to propose an improved method of prediction of Gibbs free energy of forma-

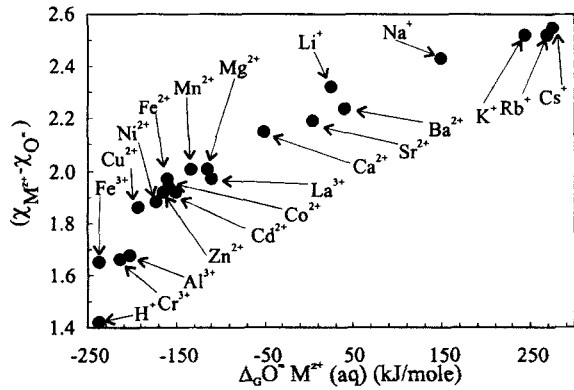


Figure 1. Relationship between $(\chi_{M^{z+}} - \chi_{O^{2-}})$ from Martynov and Batsanov (1980) versus $\Delta_G O^= M^{z+}(aq)$.

tion of hydrated clay minerals based on the parameter $\Delta_G O^= M^{z+}(aq)$ as defined initially by Tardy and Garrels (1977). The method is extended to all elements.

HISTORICAL DEVELOPMENT OF THE PARAMETER $\Delta_G O^= M^{z+}$

Both previous and proposed revisions for evaluating the Gibbs free energies of formation are based on the parameter $\Delta_G O^= M^{z+}(aq)$. This parameter characterizes a given cation M^{z+} and is defined as the difference between the Gibbs free energy of formation of the corresponding oxides [$\Delta G_f^\circ MO_x(c)$] and the Gibbs free energy of formation of the corresponding aqueous cation [$\Delta G_f^\circ M^{z+}(aq)$]:

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

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 ($x = z/2$), so that the difference in Equation (1) refers to one oxygen atom. A set of internally consistent values of $\Delta_G O^= M^{z+}(aq)$ is proposed here (Table 1). These values are mostly from Robie

Table 2. General equation of Gibbs free energy of formation from the oxides of a muscovite-like $KAl_2(Si_3Al)O_{10}(OH)_2$.

$$\Delta G_{ox}^\circ = -12 \left\{ \begin{aligned} & \frac{6}{12} \times \frac{0.5}{12} [\Delta_G O^= K^+(l) - \Delta_G O^= Si^{4+}(clay)] + \frac{1.5}{12} \times \frac{0.5}{12} [\Delta_G O^= K^+(l) - \Delta_G O^= Al^{3+}(t)] \\ & + \frac{3}{12} \times \frac{0.5}{12} [\Delta_G O^= K^+(l) - \Delta_G O^= Al^{3+}(o)] + \frac{1}{12} \times \frac{0.5}{12} [\Delta_G O^= K^+(l) - \Delta_G O^= H^+(clay)] \\ & + \frac{3}{12} \times \frac{6}{12} [\Delta_G O^= Al^{3+}(o) - \Delta_G O^= Si^{4+}(clay)] + \frac{3}{12} \times \frac{1.5}{12} [\Delta_G O^= Al^{3+}(o) - \Delta_G O^= Al^{3+}(t)] \\ & + \frac{3}{12} \times \frac{1}{12} [\Delta_G O^= Al^{3+}(o) - \Delta_G O^= H^+(clay)] + \frac{6}{12} \times \frac{1}{12} [\Delta_G O^= Si^{4+}(clay) - \Delta_G O^= H^+(clay)] \\ & + \frac{1.5}{12} \times \frac{1}{12} [\Delta_G O^= Al^{3+}(t) - \Delta_G O^= H^+(clay)] + \frac{6}{12} \times \frac{1.5}{12} [\Delta_G O^= Si^{4+}(clay) - \Delta_G O^= Al^{3+}(t)] \end{aligned} \right\}$$

Table 3. Equation of Gibbs free energy of formation from the oxides, based on short-range interactions, of a muscovite-like $KAl_2(Si_3Al)O_{10}(OH)_2$.

$$\Delta G_{ox}^{\circ} = -12 \left\{ \frac{6}{12} \times \frac{0.5}{12} [\Delta_G O^{\circ} K^+(l) - \Delta_G O^{\circ} Si^{4+}(clay)] + \frac{1.5}{12} \times \frac{0.5}{12} [\Delta_G O^{\circ} K^+(l) - \Delta_G O^{\circ} Al^{3+}(t)] \right. \\ \left. + \frac{3}{12} \times \frac{6}{12} [\Delta_G O^{\circ} Al^{3+}(o) - \Delta_G O^{\circ} Si^{4+}(clay)] + \frac{3}{12} \times \frac{1.5}{12} [\Delta_G O^{\circ} Al^{3+}(o) - \Delta_G O^{\circ} Al^{3+}(t)] \right. \\ \left. + \frac{3}{12} \times \frac{1}{12} [\Delta_G O^{\circ} Al^{3+}(o) - \Delta_G O^{\circ} H^+(clay)] + \frac{6}{12} \times \frac{1.5}{12} [\Delta_G O^{\circ} Si^{4+}(clay) - \Delta_G O^{\circ} Al^{3+}(t)] \right\}$$

and Hemingway (1995) for oxides and from Shock and Helgeson (1988) for aqueous cations. Some values [e.g., $(NH_4)_2O$, Cr^{3+} , La^{3+}] were obtained from other sources.

For double oxides, an additional parameter is introduced, $\Delta G_{ox}^{\circ}[(M_i)_{n_i}(M_j)_{n_j}O_N]$ which is the Gibbs free energy of formation of a given compound $(M_i)_{n_i}(M_j)_{n_j}O_N$ as determined from the constituent oxides $M_iO_{x_i}$ and $M_jO_{x_j}$, where $M_i^{z_i+}$ and $M_j^{z_j+}$ are two cations for which $z_i = 2x_i$ and $z_j = 2x_j$:

$$\Delta G_{ox}^{\circ}[(M_i)_{n_i}(M_j)_{n_j}O_N] \\ = \Delta G_f^{\circ}[(M_i)_{n_i}(M_j)_{n_j}O_N](c) - n_i \Delta G_f^{\circ} M_i O_{x_i}(c) \\ - n_j \Delta G_f^{\circ} M_j O_{x_j}(c) \quad (2)$$

The total number of oxygen atoms, N , of the compound is equal to the sum of the number of oxygen atoms n_i and n_j , respectively, related to the cations M_i and M_j in each oxide ($M_iO_{x_i}$ and $M_jO_{x_j}$):

$$N = n_i x_i + n_j x_j$$

and thus,

$$X_i = n_i x_i / N \quad (4)$$

$$X_j = n_j x_j / N \quad (5)$$

$$X_i + X_j = 1. \quad (6)$$

The general relationship determined by Tardy (1979) for the Gibbs free energies is:

Table 4. Values of parameter $\Delta_G O^{\circ} M^{z+}(clay)$ obtained by minimization.

Ions	$\Delta_G O^{\circ} (M^{z+}(clay))$ (kJ/mole)	Ions	$\Delta_G O^{\circ} M^{z+}(clay)$ (kJ/mole)
$K^+(l)$	425.77	$Fe^{2+}(o)$	-134.40
$Na^+(l)$	267.19	$Al^{3+}(o)$	-161.23
$Li^+(l)$	77.54	$Fe^{3+}(o)$	-164.05
$Mg^{2+}(l)$	-100.0	$Si^{4+}(clay)$	-166.09
$Ca^{2+}(l)$	-32.34	$Al^{3+}(t)$	-197.31
$Mg^{2+}(o)$	-112.0	$H^+(clay)$	-220.0

¹l, o, and t denote interlayer, octahedral, and tetrahedral sites, respectively.

$$\Delta G_{ox}^{\circ} (M_i)_{n_i} (M_j)_{n_j} O_N \\ = -\alpha N (X_i X_j) [\Delta_G O^{\circ} M_i^{z_i+}(aq) - \Delta_G O^{\circ} M_j^{z_j+}(aq)] \quad (7)$$

where N is the total number of oxygen atoms in the compound; 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 $M_iO_{x_i}$ and $M_jO_{x_j}$; $\Delta_G O^{\circ} M_i^{z_i+}(aq)$ and $\Delta_G O^{\circ} M_j^{z_j+}(aq)$ are, respectively, the $\Delta_G O^{\circ}$ parameter as calculated for cations $M_i^{z_i+}$ and $M_j^{z_j+}$ in their aqueous states according to Equation (1); and α is an empirical coefficient that characterizes a given family of compounds. For example, for $Ca_3Si_2O_7$, the α value was determined at -1.01 (Tardy and Garrels, 1977); $\Delta_G O^{\circ} Ca^{2+}(aq) = -50.31$ kJ/mole (Table 1); $\Delta_G O^{\circ} Si^{4+}(aq) = -188.08$ kJ/mole (Tardy and Garrels, 1977); so that:

$$\Delta G_{ox}^{\circ} (Ca_3Si_2O_7) = -(7)(1.01)(3/7)(4/7) \\ \times [\Delta_G O^{\circ} Ca^{2+}(aq) - \Delta_G O^{\circ} Si^{4+}(aq)] \\ = -238.5 \text{ kJ/mole} \quad (8)$$

and $\Delta G_f^{\circ} (Ca_3Si_2O_7)(c) = 3\Delta G_f^{\circ} CaO(c) + 2\Delta G_f^{\circ} SiO_2(c) + \Delta G_{ox}^{\circ} (Ca_3Si_2O_7)(c) = -3760.4$ kJ/mole, a value close to $\Delta G_f^{\circ} (Ca_3Si_2O_7)(c) = -3748.1$ kJ/mole (Robie and Hemingway, 1995).

Equation (7) was compared to many compounds containing two cations: silicates (Tardy and Garrels, 1977); hydroxides (Tardy and Garrels, 1976); phosphates (Vieillard, 1978; Tardy and Vieillard, 1977); and nitrates, sulfates, and carbonates (Gartner, 1979; Tardy and Gartner, 1977). Gibbs free energy of formation of minerals as 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 stoichiometric coefficient $N(X_i X_j)$, and (3) the difference $[\Delta_G O^{\circ} M_i^{z_i+}(aq) - \Delta_G O^{\circ} M_j^{z_j+}(aq)]$.

Because the electronegativity of an atom is its ability to attract valence electrons, Martynov and Batsanov (1980) defined the electronegativity, $\chi_{M^{z+}}$, as the square root of the average ionization potential of the valence electrons. This scale of electronegativity gives good agreement with those of Pauling (1960) and Mul-

Table 5. Chemical composition and experimental or calculated solubility products as calculated or predicted by Gibbs free energies of formation at 298.15 K of some clay minerals.

Mineral	Formula
Clay Spur Wyoming ¹	$(K_{0.02}Na_{0.27}Ca_{0.1})(Mg_{0.22}Al_{1.52}Fe^{3+}_{0.19})(Si_{3.94}Al_{0.06})O_{10}(OH)_2$
Arizona Mont. Cheto ¹	$(K_{0.02}Na_{0.02}Ca_{0.195})(Mg_{0.33}Al_{1.52}Fe^{3+}_{0.14})(Si_{3.93}Al_{0.07})O_{10}(OH)_2$
K Beidellite ^{2, 3}	$(K_{0.365}Na_{0.07}Ca_{0.01})(Mg_{0.205}Fe^{2+}_{0.055}Al_{1.41}Fe^{3+}_{0.415})(Si_{3.55}Al_{0.45})O_{10}(OH)_2$
Mg Beidellite ^{2, 3}	$(K_{0.095}Na_{0.07}Mg_{0.135}Ca_{0.01})(Mg_{0.205}Fe^{2+}_{0.055}Al_{1.41}Fe^{3+}_{0.415})(Si_{3.55}Al_{0.45})O_{10}(OH)_2$
Smectite ⁴	$(Mg_{0.255})(Mg_{0.27}Al_{1.345}Fe^{3+}_{0.405})(Si_{3.7}Al_{0.3})O_{10}(OH)_2$
Mg Belle Fourche ^{2, 5}	$(Mg_{0.135})(Mg_{0.29}Al_{1.515}Fe^{3+}_{0.225})(Si_{3.935}Al_{0.065})O_{10}(OH)_2$
Mg Aberdeen ^{2, 5}	$(Mg_{0.208})(Mg_{0.445}Al_{1.29}Fe^{3+}_{0.335})(Si_{3.82}Al_{0.18})O_{10}(OH)_2$
Colony ⁶	$(Mg_{0.195})(Mg_{0.29}Al_{1.52}Fe^{3+}_{0.22})(Si_{3.81}Al_{0.19})O_{10}(OH)_2$
Colony I ⁷	$(Mg_{0.185})(Mg_{0.26}Al_{1.58}Fe^{3+}_{0.19})(Si_{3.8}Al_{0.2})O_{10}(OH)_2$
Colony II ⁷	$(Mg_{0.21})(Mg_{0.29}Al_{1.52}Fe^{3+}_{0.21})(Si_{3.81}Al_{0.19})O_{10}(OH)_2$
Castle rock ⁷	$(Mg_{0.21})(Mg_{0.46}Al_{1.52}Fe^{3+}_{0.14})(Si_{3.68}Al_{0.32})O_{10}(OH)_2$
Upton ⁷	$(Mg_{0.17})(Mg_{0.24}Al_{1.55}Fe^{3+}_{0.2})(Si_{3.93}Al_{0.07})O_{10}(OH)_2$
Belle Fourche ^{8, 9}	$(K_{0.46})(Mg_{0.305}Al_{1.575}Fe^{3+}_{0.14})(Si_{3.785}Al_{0.215})O_{10}(OH)_2$
Nontronite, Saponite, Beidellite, Vermiculite, and Glauconite	
Palabora Vermiculite ^{10, 11}	$(Mg_{0.31})(Mg_{2.65}Fe^{2+}_{0.075}Fe^{3+}_{0.235})(Si_{3.145}Al_{0.855})O_{10}(OH)_2$
Libby Vermiculite ^{10, 11}	$(Mg_{0.218})(Mg_{2.61}Fe^{2+}_{0.015}Al_{0.08}Fe^{3+}_{0.295})(Si_{3.19}Al_{0.81})O_{10}(OH)_2$
Nontron. Nlle Caléd. ^{10, 12}	$(Mg_{0.135})(Mg_{0.315}Al_{0.07}Fe^{3+}_{1.720})(Si_{3.73}Al_{0.27})O_{10}(OH)_2$
Nontron. Lake Chad ¹⁰	$(Ca_{0.220})(Mg_{0.21}Fe^{3+}_{1.77})(Si_{3.83}Al_{0.17})O_{10}(OH)_2$
Beidellite ¹⁰	$(Ca_{0.133})(Mg_{0.26}Al_{1.327}Fe^{3+}_{0.50})(Si_{3.733}Al_{0.267})O_{10}(OH)_2$
Saponite ^{10, 13}	$(Na_{0.19})(Mg_{1.9}Al_{0.16}Fe^{3+}_{0.51})(Si_{4.0})O_{10}(OH)_2$
Glauconite ¹⁰	$(K_{0.8})(Mg_{0.3}Al_{1.20}Fe^{3+}_{0.45})(Si_{3.65}Al_{0.35})O_{10}(OH)_2$
Exchanged Montmorillonite	
Li-Camp Berteaux ²	$(Li_{0.335})(Mg_{0.32}Fe^{2+}_{0.015}Al_{1.46}Fe^{3+}_{0.205})(Si_{4.0})O_{10}(OH)_2$
Na-Camp Berteaux ²	$(Na_{0.335})(Mg_{0.32}Fe^{2+}_{0.015}Al_{1.46}Fe^{3+}_{0.205})(Si_{4.0})O_{10}(OH)_2$
K-Camp Berteaux ²	$(K_{0.335})(Mg_{0.32}Fe^{2+}_{0.015}Al_{1.46}Fe^{3+}_{0.205})(Si_{4.0})O_{10}(OH)_2$
Mg-Camp Berteaux ²	$(Mg_{0.168})(Mg_{0.32}Fe^{2+}_{0.015}Al_{1.46}Fe^{3+}_{0.205})(Si_{4.0})O_{10}(OH)_2$
Ca-Camp Berteaux ²	$(Ca_{0.168})(Mg_{0.32}Fe^{2+}_{0.015}Al_{1.46}Fe^{3+}_{0.205})(Si_{4.0})O_{10}(OH)_2$
Li-Wyoming ²	$(Li_{0.39})(Mg_{0.275}Al_{1.525}Fe^{3+}_{0.21})(Si_{3.855}Al_{0.145})O_{10}(OH)_2$
Na-Wyoming ²	$(Na_{0.39})(Mg_{0.275}Al_{1.525}Fe^{3+}_{0.21})(Si_{3.855}Al_{0.145})O_{10}(OH)_2$
K-Wyoming ²	$(K_{0.39})(Mg_{0.275}Al_{1.525}Fe^{3+}_{0.21})(Si_{3.855}Al_{0.145})O_{10}(OH)_2$
Li-Chambers ²	$(Li_{0.46})(Mg_{0.535}Fe^{2+}_{0.008}Al_{1.33}Fe^{3+}_{0.215})(Si_{3.82}Al_{0.18})O_{10}(OH)_2$
Na-Chambers ²	$(Na_{0.46})(Mg_{0.535}Fe^{2+}_{0.008}Al_{1.33}Fe^{3+}_{0.215})(Si_{3.82}Al_{0.18})O_{10}(OH)_2$
K-Chambers ²	$(K_{0.46})(Mg_{0.535}Fe^{2+}_{0.008}Al_{1.33}Fe^{3+}_{0.215})(Si_{3.82}Al_{0.18})O_{10}(OH)_2$
Ca-Chambers ²	$(Ca_{0.21})(Mg_{0.535}Fe^{2+}_{0.008}Al_{1.33}Fe^{3+}_{0.215})(Si_{3.82}Al_{0.18})O_{10}(OH)_2$
Na-Bayard ²	$(Na_{0.462})(Mg_{0.3}Al_{1.57}Fe^{3+}_{0.076})(Si_{4.0})O_{10}(OH)_2$
Idealized Clay	
Na-Montmorillonite ¹⁴	$(Na_{0.33})(Mg_{0.33}Al_{1.67})(Si_{4.0})O_{10}(OH)_2$
K-Montmorillonite ¹⁴	$(K_{0.33})(Mg_{0.33}Al_{1.67})(Si_{4.0})O_{10}(OH)_2$
Mg-Montmorillonite ¹⁴	$(Mg_{0.165})(Mg_{0.33}Al_{1.67})(Si_{4.0})O_{10}(OH)_2$
Ca-Montmorillonite ¹⁴	$(Ca_{0.165})(Mg_{0.33}Al_{1.67})(Si_{4.0})O_{10}(OH)_2$
Na-Beidellite ¹⁴	$(Na_{0.33})(Al_{2.0})(Si_{4.0})O_{10}(OH)_2$
K-Beidellite ¹⁴	$(K_{0.33})(Al_{2.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Mg-Beidellite ¹⁴	$(Mg_{0.165})(Al_{2.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Ca-Beidellite ¹⁴	$(Ca_{0.165})(Al_{2.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
K-Saponite ¹⁴	$(K_{0.33})(Mg_{3.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Na-Saponite ¹⁴	$(Na_{0.33})(Mg_{3.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Mg-Saponite ¹⁴	$(Mg_{0.165})(Mg_{3.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Ca-Saponite ¹⁴	$(Ca_{0.165})(Mg_{3.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
K-Nontronite ¹⁴	$(K_{0.33})(Fe^{3+}_{2.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Na-Nontronite ¹⁴	$(Na_{0.33})(Fe^{3+}_{2.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Mg-Nontronite ¹⁴	$(Mg_{0.165})(Fe^{3+}_{2.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Ca-Nontronite ¹⁴	$(Ca_{0.165})(Fe^{3+}_{2.0})(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Smectite low Fe/Mg ¹⁴	$(K_{0.2}Na_{0.1}Ca_{0.02})(Mg_{0.9}Fe^{2+}_{0.29}Al_{1.017}Fe^{3+}_{0.16})(Si_{3.75}Al_{0.25})O_{10}(OH)_2$
Smectite high Fe/Mg ¹⁴	$(K_{0.2}Na_{0.1}Ca_{0.025})(Mg_{1.15}Fe^{2+}_{0.5}Al_{0.75}Fe^{3+}_{0.2})(Si_{3.5}Al_{0.5})O_{10}(OH)_2$
Idealized Montmorillonites	
Mg-Montmorillonite ¹⁵	$(K_{0.3})(Mg_{0.3}Al_{1.7})(Si_{4.0})O_{10}(OH)_2$
Fe ⁺³ -Montmorillonite ¹⁵	$(K_{0.3})(Al_{1.5}Fe^{3+}_{0.4})(Si_{4.0})O_{10}(OH)_2$
Fe ⁺² -Montmorillonite ¹⁵	$(K_{0.3})(Fe^{2+}_{0.3}Al_{1.7})(Si_{4.0})O_{10}(OH)_2$
Al-Montmorillonite ¹⁵	$(K_{0.3})(Al_{1.9})(Si_{4.0})O_{10}(OH)_2$

Table 5. Extended.

Log K	ΔG_f° , calc. kJ/mole	ΔG_f° , predict. kJ/mole	Error (%)
6.70	-5227.63	-5241.15	-0.26
9.22	-5250.70	-5273.05	-0.43
7.26	-5218.08	-5227.64	-0.18
7.30	-5202.88	-5215.35	-0.24
1.62	-5212.48	-5197.91	0.28
0.28	-5223.34	-5209.24	0.27
2.75	-5220.50	-5210.08	0.20
2.11	-5259.70	-5246.49	0.25
3.24	-5265.17	-5258.15	0.13
2.7	-5262.98	-5251.85	0.21
6.6	-5333.47	-5327.54	0.11
3.5	-5216.59	-5219.44	-0.05
4.22	-5324.61	-5312.90	0.22
38.49	-5545.18	-5573.79	-0.52
31.65	-5534.68	-5542.26	-0.14
-6.16	-4618.66	-4630.42	-0.25
-8.44	-4598.17	-4599.44	-0.03
3.32	-5144.51	-5150.17	-0.11
14.73	-5196.94	-5206.83	-0.19
0.82	-5277.31	-5242.81	0.65
1.82	-5231.89	-5221.80	0.19
1.79	-5221.79	-5211.96	0.19
1.58	-5229.85	-5220.64	0.18
1.78	-5210.13	-5203.33	0.13
1.85	-5226.57	-5216.90	0.19
3.03	-5269.69	-5259.76	0.19
3.02	-5257.80	-5248.08	0.18
2.93	-5266.32	-5258.00	0.16
5.12	-5306.47	-5293.26	0.25
5.09	-5292.51	-5279.42	0.25
4.85	-5303.37	-5291.06	0.23
5.17	-5298.72	-5286.24	0.24
1.51	-5297.73	-5276.44	0.40
3.06	-5315.49	-5302.64	0.24
2.72	-5324.19	-5311.19	0.24
2.98	-5304.43	-5294.14	0.19
3.06	-5320.23	-5307.16	0.25
6.38	-5350.05	-5352.46	-0.04
6.05	-5358.73	-5360.65	-0.04
6.30	-5338.98	-5344.80	-0.11
6.32	-5355.18	-5357.66	-0.05
26.55	-5628.42	-5594.99	0.59
26.88	-5619.75	-5586.80	0.59
26.80	-5608.68	-5579.13	0.53
28.82	-5613.46	-5592.00	0.38
-11.80	-4517.94	-4516.52	0.03
-11.47	-4509.27	-4508.33	0.02
-11.55	-4498.19	-4500.67	-0.05
-11.53	-4514.39	-4513.53	0.02
9.55	-5286.92	-5276.70	0.19
16.29	-5286.49	-5286.21	0.01
4.20	-5308.3	-5305.85	0.05
-1.29	-5112.4	-5110.55	0.04
3.23	-5204.8	-5204.02	0.02
1.94	-5282.5	-5279.08	0.06

liken (1934). The relationship between the parameter $\Delta_G O^\circ M^{z+}(aq)$ with the difference of electronegativity between cation and oxygen (Figure 1) shows the dependence of a cation with the oxygen affinity. The parameter $\Delta_G O^\circ M^{z+}(aq)$ is also related to the enthalpy of dissolution of the corresponding oxide according to the relation: $MO_x(c) + 2xH^+(aq) \rightarrow M^{z+}(aq) + H_2O(l)$. When two cations have the same oxygen affinity, the Gibbs free energy of formation of a compound from the two oxides must be equal to or near zero. The lowest Gibbs free energies of formation from oxides are obtained for the electropositive cations, which show a $\Delta_G O^\circ M^{z+}(aq)$ value very different from $\Delta_G O^\circ Si^{4+}(aq)$. Compared to their constituent oxides, the corresponding compounds are the most stable.

Equation (7), as applied to numerous minerals, yields a statistical deviation of 35 kJ/mole (per one atom M_i) and depends on the family of compounds considered. These observed deviations are related to the parameter $\Delta_G O^\circ M^{z+}(aq)$, which characterizes a cation in the aqueous state and not in a crystalline environment.

To make the technique more general and to increase its accuracy, Vieillard (1982, 1994a, 1994b) and Vieillard and Tardy (1988a) proposed a method to predict enthalpy of formation, ΔH_f° (instead of ΔG_f°) of minerals based on their crystal structures by introducing a new empirical parameter, $\Delta_H O^\circ M^{z+}(comp)$. This parameter represents the electronegativity of the cation M^{z+} and is defined as:

$$\Delta_H O^\circ M^{z+}(comp) = \Delta_H O^\circ M^{z+}(ox) + \delta \Delta_H O^\circ M^{z+} \quad (9)$$

where $\Delta_H O^\circ M^{z+}(ox)$ refers to cation M^{z+} in the MO_x crystalline oxide environment and is equivalent to:

$$\begin{aligned} \Delta_H O^\circ M^{z+}(ox) \\ = 1/x[\Delta H_f^\circ MO_x(c) - \Delta H_f^\circ M^{z+}(ox)] \quad (10) \end{aligned}$$

where $\Delta H_f^\circ M^{z+}(ox)$ is the enthalpy of formation of M^{z+} in the corresponding pure crystal oxide and is an unknown. The parameter $\Delta_H O^\circ M^{z+}(ox)$ characterizes the electronegativity of the cation in the oxide crystalline environment. Although, $\Delta_H O^\circ M^{z+}(ox)$ is not known, it may be evaluated for each cation. The second term, $\delta \Delta_H O^\circ M^{z+}$, of Equation (9), representing the difference between $\Delta_H O^\circ M^{z+}(comp)$ and $\Delta_H O^\circ M^{z+}(ox)$, is a correction term that is a function of the modification in the crystal environment during the transfer from an oxide $M_{2/z}O$ to a compound. The correction, $\delta \Delta_H O^\circ M^{z+}$, for cation M^{z+} appears to be related to several parameters (*i.e.*, shortest bond length of a cation to an oxygen atom, polarizabilities, Madelung constant, repulsion constant) (Vieillard, 1982, 1994a; Vieillard and Tardy, 1988a).

Subsequently, Vieillard and Tardy (1988b, 1989) showed that the parameter $\Delta_H O^\circ M^{z+}(comp)$ is a parabolic function of χ_M , the electronegativity of the cat-

Table 5. Continued.

Mineral	Formula
Natural Illites	
Beavers Bend I ¹	(K _{0.6} Na _{0.04})(Mg _{0.16} Al _{1.433} Fe ³⁺ _{0.42})(Si _{3.48} Al _{0.52} O ₁₀ (OH) ₂
Beavers Bend II ¹⁶	(K _{0.53})(Mg _{0.13} Al _{1.663} Fe ³⁺ _{0.2})(Si _{3.62} Al _{0.38} O ₁₀ (OH) ₂
Fithian I ¹⁶	(K _{0.64})(Mg _{0.18} Al _{1.54} Fe ³⁺ _{0.29})(Si _{3.51} Al _{0.49} O ₁₀ (OH) ₂
Fithian II ¹	(K _{0.59} Na _{0.02} Ca _{0.01})(Mg _{0.23} Al _{1.54} Fe ³⁺ _{0.29})(Si _{3.47} Al _{0.53} O ₁₀ (OH) ₂
Goose lake ¹⁶	(K _{0.59})(Mg _{0.15} Al _{1.58} Fe ³⁺ _{0.24})(Si _{3.65} Al _{0.35} O ₁₀ (OH) ₂
Marble Head ¹⁷	(K _{0.69} Na _{0.03} Ca _{0.05})(Mg _{0.33} Fe ²⁺ _{0.07} Al _{1.56} Fe ³⁺ _{0.04})(Si _{3.58} Al _{0.42} O ₁₀ (OH) ₂
Grundite ¹⁷	(K _{0.56} Na _{0.04})(Mg _{0.24} Al _{1.50} Fe ³⁺ _{0.40})(Si _{3.22} Al _{0.78} O ₁₀ (OH) ₂
Rock Island ¹⁷	(K _{0.59} Na _{0.03} Ca _{0.03})(Mg _{0.26} Fe ²⁺ _{0.08} Al _{1.62} Fe ³⁺ _{0.07})(Si _{3.57} Al _{0.43} O ₁₀ (OH) ₂
Idealized Illites	
Illite IS ⁸	(K _{0.5})(Mg _{0.22} Al _{1.78})(Si _{3.72} Al _{0.28} O ₁₀ (OH) ₂
Illite ISII ⁸	(K _{0.69})(Mg _{0.16} Al _{1.84})(Si _{3.47} Al _{0.53} O ₁₀ (OH) ₂
End member illite ⁸	(K _{0.85})(Mg _{0.12} Al _{1.88})(Si _{3.27} Al _{0.73} O ₁₀ (OH) ₂
Illite K 0.81 ¹⁸	(K _{0.81} Al _{2.0})(Si _{3.19} Al _{0.81} O ₁₀ (OH) ₂
Illite K 0.81 ¹⁹	(K _{0.81} Al _{2.0})(Si _{3.19} Al _{0.81} O ₁₀ (OH) ₂
Illite K 0.34 ¹⁹	(K _{0.34} Al _{2.0})(Si _{3.66} Al _{0.34} O ₁₀ (OH) ₂

¹ Huang and Keller (1973).² Mattigod and Sposito (1978).³ Misra and Upchurch (1976).⁴ Carson *et al.* (1976).⁵ Kittrick (1971a).⁶ Weaver *et al.* (1971).⁷ Weaver *et al.* (1976).⁸ Aja (1995).⁹ Peryea and Kittrick (1986).¹⁰ Tardy and Fritz (1981).¹¹ Kittrick (1973).¹² Tardy *et al.* (1974b).¹³ Tardy *et al.* (1974a).¹⁴ Wolery and Daveler (1992).¹⁵ Chermak and Rimstidt (1989).¹⁶ Rouston and Kittrick (1971).¹⁷ Reesman (1974).¹⁸ Mattigod and Kittrick (1979).¹⁹ Rosenberg and Kittrick (1990).

ion M^{z+} (Pauling, 1960) in the considered crystal structure. For two cations M_i^{z_i+} and M_j^{z_j+}, the difference between the two Δ_HO⁻ parameters is equal to the difference of the two electronegativities:

$$[\Delta_{\text{H}}\text{O}^{\ominus} \text{M}_i^{z_i+}(\text{comp}) - \Delta_{\text{H}}\text{O}^{\ominus} \text{M}_j^{z_j+}(\text{comp})] = 96.483(\chi_{\text{M}_i} - \chi_{\text{M}_j})^2. \quad (11)$$

This method was used to predict the enthalpy of formation of talc, annite, pyrophyllite, paragonite, and muscovite for which crystal-structure data are available (Vieillard, 1994a, 1994b). In hydrated clay minerals, particles are poorly crystallized and crystal structures are not known precisely. Thus, a new method of prediction of Gibbs free energies is proposed. The method is based on the enthalpy of formation by considering a new scale for Δ_GO⁻ of the cation in clay minerals.

METHODOLOGY

Gibbs free energies of formation from constituent oxides, ΔG_{ox}^o

Consider a hydrated clay mineral whose chemical formula is expressed as following: (M₁, M₂, M₃)(Mg_{0.1}, Fe_{0.2}²⁺, Al_{0.3}, Fe_{0.4}³⁺)(Si_(4-t)Al_t)O₁₀(OH)₂ where subscripts 1, o, and t denote, respectively, the interlayer, octahedral, and tetrahedral sites and where the numerals represent stoichiometric amounts of cation M_i having a charge z_i. Interlayer sites may be occupied by hydrated cations, such as Li⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺, although the hydration number is not involved in the

calculation. Octahedral sites are occupied by several cations such as Li⁺, Mg²⁺, Fe²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Al³⁺, and Fe³⁺, and the tetrahedral site contains Si and Al. The Gibbs free energy of formation of a hydrated clay mineral, ΔG_f^o (Hydrated Clay Mineral) is a summation of Gibbs free energies of formation of the different constituent oxides and a second term, ΔG_{ox}^o, designating Gibbs free energies of formation from constituent oxides:

$$\Delta G_f^o(\text{Hydrated Clay Mineral}) = \sum_{i=1}^{i=n_s} (n_i) \Delta G_f^o(\text{M}_i\text{O}_{x_i}) + \Delta G_{\text{ox}}^o \quad (12)$$

where the Gibbs free energies of formation of oxides are given in Table 1.

The Gibbs free energy of formation from the oxides, ΔG_{ox}^o is calculated by the following equation, which is analogous to those of the enthalpy of formation given by Vieillard (1994a):

$$\Delta G_{\text{ox}}^o = -12 \left\{ \sum_{i=1}^{i=n_s-1} \sum_{j=i+1}^{j=n_s} X_i X_j [\Delta_{\text{G}}\text{O}^{\ominus} \text{M}_i^{z_i+}(\text{clay}) - \Delta_{\text{G}}\text{O}^{\ominus} \text{M}_j^{z_j+}(\text{clay})] \right\} \quad (13)$$

where X_i and X_j are the molar fraction of oxygen related to the cations M_i^{z_i+} and M_j^{z_j+} in the individual oxides M_iO_{x_i} and M_jO_{x_j}, respectively:

Table 5. Continued Extended.

Log K	ΔG_f° calc. kJ/mole	ΔG_f° predict. kJ/mole	Error (%)
12.58	-5235.78	-5268.00	-0.62
6.44	-5317.49	-5317.04	0.01
7.46	-5320.93	-5318.52	0.05
3.13	-5370.13	-5344.33	0.48
5.80	-5303.36	-5300.13	0.06
		-5417.56	
		-5339.99	
		-5386.79	
4.36	-5402.52	-5383.21	0.31
12.04	-5446.53	-5452.32	-0.11
16.04	-5495.96	-5507.60	-0.21
16.80	-5494.65	-5511.74	-0.31
17.24	-5492.15	-5511.74	-0.36
3.70	-5376.26	-5363.88	0.23

$$X_i = (1/12)(n_i x_i) \quad (14)$$

$$X_j = (1/12)(n_j x_j) \quad (15)$$

The total number of oxygen atoms of the compound must equal 12:

$$\sum_{i=1}^{i=n_s} n_i x_i = 12. \quad (16)$$

The parameters $\Delta_G O^\circ = M_i^{z_i+}(\text{clay})$ and $\Delta_G O^\circ = M_j^{z_j+}(\text{clay})$ characterize the electronegativity of cations $M_i^{z_i+}$ and $M_j^{z_j+}$, respectively, in a specific site. These terms are initially dependent on structural parameters such as bond length, average bond length, and polarizability (Vieillard, 1982, 1994a) and they are assumed to be constant here.

In smectites, such as Mg-rich smectite from Belle Fourche or Mg-rich smectite from Aberdeen (Kittrick, 1971a), the Mg^{2+} ion is located in two sites: interlayer or hydrated sites (index l) and octahedral sites (index o), which have different structural surroundings. This implies that terms, such as $\Delta_G O^\circ = Mg^{2+}(l)$ and $\Delta_G O^\circ = Mg^{2+}(o)$, are characteristic of the electronegativity of the Mg^{2+} ion in the two sites, respectively, and these terms are not equal. Similarly, octahedral aluminum $\Delta_G O^\circ = Al^{3+}(o)$, tetrahedral aluminum $\Delta_G O^\circ = Al^{3+}(t)$, and interlayer aluminum $\Delta_G O^\circ = Al^{3+}(l)$ are unequal in Al-exchanged montmorillonite (Kittrick, 1971b, 1971c).

In the general equation, the interaction energy is defined by the difference of $\Delta_G O^\circ = M_i^{z_i+}(\text{clay})$ $\Delta_G O^\circ = M_j^{z_j+}(\text{clay})$, and this term characterizes short-range and long-range interactions between the different sites. The interaction energy is positive and can be assumed to be equal:

$$\begin{aligned} [\Delta_G O^\circ = M_i^{z_i+}(\text{clay}) - \Delta_G O^\circ = M_j^{z_j+}(\text{clay})] \\ = 96.483(\chi_{M_i} - \chi_{M_j})^2. \end{aligned} \quad (17)$$

For example, if a poorly crystallized muscovite-like clay, $KAl_2(Si_3Al)O_{10}(OH)_2$, is chosen, five sites are defined as follows: K in the interlayer site, Al in octahedral coordination, the tetrahedral polyhedron which is occupied by Al^{3+} and Si^{4+} , and a hydrogen site of the hydroxyl (OH). If we consider this compound as a sum of oxides: $KAl_2(Si_3Al)O_{10}(OH)_2 \rightarrow 0.5K_2O + Al_2O_3(o) + 3SiO_2 + 0.5Al_2O_3(t) + H_2O$ with the molar fraction of oxygen bound to the following oxides K_2O , Al_2O_3 (octahedral coordination), SiO_2 , Al_2O_3 (tetrahedral coordination), and H_2O being, respectively, 0.5/12, 3/12, 6/12, 1.5/12, and 1/12; the calculated equation of ΔG_{ox}° is given in Table 2.

The equation for the Gibbs free energies of formation from constituent oxides is comprised of the summation of different interaction terms between any two different cations located within and between different sites (interlayer, octahedral, tetrahedral, and hydrogen), so that the total number of interaction terms is calculated from the number of cations n_s , located in different sites of the clay mineral by the following expression:

$$\begin{aligned} \text{Bulk number of interaction terms} \\ = n_s(n_s - 1)/2. \end{aligned} \quad (18)$$

For the muscovite-like compound, the total number of cations located in different sites is five [K^+ , $Al^{3+}(o)$, Si^{4+} , $Al^{3+}(t)$, and H^+] which gives ten unique interaction terms in the equation of ΔG_{ox}° .

Short-range interactions

Vieillard (1994a) applied the principles of Pauling (1960) regarding the predominance of nearest-neighbor interactions (short-range interactions) observed in a crystal structure in the calculation of enthalpy of formation. Thus, for the muscovite-like compound, there is neither a common oxygen atom between silicon and hydrogen, nor common oxygen atoms between tetrahedral aluminum and hydrogen, between potassium and hydrogen, or between potassium and octahedral aluminum atoms. The presence of a non-bridging oxygen between any two adjacent polyhedra in any mineral implies that long-range interaction energy terms between the two sites are not required, and consequently:

$$[\Delta_G O^\circ = M_i^{z_i+}(\text{clay}) - \Delta_G O^\circ = M_j^{z_j+}(\text{clay})] = 0. \quad (19)$$

For the muscovite-like example, the following four interaction terms:

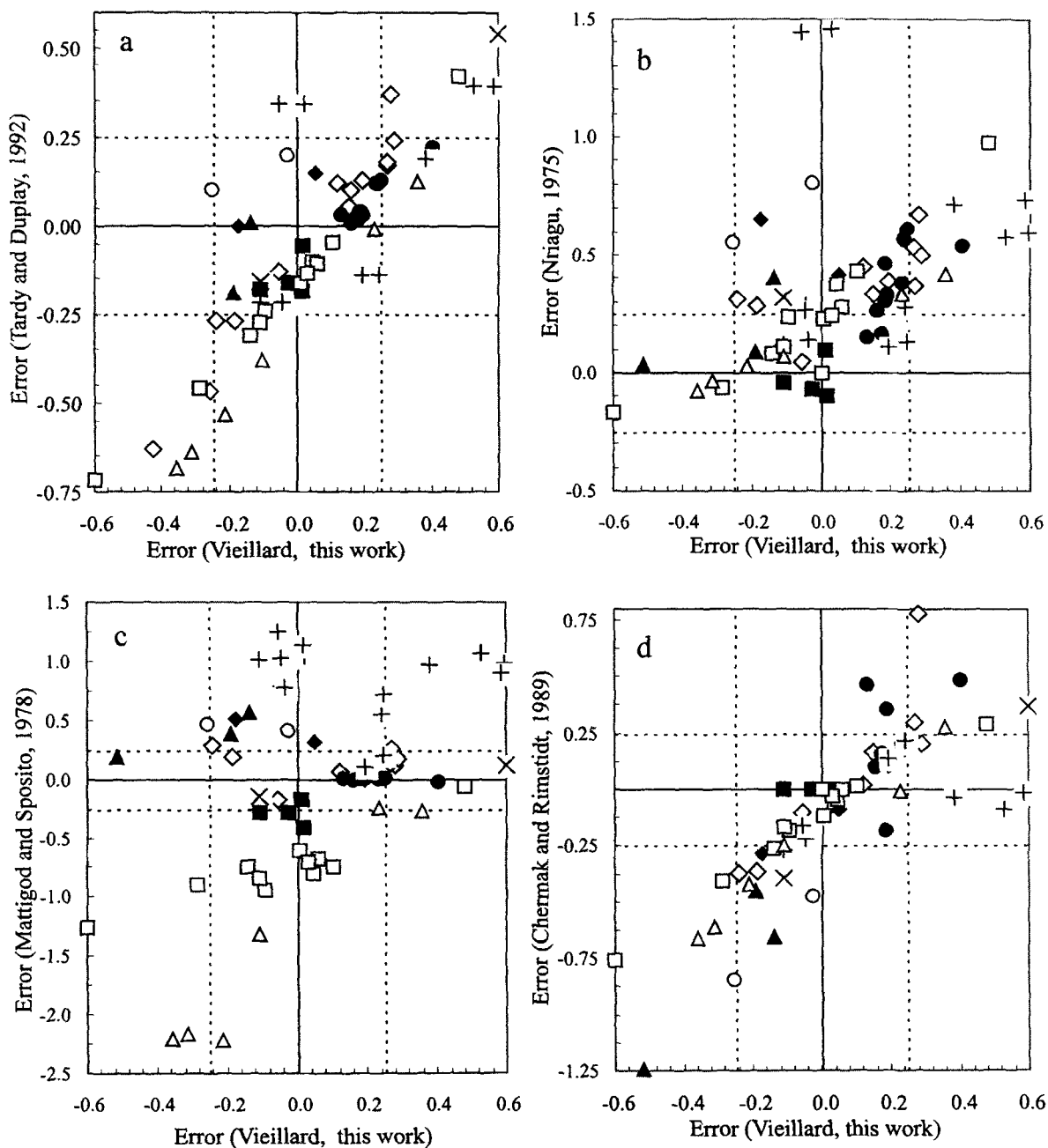


Figure 2. Plots of the percentage errors for determinations from different methods of prediction of Gibbs free energies of formation against the percentage errors for values from the model presented here. The horizontal and vertical dashed lines represent a $\pm 0.25\%$ error in each model using: a) Method of Tardy and Duplay (1992); b) Method of Nriagu (1975); c) Method of Mattigod and Sposito (1978); d) Method of Chermak and Rimstidt (1989). \diamond smectites from well-known localities [e.g., Clay Spur, Cheto (Huang and Keller, 1973); Beidellite (Misra and Upchurch, 1976); Belle Fourche, Aberdeen (Kittrick, 1971a; Peryea and Kittrick, 1986); Colony, Castle Rock, Upton (Weaver *et al.*, 1976)]; \blacktriangle saponite and vermiculite (Tardy and Fritz, 1981); \circ nontronite (Tardy and Fritz, 1981); \times beidellite and glauconite (Tardy and Fritz, 1981); \bullet exchanged montmorillonites (Mattigod and Sposito, 1978); $+$ idealized clay (Wolery and Daveler, 1992); \blacklozenge smectites (Wolery and Daveler, 1992); \blacksquare idealized montmorillonites (Chermak and Rimstidt, 1989); \square natural illites; \triangle idealized illites.

Table 6. Values of $\Delta_G O^- M^{z+}(l)$ for Cs⁺, Rb⁺, Ba²⁺, Sr²⁺, and H⁺ in the interlayer site obtained by minimization.

Ions	$\Delta_G O^- M^{z+}(\text{clay})$ (kJ/mole)	Ions	$\Delta_G O^- M^{z+}(\text{clay})$ (kJ/mole)
Cs ⁺ (l)	565.9	Ba ²⁺ (l)	157.6
Rb ⁺ (l)	528.1	Sr ²⁺ (l)	123.4
		H ⁺ (l)	-154.2

$$\begin{aligned}
 &[\Delta_G O^- K^+(l) - \Delta_G O^- Al^{3+}(o)] \\
 &= [\Delta_G O^- K^+(l) - \Delta_G O^- H^+(\text{clay})] \\
 &= [\Delta_G O^- Si^{4+}(\text{clay}) - \Delta_G O^- H^+(\text{clay})] \\
 &= [\Delta_G O^- Al^{3+}(t) - \Delta_G O^- H^+(\text{clay})] = 0 \quad (20)
 \end{aligned}$$

go to zero in the general expression of ΔG_{ox}^o (Table 3). This equation allows an evaluation of the Gibbs free energies of formation from the constituent oxides of $KAl_2(Si_3Al)O_{10}(OH)_2$. The equation contains one intrasite interaction term (energy between silicon and aluminum within the tetrahedral sites) and five intersite interaction terms [energies between K⁺(l) and Al³⁺(t), K⁺(l) and Si⁴⁺(clay), Al³⁺(o) and Si⁴⁺(t), Al³⁺(o) and Al³⁺(t), Al³⁺(o) and H⁺(clay)]. Generally, as natural clay minerals often show isomorphous substitution, the equation of the Gibbs free energies of formation from oxides may have several interaction terms between any two cations. The number of intersite and intrasite interaction terms can be determined from:

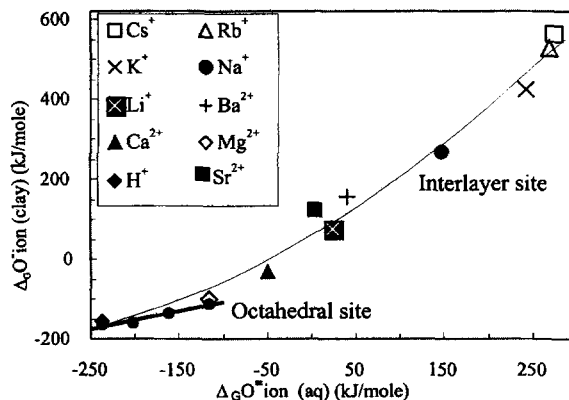


Figure 3. Relationship between $\Delta_G O^- M^{z+}(\text{clay})$ and $\Delta_G O^- M^{z+}(\text{aq})$ for interlayer cations.

Number of intrasite interaction terms

$$= n_i(n_i - 1)/2 + n_o(n_o - 1)/2 + n_t(n_t - 1)/2 \quad (21)$$

Number of intersite interaction terms

$$= n_i n_t + n_o n_t + n_o \quad (22)$$

where n_i , n_o , and n_t are the number of different cations occupying interlayer, octahedral, and tetrahedral sites, respectively. The addition of Equations (21) and (22) gives the total number of interaction terms involved in the calculation of Gibbs free energies from constituent oxides of any known chemical composition of a clay mineral. This number is always lower than the bulk-number interaction terms defined in Equation (18). For the muscovite-like compound, $n_i = 1$, $n_o = 1$, and n_t

Table 7. Chemical composition, experimental or calculated solubility products, calculated and predicted Gibbs free energies of formation of proton, alkaline, and earth-alkaline exchanged clay minerals.

Sample	Formula	Log K	ΔG_f^o calc. (kJ/mol)	ΔG_f^o predict. (kJ/mol)	Error (%)
H-exch. Camp Berteaux ¹	$(H_{0.335})(Mg_{0.32}Fe^{2+}_{0.015}Al_{1.46}Fe^{3+}_{0.205})(Si_{4.0}O_{10}(OH)_2)$	1.70	-5134.56	-5138.77	-0.08
Rb-exch. Camp Berteaux ²	$(Rb_{0.335})(Mg_{0.32}Fe^{2+}_{0.015}Al_{1.46}Fe^{3+}_{0.205})(Si_{4.0}O_{10}(OH)_2)$	1.31	-5231.92	-5228.38	0.07
Cs-exch. Camp Berteaux ²	$(Cs_{0.335})(Mg_{0.32}Fe^{2+}_{0.015}Al_{1.46}Fe^{3+}_{0.205})(Si_{4.0}O_{10}(OH)_2)$	1.18	-5235.18	-5233.99	0.02
Rb-exch. Wyoming ²	$Rb_{0.39}(Mg_{0.275}Al_{1.525}Fe^{3+}_{0.21})(Si_{3.855}Al_{0.145}O_{10}(OH)_2)$	2.84	-5267.47	-5267.74	-0.01
Cs-exch. Wyoming ²	$Cs_{0.39}(Mg_{0.275}Al_{1.525}Fe^{3+}_{0.21})(Si_{3.855}Al_{0.145}O_{10}(OH)_2)$	2.71	-5271.10	-5274.27	-0.06
Rb-exch. Chambers ²	$Rb_{0.46}(Mg_{0.535}Fe^{2+}_{0.008}Al_{1.33}Fe^{3+}_{0.215})(Si_{3.82}Al_{0.18}O_{10}(OH)_2)$	4.64	-5305.28	-5302.76	0.05
Cs-exch. Chambers ²	$Cs_{0.46}(Mg_{0.535}Fe^{2+}_{0.008}Al_{1.33}Fe^{3+}_{0.215})(Si_{3.82}Al_{0.18}O_{10}(OH)_2)$	4.46	-5309.74	-5310.47	-0.01
Ba-exch. Chambers ²	$Ba_{0.23}(Mg_{0.535}Fe^{2+}_{0.008}Al_{1.33}Fe^{3+}_{0.215})(Si_{3.82}Al_{0.18}O_{10}(OH)_2)$	4.93	-5301.97	-5296.01	0.11
Sr-exch. Chambers ²	$Sr_{0.23}(Mg_{0.535}Fe^{2+}_{0.008}Al_{1.33}Fe^{3+}_{0.215})(Si_{3.82}Al_{0.18}O_{10}(OH)_2)$	5.64	-5298.62	-5300.10	-0.03
Cs-exch. Bayard ²	$Cs_{0.462}(Mg_{0.3}Al_{1.57}Fe^{3+}_{0.076})(Si_{4.0}O_{10}(OH)_2)$	0.74	-5315.80	-5306.82	0.17
Sr-exch. Bayard ²	$Sr_{0.231}(Mg_{0.3}Al_{1.57}Fe^{3+}_{0.076})(Si_{4.0}O_{10}(OH)_2)$	1.62	-5306.34	-5296.96	0.18
H-exch. Beidellite ³	$(H_{0.33})(Al_2)(Si_{3.67}Al_{0.33}O_{10}(OH)_2)$	2.64	-5284.95	-5281.32	0.07
Cs-exch. Beidellite ³	$(Cs_{0.33})(Al_2)(Si_{3.67}Al_{0.33}O_{10}(OH)_2)$	3.16	-5378.16	-5375.21	0.05
H-exch. Saponite ³	$(H_{0.33})(Mg_3)(Si_{3.67}Al_{0.33}O_{10}(OH)_2)$	25.85	-5539.21	-5515.66	0.42
Cs-exch. Saponite ³	$(Cs_{0.33})(Mg_3)(Si_{3.67}Al_{0.33}O_{10}(OH)_2)$	25.57	-5636.99	-5609.55	0.49
H-exch. Nontronite ³	$(H_{0.33})(Fe^{3+}_2)(Si_{3.67}Al_{0.33}O_{10}(OH)_2)$	-12.82	-4430.55	-4437.19	-0.15
Cs-exch. Nontronite ³	$(Cs_{0.33})(Mg^{2+}_{0.33}Fe^{3+}_{1.67})(Si_4O_{10}(OH)_2)$	5.80	-4522.47	-4619.59	-2.15

¹ Benson (1982); Bruggenwert and Kamphorst (1979).

² Mattigod and Sposito (1978).

³ Wolery and Daveler (1992).

Table 8. Values of $\Delta_G O^- M^{z+}(l)$ of different ions in the interlayer site as determined from Equation (23).

Ions	$\Delta_G O^- M^{z+}(\text{clay})$ (kJ/mole)	Ions	$\Delta_G O^- M^{z+}(\text{clay})$ (kJ/mole)
$(\text{NH}_4)^+(l)$	-28.4	$\text{Cd}^{2+}(l)$	-102.6
$\text{Mn}^{2+}(l)$	-88.0	$\text{Zn}^{2+}(l)$	-121.0
$\text{Cu}^{2+}(l)$	-136.7	$\text{Al}^{3+}(l)$	-143.3
$\text{Co}^{2+}(l)$	-110.0	$\text{La}^{3+}(l)$	-65.6
$\text{Ni}^{2+}(l)$	-114.8		

= 2, there are six interaction terms in the Gibbs free energy of formation from constituent oxides (Table 3).

RESULTS

Thermodynamic set of data of clay minerals

Numerous data for the Gibbs free energies of formation of clay minerals are compiled elsewhere (Matigod and Sposito, 1978; Chermak and Rimstidt, 1989; Tardy and Fritz, 1981; Wolery, 1978) and much of the data are inconsistent. To provide an internally consistent set of data, Gibbs free energies for each clay mineral are calculated from an experimental solubility product with the use of a set of thermodynamic data of ions (Table 1). Gibbs free energies of 44 hydrated end-member clay minerals from Tardy and Duplay (1992) are recalculated from the estimated solubility products with ΔG_f° of ions (Table 1). These values are used here to determine the importance of the hydration of interlayer cations in different clay minerals.

Minimization

Parameter $\Delta_G O^- M^{z+}$ of 12 cations characterizing the occurrence in different sites were determined by minimization of the difference between calculated Gibbs free energies of formation from oxides and those computed by the general Equation (13). These

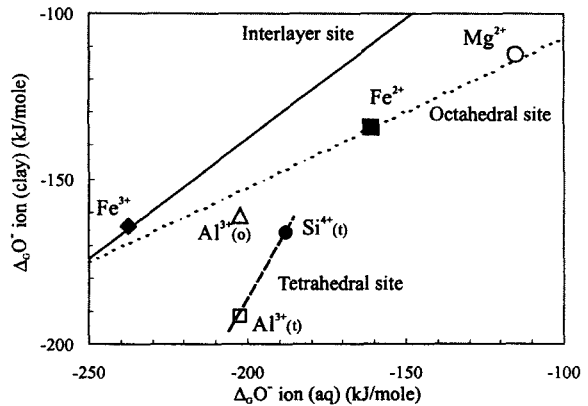


Figure 4. Relationship between $\Delta_G O^- M^{z+}(\text{clay})$ and $\Delta_G O^- M^{z+}(\text{aq})$ for octahedral and tetrahedral cations.

elements included Li^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} in the interlayer or hydrated site, Mg^{2+} , Fe^{2+} , Al^{3+} , and Fe^{3+} in octahedral sites, Si^{4+} and Al^{3+} in tetrahedral sites, and H^+ in the hydroxyl. Constraints of minimization involve short-range interactions and positive-value terms of interaction energies between two different cations in accordance with Equation (17).

The minimization is optimized by fixing $\Delta G_f^\circ \text{H}_2\text{O}$ at -220.0 kJ/mole, which is a value slightly different from that of ice II, $\Delta G_f^\circ = -235.56$ kJ/mole (Mercury *et al.*, 2000). This variation is based on the differences between the proton of the hydroxyl groups in the 2:1 layer vs. the proton of ice. By assuming that $\Delta G_f^\circ \text{H}^+(c) = 0$; $\Delta_G O^- \text{H}^+(\text{clay})$ is equal to -220.0 kJ/mole, which represents the reference value for $\Delta_G O^- M^{z+}(\text{clay})$ for different cations located in different sites of a clay mineral. These values obtained by minimization are given in Table 4 and they contribute to the determination of Gibbs free energy of formation from con-

Table 9. Chemical composition, experimental or calculated solubility products, calculated and predicted Gibbs free energies of formation of some transition elements and Al-exchanged clay minerals.

Sample	Formula	Log K	ΔG_f° calc. (kJ/mol)	ΔG_f° predict. (kJ/mol)	Error (%)
NH_4 -exch. Camp Berteaux ¹	$(\text{NH}_4)_{0.335}(\text{Mg}_{0.32}\text{Fe}^{2+}_{0.015}\text{Al}_{1.46}\text{Fe}^{3+}_{0.205})(\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2)$	1.49	-5162.36	-5149.96	0.24
Mn -exch. Camp Berteaux ¹	$(\text{Mn}_{0.168})(\text{Mg}_{0.32}\text{Fe}^{2+}_{0.015}\text{Al}_{1.46}\text{Fe}^{3+}_{0.205})(\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2)$	1.77	-5172.37	-5170.10	0.04
Cu -exch. Camp Berteaux ¹	$(\text{Cu}_{0.168})(\text{Mg}_{0.32}\text{Fe}^{2+}_{0.015}\text{Al}_{1.46}\text{Fe}^{3+}_{0.205})(\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2)$	1.74	-5123.43	-5125.37	-0.04
Co -exch. Camp Berteaux ¹	$(\text{Co}_{0.168})(\text{Mg}_{0.32}\text{Fe}^{2+}_{0.015}\text{Al}_{1.46}\text{Fe}^{3+}_{0.205})(\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2)$	1.73	-5143.49	-5142.73	0.01
Ni -exch. Camp Berteaux ¹	$(\text{Ni}_{0.168})(\text{Mg}_{0.32}\text{Fe}^{2+}_{0.015}\text{Al}_{1.46}\text{Fe}^{3+}_{0.205})(\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2)$	1.74	-5141.97	-5141.69	0.01
Cd -Exch. Camp Berteaux ¹	$(\text{Cd}_{0.168})(\text{Mg}_{0.32}\text{Fe}^{2+}_{0.015}\text{Al}_{1.46}\text{Fe}^{3+}_{0.205})(\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2)$	1.75	-5147.26	-5146.00	0.02
Zn -exch. Camp Berteaux ¹	$(\text{Zn}_{0.168})(\text{Mg}_{0.32}\text{Fe}^{2+}_{0.015}\text{Al}_{1.46}\text{Fe}^{3+}_{0.205})(\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2)$	1.74	-5159.01	-5159.30	-0.01
Al-exch. Aberdeen ²	$\text{Al}_{0.138}(\text{Mg}_{0.445}\text{Al}_{1.29}\text{Fe}_{0.335}^{3+})(\text{Si}_{3.82}\text{Al}_{0.18}\text{O}_{10}(\text{OH})_2)$	1.35	-5201.73	-5195.46	0.12
Al-exch. Belle Fourche ³	$\text{Al}_{0.088}(\text{Mg}_{0.29}\text{Al}_{1.515}\text{Fe}_{0.225}^{3+})(\text{Si}_{3.935}\text{Al}_{0.065}\text{O}_{10}(\text{OH})_2)$	-1.06	-5213.89	-5199.86	0.27
Le County N ^o 1 ⁴	$(\text{Al}_{0.12}\text{Mg}_{0.045})(\text{Mg}_{0.48}\text{Al}_{1.155}\text{Fe}_{0.435}^{3+})(\text{Si}_{3.825}\text{Al}_{0.175}\text{O}_{10}(\text{OH})_2)$	4.24	-5147.78	-5159.10	-0.22
Le County N ^o 2 ⁴	$(\text{Al}_{0.09}\text{Mg}_{0.105})(\text{Mg}_{0.41}\text{Al}_{1.38}\text{Fe}_{0.215}^{3+})(\text{Si}_{3.915}\text{Al}_{0.085}\text{O}_{10}(\text{OH})_2)$	7.70	-5203.46	-5227.48	-0.46
Clarke County N ^o 4 ⁴	$(\text{Al}_{0.12}\text{Mg}_{0.05})(\text{Mg}_{0.43}\text{Al}_{1.15}\text{Fe}_{0.425}^{3+})(\text{Si}_{3.935}\text{Al}_{0.065}\text{O}_{10}(\text{OH})_2)$	1.14	-5132.24	-5132.33	0.00

¹ Benson (1982); Bruggenwert and Kamphorst (1979).

² Kittrick (1971b).

³ Kittrick (1971a).

⁴ Karathanasis and Hajek (1983).

Table 10. Values of $\Delta_G O^- M^{2+}(o)$ of Li^+ , and transition element ions located in the octahedral site, determined from Equation (24).

Ions	$\Delta_G O^- M^{2+}(aq)$ (kJ/mole)	$\Delta_G O^- M^{2+}(clay)$ (kJ/mole)
$Li^+(o)$	+24.0	-50.71
$Mn^{2+}(o)$	-134.7	-122.9
$Zn^{2+}(o)$	-173.1	-140.3
$Ni^{2+}(o)$	-165.5	-136.8
$Cr^{3+}(o)$	-213.5	-158.6

stituent oxides. Consequently, the determined Gibbs free energies of formation of the clay minerals may be compared with experimental (or calculated) values (Table 5).

Precision of the method of prediction

Figure 2 compares this method with other methods of predicted values (Tardy and Duplay, 1992; Nriagu, 1975; Mattigod and Sposito, 1978; Chermak and Rim-

Table 11. Detailed computation of ΔG°_{ox} of aluminum-exchanged montmorillonite from Aberdeen (Kittrick, 1971b).

¹ Nature of interactions terms	$[\Delta_G O^- M_i^{2+}(clay) - \Delta_G O^- M_j^{2+}(clay)]$ (kJ/mole)		² Interaction energy (kJ/mole)
	12 $X_i X_j$		
Within octahedral site			
$Mg^{2+}(o) - Al^{3+}(o)$	0.072	49.23	-3.53
$Mg^{2+}(o) - Fe^{3+}(o)$	0.019	52.05	-0.97
$Al^{3+}(o) - Fe^{3+}(o)$	0.081	2.82	-0.23
Within tetrahedral site			
$Si^{4+}(t) - Al^{3+}(t)$	0.172	31.22	-5.37
Between octahedral site and hydroxyl			
$Mg^{2+}(o) - H(clay)$	0.037	108.0	-4.01
$Al^{3+}(o) - H(clay)$	0.161	58.77	-9.48
$Fe^{3+}(o) - H(clay)$	0.042	55.95	-2.34
Between octahedral and tetrahedral sites			
$Mg^{2+}(o) - Si^{4+}(t)$	0.283	54.09	-15.32
$Mg^{2+}(o) - Al^{4+}(t)$	0.010	85.31	-0.85
$Al^{3+}(o) - Si^{4+}(t)$	1.232	4.86	-5.99
$Al^{3+}(o) - Al^{3+}(t)$	0.044	36.08	-1.57
$Fe^{3+}(o) - Si^{4+}(t)$	0.320	2.04	-0.65
$Fe^{3+}(o) - Al^{3+}(t)$	0.011	33.26	-0.38
Between interlayer and tetrahedral sites			
$Al^{3+}(l) - Si^{4+}(t)$	0.132	22.88	-3.02
$Al^{3+}(l) - Al^{3+}(t)$	0.005	54.10	-0.25
			$\Delta G^\circ_{ox} (kJ/mole) = -53.96$

¹ l, o, and t denote interlayer, octahedral, and tetrahedral sites, respectively.

² Product of the two first columns, i.e., equal to $-12X_i X_j \{[\Delta_G O^- M_i^{2+}(clay) - \Delta_G O^- M_j^{2+}(clay)]\}$.

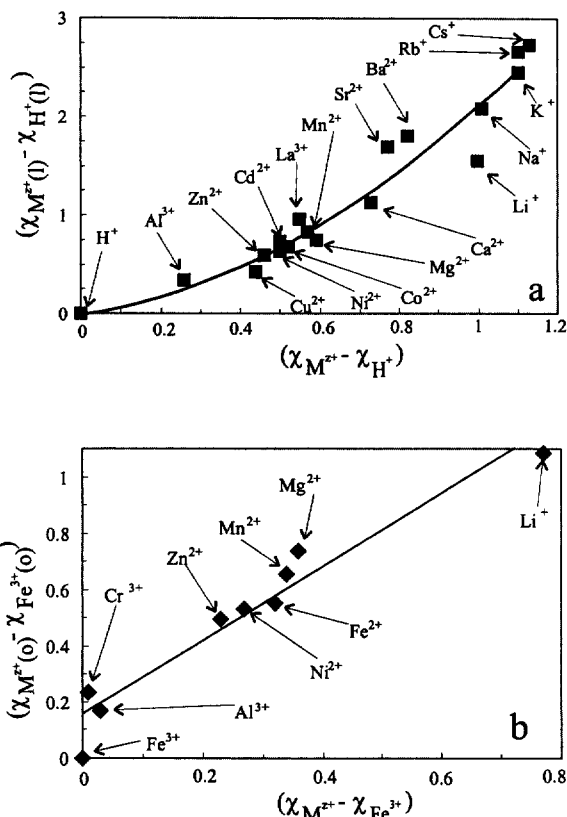


Figure 5. Relationship between predicted difference of electronegativities in clay minerals and theoretical difference of electronegativities (Martynov and Batsanov, 1980): a) $(\chi_{M^{2+}(l)} - \chi_{H^+(l)})$ in interlayer site (this study, vertical axis) versus theoretical values of $(\chi_{M^{2+}} - \chi_{H^+})$ from Martynov and Batsanov (1980); b) $(\chi_{M^{2+}(o)} - \chi_{Fe^{3+}(o)})$ in octahedral site (this study, vertical axis) versus $(\chi_{M^{2+}} - \chi_{Fe^{3+}})$ from Martynov and Batsanov (1980).

stidt, 1989). Figure 2 shows a plot of standard errors of estimation using the model presented here and the average error obtained for each of the four different methods given previously. The horizontal and vertical dashed lines show the $\pm 0.25\%$ error for each model. Data from ten sets of minerals: smectites from different well-known localities [e.g., Clay Spur, Cheto (Huang and Keller, 1973), Belle Fourche, Aberdeen (Kittrick, 1971a), Colony, Castle Rock, Upton (Weaver *et al.*, 1976)]; saponite and vermiculite (Tardy and Fritz, 1981); nontronite, glauconite, and beidellite (Tardy and Fritz, 1981); cation-exchanged montmorillonite [e.g., Camp Berteaux, Chambers, and Bayard (Mattigod and Sposito, 1978)]; idealized clay minerals (Wolery and Daveler, 1992); idealized montmorillonite (Chermak and Rimstidt, 1989); and natural and idealized illites are used for determining the accuracy of prediction.

The method of Tardy and Duplay (1992) shows a greater spread in Figure 2a than those used here; this result is related to the lack of internal consistency of the Gibbs free energies and the model for ideal solid solution used by these authors is apparently too simple.

The method of Nriagu (1975) (Figure 2b) gives moderate prediction errors for the entire range of data ($>0.5\%$) except for idealized nontronite (Wolery and Daveler, 1992) where the error is underestimated. The main reason for these variations is related to the un-

derestimation of Gibbs free energies of formation of some Fe-rich montmorillonite.

All smectites from well-known localities and cation-exchanged montmorillonites are within 0.25% error for the method of Mattigod and Sposito (1978) (Figure 2c). Nontronite, saponite, and beidellite (Tardy and Fritz, 1981), some smectites (Wolery and Daveler, 1992), and natural illites give predicted errors within 0.5–1%. For some idealized clay minerals and idealized illites, the method of prediction shows an error of >1%, indicating either inconsistent Gibbs free energies of formation for these compounds or problems in the computation of the term δ related to the CEC.

The method of Chermak and Rimstidt (1989) (Figure 2d) initially tested on silicate minerals, gives good accuracy to within a 1% limit. Predicted Gibbs free energies of natural nontronite and vermiculite appear slightly overestimated.

Extension to other cations in exchangeable clay minerals

Gibbs free energies of formation of H-, Rb-, Cs-, Sr-, and Ba-exchangeable montmorillonites (Camp Bertaux, Chambers, Wyoming, and Bayard) of Mattigod and Sposito (1978) and those of idealized clay minerals (beidellite, saponite, and nontronite) of Wolery and Daveler (1992) were recalculated with the new set of Gibbs free energies of formation of ions to maintain an internally consistent set of data.

The determination of $\Delta_G O^- M^{z+}$ for these five cations in the interlayer site (Table 6) was performed by minimization of the difference between experimental and calculated Gibbs free energies of formation from the oxides, with the same constraints given below. From values of $\Delta_G O^- M^{z+}$ and values from Tables 1 and 4, Gibbs free energies of formation of alkaline and earth-alkaline exchangeable cations were calculated and the results are in excellent agreement with those by different authors (Table 7).

DISCUSSION

Values of $\Delta_G O^- M^{z+}(\text{clay})$, obtained from minimization (Tables 4 and 6) are greater than $\Delta_G O^- M^{z+}(\text{aq})$; $\Delta_G O^- M^{z+}(\text{clay})$ is higher for cations that are more electropositive. Among values of $\Delta_G O^- M^{z+}(\text{clay})$ corresponding to different sites in the clay mineral, three sets of values are observed corresponding to the interlayer, octahedral, and tetrahedral sites.

Interlayer sites

The relation between $\Delta_G O^- M^{z+}(\text{aq})$ and $\Delta_G O^- M^{z+}(\text{l})$ in the interlayer site for alkaline, earth-alkaline cations, and H⁺ (Figure 3) is:

$$\Delta_G O^- M^{z+}(\text{l}) = 62.493 + 1.31608[\Delta_G O^- M^{z+}(\text{aq})] + 0.001479[\Delta_G O^- M^{z+}(\text{aq})]^2 \quad (23)$$

with a regression coefficient of 0.9909, for ten points

and a standard error of ± 34 kJ/mole. Thus, values of $\Delta_G O^- M^{z+}(\text{l})$ for NH₄⁺, Mn²⁺, Co²⁺, Ni²⁺, Cd²⁺, Zn²⁺, Al³⁺, and La³⁺ located in the interlayer sites can be determined from Equation (23) from known values of $\Delta_G O^- M^{z+}(\text{aq})$ (Table 1), and these values are given in Table 8. With these values of $\Delta_G O^- M^{z+}(\text{clay})$ for exchangeable ions, Gibbs free energies of formation of some various exchangeable cations may be calculated. The results are in excellent agreement with experimental values (Table 9).

For aluminum, $\Delta_G O^- M^{z+}(\text{clay})$ exhibits three values: $\Delta_G O^- \text{Al}^{3+}(\text{l}) = -143.3$ kJ/mole in the interlayer site; $\Delta_G O^- \text{Al}^{3+}(\text{o}) = -161.23$ kJ/mole in the octahedral site, and $\Delta_G O^- \text{Al}^{3+}(\text{t}) = -197.31$ kJ/mole in the tetrahedral site. These differences are related to the different environment of aluminum. The polyhedral volume, defined as the space enclosed by constructing planes through each set of three adjacent coordinating oxygen atoms about aluminum, is very large in interlayer sites, and less so in octahedral sites and in tetrahedral sites. This trend occurs also for magnesium in interlayer and octahedral sites.

Octahedral sites

A relationship between $\Delta_G O^- M^{z+}(\text{o})$ and $\Delta_G O^- M^{z+}(\text{aq})$ is observed for four cations Mg²⁺, Fe²⁺, Al³⁺, and Fe³⁺ (Figure 4):

$$\Delta_G O^- M^{z+}(\text{o}) = -61.618 + 0.454[\Delta_G O^- M^{z+}(\text{aq})] \quad (24)$$

with a regression coefficient of 0.974 for four points and an error of prediction of ± 12.5 kJ/mole. From Equation (24), values of $\Delta_G O^- M^{z+}(\text{o})$ of cations such as Li⁺, Mn²⁺, Ni²⁺, Co²⁺, Zn²⁺ and Cr³⁺ are determined from known values of $\Delta_G O^- M^{z+}(\text{aq})$ (Table 10). These values contribute to the prediction of Gibbs free energies of clay minerals with transition metals and Li located in octahedral sites as in hectorite, saunconite, and stevensite.

Tetrahedral sites

The parameter $\Delta_G O^- \text{Al}^{3+}(\text{t})$ is more negative than $\Delta_G O^- \text{Si}^{4+}(\text{t})$; the difference between the two $\Delta_G O^-$ parameters is always positive with a value of 31.22 kJ/mole. In any clay mineral M₁M₆(Si_(4-y)Al_y)O₁₀(OH)₂, an interaction term between Al³⁺(t) and Si⁴⁺(t) appears in the general equation of Gibbs free energies from constituent oxides [Equation (13)]:

$$\left[\frac{2(4-y)}{12} \right] \left[\frac{1.5y}{12} \right] [\Delta_G O^- \text{Si}^{4+}(\text{clay}) - \Delta_G O^- \text{Al}^{3+}(\text{t})] \quad (25)$$

where $2(4-y)/12$ and $1.5y/12$ are the molar fraction of oxygen atoms related to Si⁴⁺(t) and Al³⁺(t) in SiO₂ and Al₂O₃, respectively. This intrasite interaction term is the supplementary energy in the Gibbs free energy of formation from constituent oxides. This supplement-

tary energy indicates that substitution of silicon by aluminum ($\text{Si}_{(4-y)}\text{Al}_y$) makes the Gibbs energies of formation from constituent oxides more negative than those of clay minerals without substitutions in the tetrahedral site (Si_4).

Thus, the prediction of $\Delta_{\text{G}}\text{O}^- \text{Fe}^{3+}(\text{t})$ in tetrahedral sites is currently not possible because of the imprecise knowledge of $\Delta_{\text{G}}\text{O}^- \text{Si}^{4+}(\text{aq})$ which varies from -191.4 to -187.4 kJ/mole (Tardy and Garrels, 1977; Gartner, 1979). The evaluation of $\Delta_{\text{G}}\text{O}^- \text{Fe}^{3+}(\text{t})$ can be provided from Gibbs free energies of formation of Fe-bearing clay minerals with Fe^{3+} in the tetrahedral position, but these data are not available.

Electronegativity scale

From Equation (17), the values of $\Delta_{\text{G}}\text{O}^- \text{M}^{z+}(\text{l})$ for the interlayer sites (Tables 4, 6, and 8) exhibit an electronegative scale based on the following difference:

$$(\chi_{\text{M}^{z+}(\text{l})} - \chi_{\text{H}^+(\text{l})}) \\ = \{[\Delta_{\text{G}}\text{O}^- \text{M}_i^{z+}(\text{l}) - \Delta_{\text{G}}\text{O}^- \text{H}^+(\text{l})]/96.483\}^{1/2} \quad (26)$$

where the most electronegative ion, $\text{H}^+(\text{l})$, represents the proton (*i.e.*, H_3O^+) in the interlayer site. The values of $(\chi_{\text{M}^{z+}(\text{l})} - \chi_{\text{H}^+(\text{l})})$ for the interlayer site (Figure 5a) show a greater scale than those of Martinov and Batsanov (1980) because of the presence of H_2O molecules around the cations.

Similarly, in octahedral sites, where Fe^{3+} is the most electronegative cation, the values of $(\chi_{\text{M}^{z+}(\text{o})} - \chi_{\text{Fe}^{3+}(\text{o})})$ are calculated from the values of $\Delta_{\text{G}}\text{O}^- \text{M}^{z+}(\text{o})$ (Tables 4 and 10) by the following difference:

$$(\chi_{\text{M}^{z+}(\text{o})} - \chi_{\text{Fe}^{3+}(\text{o})}) \\ = \{[\Delta_{\text{G}}\text{O}^- \text{M}_i^{z+}(\text{o}) - \Delta_{\text{G}}\text{O}^- \text{Fe}^{3+}(\text{o})]/96.483\}^{1/2}. \quad (27)$$

The values of $(\chi_{\text{M}^{z+}(\text{o})} - \chi_{\text{Fe}^{3+}(\text{o})})$ for the octahedral coordination (Figure 5b) exhibit a similar scale as that found by Martinov and Batsanov (1980), indicating weak differences within the octahedral sites.

Example of calculation of Gibbs free energies of two different clay minerals

An aluminum-exchanged clay from Aberdeen was chosen, because the solubility product was determined by Kittrick (1971b). The chemical formula is: $\text{Al}_{0.138}(\text{Mg}_{0.445}\text{Al}_{1.29}\text{Fe}_{0.335}^{3+})(\text{Si}_{3.82}\text{Al}_{0.18})\text{O}_{10}(\text{OH})_2$ and it has aluminum located in three sites. The effective number of interaction energy terms between two cations is known from the numbers of different cations occupying the three sites: $n = 1$, $n_o = 3$, and $n_t = 2$ [Equations (21) and (22)]. Thus, the Gibbs free energy of formation from constituent oxides will contain 15 effective interaction terms: four intrasite terms and 11 intersite terms. Details of computation are given in Table 11. The calculated Gibbs free energy of formation

from constituent oxides is -53.96 kJ/mole. The Gibbs free energies of formation from elements is $\Delta G_f^\circ = -5195.45$ kJ/mole, a value very close to the experimental value of -5201.7 kJ/mole as calculated from the solubility product.

Ni-rich stevensite, $\text{Na}_{0.2}\text{Ni}_{2.9}\text{Si}_4\text{O}_{10}(\text{OH})_2$, synthesized by Decarreau (1983) has a measured solubility and thus can be used as a test case also. From its chemical composition, the Gibbs free energy of formation from constituent oxides has three effective intersite terms:

$$\Delta G_{\text{ox}}^\circ = -\frac{0.1 \times 8}{12}[\Delta_{\text{G}}\text{O}^- \text{Na}^+(\text{l}) - \Delta_{\text{G}}\text{O}^- \text{Si}^{4+}(\text{clay})] \\ - \frac{2.9 \times 1}{12}[\Delta_{\text{G}}\text{O}^- \text{Ni}^{2+}(\text{o}) - \Delta_{\text{G}}\text{O}^- \text{H}^+(\text{clay})] \\ - \frac{2.9 \times 8}{12}[\Delta_{\text{G}}\text{O}^- \text{Ni}^{2+}(\text{o}) - \Delta_{\text{G}}\text{O}^- \text{Si}^{4+}(\text{clay})]. \quad (28)$$

With the predicted value of $\Delta_{\text{G}}\text{O}^- \text{Ni}^{2+}$ in the octahedral site (Table 10), Equation (29) gives $\Delta G_{\text{ox}}^\circ = -105.6$ kJ/mole and the Gibbs free energy of formation from elements is $\Delta G_f^\circ = -4400.6$ kJ/mole, a value very close to the experimental, -4406.84 kJ/mole, as calculated from the solubility product.

CONCLUSIONS

Note that Gibbs free energies of clay minerals are obtained mostly from experimental measurements. Thus, errors of ΔG_f° are related to time of contact, temperature, ionic strength, and pH. Also, assumptions of equilibrium or non-equilibrium are very approximate and must be considered carefully. This work shows that a model based on the prediction of Gibbs free energies of formation from $\Delta_{\text{G}}\text{O}^- \text{M}^{z+}(\text{clay})$, a parameter assumed to be constant within three sites of a clay mineral, can give very good results if the formalism of the Gibbs free energy of formation from constituent oxides uses an approach from short-range interactions.

For a model involving long-range interactions, the constancy of $\Delta_{\text{G}}\text{O}^- \text{M}^{z+}$ for cations in different sites is questionable and accurate results depend on the environment around the cations and on the degree of hydration, with the latter being different depending on the type of interlayer cation.

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