A method of estimating the Gibbs free energies of formation of hydrated and dehydrated clay minerals

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Abstract—Clay minerals are commonly hydrated, and water molecules are attached in two different interlayer and interparticle hydration sites. Both sites contribute to the hydration energy involved when a dry clay aggregate is placed in contact with water or when a wet and swollen aggregate is placed in a dry atmosphere. The amounts of adsorbed water, and the hydration energy as well, vary as functions of the activity of water in which particle aggregates are placed. Integration of dehydration isotherms, established for different samples of various compositions of clay minerals, was used to evaluate the Gibbs free energies of hydration at different hydration stages, i.e., from the water-saturated phases to the dry states.

The proposed model of estimating Gibbs free energies is based on the following steps and assumptions:

(1) Hydrated and dehydrated clay minerals are ideal solid solutions, as presented by TARDY and FRITZ (1981);

(2) In each of the series of phyllosilicates (talc, mica, and celadonites), hydrated, dehydrated, and well-crystallized Gibbs free energies of formation from the oxides are linearly dependent on the parameters $\Delta O_{M^{z+}}^{2-}$ related to the electronegativity of the cation M^{z+} in the octahedral position;

(3) In each of the mineral series, hydration energies are proportional to the layer charge; and

(4) In each of the mineral series of the same charge and same interlayer cation, the hydration energy is also proportional to $\Delta O_{M^{z+}}^{2-}$.

The principal results of the model are (1) poorly crystallized but hydrated clay minerals of a given chemical composition; (2) poorly crystallized, dehydrated clay minerals; and (3) dry, largely sized, well-crystallized phyllosilicates of the same chemical composition, all of which differ largely in their Gibbs free energies of formation and in their stability fields in natural conditions. Furthermore, the solubility products and the corresponding cation exchange constants of these minerals are dependent on the activity of water in which the equilibrium reactions take place. These parameters also depend on the tetrahedral, octahedral, or total interlayer charge, and finally on the nature of the cation located in the octahedral layer (i.e., Mg^{2+}, Fe^{2+}, Al^{3+}, or Fe^{3+}). It is also proposed that for a given interlayer cation (Li^+, Na^+, K^+, Mg^{2+}, or Ca^{2+}) and for a given octahedral composition (Mg^{2+}, Fe^{2+}, Al^{3+}, or Fe^{3+}), the hydration energy generally increases with the layer charge so that most of the minerals of high charge are hydrophylic and should hydrate spontaneously in water. However, the hydration energy of K^+-exchanged nontronites (Fe^{3+}) and beidellites (Al^{3+}), both dioctahedral, decreases with the layer charge so that illite and glauconite, muscovite, and ferrimuscovite presumably appear as hydrophobic and should not hydrate spontaneously when placed in contact with water.
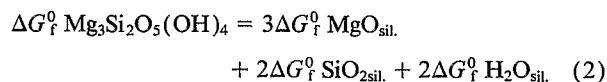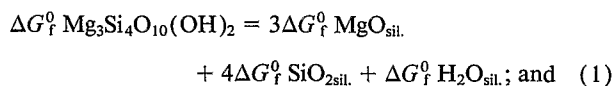
INTRODUCTION

KNOWLEDGE OF THE HYDRATION states of clay minerals such as smectites, vermiculites, illites, and celadonites is an important step towards the understanding of the conditions of smectites transformation into illites and towards the prediction of the behavior of such minerals when they are placed in various environments differing by temperature, pressure, and fluid chemistry (POWERS, 1967; BURST, 1969; PERRY and HOWER, 1972; COLTEN-BRADLEY, 1987). In this paper, attention is drawn to the important shift of solubility products induced by changes of activity of water and on the important

differences in Gibbs free energies that occur between hydrated clay minerals and their corresponding dry states.

In the literature, most of the data available on well-crystallized and large grain size phyllosilicates refer to their dry states (see, for example, HELGESON et al., 1978). On the other hand, most of the data available for poorly crystallized or small grain size phyllosilicates (i.e., clay minerals) are derived directly or indirectly from solubility measurements. These latter data are of the fully hydrated states of the minerals even if H_2O is not currently taken into consideration when equilibrium reactions are written (see TARDY et al., 1987, for the review of Gibbs free energies of formation and of

solubility products of clay minerals). This procedure is justified if the calculations refer to equilibria in dilute conditions and in large amounts of water, at the atmospheric pressure (1 bar); therefore, the activity of water can be assumed to be equal to one. However, this assumption is not always true, especially in soils, brines, or capillaries of compacted clay materials in which water activity can be considered as different from one. Consequently, water amounts have to be taken into consideration both in equilibrium reactions, and water activity has to be considered in thermodynamic calculations.

About fifteen years ago, we published in *Geochimica et Cosmochimica Acta,* together with Robert M. Garrels, our method of estimating the Gibbs energies of formation of layer silicates (TARDY and GARRELS, 1974). Its major purpose was to find appropriate values for 2:1 clay minerals which exhibit a large variety of chemical compositions of tetrahedral, octahedral, and interlayer occupations, and of distribution of the layer charge. Our method was based on a very simple statement. The Gibbs free energy of formation from the elements of a given layer silicate is estimated as equal to the sum of the Gibbs free energy of formation from the elements of its constituent "silicated oxides" such as for talc or chrysotile:

$$\Delta G_f^0 \ Mg_3Si_4O_{10}(OH)_2 = 3\Delta G_f^0 \ MgO_{sil.}$$
$$+ 4\Delta G_f^0 \ SiO_{2sil.} + \Delta G_f^0 \ H_2O_{sil.}; \text{ and} \quad (1)$$
$$\Delta G_f^0 \ Mg_3Si_2O_5(OH)_4 = 3\Delta G_f^0 \ MgO_{sil.}$$
$$+ 2\Delta G_f^0 \ SiO_{2sil.} + 2\Delta G_f^0 \ H_2O_{sil.} \quad (2)$$

ΔG_f^0 of a given silicated oxide is determined and is the same for all layer silicates considered. The Gibbs free energy of silication of each of the silicated oxides was found to be proportional to the corresponding cation electronegativity: The higher the electronegativity, the larger (less negative) the Gibbs free energy of silicatation of the free oxides.

Despite its simplicity, our paper has achieved a large success. However, most of the critics and users have considered the methodological viewpoint for estimating Gibbs free energies and not the other side of the conclusions which involves the necessary changes of solubility and natural stability of clay minerals as a function of their chemical composition. Taken as an example, the solubility is smaller; and the natural stability field is larger for a nontronite (Fe^{3+}-dioctahedral smectite) than for a beidellite (Al^{3+}-dioctahedral smectite) than for a ferrous saponite (Fe^{2+}-trioctahedral smectite) than for a saponite (Mg^{2+}-trioctahedral smectite) of the same tetrahedral charge and the same interlayer occupation. The larger the stability field, the lower the solubility product.

The initial principle of estimation as presented by TARDY and GARRELS (1974) was substantially revised in two further papers (TARDY and GARRELS, 1976, 1977). The new method is based on the fact that within a family of compounds (i.e., metasilicates, orthosilicates, etc.), Gibbs free energies of formation of compounds from their constituent oxides are linearly dependent on a parameter called $\Delta O_{M^{z+}}^{2-}$, which is a function of the electronegativity of the constituent cations (M^{z+}).

The new method of estimation, which has been applied to a large number of mineral families, is applied here to present internally consistent data sets concerning several kinds of phyllosilicates.

GARRELS and TARDY (1982) have presented leg diagrams characterizing Born-Haber cycles for different cations and have proposed a method to calculate the energies required to move cations from the dry interlayers of micas into hydrated interlayer spaces of clay minerals. Furthermore, differences in the hydration energy separating different interlayer cations have been established so that it could be demonstrated that cation exchange constants measured in solutions where the activity of water is equal to 1 ($a_w = 1$) change considerably when the activity of water decreases ($a_w < 1$) and especially when clay layers are dry. Let us consider a phyllosilicate framework written as X-characterized by a layer charge of 1 and saturated by a cation either by 1.0 Na^+ or by 0.5 Ca^{2+}, each of these being hydrated respectively with n_1 or n_2 moles of hydration water. The Na-Ca cation exchange reaction may be written as follows:

$$Na\text{-}X \cdot n_1H_2O + 0.5Ca_{(aq)}^{2+}$$
$$= Ca_{0.5}\text{-}X \cdot n_2H_2O + Na_{(aq)}^+ + (n_1 - n_2)H_2O. \quad (3)$$
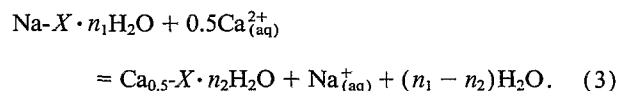
The corresponding expression of the mass action law is written as follows:

$$K_{ex} = [Na_{(aq)}^+] \cdot [Ca_{0.5}\text{-}X \cdot n_2H_2O] \cdot [H_2O]^{(n_1-n_2)}/$$
$$[Ca_{(aq)}^{2+}]^{0.5} \cdot [Na\text{-}X \cdot n_1H_2O], \quad (4)$$

in which K_{ex} is the thermodynamic exchange constant; and terms between brackets are the activity of ions, the activity of water, and the activities of hydrated phases. In natural conditions such as in brines or capillaries, water activity is generally smaller than 1. Consequently, the term $[H_2O]^{(n_1-n_2)}$ must not be neglected nor the fact that n_1 and n_2 may also vary as a function of water activity itself. Therefore, the thermodynamic treatment of these types of reactions requires a precise knowledge of the Gibbs free energies of formation of the dry phases as well as their hydrated counterparts. Furthermore, the number of water molecules attached to the dry phase should also be known.

In addition, TARDY and TOURET (1987) have demonstrated that changes in cation exchange selectivities as a function of water activity are strongly dependent on the nature of the layer in which the exchange takes place. In other words, the solubility products of hydrated clay minerals, solubility products of dehydrated clay minerals, and Gibbs free energies of hydration are all functions of the chemical composition of the layer involved, i.e., tetrahedral, octahedral, and interlayer occupation.

A compilation of data available in the literature as well as results of recent clay dehydration experiments (TOURET, 1988) permit the presentation of a complete set of evaluated solubility products and Gibbs free energies of formation for (1) poorly crystallized, hydrated clay minerals and (2) for poorly crystallized, dehydrated clay minerals; and permit the

comparison of these results with those for (3) well-crystallized, dehydrated phyllosilicates.

LINEAR RELATIONSHIPS BETWEEN GIBBS FREE ENERGY OF FORMATION FROM OXIDES AND CATION ELECTRONEGATIVITY

The chemical composition of a great number of 2:1 clay minerals including smectites, vermiculites, illites, etc., can be described in terms of ideal mixtures of forty-four components, including the following:

1) four uncharged phyllosilicates in the series talc-pyrophyllite (Mg_3^{2+}, Fe_3^{2+}, Al_2^{3+}, Fe_2^{3+}) $Si_4O_{10}(OH)_2$;

2) four tetrahedrally charged K^+-micas in the series phlogopite-muscovite K^+-(Mg_3^{2+}, Fe_3^{2+}, Al_2^{3+}, Fe_2^{3+}) $AlSi_3O_{10}(OH)_2$; and

3) four octahedrally charged K^+-micas in the celadonite series K^+-($Mg_{2.5}^{2+}$, $Fe_{2.5}^{2+}$, $Al_{1.667}^{3+}$, $Fe_{1.667}^{3+}$) $Si_4O_{10}(OH)_2$.

Furthermore, K^+-ions in interlayers can be replaced by Li^+, Na^+, $Mg_{0.5}^{2+}$, or $Ca_{0.5}^{2+}$ within the dehydrated series of vermiculites (TARDY and FRITZ, 1981; FRITZ, 1985).

In natural conditions, these minerals may be hydrated or dehydrated and well crystallized or poorly crystallized so that the number of Gibbs free energy values required to describe the stability of the systems is almost infinite. Furthermore, most of the values required have to be estimated from a relatively small number of data experimentally determined.

In their original method for the estimation of the Gibbs free energy of formation of phyllosilicates, TARDY and GARRELS (1974) used an empirical relationship derived by plotting the difference between the Gibbs free energy of formation from the elements of various oxides within silicate structures (ΔG_f^0 sil.), and the Gibbs free energy of formation from the elements of oxides as free phases, against the electronegativity of cations. However, electronegativities (GORDY and THOMAS, 1956; PAULING, 1960) used at that time do not appear to be accurate enough to make reliable estimations of the Gibbs free energy. As a result, electronegativities are replaced by a new parameter termed $\Delta O_{M^{z+}}^{2-}$ which is related to electronegativity but more precisely determined.

In fact, TARDY and GARRELS (1976, 1977) and TARDY (1978) have shown that for a series of compounds of a same formula type such as $MSiO_3$, M_2SiO_4, etc., the parameter ΔG_f^0 ox is equal to the Gibbs free energy of formation of each compound from its constituent free oxides and appears to be proportional to the parameter $\Delta O_{M^{z+}}^{2-}$ which characterizes each cation M^{z+}. The parameter $\Delta O_{M^{z+}}^{2-}$ is defined (TARDY and GARRELS, 1976) as

$$\Delta O_{M^{z+}}^{2-} = (1/x)[\Delta G_f^0 \, MO_{x(c)} - \Delta G_f^0 \, M_{(aq)}^{z+}] \text{ (kJ/mol)},$$
(5)

where z is the charge of the cation M^{z+} ($x = z/2$), MO_x is the corresponding oxide, and $M_{(aq)}^{z+}$ stands for the cation in the aqueous state.

Subsequently, VIEILLARD and TARDY (1988a,b, 1989) have shown that the parameter $\Delta O_{M^{z+}}^{2-}$ is a parabolic function of χ_M, the electronegativity of the cation M^{z+} (of PAULING,

1960) in the considered crystal structure. For two cations $M1^{z1+}$ and $M2^{z2+}$, the difference between the two ΔO^{2-} parameters is equal to the square of the difference of the two electronegativities:

$$(\Delta O_{M1^{z1+}}^{2-} - \Delta O_{M2^{z2+}}^{2-}) = (\chi_{M1^{z1+}} - \chi_{M2^{z2+}})^2. \quad (6)$$

Henceforth, the parameter $\Delta O_{M^{z+}}^{2-}$ will be considered as strictly related to the electronegativity of cations and will be used as a good tool for establishing sets of internally consistent Gibbs free energies for the estimation of the unknown Gibbs free energies of formation of minerals and Gibbs free energies of hydration as shown further ahead.

The first series of data (Table 1) lists the Gibbs free energies of formation, from the elements, of aqueous ions and oxides that constitute the common phyllosilicates and corresponding values of the parameters $\Delta O_{M^{z+}}^{2-}$ for each cation.

The reference oxide for structural water is taken as H_2O metastable ice ($\Delta G_{f \, ice}^0 = -223.8$ kJ/mol, at 298.15 K; ROBIE and WALDBAUM, 1968). Other sources are from ROBIE et al. (1978) and WAGMAN et al. (1982).

In Table 2 (column 3) the solubility products of well-crystallized phyllosilicates calculated by FRITZ (1981) and selected by HELGESON et al. (1978) for micas and other minerals in the series talc-pyrophyllite are given. For the well-crystallized and dehydrated phyllosilicates (starred values of Table 2), the Gibbs free energies of formation from the oxides were recalculated in order to fit the $\Delta O_{M^{z+}}^{2-}$ linear relationship of TARDY and GARRELS (1976, 1977) as shown on Figs. 1, 2, and 3.

SOLID SOLUTIONS

Chemical compositions for 2:1 phyllosilicates such as smectites, vermiculites, micas, and celadonites can be described by four uncharged mineral species in the talc-pyrophyllite series, four fully charged mineral species saturated by K^+ in the series of celadonites, and four fully charged mineral species saturated by K^+ in the series of micas. Besides K^+, interlayers can be occupied by Li^+, Na^+, Mg^{2+}, or Ca^{2+}.

Any kind of clay mineral in the series of smectites (low charge), vermiculites (high charge), illites, micas (high tetrahedral charge), and celadonites (high octahedral charge) can be considered as a mixture of these different components.

Several models for estimating Gibbs free energies of formation of complex clay minerals from simple components were proposed. TRUESDELL and CHRIST (1968) and STOESSEL (1979, 1981) adopted a regular solid-solution model to calculate the thermodynamic consequences of compositional variations in montmorillonites and illites. HELGESON and MACKENZIE (1970) have adopted an ideal solid-solution model, while AAGAARD and HELGESON (1983) proposed an ideal mixing of atoms on homological sites in montmorillonites and illites. All these models have been applied to a rather small number of endmembers (or mineral components) and fail somewhat to simulate the observations (MERINO and RANSOM, 1982).

In contrast, TARDY and FRITZ (1981) proposed an ideal multicomponent mixing model which simulates the vari-

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TABLE 1. Gibbs free energies of formation (ΔG_f^0, kJ/mol) of aqueous ions and oxides, as well as corresponding values for the parameter $\Delta O_{M^{z+}}^{2-} = (1/x)[\Delta G_f^0\ MO_x - \Delta G_f^0\ M^{z+}(aq)]$, determined by TARDY and GARRELS (1976, 1977).

Ions and oxides	ΔG_f^0 (kJ/mol)	References	Ions and oxides	ΔG_f^0 (kJ/mol)	References
Al^{3+}	– 489.4	(1)	Li^+	– 293.3	(1)
Al_2O_3 (corundum)	– 1582.2	(1)	Li_2O	– 561.2	(1)
$\Delta O_{Al^{3+}}^{2-}$	– 201.13		$\Delta O_{Li^+}^{2-}$	+ 25.4	(1)
Ca^{2+}	– 553.6	(2)	Mg^{2+}	– 454.8	(1)
CaO (lime)	– 604.0	(2)	MgO (periclase)	– 569.2	(1)
$\Delta O_{Ca^{2+}}^{2-}$	– 50.4		$\Delta O_{Mg^{2+}}^{2-}$	– 114.4	(1)
H^+	0	(1)	K^+	– 282.5	(1)
$H_2O_{(c)}$ (metastable ice)	– 223.8	(3)	K_2O	– 322.1	(1)
$H_2O_{(l)}$ (liquid water)	– 237.1	(1)	$\Delta O_{K^+}^{2-}$	+ 242.9	(1)
$\Delta O_{H^+}^{2-}$	– 223.8				
Fe^{2+}	– 78.9	(1)	$SiO_{2(aq)}$	– 833.8	(1)
FeO (stoichiometric)	– 251.2	(1)	$SiO_{2(c)}$ (quartz)	– 856.3	(1)
$\Delta O_{Fe^{2+}}^{2-}$	– 172.3		$\Delta O_{Si^{4+}}^{2-}$		
Fe^{3+}	– 4.7	(2)	Na^+	– 261.9	(1)
Fe_2O_3 (hematite)	– 742.2	(2)	Na_2O	– 376.1	(1)
$\Delta O_{Fe^{3+}}^{2-}$	– 244.27	(2)	$\Delta O_{Na^+}^{2-}$	+ 147.7	(1)

(1) ROBIE et al. (1978)

(2) WAGMAN et al. (1982)

(3) ROBIE and WALDBAUM (1968)

ability of clay mineral compositions as they appear in natural conditions. In this model, it is supposed that the endmembers mix ideally so that the Gibbs free energy of any kind of phyllosilicate can be easily calculated from the data set of the forty-four mineral components.

As shown by TARDY et al. (1987), stability fields of hydrated natural clay minerals are primarily dependent on their chemical composition. In general, Mg^{2+}-trioctahedral minerals are the most soluble, while Fe^{3+}-dioctahedral phases are the least soluble species. Solubility products in each series decrease from Mg^{2+}, Fe^{2+}, and Al^{3+} to Fe^{3+} minerals such as talc, minnesotaite, pyrophyllite, and ferripyrophyllite in a series of uncharged minerals, or saponite, beidellite, and nontronite in a series of poorly charged minerals for example.

This model of multicomponent ideal solid solution was used (1) to evaluate the Gibbs free energies of formation of hydrated and poorly crystallized clay minerals endmembers,

presented by TARDY et al. (1987) and shown in the next paragraph, as well as (2) to calculate the contribution of each of these different endmembers in the hydration energies measured for clay minerals listed in Table 5.

ESTIMATION OF GIBBS FREE ENERGIES OF FORMATION OF HYDRATED CLAY MINERALS

Clay minerals in common natural conditions are hydrated, poorly crystallized, and of small size. Their Gibbs free energies of formation differ substantially from those of nonhydrated and well-crystallized phyllosilicates of the same chemical composition.

A Set of Measured Values

TARDY and GARRELS (1974), CHEN (1975), NRIAGU (1975), MATTIGOD and SPOSITO (1978), STOESSEL (1979,

TABLE 2. Data for well-crystallized phyllosilicates: (1) Gibbs free energies of formation from the elements (ΔG^0_f, kJ/mol), (2) Gibbs free energies of formation from the constituent oxides (ΔG^0_f ox, kJ/mol), and (3) Solubility products (log K_{sp}). Data are from HELGESON et al. (1978) and FRITZ (1981). Starred values (∗) are estimated by the method of TARDY and GARRELS (1974) and readjusted by the ΔO^{2-} method of TARDY and GARRELS (1976, 1977) and of TARDY (1982) (see Fig. 1).

	$\Delta G°_f$	$\Delta G°_f(ox)$	log K_{sp}
$Mg_3\,Si_4\,O_{10}(OH)_2$	− 5524.9	− 168.3	21.6
$Fe_3\,Si_4\,O_{10}(OH)_2$	− 4479.0	− 76.4	7.2
$Al_2\,Si_4\,O_{10}(OH)_2$	− 5256.3	− 25.1	1.1
$Fe_2\,Si_4\,O_{10}(OH)_2$	− 4348.7∗	+ 42.5∗	− 9.8
$K\,Mg_3\,Al\,Si_3\,O_{10}(OH)_2$	− 5842.1	− 389.7	38.2
$K\,Fe_3\,Al\,Si_3\,O_{10}(OH)_2$	− 4800.3	− 301.9	23.2
$K\,Al_2\,Al\,Si_3\,O_{10}(OH)_2$	− 5591.6	− 264.5	14.6
$K\,Fe_2\,Al\,Si_3\,O_{10}(OH)_2$	− 4685.5∗	− 198.5∗	3.5∗
$K\,Mg_{2.5}\,Si_4\,O_{10}(OH)_2$	− 5569.0∗	− 336.0∗	23.5∗
$K\,Fe_{2.5}\,Si_4\,O_{10}(OH)_2$	− 4699.0∗	− 261.0∗	11.3∗
$K\,Al_{1.667}\,Si_4\,O_{10}(OH)_2$	− 5353.0∗	− 225.0∗	5.0∗
$K\,Fe_{1.667}\,Si_4\,O_{10}(OH)_2$	− 4595.3∗	− 167.0∗	− 3.7∗

∗ Estimated

1981), AAGAARD and HELGESON (1983), and SPOSITO (1986) have described methods for estimating the Gibbs free energies of formation of clay minerals. Some recent solubility measurements have been made by MAY et al. (1986); while TARDY and FRITZ (1981), FRITZ (1981), TARDY (1982), TARDY et al. (1987), and DUPLAY (1988) have attempted to improve solubility product values by testing their ability, through computer equilibrium simulations to reproduce
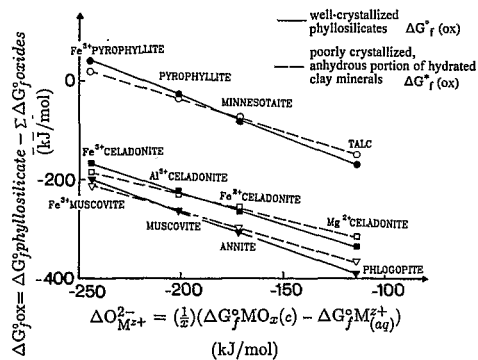

FIG. 1. Linear relationships between ΔG^0_f ox (kJ/mol) (Gibbs free energy of formation from the oxides) and $\Delta O^{2-}_{M^{z+}}$ (kJ/mol) characterizing the electronegativity of the cation M^{z+} (Mg^{2+}, Fe^{2+}, Al^{3+}, or Fe^{3+}) located in octahedral position for (1) well-crystallized, dehydrated phyllosilicates (ΔG^0_f ox) and (2) dehydrated portion of poorly crystallized and fully hydrated corresponding clay minerals ΔG^*_f ox (hyd.) in the different families of talc-Fe^{3+}-pyrophyllite, Mg^{2+}-celadonite-Fe^{3+}-celadonite, and phlogopite-Fe^{3+}-muscovite.
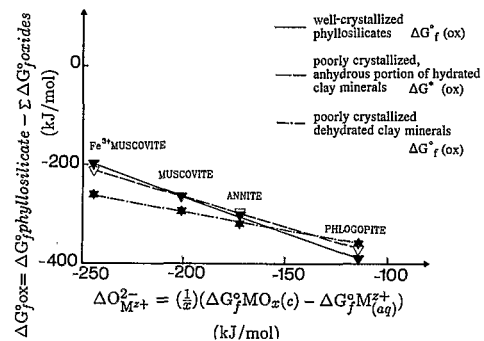

FIG. 2. Linear relationships between ΔG^0_f ox (kJ/mol) (Gibbs free energy of formation from the oxides) and $\Delta O^{2-}_{M^{z+}}$ (kJ/mol) characterizing the electronegativity of the cation M^{z+} (Mg^{2+}, Fe^{2+}, Al^{3+}, and Fe^{3+}) located in octahedral position for (1) well-crystallized phyllosilicates; (2) dehydrated portion of poorly crystallized, small, and fully hydrated clay minerals (ΔG^*_f ox); and (3) poorly crystallized, small, dehydrated clay minerals in the series of micas: phlogopite, annite, muscovite, and Fe^{3+}-muscovite.
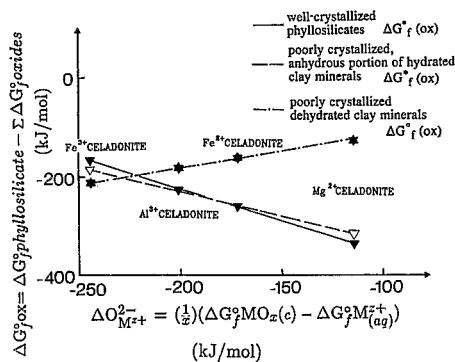
FIG. 3. Linear relationships between ΔG_f^0 ox (kJ/mol) (Gibbs free energy of formation from the oxides) and $\Delta O_{M^{z+}}^{2-}$ (kJ/mol) characterizing the electronegativity of the cation M^{z+} (Mg^{2+}, Fe^{2+}, Al^{3+}, and Fe^{3+}) located in octahedral position for (1) well-crystallized phyllosilicates (ΔG_f^0 ox); (2) poorly crystallized, small, hydrated clay minerals (ΔG_f^* ox); and (3) poorly crystallized, small, dehydrated clay minerals (ΔG_f^0 ox) in the series of celadonites.

closely various situations observed in natural weathering, sedimentation, diagenesis, and hydrothermal processes. The latter might be considered as the most reliable data set available at the moment.

Table 3 gives, respectively, the Gibbs free energies of formation from the elements (ΔG_f^*, column 1) and from the oxides (ΔG_f^* ox, column 3), and the solubility product (log K_{sp}, column 5) of four uncharged and eight K^+-exchanged poorly crystallized, fully hydrated clay minerals. In the first set (columns 1, 3, and 5, respectively), values are from TARDY et al. (1987). They are called measured values.

A Set of Idealized Values of K^+-exchanged Clay Minerals

As demonstrated by TARDY and FRITZ (1981), for phyllosilicates in the talc-pyrophyllite and phlogopite-muscovite series, ΔG_f^0 ox (phyllosilicates) are precisely and linearly correlated to the parameter $\Delta O_{M^{z+}}^{2-}$, which characterizes the cations Mg^{2+}, Fe^{2+}, Al^{3+}, and Fe^{3+}.

TABLE 3. Data for poorly crystallized and hydrated clay minerals: (1) and (2), Gibbs free energies of formation from the elements, (ΔG_f^*, kJ/mol); (3) and (4), Gibbs free energies of formation from the constituent oxides (ΔG_f^* ox, kJ/mol); and (5) and (6), solubility products (log K_{sp}). Values listed in columns (1), (3), and (5) (●) are those of TARDY et al. (1987). Values listed in columns (2), (4), and (6) (●●) are adjusted to fit the ΔG_f^0 ox $- \Delta O^{2-}$ linear relationship of TARDY and GARRELS (1976, 1977).

	ΔG_f°		$\Delta G_{f(ox)}^*$		log K_{sp}	
	(1) ●	(2) ●●	(3) ●	(4) ●●	(5) ●	(6) ●●
$Mg_3 Si_4 O_{10}(OH)_2$	− 5504.4	− 5504.4	− 147.8	− 147.8	25.16	25.16
$Fe_3 Si_4 O_{10}(OH)_2$	− 4479.0	− 4475.6	− 76.4	− 73.0	7.24	7.83
$Al_2 Si_4 O_{10}(OH)_2$	− 5256.7	− 5267.2	− 25.5	− 36.0	1.00	− 0.84
$Fe_2 Si_4 O_{10}(OH)_2$	− 4371.2	− 4371.2	+ 20.0	+ 20.0	− 13.70	− 13.70
$K Mg_3 Al Si_3 O_{10}(OH)_2$	− 5821.1	− 5821.1	− 368.7	− 368.7	41.91	41.91
$K Fe_3 Al Si_3 d_{10}(OH)_2$	− 4799.8	− 4797.5	− 301.4	− 299.1	23.27	23.67
$K Al_2 Al Si_3 O_{10}(OH)_2$	− 5579.6	− 5591.1	− 252.6	− 264.1	16.66	14.65
$K Fe_2 Al Si_3 O_{10}(OH)_2$	− 4699.1	− 4699.1	− 212.1	− 212.1	1.09	1.09
$K Mg_{2.5} Si_4 O_{10}(OH)_2$	− 5549.4	− 5549.4	− 316.4	− 316.4	26.93	26.93
$K Fe_{2.5} Si_4 O_{10}(OH)_2$	− 4696.3	− 4696.0	− 258.3	− 258.0	11.75	11.80
$K Al_{1.667} Si_4 O_{10}(OH)_2$	− 5345.2	− 5357.2	− 217.2	− 229.2	6.35	4.25
$K Fe_{1.667} Si_4 O_{10}(OH)_2$	− 4613.7	− 4613.9	− 185.4	− 185.6	− 6.97	− 7.00

Note : ΔG^*f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text) ; for talc, pyrophyllite and other uncharged minerals $\Delta G^*f = \Delta G^\circ f$

TABLE 4. Exchange constants; difference in Gibbs free energies of exchange [ΔG^* M-K(hyd.) = ΔG_f^* K-X(hyd.) − ΔG_f^* M-X(hyd.)], according to Eqn. (44); and Gibbs free energy of cation exchange from TARDY and GARRELS (1974) and GARRELS and TARDY (1982).

logK exchange	Difference ΔG^* M-K(hyd.)	ΔG° exchange
log[Na$^+$]/[K$^+$] = 0.8	ΔG^*(Na-K) = −25.2 kJ/mol	−4.566 kJ/mol
log[Li$^+$]/[K$^+$] =0.9	ΔG^*(Li-K) = + 5.7 kJ/mol	−5.137 kJ/mol
log[Ca^{2+}]0.5/[K$^+$] = 0.725	ΔG^*(Ca0.5-K) = − 9.8 kJ/mol	−4.138 kJ/mol
log[Mg^{2+}]0.5/[K$^+$] = 0.725	ΔG^*(Mg0.5-K) = − 59.2 kJ/mol	−4.138 kJ/mol

Data in Table 1 were used to calculate the parameter ΔG_f^0 ox (phyllosilicate), defined by TARDY and GARRELS (1976, 1977) as the Gibbs free energy of formation of a mineral from its constituent oxides (Table 3, column 4):

ΔG_f^0 ox (phyllosilicate)

$$= \Delta G_f^0(\text{phyllosilicate}) - \Sigma G_f^0(\text{oxides}) \quad (\text{kJ/mol}). \quad (7)$$

In this relationship, "phyllosilicate" stands for all kinds of minerals showing formulas identical to those of Table 3.

ΔG_f^0 ox(phyllosilicate) is linearly dependent on the parameter $\Delta O_{M^{z+}}^{2-}$, as represented in Figs. 1, 2, and 3. Assuming that the Gibbs free energies of formation of Mg^{2+} and Fe^{3+} endmembers are correct, a subsequent adjustment is applied to the Al^{3+} (about −12 kJ/mol) and to the Fe^{2+} (about +4 kJ/mol) endmember in order to perfectly fit the linear relationship and to obey the condition fixed by the model.

Gibbs free energies from the elements and from the oxides as well as solubility products of K^+-exchanged clay minerals (K^+-X) are given in Table 3 (columns 2, 4, and 6). These numbers refer to the dehydrated portions of the fully hydrated clay minerals.

Cation Exchange Reactions

Considerable amounts of data are available for cation-exchange reactions in clay minerals. A large number of constants were collected by BRUGGENWERT and KAMPHORST (1982). Important scatters observed on cation-exchange constants and hydration energies are probably due to the same reasons, i.e., degree of hydration, chemical composition, degree of crystallinity, grain size, etc., which, nevertheless, are not precisely identified.

The data set of cation exchange constants, the same for all clay minerals, as selected and recommended by TARDY and GARRELS (1974) and GARRELS and TARDY (1982) is reported in Table 4. The scatter of the exchange constants does not affect the Gibbs free energy of exchange by more than 10 kJ/mol.

DEHYDRATION ISOTHERMS OF CLAY MINERALS

. Clay minerals are hydrated with variable amounts of water molecules attached to three different sites of hydration. Individual layers which form particles are separated by interlayer spaces. Individual particles which form aggregates are separated by interparticle spaces, and aggregates are separated

by interaggregate spaces. At saturation particularly [i.e., at equilibrium with pure liquid water at 1 bar total pressure, which defines the standard state for water ($a_w = 1$)], smectites and even vermiculites clearly show these three sites of hydration simultaneously developed. The three spaces—and not only the interlayers—have to be, thermodynamically speaking, considered as components of the clay-water systems (QUIRK, 1968; MERING, 1975; TESSIER and BERRIER, 1978; TESSIER and QUIRK, 1979; PONS et al., 1980, 1981a,b, 1982; TESSIER, 1984; BEN RHAIEM et al., 1986, 1987; TOURET, 1988).

Interlayer Spaces

In a given particle, the distribution of hydrated interlayer spaces is variable and can be regular or, more commonly, random. A few interlayers may remain dry (d001 = 10 Å), some admit only one water layer (d001 = 12.5 Å), while others admit two (d001 = 15.6 Å) or three (d001 = 18.6 Å) or more water monolayers.

At saturation with water, the distribution of hydrated interlayer spaces and the amount of interlayer water change from one clay mineral to another as a function of the chemical composition of the clay mineral layer and of the nature of the interlayer cation (PONS, 1980; BEN RHAIEM, 1983; BEN RHAIEM et al., 1986; TESSIER, 1984; TOURET, 1988).

When the activity of water diminishes and dehydration takes place, the amount of interlayer water decreases and, as demonstrated by TOURET (1988), the relative distribution of water in interlayer spaces also changes. Therefore, some interlayers remain hydrated even at very low activities of water (Fig. 6).

Interparticle Hydration Sites

Between the different particles that constitute an aggregate, the interparticle water is trapped in large pores (500 Å). At saturation with H_2O, the amount of interparticle water may be greater than the amount of interlayer water. The size of the interparticle spaces is also variable with the chemical composition of the phyllosilicate layer considered, the activity of water, and the nature of the cations present in solution. When the activity of water diminishes, the amount of the interparticle water decreases and rapidly becomes smaller than the amount of interlayer water. Therefore, both interlayer and interparticle water are part of the hydration of the

clay minerals and need not to be considered independently. Both types of water always take part together in hydration-dehydration processes.

Hydration-Dehydration Isotherms

Hydration or dehydration isotherms are obtained by plotting the total amount of water adsorbed in clay-water systems as a function of the relative humidity of the atmosphere in which hydration or dehydration takes place. In an hydration process, the amount of water adsorbed increases together with the relative humidity of the atmosphere. In a dehydration process, on the contrary, the amount of water adsorbed decreases together with the humidity of the atmosphere (Fig. 6). Hydration and dehydration processes are generally not reversible and are almost always hysteretic.

After a complete or even moderate dehydration, clay minerals can generally not recover their original properties and particularly their swelling characters. As demonstrated by TESSIER (1984), TESSIER and BERRIER (1978), and BEN RHAIEM et al. (1987), the reason is that interaggregate and interparticle pores after collapse seem cemented and do not open again at contact with water. Rehydration after drastic stirring is kinetically very slow compared to dehydration. This is the reason why we (GARRELS and TARDY, 1982) recommend the use of dehydration isotherms instead of hydration isotherms in our calculations of the Gibbs free energy of hydration of clay minerals.

Gibbs Free Energy of Hydration

The standard molal Gibbs free energy of formation of a hydrated clay mineral is calculated as follows (BARSHAD, 1955; VAN OLPHEN, 1965, 1977; TARDY et al., 1980; TARDY and TOURET, 1987):

$$\Delta G_f^0(\text{hydrated clay}) = \Delta G_f^0(\text{dry clay} \cdot n\text{H}_2\text{O})$$

$$= \Delta G_f^0(\text{dry clay}) + \Delta G(\text{hydration}), \quad (8)$$

where $\Delta G(\text{hydration})$ is obtained by integrating the following expression along the corresponding experimental isotherm, from $a_w = 1$ to $a_w = 0$:

$$\Delta G_f^0(\text{hydration}) = RT \int_0^n \text{Ln } a_w dn$$

$$= RT \int_0^n \text{Ln } (p/p_0)dn, \quad (9)$$

where n is the maximum number of moles adsorbed at equilibrium with a given activity of water a_w. The activity of water is considered (see GARRELS and CHRIST, 1965) equal to the relative humidity of the atmosphere in which hydrated clay minerals equilibrate:

$$a_w = RH = p/p_0,$$

where p is the partial pressure of water vapour in the atmosphere, and p_0 the corresponding partial pressure of saturation with pure liquid water in its standard state ($P = 1$ bar at any temperature).

THERMODYNAMIC RELATIONS

The following equations are all derived for hydrated and dehydrated phases represented for simplicity by $MX \cdot n\text{H}_2\text{O}$ and MX.

Hydrated Phase Relationships

Consider the dissolution of the hydrated phase:

$$MX \cdot n\text{H}_2\text{O} = M_{(aq)}^+ + X_{(aq)}^- + n\text{H}_2\text{O}_{(l)}, \quad (10)$$
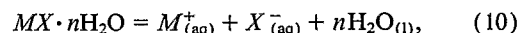
in which M^+ stands for an interlayer cation and X^- the anionic framework.

The solubility product for this reaction is written as follows:

$$K_{sp}(MX \cdot n\text{H}_2\text{O}) = [M_{(aq)}^+][X_{(aq)}^-][\text{H}_2\text{O}]^n/[MX \cdot n\text{H}_2\text{O}], \quad (11)$$

where brackets denote thermodynamic activities.
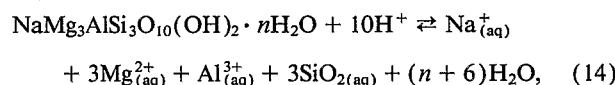
As applied to a hydrated salt, for example $MgCl_2 \cdot 6\text{H}_2\text{O}$, Eqns. (10) and (11) would be as follows, respectively:

$$MgCl_2 \cdot 6\text{H}_2\text{O} \rightleftarrows Mg_{(aq)}^{2+} + Cl_{(aq)}^- + 6\text{H}_2\text{O}_{(l)}, \quad (12)$$
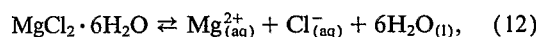
and

$$K_{sp}(MgCl_2 \cdot 6\text{H}_2\text{O}) = [Mg^{2+}(aq)][Cl^-(aq)][\text{H}_2\text{O}]^6. \quad (13)$$

As applied to a hydrated clay mineral, for example $NaMg_3AlSi_3O_{10}(OH)_2 \cdot n\text{H}_2\text{O}$, Eqns. (10) and (11) would be as follows, respectively:

$$NaMg_3AlSi_3O_{10}(OH)_2 \cdot n\text{H}_2\text{O} + 10\text{H}^+ \rightleftarrows Na_{(aq)}^+$$

$$+ 3Mg_{(aq)}^{2+} + Al_{(aq)}^{3+} + 3SiO_{2(aq)} + (n+6)\text{H}_2\text{O}, \quad (14)$$

and

$$K_{sp} = [Na_{(aq)}^+][Mg_{(aq)}^{2+}]^3[Al_{(aq)}^{3+}][SiO_{2(aq)}]^3$$

$$\times [\text{H}_2\text{O}_{(l)}]^{n+6}/[\text{H}_{(aq)}^+]^{10}, \quad (15)$$

or

$$\log K_{sp} = \log [Na^+]/[\text{H}^+] + 3 \log [Mg^{2+}]/[\text{H}^+]^2$$

$$+ \log [Al^{3+}]/[\text{H}^+]^3 + 3 \log [SiO_2] + (n+6) \log [\text{H}_2\text{O}]. \quad (16)$$

In Eqns. (12) and (13), the simplified $MX \cdot n\text{H}_2\text{O}$ notation, $[M_{(aq)}^+]$ and $[X_{(aq)}^-]$, would correspond to the following:

$$[M_{(aq)}^+] = [Na_{(aq)}^+], \quad (17)$$

and

$$[X_{(aq)}^-] = [Mg_{(aq)}^{2+}]^3[Al_{(aq)}^{3+}][SiO_{2(aq)}]^3$$

$$\times [\text{H}_2\text{O}_{(l)}]^{n+6}/[\text{H}_{(aq)}^+]^{10}. \quad (18)$$

The algebraic form and charge on the terms $[M_{(aq)}^+]$ and $[X_{(aq)}^-]$ are not critical to the following derivations because the terms retain the same form throughout. However, in terms of using free energy data, the form of the reaction and K_{sp} equation to which they refer are critical. Equations (14) and (15) represent the dissolution reaction and solubility product, K_{sp}, to which all of the free energy data in Tables 2 through

11 refer, namely the reaction with $H^+_{(aq)}$ to produce free cations, $SiO_{2(aq)}$ and $H_2O_{(1)}$.

Returning to the MX form of Eqns. (10) and (11), we can write the following:

$$-RTLn K_{sp}(MX \cdot nH_2O) = \Delta G^0_{R(10)} = \Delta G^0_f M^+_{(aq)}$$
$$+ \Delta G^0_f X^-_{(aq)} + n\Delta G^0_f H_2O - \Delta G^0_f MX \cdot nH_2O. \quad (19)$$

If the number of water molecules, nH_2O, is known, Eqn. (19) can be used to calculate $\Delta G^0_f MX \cdot nH_2O$ from a measured value of K_{sp}; or alternatively, K_{sp} can be calculated from $\Delta G^0_f MX \cdot nH_2O$. Note that K_{sp} can be measured in a dilute solution with $a_{H_2O} = 1$ even if nH_2O is unknown. However, with nH_2O unknown, the free energy of formation $\Delta G^0_f MX \cdot nH_2O$ cannot be calculated from K_{sp} or vice versa.

Anhydrous Portion of Hydrated Phases

Another parameter of considerable utility can be calculated, however, defined by the following equation:

$$\Delta G^*_f MX(hyd.) \equiv \Delta G^0_f MX \cdot nH_2O - n\Delta G^0_f H_2O_{(1)}. \quad (20)$$

The notation $\Delta G^*_f MX(hyd.)$ is cumbersome, but we maintain it to emphasize the fact that $\Delta G^*_f MX(hyd.)$ is a calculated free energy that refers to a physically hypothetical state $MX(hyd.)$ that might be considered as "the anhydrous portion of a hydrated phase." Whatever its physical interpretation, the parameter $\Delta G^*_f MX(hyd.)$ is defined rigorously by Eqn. (20).

Using the definition of $\Delta G^*_f MX(hyd.)$, Eqn. (18) can be rewritten as follows:

$$-RTLn K_{sp}(MX \cdot nH_2O) = \Delta G^0_{R(10)}$$
$$= \Delta G^0_f M^+_{(aq)} + \Delta G^0_f X^-_{(aq)} - \Delta G^*_f MX(hyd.). \quad (21)$$

If K_{sp} is known, $\Delta G^*_f MX(hyd.)$ can be calculated from Eqn. (21), even if nH_2O is not known. Of far more importance, however, is the fact that if an independent source of information is available that allows calculation of $\Delta G^*_f MX(hyd.)$, the solubility products, K_{sp}, can be calculated from $\Delta G^*_f MX(hyd.)$. As discussed below, $\Delta G^*_f MX(hyd.)$ can be calculated from a knowledge of hydration energies and the standard free energies of the dehydrated phases.

Hydration Energy

For the reaction of a dehydrated phase plus water,

$$MX(dehyd.) + nH_2O = MX \cdot nH_2O \quad (22)$$
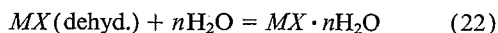
the Gibbs free energy of hydration is given by the following:

$$\Delta G^0(hydration) = \Delta G^0_{R(22)} = \Delta G^0_f MX \cdot nH_2O$$
$$- \Delta G^0_f MX(dehyd.) - n\Delta G^0_f H_2O_{(1)}. \quad (23)$$

Introducing the definition of $\Delta G^*_f MX(hyd.)$ from Eqn. (20) in Eqn. (23) gives the following:

$$\Delta G^*_f MX(hyd.) = \Delta G^0_f MX(dehyd.) + \Delta G^0(hydration). \quad (24)$$

Introducing $\Delta G^*_f MX(hyd.)$ from Eqn. (24) in Eqn. (21) yields the following:

$$-RTLn K_{sp}(MX \cdot nH_2O)$$
$$= \Delta G^0_{R(10)} = \Delta G^0_f M^+_{(aq)} + \Delta G^0_f X^-_{(aq)}$$
$$- \Delta G^*_f MX(dehyd.) - \Delta G^0(hydration). \quad (25)$$

Thus, if the free energy of hydration is known, the parameter $\Delta G^*_f MX(hyd.)$ can be calculated for the hydrated phase; and thus the K_{sp} for the hydrated phase can be calculated without knowing the amount of water in it. This also holds true if the parameter $\Delta G^*_f MX(hyd.)$ is obtained from other sources, such as estimated from the linear plots of ΔG^*_f ox vs $\Delta O^{2-}_{M^{z+}}$ in Figs. 1–3.

As expected from the above, the K_{sp}'s of the hydrated and dehydrated phases are directly related. For a dehydrated phase MX,

$$MX(dehyd.) = M^+_{(aq)} + X^-_{(aq)} \quad (26)$$
$$-RTLn K_{sp}MX(dehyd.) = \Delta G^0_{R(26)}$$
$$= \Delta G^0_f M^+_{(aq)} + \Delta G^0_f X^-_{(aq)} - \Delta G^0_f MX(dehyd.). \quad (27)$$

or

$$\Delta G^0_f MX(dehyd.) = RTLn K_{sp}MX(dehyd.)$$
$$+ \Delta G^0_f M^+_{(aq)} + \Delta G^0_f X^-_{(aq)}. \quad (28)$$

Introducing $\Delta G^0_f MX(dehyd.)$ from Eqn. (28) into Eqn. (25) gives

$$\Delta G^0_{R(10)} = - RTLn K_{sp}(MX \cdot nH_2O)$$
$$= \Delta G^0_f M^+_{(aq)} + \Delta G^0_f X^-_{(aq)} - \Delta G^0(hydration)$$
$$- (RTLn K_{sp}MX(dehyd.) + \Delta G^0_f M^+_{(aq)}$$
$$+ \Delta G^0_f X^-_{(aq)}), \quad (29)$$

So that

$$\Delta G^0_{R(10)} = - RTLn K_{sp}(MX \cdot nH_2O)$$
$$= - RTLn K_{sp}MX(dehyd.) - \Delta G^0(hydration), \quad (30)$$

or

$$RT(Ln K_{sp}(MX \cdot nH_2O) - Ln K_{sp}MX(dehyd.))$$
$$= \Delta G^0(hydration). \quad (31)$$

Equation (31) is really the fundamental thermodynamic relationship between the hydrated and dehydrated phases and hydration free energy. The fact that this relationship exists and can be used without an explicit knowledge of the amount of water in the hydrated phase is at first surprising. However, the mass of water is in fact implicit in the numerical value of the hydration free energy, which is obtained by integration of the hydration isotherm (see Fig. 6).

Gibbs Free Energy and Solubility Products of Hydrates and Hydrated Clay Minerals: Example of Calculation

Hydrated and dehydrated clay minerals can be compared to series of hydrates such as $MgCl_2$, $MgCl_2 \cdot H_2O$,

$MgCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 4H_2O$, and $MgCl_2 \cdot 6H_2O$. The difference is that hydrates have discrete compositions, while clay minerals show continuous variations in water content (Fig. 6). Therefore, thermodynamic calculations are similar. In pure water at 1 bar pressure (conventional standard state for

water, $a_w = 1$) only $MgCl_2 \cdot 6H_2O$ and water-saturated clay minerals are the stable phases. In pure water, dehydrated phases, i.e., $MgCl_2$ or $MgCl_2$(dehyd.), are less stable than hydrated minerals (data from WAGMAN et al., 1982). Differences in solubility products (K_{sp}) are directly related to hydration energies, as illustrated as follows for $MgCl_2$ and $MgCl_2 \cdot 6H_2O$:

$$\Delta G_f^0 \, MgCl_2 \cdot 6H_2O = \Delta G_f^0 \, MgCl_2 + \Delta G(\text{hydration}) + 6\Delta G_f^0 \, H_2O_{(l)}$$
$$-2115.56 \quad = \quad -592.3 \quad - \quad 100.061 \quad - 1423.2 \; (\text{kJ/mol}), \tag{32}$$

and

$$\Delta G_f^* \, MgCl_2(\text{hyd.}) = -2115.56 + 1423.2 \; \text{kJ/mol} = -692.36 \; \text{kJ/mol} \tag{33}$$

$$= \Delta G_f^0 \, MgCl_2 + \Delta G^0(\text{hydration}).$$

In pure water, at 25°C,

$$2.303 \, RT[\log K_{sp} \, (MgCl_2 \cdot 6H_2O) - \log K_{sp} \, (MgCl_2)] = \Delta G^0(\text{hydration})$$
$$5.707 \qquad (4.448 \quad - \quad 21.981) \qquad = -100.061 \; \text{kJ/mol}. \tag{34}$$

In this expression, the solubility products are written as follows:

$$\log K_{sp} \, (MgCl_2 \cdot 6H_2O) = \log [Mg^{2+}_{(aq)}]2 \log [Cl^-_{(aq)}] + 6 \log [H_2O]$$

$$= 4.448, \tag{35}$$

and

$$\log K_{sp} \, (MgCl_2) = \log [Mg^{2+}_{(aq)}] + 2 \log [Cl^-_{(aq)}]$$

$$= 21.981, \tag{36}$$

in which terms in brackets stand for activity of species. In the above expression, $MgCl_2$ and $MgCl_2$(dehyd.) stand for the same dehydrated phase.

Hydration energies or Gibbs free energies of hydrated and dehydrated clay minerals are computed similarly here, as follows:

$\Delta G_f^*(\text{hydrated clay})$

$$= \Delta G_f^0(\text{dehydrated clay}) + \Delta G(\text{hydration}). \tag{37}$$

As an example, let us consider the data listed in the first line of Table 7. The mineral involved is a trioctahedral Na-vermiculite poorly crystallized. The dissolution equation and the solubility product were given in Eqns. (14) and (15).

$\Delta G_f^* \, NaMg_3AlSi_3O_{10}(OH)_2(\text{hyd.})$

$$= \Delta G_f^0 \, NaMg_3AlSi_3O_{10}(OH)_2(\text{dehyd.})$$

$$+ \Delta G^0(\text{hydration})$$

$$-5795.9 \; \text{kJ/mol} = -5774.9 - 21 \; \text{kJ/mol}, \tag{38}$$

or

$\Delta G^0(\text{hydration}) = -5.707 \{ \log K_{sp} \, \text{Na-vermiculite(hyd.)}$

$$- \log K_{sp} \, \text{Na-vermiculite(dehyd.)} \}$$

$$= -5.707 \times 3.679 = -21 \; \text{kJ/mol}. \tag{39}$$

Again, the solubility products and the corresponding Gibbs free energies of formation from the elements of hydrated and dehydrated Na-vermiculite are defined in water of standard state ($a_w = [H_2O] = 1$).

Cation Exchange Reactions

The concept applied to hydration water in exchange reactions is similar to the one developed in the preceding paragraph for the solubility product, and the exchange constants are determined for reactions similar to Eqn. (3):

$Na\text{-}X \cdot n_1H_2O + K^+_{(aq)}$

$$= K\text{-}X \cdot n_2H_2O + Na^+_{(aq)} + (n_1 - n_2)H_2O; \tag{40}$$
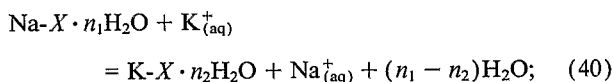
and

$K_{R(40)} = [Na^+_{(aq)}][K\text{-}X \cdot n_2H_2O][H_2O]^{(n_1-n_2)}/$

$$[K^+_{(aq)}][Na\text{-}X \cdot n_1H_2O]. \tag{41}$$

Again, $K_{R(40)}$ can be measured if [solids] = 1, if [H_2O] = 1, or if $n_1 = n_2$. Algebraically, we can write the following:

$-RTLnK_{R(40)} = \Delta G_{R(40)}^0 = \Delta G_f^0 \, Na^+_{(aq)} - \Delta G_f^0 \, K^+_{(aq)}$

$$- (\Delta G_f^0 \, Na\text{-}X \cdot n_1H_2O - n_1\Delta G_f^0 \, H_2O)$$

$$+ (\Delta G_f^0 \, K\text{-}X \cdot n_2H_2O - n_2\Delta G_f^0 \, H_2O). \tag{42}$$

We can again define the parameters $\Delta G_f^* \, K\text{-}X(\text{hyd.})$ and $\Delta G_f^* \, Na\text{-}X(\text{hyd.})$ from Eqn. (20) and substitute in Eqn. (42) the following:

TABLE 5. Gibbs free energies of hydration ΔG^0 (hydration) of clay minerals computed from dehydration isotherms and selected by GARRELS and TARDY (1982), TARDY and TOURET (1987), and TOURET (1988). The first set of data, "measured" data, is derived from experiments; the second set, "calculated" data, is calculated from the model presented in this paper.

Mineral name, reference and simplified formula	Interlayer charge = Octahedral + Tetrahedral			Type of data	ΔG hydration (kJ/mol)				
					Li	Na	K	Ca	Mg
Vermiculite (TOURET, 1988)				measured	-56	-29	-21	-44	-35
$M_{0.81}(Al_{0.16} Fe^{3+}_{0.24} Mg_{2.40})(Al_{0.81} Si_{3.19})O_{10}(OH)_2$	0.81	0.00	0.81	calculated	-42	-26	-17	-43	-35
Vermiculite (VAN OLPHEN, 1965)				measured		-22			
$Na_{0.80}(Al_{0.60} Mg_{2.10})(Al_{0.8} Si_{3.2})O_{10}(OH)_2$	0.80	0.00	0.80	calculated	-45	-26	-17	-43	-35
Vermiculite (OVCHARENKO et al., 1967)				measured	-38	-25	-22		-46
$M_{0.66}(Mg_3)(Al_{0.66} Si_{3.34})O_{10}(OH)_2$	0.66	0.00	0.66	calculated	-38	-29	-22	-45	-39
Beidellite (SUQUET, 1978)				measured		-38		-53	
$M_{0.54}(Al_{1.76} Mg_{0.285})(Al_{0.39} Si_{3.61})O_{10}(OH)_2$	0.54	0.15	0.39	calculated	-82	-39	-19	-53	-67
Montmorillonite (TOURET, 1988)				measured	-65	-48	-29	-61	-64
$M_{0.51}(Al_{1.40} Fe^{3+}_{0.17} Mg_{0.40})(Al_{0.02} Si_{3.98})O_{10}(OH)_2$	0.51	0.59	0.02	calculated	-77	-49	-27	-70	-63
Saponite (SUQUET, 1978)				measured		-35		-47	
$M_{0.45}(Fe^{3+}_{0.24} Mg_{2.64})(Al_{0.45} Si_{3.55})O_{10}(OH)_2$	0.45	0.00	0.45	calculated	-47	-37	-28	-50	-47
Smectite (TOURET, 1988)				measured	-62	-46	-43	-58	-59
$M_{0.44}(Al_{1.52} Fe^{3+}_{0.16} Mg_{0.34})(Al_{0.16} Si_{3.84})O_{10}(OH)_2$	0.44	0.28	0.16	calculated	-67	-48	-27	-63	-60
Nontronite (TOURET, 1988)				measured	-88	-64	-37	-62	-64
$M_{0.40}(Al_{0.18} Fe^{3+}_{1.71} Mg_{0.08})(Al_{0.29} Si_{3.71})O_{10}(OH)_2$	0.40	0.11	0.29	calculated	-89	-65	-36	-62	-68
Montmorillonite (TOURET, 1988)				measured	-88	-64	-37	-62	-64
$M_{0.39}(Al_{1.52} Fe^{3+}_{0.20} Mg_{0.24})(Al_{0.03} Si_{3.97})O_{10}(OH)_2$	0.39	0.36	0.03	calculated	-61	-40	-24	-47	-52
Hectorite (TARDY et al., 1980)				measured	-36	-26	-21	-43	-46
$M_{0.29}(Al_{0.21} Mg_{2.57})(Al_{0.06} Si_{3.94})O_{10}(OH)_2$	0.29	0.23	0.06	calulated	-45	-37	-32	-49	-49
Hectorite (TOURET, 1988)				measured	-47	-29	-31	-27	-32
$M_{0.28}(Al_{0.21} Mg_{2.57})(Al_{0.05} Si_{3.95})O_{10}(OH)_2$	0.28	0.23	0.05	calculated	-45	-37	-32	-49	-49

$$-RT\mathrm{Ln}K_{R(40)} = \Delta G^0_f \, Na^+_{(aq)} - \Delta G^0_f \, K^+_{(aq)}$$
$$+ \Delta G^*_f \, K\text{-}X(\text{hyd.}) - \Delta G^*_f \, Na\text{-}X(\text{hyd.}). \quad (43)$$

For further convenience, we can define the following:

$$\Delta G^* \, Na\text{-}K(\text{hyd.})$$
$$= \Delta G^*_f \, K\text{-}X(\text{hyd.}) - \Delta G^*_f \, Na\text{-}X(\text{hyd.}). \quad (44)$$

And finally, we obtain for unit activity of solids and liquids,

$$-RT\mathrm{Ln}K_{R(40)}$$
$$= -RT\mathrm{Ln}[Na^+_{(aq)}]/[K^+_{(aq)}] = \Delta G^0_{Na\text{-}K} \text{ (exchange)}$$
$$= \Delta G^0_f \, Na^+_{(aq)} - \Delta G^0_f \, K^+_{(aq)} + \Delta G^*(Na\text{-}K). \quad (45)$$

As an example, calculations with data of Tables 3, 4, and 7 yield the following:

$$\Delta G^* \, (Na\text{-}K)(\text{hyd.})$$
$$= \Delta G^*_f \, K\text{-}X(\text{hyd.}) - \Delta G^*_f \, Na\text{-}X(\text{hyd.})$$
$$= -5821.1 + 5795.9 \text{ (kJ/mol)} = -25.2 \text{ (kJ/mol)} \quad (46)$$

$\Delta G^*_f \, Na\text{-}X(\text{hyd.})$ are thus determined by calculating the difference between $\Delta G^*_f \, K\text{-}X(\text{hyd.})$ and the cation exchange energy $\Delta G^*(Na\text{-}K)(\text{hyd.})$, which is -25.2 kJ/mol.

Furthermore,

$$-RT\mathrm{Ln}[Na^+_{(aq)}]/[K^+_{(aq)}] = \Delta G^* \, (Na\text{-}K)(\text{hyd.})$$
$$+ \Delta G^0_f \, Na^+_{(aq)} - \Delta G^0_f \, K^+_{(aq)} = -25.2 - 261.9$$
$$+ 282.5 \text{ (kJ/mol)} = -4.566 \text{ (kJ/mol).} \quad (47)$$

At 25°C,

$$\log [Na^+_{(aq)}]/[K^+_{(aq)}] = 4.566/5.707 = 0.8. \quad (48)$$

TABLE 6. (1) Gibbs free energies of hydration of K$^+$-micas of small size calculated from data of Table 4. Gibbs free energies of formation from the elements of (2) hydrated K$^+$-micas as given in column 2 of Table 3; (3) dehydrated K$^+$-micas of small size, calculated by the difference (3) = (2) − (1); (4) well-crystallized phyllosilicates of large size as given in column 1 of Table 2; (5) difference (5) = (2) − (4); and (6) difference (6) = (3) − (4).

Clay Minerals	$\Delta G°$ hyd.	ΔG^*_f K-X hyd.	$\Delta G°_f$ K-X dehy.	$\Delta G°_f$ cryst.	Diff. (2)-(4)	Diff. (5)=(3)-(4)
	(1)	(2)	(3)	(4)	(5)	(6)
K Mg$_3$ Al Si$_3$ O$_{10}$(OH)$_2$	− 10	− 5821.1	− 5811.1	− 5842.1	+ 21.0	+ 31.0
K Fe$_3$ Al Si$_3$ O$_{10}$(OH)$_2$	+ 17	− 4797.5	− 4814.5	− 4800.3	+ 2.8	− 14.2
K Al$_2$ Al Si$_3$ O$_{10}$(OH)$_2$	+ 30	− 5591.1	− 5621.1	− 5591.6	+ 0.5	− 29.5
K Fe$_2$ Al Si$_3$ O$_{10}$(OH)$_2$	+ 50	− 4699.1	− 4749.1	− 4685.5	− 13.6	− 63.6
K Mg$_{2.5}$ Si$_4$ O$_{10}$(OH)$_2$	− 187	− 5549.4	− 5362.4	− 5569.0	+ 19.6	+ 206.6
K Fe$_{2.5}$ Si$_4$ O$_{10}$(OH)$_2$	− 99	− 4696.0	− 4597.0	− 4699.0	+ 3.2	+ 102.0
K Al$_{1.667}$ Si$_4$ O$_{10}$(OH)$_2$	− 50	− 5357.2	− 5307.2	− 5353.0	− 4.2	+ 45.8
K Fe$_{1.667}$ Si$_4$ O$_{10}$(OH)$_2$	+ 28	− 4613.9	− 4641.9	− 4595.3	− 18.6	− 46.6

Note : ΔG^*f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

TABLE 7. (1) Gibbs free energies of hydration of Na-X micas (kJ/mol). Gibbs free energies of formation from the elements (kJ/mol) at 298.15 K and 1 bar total pressure: (2) K-X hydrated; (3) Na-X hydrated; (4) Na-X dehydrated; (5) K-X dehydrated; and (6) difference (4) − (5) = (6).

Clay Minerals	$\Delta G°$ hyd.	ΔG^*_f K-X hyd.	ΔG^*_f Na-X hyd.	$\Delta G°_f$ Na-X dehy.	$\Delta G°_f$ K-X dehy.	Diff. (4)-(5)
	(1)	(2)	(3)	(4)	(5)	(6)
Na Mg$_3$ Al Si$_3$ O$_{10}$(OH)$_2$	− 21	− 5821.1	− 5795.9	− 5774.9	− 5811.1	+ 36.2
Na Fe$_3$ Al Si$_3$ O$_{10}$(OH)$_2$	− 21	− 4797.5	− 4772.3	− 4751.3	− 4814.5	+ 63.2
Na Al$_2$ Al Si$_3$ O$_{10}$(OH)$_2$	− 21	− 5591.1	− 5565.9	− 5544.9	− 5621.1	+ 76.2
Na Fe$_2$ Al Si$_3$ O$_{10}$(OH)$_2$	− 21	− 4699.1	− 4673.9	− 4652.9	− 4749.1	+ 96.2
Na Mg$_{2.5}$ Si$_4$ O$_{10}$(OH)$_2$	− 190	− 5549.4	− 5524.2	− 5334.2	− 5362.4	+ 28.2
Na Fe$_{2.5}$ Si$_4$ O$_{10}$(OH)$_2$	− 125	− 4696.0	− 4670.8	− 4545.8	− 4597.0	+ 51.2
Na Al$_{1.667}$ Si$_4$ O$_{10}$(OH)$_2$	− 95	− 5357.2	− 5332.0	− 5237.0	− 5307.2	+ 70.2
Na Fe$_{1.667}$ Si$_4$ O$_{10}$(OH)$_2$	− 43	− 4613.9	− 4588.7	− 4545.7	− 4641.9	+ 96.2

Note : ΔG^*f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

TABLE 8. (1) Gibbs free energies of hydration of Li-X micas (kJ/mol). Gibbs free energies of formation (kJ/mol) at 298.15 K and 1 bar total pressure: (2) Li-X hydrated and (3) Li-X dehydrated; (3) = (2) − (1).

	ΔG° hyd.	ΔG^*_f Li-X hyd.	ΔG°_f Li-X dehyd.
Minerals	(1)	(2)	(3)
Li Mg$_3$ AlSi$_3$ O$_{10}$(OH)$_2$	− 35	− 5826.8	− 5791.8
Li Fe$_3$ AlSi$_3$ O$_{10}$(OH)$_2$	− 51	− 4803.2	− 4752.2
Li Al$_2$ AlSi$_3$ O$_{10}$(OH)$_2$	− 60	− 5596.8	− 5536.8
Li Fe$_2$ AlSi$_3$ O$_{10}$(OH)$_2$	− 71	− 4704.8	− 4633.8
Li Mg$_{2.5}$ Si$_4$ O$_{10}$(OH)$_2$	− 194	− 5555.1	− 5361.1
Li Fe$_{2.5}$ Si$_4$ O$_{10}$(OH)$_2$	− 168	− 4701.7	− 4533.7
Li Al$_{1.667}$ Si$_4$ O$_{10}$(OH)$_2$	− 153	− 5362.9	− 5209.9
Li Fe$_{1.667}$ Si$_4$ O$_{10}$(OH)$_2$	− 134	− 4619.6	− 4485.6

Note : ΔG^*f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

One obtains, finally, the following:

log K_{sp} Na-vermiculite(hyd.)

$= \log K_{sp}$ K-vermiculite(hyd.) $+ \log [Na^+_{(aq)}]/[K^+_{(aq)}]$

$$42.71 = 41.91 + 0.8 \quad (49)$$

Therefore, all exchange free energies in Table 3 and onward are for the anhydrous portion of hydrated phases.

Equations (43)–(45) provide the relationships between $K_{R(40)}$, ΔG^*_f K-X(hyd.) and ΔG^*_f Na-X(hyd.), which once again do not require an explicit knowledge of the amount of water in the hydrated phases.

Data Presentation in Tables 3–11

The equations derived above are used in this paper as follows. Table 2 presents standard thermodynamic data for well-crystallized dehydrated phyllosilicates. Table 3 presents data for poorly crystallized hydrated clay minerals (uncharged and K-exchanged); the data include measured K_{sp}'s from the solubility data, values of ΔG^*_f K-X(hyd.) calculated from the K_{sp}'s, and values of ΔG^*_f K-X(hyd.) after adjustment to a linear relationship with $\Delta O^{2-}_{M^{z+}}$. Table 4 presents measured values of exchange constants and values of ΔG^* M-K(hyd.) and ΔG^* M-K (exchange) calculated from them. Table 5 presents hydration energies, ΔG^0(hydration). Table 6 calculates ΔG^*_f K-X(hyd.) from ΔG^0(hydration) and ΔG^*_f K-

TABLE 9. (1) Gibbs free energies of hydration of Ca$_{0.5}$-X micas (kJ/mol). Gibbs free energies of formation (kJ/mol) at 298.15 K and 1 bar total pressure: (2) Ca$_{0.5}$-X hydrated and (3) Ca$_{0.5}$-X dehydrated; (3) = (2) − (1).

	ΔG° hyd.	ΔG^*_f Ca$_{0.5}$-X hyd ·	ΔG°_f Ca$_{0.5}$-X dehyd.
Minerals	(1)	(2)	(3)
Ca$_{0.5}$ Mg$_3$ AlSi$_3$ O$_{10}$(OH)$_2$	− 40	− 5811.3	− 5771.3
Ca$_{0.5}$ Fe$_3$ AlSi$_3$ O$_{10}$(OH)$_2$	− 28	− 4787.7	− 4759.7
Ca$_{0.5}$ Al$_2$ AlSi$_3$ O$_{10}$(OH)$_2$	− 22	− 5581.3	− 5559.3
Ca$_{0.5}$ Fe$_2$ AlSi$_3$ O$_{10}$(OH)$_2$	− 13	− 4689.3	− 4676.3
Ca$_{0.5}$ Mg$_{2.5}$ Si$_4$ O$_{10}$(OH)$_2$	− 230	− 5539.6	− 5309.6
Ca$_{0.5}$ Fe$_{2.5}$ Si$_4$ O$_{10}$(OH)$_2$	− 166	− 4686.2	− 4520.2
Ca$_{0.5}$ Al$_{1.667}$ Si$_4$ O$_{10}$(OH)$_2$	− 134	− 53487.4	− 5213.4
Ca$_{0.5}$ Fe$_{1.667}$ Si$_4$ O$_{10}$(OH)$_2$	− 86	− 4604.1	− 4518.1

Note : ΔG^*f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

TABLE 10. (1) Gibbs free energies of hydration of $Mg_{0.5}$-X micas (kJ/mol). Gibbs free energies of formation (kJ/mol) at 298.15 K and 1 bar total pressure: (2) $Mg_{0.5}$-X hydrated and (3) $Mg_{0.5}$-X dehydrated; (3) = (2) − (1).

Minerals	ΔG° hyd.	ΔG^*_f $Mg_{0.5}$-X hyd.	ΔG°_f $Mg_{0.5}$-X dehyd.
	(1)	(2)	(3)
$Mg_{0.5}$ Mg_3 $AlSi_3$ $O_{10}(OH)_2$	~ 30	~ 5761.9	~ 5731.9
$Mg_{0.5}$ Fe_3 $AlSi_3$ $O_{10}(OH)_2$	~ 30	~ 4738.3	~ 4708.3
$Mg_{0.5}$ Al_2 $AlSi_3$ $O_{10}(OH)_2$	~ 30	~ 5531.9	~ 5501.9
$Mg_{0.5}$ Fe_2 $AlSi_3$ $O_{10}(OH)_2$	~ 30	~ 4639.9	~ 4609.9
$Mg_{0.5}$ $Mg_{2.5}$ Si_4 $O_{10}(OH)_2$	~ 255	~ 5490.2	~ 5235.2
$Mg_{0.5}$ $Fe_{2.5}$ Si_4 $O_{10}(OH)_2$	~ 184	~ 4636.8	~ 4452.8
$Mg_{0.5}$ $Al_{1.667}$ Si_4 $O_{10}(OH)_2$	− 15	~ 5298.	~ 5148.
$Mg_{0.5}$ $Fe_{1.667}$ Si_4 $O_{10}(OH)_2$	~ 95	~ 4554.7	~ 4459.7

Note : ΔG^*f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

X(hyd.) in Table 3. Tables 7–10 present values of ΔG^*_f M-X(hyd.) and ΔG^0_f M-X(dehyd.) with $M = Na^+$, Li^+, 0.5 Ca^{2+}, and 0.5 Mg^{2+}. These data are calculated from the ΔG^*_f K-X(dehyd.) data in Table 3, the exchange data in Table 4, and the ΔG^0(hydration) data of Table 5. Finally, Table 11 presents calculated values for ΔG^*_f M-X(hyd.), ΔG^0_f M-X(dehyd.), log $K_{sp}MX \cdot nH_2O$, log $K_{sp}M$-X(dehyd.), and ΔG^0(hydration) with $M = K^+$, Na^+, Li^+, $Ca^{2+}_{0.5}$, and $Mg^{2+}_{0.5}$ for phases of varying layer charge, calculated via the multicomponent mixing model of TARDY and FRITZ (1981).

Finally, at that point, we have a complete set of what we call modelized Gibbs free energies for twelve endmembers in the series phlogopite-talc-celadonite or muscovite-pyrophyllite-celadonite K^+-saturated, for each of the four cations (Mg^{2+}, Fe^{2+} trioctahedral and Al^{3+}, Fe^{3+} dioctahedral) and thirty-two minerals of the same kinds but saturated by Li^+, Na^+, Mg^{2+}, and Ca^{2+}. All correspond to poorly crystallized and fully hydrated phyllosilicates. They are all internally consistent in such a way that Gibbs free energies of formation from the oxides of K^+-saturated clays fit linear relationships with the parameters $\Delta O^{2-}_{M^{z+}}$ characterizing octahedral cations (Mg^{2+}, Fe^{2+}, Al^{3+}, Fe^{3+}) as shown in Figs. 1, 2, and 3. The same kinds of linear relationships are obviously obtained for Li^+-, Na^+-, Mg^{2+}-, and Ca^{2+}-saturated phyllosilicates.

Thermodynamic Properties of Smectites, Vermiculites, and Illites

Data calculated in Tables 3–10 are used to estimate thermodynamic properties of smectites (interlayer charge: 0.2), vermiculites, or illites (interlayer charge: 0.8), shown in Table

11. Let us consider, for example, the first line of Table 11a referring to a trioctahedral K-exchanged smectite. ΔG^*_f $K_{0.2}Mg_3Al_{0.2}Si_{3.8}O_{10}(OH)_2$ is calculated from data listed in the first and fifth lines in column 2 of Table 3 on the base of an ideal solid solution, as follows:

ΔG^*_f $K_{0.2}Mg_3Al_{0.2}Si_{3.8}O_{10}(OH)_2$(hyd.)

$= 0.2\Delta G^*_f$ $KMg_3AlSi_3O_{10}(OH)_2$(hyd.)

$\qquad + 0.8\Delta G^*_f$ $Mg_3Si_4O_{10}(OH)_2$(hyd.)

$\qquad + 5.707(0.2 \log 0.2 + 0.8 \log 0.8)$

$= 0.2(-5821.1) + 0.8(-5504.4)$

$\qquad + 5.707(-0.217) = -5569.0$ kJ/mol.

ΔG^*_f $K_{0.2}Mg_3Al_{0.2}Si_{3.8}O_{10}(OH)_2$(dehyd.) (column 3) is calculated by Eqn. (37), as follows:

$$-5569.0 + 38 = -5531.0 \text{ kJ/mol.}$$

The parameters of interest and ultimate applicability to mineral stability studies are the K_{sp}'s that can be obtained from the calculated "anhydrous" and "dehydrated" free energy values.

A final word of caution must be introduced here. Almost all of the calculations presented in this paper, for both hydration and clay mineral free energies, invoke a mixing model, implicitly or explicitly, somewhere in the calculation sequence. In these derivations, solid solution is assumed among a large number of endmembers, and the solid phases are thus assumed to be of variable composition during the free energy

calculations. However, in the final step towards application of the data—calculation of the K_{sp}'s and their use in evaluating mineral stabilities—the explicit assumption is that the minerals are now behaving as phases of fixed composition; thermodynamically, they have become one-component phases. Their reactions in an aqueous phase are thus subject to the constraints of stoichiometric saturation (THORSTENSON and PLUMMER, 1977; GLYNN and REARDON, 1990), a subset of the more general equilibrium constraints between phases of variable composition. This dichotomy of assumptions between calculation and application must be kept in mind when the data are used.

GIBBS FREE ENERGY OF HYDRATION OF CLAY MINERALS

One of the first synthetic records of hydration energies of several clay minerals was presented by GARRELS and TARDY (1982) by integrating along dehydration and hydration isotherms presented by MOONEY et al. (1952), VAN OLPHEN (1965), OVCHARENKO et al. (1967), GLAESER et al. (1967), GLAESER and MERING (1968), TARASEVICH et al. (1968), SUQUET (1978), PROST (1975), and TARDY et al. (1980). Later on, TARDY and TOURET (1987) and TOURET (1988) computed new hydration energies from dehydration isotherms which, for the most part, are from measurements of KAMEL (1980) and TURKI (1987).

Gibbs free energies of hydration computed from dehydration isotherms are presented in Table 5.

Results

As already pointed out by GARRELS and TARDY (1982), the Gibbs free energy of hydration of various clay minerals saturated by various cations shows a large spread in values which can be attributed to the nature of the interlayer cation and to the interlayer charge. Furthermore, the more recent measurements from TARDY and TOURET (1987) and TOURET (1988) (Table 5) suggest that the spread is also a function of the localization of the charge (tetrahedral or octahedral) and a function of the composition of the octahedral layer (trioctahedral: Mg^{2+}, Fe^{2+}, or dioctahedral: Al^{3+}, Fe^{3+}). In fact, the examination of measured values listed in Table 5 suggests the following tendencies:

1) There is a general trend for the hydration energy to be more important, i.e., more negative, when the octahedral net charge that is less than 6 increases; the general trend for the hydration energy is less important, i.e., less negative, when the tetrahedral net charge that is less than 6 increases.

2) These relations are in fact complex and depend on the nature of the octahedral composition (trioctahedral Mg_3^{2+} or Fe_3^{2+} or dioctahedral Al_2^{3+} or Fe_2^{3+}) and also on the nature of the interlayer cation, i.e., hydrated, such as Mg^{2+} or Li^+, or dehydrated, such as K^+.

3) Highly charged Li^+- or Mg^{2+}-vermiculites may show hydration energies more important (i.e., more negative) than those of Li^+- or Mg^+-hectorites of low interlayer charges.

On the contrary, the hydration energies of K^+-vermiculites are less important (less negative) than these for K^+-hectorites. K^+-hectorites and K^+-Wyoming montmorillonites appear as highly hydrated, despite the fact that the potassium ion is generally dehydrated.

4) For trioctahedral clay minerals such as saponite and vermiculite, the Gibbs free energy of hydration diminishes (i.e., is less negative) as the tetrahedral charge increases.

5) For dioctahedral clay minerals such as montmorillonite and beidellite, the Gibbs free energy of hydration is less important (i.e., less negative) for dehydrated cations such as K^+ and more important (i.e., more negative) for hydrated cations such as Li^+ or Mg^{2+}, as the tetrahedral charge increases and the octahedral charge decreases.

6) There are few data to support the line drawn by plotting hydration energy vs. interlayer charge for aluminous K^+ interlayered silicates. However, GARRELS and TARDY (1982) pointed out that the Gibbs free energy of hydration of K^+-smectites, K^+-vermiculites, and K^+-micas in the aluminous series decreases together with the tetrahedral and the layer charge. Furthermore, the point of zero hydration energy at an interlayer charge of 0.8 is well established (BARSHAD, 1954). Together, these two observations mean that the Gibbs free energy of hydration of K^+ dioctahedral micas (tetrahedral charge = interlayer charge = 1) is probably positive, which suggests that these micas cannot spontaneously hydrate in water at room temperature (GARRELS and TARDY, 1982).

Bases for a Model

From our point of view, such relationships are of the highest importance and appear as encouragements for creating a model, which allows for estimation of hydration energies for all kinds of clay minerals, as a function of the following:

1) the layer charge,

2) the source of the charge (tetrahedral, as in micas, or octahedral, as in celadonites),

3) the nature of the octahedral cation (Mg^{2+}, Fe^{2+}, Al^{3+}, and Fe^{3+}),

4) the nature of the interlayer cation (Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}), and

5) the size and crystallinity of the material (poorly crystallized and small, as in clay minerals; and well crystallized and large, as in micas and other well-crystallized phyllosilicates).

A Model of Estimation of Hydration Energies

Calculated Gibbs free energies of hydration given in Table 5 result from the following assumptions:

1) We assume that the poorly crystallized clay minerals are fully hydrated and are all of the same size.

2) Each of the endmembers involved is characterized by a specific hydration energy.

3) In each of the three series of phyllosilicates (talc, mica, and celadonite) and in each of the two series of minerals

TABLE 11a. Mg^{2+}-trioctahedral and tetrahedral charge. Gibbs free energies of formation (kJ/mol) at 298.15 K and 1 bar total pressure. M represents K^+, Na^+, Li^+, Ca^{2+} and Mg^{2+}, respectively. X represents a smectite (interlayer charge of 0.2) and illite or a vermiculite (interlayer charge of 0.8), respectively. X represents a phyllosilicate layer.

	$\Delta G°$ hyd.	ΔG^*_f M-X hyd.	$\Delta G°_f$ M-X dehyd.	$\Delta G^*_{f(ox)}$ M-X hyd.	$\Delta G°_{f(ox)}$ M-X dehyd.	$logK_{sp}$ M-X hyd.	$logK_{sp}$ M-X dehyd.
$K_{0.2} Mg_3 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-38	-5569.0	-5531.0	-193.2	-193.2	28.3	34.9
$Na_{0.2} Mg_3 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-40	-5563.9	-5523.9	-182.7	-142.7	28.4	35.4
$Li_{0.2} Mg_3 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-43	-5570.1	-5527.1	-170.4	-127.4	28.5	36.0
$Ca_{0.1} Mg_3 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-52	-5567.0	-5515.0	-163.0	-163.0	28.4	37.5
$Mg_{0.1} Mg_3 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-50	-5557.1	-5507.1	-156.6	-106.6	28.4	37.2
$K_{0.8} Mg_3 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	-17	-5759.0	-5742.0	-325.7	-308.7	38.3	41.3
$Na_{0.8} Mg_3 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	-25	-5738.8	-5713.8	-283.9	-258.9	39.0	43.4
$Li_{0.8} Mg_3 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	-37	-5763.6	-5726.6	-234.7	-197.7	39.0	45.5
$Ca_{0.4} Mg_3 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	-43	-5751.2	-5708.2	-205.2	-162.2	38.9	46.4
$Mg_{0.4} Mg_3 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	-35	-5711.6	-5676.6	-179.5	-144.6	38.9	45.0

Note : ΔG^*_f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

(hydrated and poorly crystallized, and dehydrated and poorly crystallized clay minerals), Gibbs free energies of formation from the oxides are linearly dependent on the parameter $\Delta O^{2-}_{M^{z+}}$ as it is presented in Figs. 1, 2, and 3.

4) In each of the four series of octahedral occupation (Mg^{2+}, Fe^{2+}, Al^{3+}, and Fe^{3+}) and in each of the two series of tetrahydrally charged or octahedrally charged minerals, hydration energies are proportional to the layer charge.

TABLE 11b. Al^{3+}-dioctahedral and tetrahedral charge. Gibbs free energies of formation (kJ/mol) at 298.15 K and 1 bar total pressure. M represents K^+, Na^+, Li^+, Ca^{2+} and Mg^{2+}, respectively. X represents a smectite (interlayer charge of 0.2) and illite or a vermiculite (interlayer charge of 0.8), respectively. X represents a phyllosilicate layer.

	$\Delta G°$ hyd.	ΔG^*_f M-X hyd.	$\Delta G°_f$ M-X dehyd.	$\Delta G^*_{f(ox)}$ M-X hyd.	$\Delta G°_{f(ox)}$ M-X dehyd.	$logK_{sp}$ M-X hyd.	$logK_{sp}$ M-X dehyd.
$K_{0.2} Al_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-50	-5333.2	-5283.2	-82.8	-32.8	69.6	78.3
$Na_{0.2} Al_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-60	-5328.2	-5268.2	-72.4	-12.4	69.7	80.2
$Li_{0.2} Al_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-74	-5334.4	-5260.4	-60.1	13.9	69.7	82.7
$Ca_{0.1} Al_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-63	-5331.3	-5268.3	-52.7	10.3	69.7	80.7
$Mg_{0.1} Al_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	-64	-5321.4	-5257.4	-46.3	17.7	69.7	80.9
$K_{0.8} Al_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	+ 10	-5527.6	-5537.6	-219.7	-229.7	11.3	9.6
$Na_{0.8} Al_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	-31	-5507.4	-5476.4	-177.9	-146.9	12.0	17.4
$Li_{0.8} Al_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	-64	-5532.1	-5468.1	-128.6	-64.6	12.0	23.2
$Ca_{0.4} Al_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	-33	-5519.8	-5486.8	-99.1	-66.1	11.9	18.7
$Mg_{0.4} Al_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	-39	-5480.2	-5441.2	-73.5	-34.5	11.9	17.7

Note : ΔG^*_f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

TABLE 11c. Fe^{3+}-dioctahedral and tetrahedral charge. Gibbs free energies of formation (kJ/mol) at 298.15 K and 1 bar total pressure. M represents K^+, Na^+, Li^+, Ca^{2+} and Mg^{2+}, respectively. X represents smectite (interlayer charge of 0.2) and illite or a vermiculite (interlayer charge of 0.8), respectively. X represents a phyllosilicate layer.

	ΔG° hyd.	ΔG^*_f M-X hyd.	ΔG°_f M-X dehyd.	$\Delta G^*_{f(ox)}$ M-X hyd.	$\Delta G^\circ_{f(ox)}$ M-X dehyd.	$logK_{sp}$ M-X hyd.	$logK_{sp}$ M-X dehyd.
$K_{0.2} Fe_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	−55	−4438.0	−4383.0	−27.6	27.4	−11.0	−1.4
$Na_{0.2} Fe_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	−69	−4433.0	−4364.0	−22.6	46.4	−10.9	1.2
$Li_{0.2} Fe_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	−78	−4439.2	−4361.2	−4.9	72.4	−10.8	2.9
$Ca_{0.1} Fe_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	−88	−4436.1	−4348.1	2.5	90.5	−10.9	4.5
$Mg_{0.1} Fe_2 Al_{0.2} Si_{3.8} O_{10}(OH)_2$	−92	−4426.2	−4334.2	2.5	90.5	−10.9	5.2
$K_{0.8} Fe_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	+23	−4634.8	−4657.8	−166.9	−189.9	−2.1	−6.1
$Na_{0.2} Fe_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	−33	−4614.6	−4581.6	−125.1	−92.1	−1.4	4.4
$Li_{0.2} Fe_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	−73	−4639.3	−4566.3	−75.8	−2.8	−1.4	11.4
$Ca_{0.1} Fe_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	−32	−4627.0	−4595.0	−45.1	−13.1	−1.3	4.3
$Mg_{0.1} Fe_2 Al_{0.8} Si_{3.2} O_{10}(OH)_2$	−46	−4587.4	−4541.4	−20.7	25.3	−1.3	6.5

Note : ΔG^*_f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

As proposed by GARRELS and TARDY (1982), the Gibbs free energy of hydration either decreases or increases or does not change with layer charge, depending on the source of the charge and the nature of the interlayer cation (Figs. 4 and 5).

5) In a series of minerals of identical charge and source of the charge, hydration energies increase or decrease together with the parameter $\Delta O^{2-}_{M^{2+}}$ characterizing the octahedral cation. For each specific endmember, hydration energies are given in column 1 of Tables 6–10.

TABLE 11d. Mg^{2+}-trioctahedral and octahedral charge. Gibbs free energies of formation (kJ/mol) at 298.15 K and 1 bar total pressure. M represents K^+, Na^+, Li^+, Ca^{2+} and Mg^{2+}, respectively. X represents a smectite (interlayer charge of 0.2) and illite or a vermiculite (interlayer charge of 0.8), respectively. X represents a phyllosilicate layer.

	ΔG° hyd.	ΔG^*_f M-X hyd.	ΔG°_f M-X dehyd.	$\Delta G^*_{f(ox)}$ M-X hyd.	$\Delta G^\circ_{f(ox)}$ M-X dehyd.	$logK_{sp}$ M-X hyd.	$logK_{sp}$ M-X dehyd.
$K_{0.2} Mg_{2.9} Si_4 O_{10}(OH)_2$	−8	−5514.6	−5506.6	−182.7	−174.7	25.3	26.7
$Na_{0.2} Mg_{2.9} Si_4 O_{10}(OH)_2$	−8	−5509.6	−5501.6	−172.3	−164.3	25.4	26.8
$Li_{0.2} Mg_{2.9} Si_4 O_{10}(OH)_2$	−9	−5515.8	−5506.8	−160.0	−151.0	25.4	27.0
$Ca_{0.1} Mg_{2.9} Si_4 O_{10}(OH)_2$	−17	−5512.7	−5495.7	−152.6	−135.6	25.4	28.4
$Mg_{0.1} Mg_{2.9} Si_4 O_{10}(OH)_2$	−24	−5502.8	−5478.8	−146.2	−122.2	25.4	29.6
$K_{0.8} Mg_{2.6} Si_4 O_{10}(OH)_2$	−142	−5541.6	−5399.6	−283.8	−141.8	26.4	51.2
$Na_{0.8} Mg_{2.6} Si_4 O_{10}(OH)_2$	−145	−5521.5	−5376.5	−242.1	−97.1	27.0	52.4
$Li_{0.8} Mg_{2.6} Si_4 O_{10}(OH)_2$	−150	−5546.2	−5396.2	−192.8	−42.8	27.1	53.3
$Ca_{0.4} Mg_{2.6} Si_4 O_{10}(OH)_2$	−180	−5533.8	−5353.8	−163.3	16.7	26.9	58.5
$Mg_{0.4} Mg_{2.6} Si_4 O_{10}(OH)_2$	−197	−5494.3	−5297.3	−137.7	59.3	26.9	61.4

Note : ΔG^*_f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

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TABLE 11e. Al^{3+}-dioctahedral and octahedral charge. Gibbs free energies of formation (kJ/mol) at 298.15 K and 1 bar total pressure. M represents K^+, Na^+, Li^+, Ca^{2+} and Mg^{2+}, respectively. X represents a smectite (interlayer charge of 0.2) and illite or a vermiculite (interlayer charge of 0.8), respectively. X represents a phyllosilicate layer.

	ΔG° hyd.	ΔG^*_f M-X hyd.	ΔG°_f M-X dehyd.	$\Delta G^*_{f(ox)}$ M-X hyd.	$\Delta G^\circ_{f(ox)}$ M-X dehyd.	$\log K_{sp}$ M-X hyd.	$\log K_{sp}$ M-X dehyd.
$K_{0.2} Al_{1.93} Si_4 O_{10}(OH)_2$	-9	-5286.4	-5277.4	-76.0	-67.0	-0.1	1.5
$Na_{0.2} Al_{1.93} Si_4 O_{10}(OH)_2$	-18	-5281.4	-5263.4	-65.6	-47.6	0.1	3.2
$Li_{0.2} Al_{1.93} Si_4 O_{10}(OH)_2$	-30	-5287.6	-5257.6	-53.3	-23.3	0.1	5.3
$Ca_{0.1} Al_{1.93} Si_4 O_{10}(OH)_2$	-25	-5284.5	-5259.5	-45.9	10.9	0.1	4.4
$Mg_{0.1} Al_{1.93} Si_4 O_{10}(OH)_2$	-30	-5274.6	-5244.6	-39.5	-9.5	0.1	5.3
$K_{0.8} Al_{1.73} Si_4 O_{10}(OH)_2$	-40	-5340.4	-5300.4	-194.0	-154.0	2.8	9.8
$Na_{0.8} Al_{1.73} Si_4 O_{10}(OH)_2$	-79	-5320.3	-5241.3	-152.3	-73.3	3.4	17.3
$Li_{0.8} Al_{1.73} Si_4 O_{10}(OH)_2$	-122	-5345.0	-5223.0	-102.9	19.1	3.5	24.9
$Ca_{0.4} Al_{1.73} Si_4 O_{10}(OH)_2$	-106	-5332.6	-5226.6	-73.4	32.6	3.3	21.9
$Mg_{0.4} Al_{1.73} Si_4 O_{10}(OH)_2$	-119	-5293.1	-5174.1	-47.8	71.2	3.3	24.2

Note : ΔG^*_f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)

6) For one given exchangeable cation, a clay mineral of a complex composition is considered as an ideal solid solution of twelve endmembers (four uncharged minerals, four micas, and four celadonites). Octahedral Fe^{2+}, generally not represented, was forgotten. The contribution of each of these endmembers in the solid solution was recalculated according to the model of TARDY and FRITZ (1981) and TARDY et al. (1987). Thus, specific hydration

TABLE 11f. Fe^{3+}-dioctahedral and octahedral charge. Gibbs free energies of formation (kJ/mol) at 298.15 K and 1 bar total pressure. M represents K^+, Na^+, Li^+, Ca^{2+} and Mg^{2+}, respectively. X represents a smectite (interlayer charge of 0.2) and illite or a vermiculite (interlayer charge of 0.8), respectively. X represents a phyllosilicate layer.

	ΔG° hyd.	ΔG^*_f M-X hyd.	ΔG°_f M-X dehyd.	$\Delta G^*_{f(ox)}$ M-X hyd.	$\Delta G^\circ_{f(ox)}$ M-X dehyd.	$\log K_{sp}$ M-X hyd.	$\log K_{sp}$ M-X dehyd.
$K_{0.2} Fe_{1.93} Si_4 O_{10}(OH)_2$	-84	-4421.0	-4337.0	-22.5	61.6	-12.6	10.8
$Na_{0.2} Fe_{1.93} Si_4 O_{10}(OH)_2$	-98	-4415.9	-4317.9	-12.0	86.1	-12.5	4.7
$Li_{0.2} Fe_{1.93} Si_4 O_{10}(OH)_2$	-116	-4422.1	-4306.1	0.4	116.4	-12.4	7.9
$Ca_{0.1} Fe_{1.93} Si_4 O_{10}(OH)_2$	-31	-4419.0	-4388.0	7.7	38.7	-12.5	-7.1
$Mg_{0.1} Fe_{1.93} Si_4 O_{10}(OH)_2$	-33	-4409.1	-4376.1	14.2	47.2	-12.5	-6.7
$K_{0.8} Fe_{1.73} Si_4 O_{10}(OH)_2$	0	-4566.6	-4566.6	-146.8	146.8	-8.6	-8.6
$Na_{0.8} Fe_{1.73} Si_4 O_{10}(OH)_2$	-57	-4546.4	-4489.4	-105.0	-48.0	-7.9	2.1
$Li_{0.8} Fe_{1.73} Si_4 O_{10}(OH)_2$	-129	-4571.2	-4442.2	-55.7	73.3	-7.9	14.7
$Ca_{0.4} Fe_{1.73} Si_4 O_{10}(OH)_2$	-72	-4558.8	-4486.8	-26.2	45.8	-8.0	4.6
$Mg_{0.4} Fe_{1.73} Si_4 O_{10}(OH)_2$	-79	-4519.2	-4440.2	-0.5	78.5	-8.0	5.9

Note : ΔG^*_f refers to the dehydrated portion of the fully hydrated clay mineral ΔG^* M-X(hyd.) (see text)
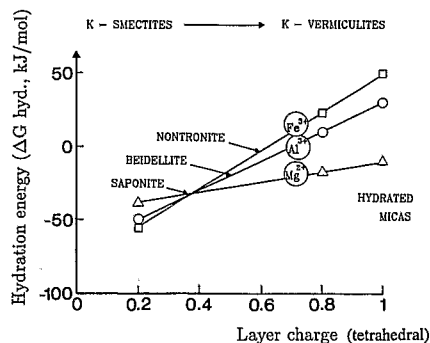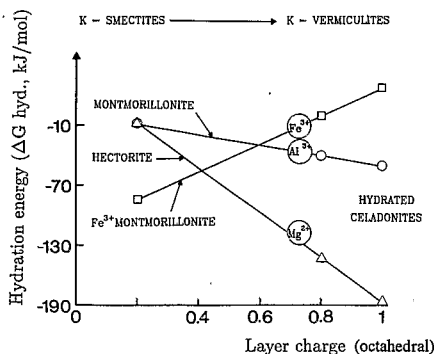
FIG. 4. Hydration energy (kJ/mol) as a function of the tetrahedral charge (equal to the layer charge) of K^+-vermiculites (tetrahedral charge between 1 and 0.6) and K^+-smectites (tetrahedral charge between 0.6 and 0.2) for three different octahedral cations (Mg^{2+}, Al^{2+}, and Fe^{3+}).

energies were added proportionally to the calculated contribution of each endmember so that we get the so-called "calculated values" listed in Table 5.

In Table 5, measured values range from -88 to -21 kJ/mol, and calculated hydration energies range from -89 to -17 kJ/mol. The correspondence between measured and calculated values is fairly good, the average error being ±6 kJ/mol. Most of the individual differences are small, whereas some of them can be very large, such as 27 kJ/mol for Li-montmorillonite of TOURET (1988).

GIBBS FREE ENERGY OF FORMATION OF DEHYDRATED CLAY MINERALS

Gibbs free energies of formation of dehydrated clay minerals M-X(dehyd.) are derived from the Gibbs free energies of formation from the elements of hydrated clay minerals (M-$X \cdot n H_2O$) and Gibbs free energies of hydration according to the following identical reactions:

$$\Delta G_f^*(\text{hydrated clay}) = \Delta G_f^0(\text{dry clay}) + \Delta G(\text{hydration}),$$
$$(50)$$

FIG. 5. Hydration energy (kJ/mol) as a function of the octahedral charge (equal to the layer charge) of K^+-vermiculites (octahedral charge between 1 and 0.6) and K^+-smectites (octahedral charge between 0.6 and 0.2) for three different octahedral cations (Mg^{2+}, Al^{3+}, and Fe^{3+}).
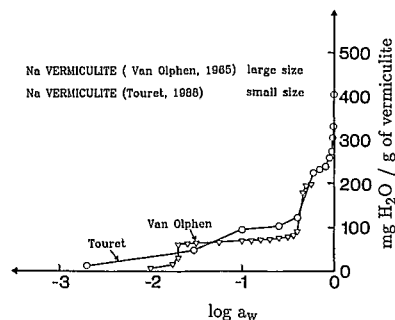

FIG. 6. Dehydration isotherms of a large Na-vermiculite (VAN OLPHEN, 1965) and fine-grained Na-vermiculite (TOURET, 1988). Notice the discrete hydration steps for data of VAN OLPHEN (1965). The first hydration step occurs at log $a_w = -1.75$, with the second developed at log $a_w = -0.35$. Data of fine-grained vermiculite by TOURET (1988) show less well-developed steps and progressive dehydration as function of water activity.

or

$$\Delta G_f^* \, M\text{-}X(\text{hyd.}) = \Delta G_f^0 \, M\text{-}X(\text{dehyd.}) + \Delta G(\text{hyd.}), \quad (51)$$

in which M stands for a given interlayer cation (K^+, Na^+, Li^+, $Ca_{0.5}^{2+}$, $Mg_{0.5}^{2+}$) and X represents one of the twelve phyllosilicate frameworks given in Table 2.

Generally, for clay minerals as for hydrates in pure water, hydrated phases are more stable than the corresponding dehydrated phases (Tables 6–10). This is true for all the minerals of mica and celadonite types saturated by Li^+, Na^+, Mg^{2+}, and Ca^{2+}. These minerals exhibit a negative hydration energy so that they hydrate spontaneously in water and change from micas to vermiculites. Vermiculites are less soluble and more stable in water than the corresponding micas. In general, vermiculites of octahedral charge are more hydrated than vermiculites of tetrahedral charge. Among them, hydration energies are more important (more negative) for trioctahedral (Mg^{2+} or Fe^{2+}) minerals than for dioctahedral minerals (Al^{3+} or Fe^{3+}) (Tables 6–10 and Figs. 4 and 5).

These considerations are also true (1) for celadonites and octahedrally charged vermiculites saturated by K^+, and (2) for phlogopite and the corresponding K^+ vermiculites.
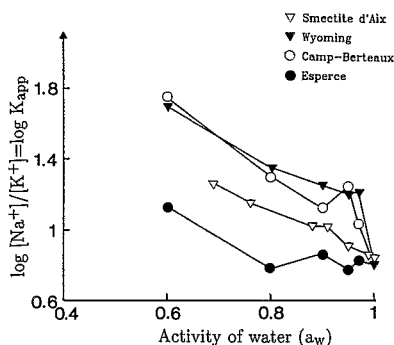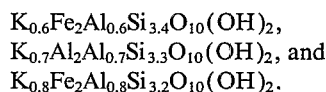

FIG. 7. Experimental change in the apparent Na-K exchange constants as function of the activity of water (TOURET, 1988). Notice that when the activity of water decreases, K_i (the dehydrated cation) is preferred to Na (the hydrated cation).

However, the contrary is observed for tetrahedrally charged K^+-micas such as annite (ΔG(hydration) = +17 kJ/mol), muscovite (ΔG(hydration) = +30 kJ/mol), and ferrimuscovite ($KFe_2AlSi_3O_{10}(OH)_2$; ΔG(hydration) = +50 kJ/mol).

Dioctahedral K^+-micas tetrahydrally charged, such as muscovite and ferrimuscovite, do not hydrate spontaneously in water and are consequently not commonly transformed into vermiculite. Only for the following three types of micas, hydration energy decreases with charge (less negative) and is equal to zero (Fig. 4):

$K_{0.6}Fe_2Al_{0.6}Si_{3.4}O_{10}(OH)_2$,
$K_{0.7}Al_2Al_{0.7}Si_{3.3}O_{10}(OH)_2$, and
$K_{0.8}Fe_2Al_{0.8}Si_{3.2}O_{10}(OH)_2$.

For higher tetrahedral charges, the Gibbs free energy of hydration is positive, and dehydrated micas are more stable than their corresponding vermiculites. This is probably the reason why, in water, glauconites are the only micas which can form at room temperature and why illite is the only one to form at relatively low diagenetic temperature (120°C).

As pointed out by TARDY and TOURET (1987), cation exchange energies are functions of hydration energies. This is well illustrated by the change of the cation exchange constant between layer silicates of paragonite-muscovite composition.

For the reaction

$$NaAl_2Si_3O_{10}(OH)_2 + K^+_{(aq)}$$
$$= KAl_2AlSi_3O_{10}(OH)_2 + N^+_{(aq)}, \quad (52)$$
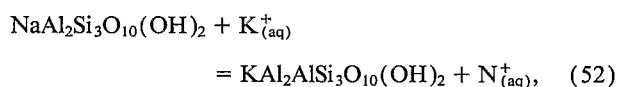
$[Na^+_{(aq)}]$ and $[K^+_{(aq)}]$ designate, respectively, the activities of aqueous cations in solution, and log $[Na^+]/[K^+]$ is the classical expression of the cation exchange reaction.

For well-crystallized paragonite-muscovite: log $[Na^+]/[K^+]$ = +3.93.
For poorly crystallized paragonite-muscovite: log $[Na^+]/[K^+]$ = +2.73.
For hydrated corresponding clay minerals: log $[Na^+]/[K^+]$ = +0.81.

When both cations are dehydrated, such as in well-crystallized and poorly crystallized paragonite and muscovite, the exchange constant is very high, which means that potassium is, by far, more preferred than sodium, or which means that, in water, muscovite is much more stable than paragonite when both are dehydrated. However, when sodium is hydrated, sodium-exchanged clay mineral is, in water, stabilized by comparison with its potassium counterpart (TOURET, 1988; Figs. 6 and 7). In other words, when dehydration takes place, either by compaction or increase of temperature and salinity, potassium in competition with other ions is selected and clay minerals tend to form illites. In the different terms of the illite series, the selection of potassium is better marked for iron-rich illites (glauconite) than for aluminous illites, than for trioctahedral illites, which never form (TARDY and TOURET, 1987; TARDY et al., 1987; TOURET, 1988).

When, on the contrary, hydration takes place in systems open to water circulation, hydrated ions such as Mg^{2+}, Ca^{2+}, or even Na^+, are selected; and clay minerals formed are vermiculites or smectites.

Changes in Gibbs Free Energy Due to Crystallinity and Grain Size

Gibbs free energies of hydrated clay minerals together with Gibbs free energies of hydration permitted estimates of Gibbs free energies of formation of dehydrated clay minerals (of small size) to be compared with Gibbs free energies of formation of corresponding well-crystallized phyllosilicates (of large size). Differences between these two energies are functions of crystallinity, grain size, and surface area (A) of particles, according to the following relationships:

ΔG_f^0 (dehydrated clay mineral of small size)

$- \Delta G_f^0$ (well-crystallized phyllosilicates of large size)

$$= \sigma A = \Delta G_{diff} \text{ (Table 6, column 6).}$$

In general, we expect that σ, the Gibbs free energy of surface, is positive so that the Gibbs free energy of formation of well crystallized and large-size phyllosilicates are generally more negative than Gibbs free energies of formation of corresponding dehydrated clay minerals of small size (Table 6, column 6). In water, phyllosilicates of large size are more stable than clay minerals of the same composition. One normally expects that crystals of small size should grow in solution and naturally evolve into large-size phyllosilicates.

However, our calculations suggest that poorly soluble phyllosilicates and particularly dioctahedral micas, such as muscovite or ferrimuscovite, for example, exhibit a negative surface Gibbs free energy so that dehydrated crystals of small size could appear more stable in water than dehydrated crystals of large size. In these conditions, dehydrated crystal growth could not consequently operate (Table 6, column 6).

Before extrapolating these results to natural conditions, one has to realize that data listed are concerning only individual components or endmembers. In natural conditions, these endmembers mix into solid solutions so that properties of natural clay minerals are combinations of those of individual endmembers. Furthermore, in natural environments, conditions of hydration are variable and determined by change in temperature, pressure, degree of compaction, and salinity of solutions.

CONCLUDING REMARKS

The Gibbs free energy of formation from the elements, the solubility product (i.e., the constant of the mass action law), and the field of stability of clay minerals are mostly dependant on the following three kinds of parameters:

1) Crystal grain size;
2) Chemical composition including layer charge, source of the charge (tetrahedral or octahedral), nature of the oc-

tahedral cation (Mg^{2+}, Fe^{2+}: trioctahedral; Al^{3+}, Fe^{3+}: dioctahedral), and nature of the interlayer cation; and

3) Hydration state and hydration energy.

These three parameters are also related and are not independent one from the other. Therefore clay minerals are hydrated, poorly, moderately, or highly hydrated so that their stability fields depend not only on temperature, pressure, and chemical composition of the system but also on the activity of water in which they equilibrate.

Three illustrations of these statements are selected here, as follows:

1) The hydration state (number of moles of H_2O per mole of mineral) and the hydration energy of a layer silicate depend on the nature of the interlayer cation. Consequently, a cation exchange reaction also involves an exchange of water. When reactions occur in water, the activity of which differs from 1 ($a_w \neq 1$), the thermodynamic exchange constant must include the activity of water in which the cation exchange reaction takes place; and the apparent exchange constant or the selectivity constant is dependent on the activity of water in which the cation exchange reaction takes place. In a cation exchange reaction and in water of high activity ($a_w \approx 1$), hydrated cations such as sodium are stabilized and favored. On the contrary, in water of low activity ($a_w \ll 1$), dehydrated cations such as potassium are stabilized; and hydrated cations such as sodium, calcium, or magnesium are defavorized. This is the reason why hydrated Na- or K-vermiculites exhibit about the same stability, while paragonite (Na-mica, dehydrated) is much less stable than muscovite (K-mica also dehydrated). Hydration stabilizes hydrated sodium and destabilizes dehydrated potassium.

2) The transformation of micas into vermiculites, or of smectites into illites, may be also regarded as an hydration-dehydration process. When temperature increases, layer dehydration takes place, and dehydrated cations such as potassium become stabilized. Illites or micas become more stable than vermiculites or smectites. When temperature decreases or water activity increases, hydration takes place and hydrated cations are stabilized, then micas of low charge can be transformed into vermiculites or smectites.

3) Questions concerning relationships between grain size effect, layer charge, and hydration energies are complex.

As pointed out by GARRELS and TARDY (1982), one may attribute 4–25 kJ/mol (i.e., per formula weight) to the increase of hydration energy due to the grain size effect, which may be significantly different from one sample to another, for example, from large-size vermiculites to small-size hectorites. It is assumed that the 21 kJ/mol represents the energy of hydrating some 370 m^2 per gram of silicate surface and corresponds to 0.140 J/m^2 as the energy involved. This number compares with the value of VAN OLPHEN (1965) of 0.150 J/m^2 for Na-vermiculite, with the value of KEENAN et al. (1951) of 0.125 J/m^2 for Li-kaolinite (that he interpreted as having an uncharged surface), and with the value of ILER (1955) of 0.130 J/m^2 for the heat of wetting of silicate sur-

faces. 120–150 kJ/m^2 (21 kJ/mol) is considered as the energy of wetting of an uncharged silicate surface.

When surfaces are charged and when cations compensating the charge are Li^+, Na^+, Mg^{2+}, or Ca^{2+}, hydration energies increase with the layer charge from 21 kJ/mol for zero charge. This is especially true for trioctahedral minerals and for Na-trioctahedral vermiculites. If, on the contrary, charged surfaces are compensated by K^+, hydration energies seem to diminish with layer charge. This is especially true for dioctahedral minerals in the series beidellite-vermiculite-illite-muscovite or nontronite-vermiculite-glauconite-celadonite.

There are not many data to support the line drawn for the hydration energy of aluminous K^+ layer silicates. However, the point of zero hydration energy at an interlayer charge of -0.8 is well established (BARSHAD, 1954). If this is accepted, it yields a positive value for the hydration of K^+ micas, which do not spontaneously hydrate in water at room temperature (GARRELS and TARDY, 1982).

Similarly, positive hydration energies have to characterize also the illitic Fe^{3+}-micas: celadonites of octahedral charge and glauconites of tetrahedral charge. Those minerals are known to remain stable as mica in seawater, at room temperature, without being transformed into hydrated vermiculites.

REFERENCES

AAGAARD P. and HELGESON H. C. (1983) Activity/composition relations among silicates and aqueous solutions: II. Chemical and thermodynamic consequences of ideal mixing of atoms on homological sites in montmorillonites, illites, and mixed layer clays. *Clays Clay Mineral.* **31**, 207–217.

BARSHAD L. (1954) Cation exchange in micaceous minerals: II. Replaceability of ammonium and potassium from vermiculite, biotite, and montmorillonite. *J. Soil Sci.* **78**, 57–76.

BARSHAD L. (1955) Adsorption and swelling properties of clay water systems. *Clays and Clay Technology* (ed. J. A. PASK and M. D. TURNER); *Calif. Div. Mines. Bull.* **169**, 70–77.

BEN RHAIEM H. (1983) Etude du comportement hydrique des montmorillonites calciques et sodiques par analyse de la diffusion des rayons X aux petits angles. Mise en évidence de la transition solide hydraté gel. Thesis, Univ. Orléans.

BEN RHAIEM H., TESSIER D., and PONS C. H. (1986) Comportement hydrique et évolution structurale et texturale des montmorillonites au cours d'un cycle de dessication-humectation: Partie I. Cas des montmorillonites Ca. *Clay Minerals* **21**, 9–29.

BEN RHAIEM H., PONS C. H., and TESSIER D. (1987) Factors affecting the microstructure of smectites: Role of cation and history of applied stresses. In *Proc. Intl. Clay Conf., Denver, 1985* (ed. L. G. SCHULTZ, H. VAN OLPHEN, and F. A. MUMPTON), pp. 292–297.

BRUGGENWERT M. G. M. and KAMPHORST A. (1982) Survey of experimental information on cation exchange in soil systems. In *Soil Chem.* (ed. G. H. BOLT) 5, pp. 141–203.

BURST J. F. (1969) Diagenesis of Gulf Coast clayed sediments and its possible relation to petroleum migration. *AAPG Bull.* **53**, 73–93.

CHEN C. H. (1975) A method of estimation of standard free energies of formation of silicate minerals, at 298,15°K. *Amer. J. Sci.* **275**, 801–817.

COLTEN-BRADLEY V. A. (1987) Role of pressure in smectite dehydration. Effects on geopressure and smectite to illite transformation. *AAPG Bull.* **71**, 1414–1427.

DUPLAY J. (1988) Géochimie des argiles et géothermométrie des populations monominérales de particules. Thesis, Univ. Strasbourg.

FRITZ B. (1981) Etude thermodynamique et modélisation des réactions hydrothermales et diagénétiques. *Sci. Géol. Mem.* **65**.

FRITZ B. (1985) Multicomponent solid solutions for clay minerals and computer modeling of weathering processes. In *The Chemistry of Weathering* (ed. J. L. DREVER); *NATO ASI series*, Vol. 149, pp. 19–34. Reidel Publishing Co.

GARRELS R. M. and CHRIST C. L. (1965) *Solutions, Minerals, and Equilibria.* Harper and Row.

GARRELS R. M. and TARDY Y. (1982) Born-Haber cycles for interlayer cations of micas. *Intl. Clay Conf., Bologne, 1981.* In *Developments in Sedimentology* (ed. H. VAN OLPHEN and F. VENIALE), Vol. 35, pp. 423–440. Elsevier.

GLAESER R. and MERING J. (1968) Domaines d'hydratation homogène des smectites. *C. R. Acad Sci.* **267**, 463–466.

GLAESER R., MANTINE I., and MERING J. (1967) Observations sur la beidellite. *Bull. Gr. Fr. Argiles* **19**, 125–130.

GLYNN P. D. and REARDON E. J. (1990) Solid solution, aqueous solution equilibria: Thermodynamic theory and representation. *Amer. J. Sci.* **290**, 164–201.

GORDY W. and THOMAS W. J. O. (1956) Electronegativities of the elements. *J. Chem. Phys.* **24**, 439–444.

HELGESON H. C. and MACKENZIE F. T. (1970) Silicate-sea water equilibria in the ocean system. *Deep-Sea Res.* **17**, 877–892.

HELGESON H. C., DELANY J. M., NESBITT H. W., and BIRD D. K. (1978) Summary and critique of the thermodynamic properties of rock forming minerals. *Amer. J. Sci.* **278A**, 1–229.

ILER R. K. (1955) *The Colloid Chemistry of Silica and Silicates.* Cornell Univ. Press.

KAMEL M. W. (1980) Etude de l'imbibition, du gonflement et du désséchement de quelques argiles. Thesis, Univ. Toulouse.

KEENAN A. G., MOONEY R. W., and WOOD L. A. (1951) The relation between exchangeable ions and water adsorption on kaolinite. *J. Phys. Colloid Chem.* **55**, 1462–1474.

MATTIGOD S. V. and SPOSITO G. (1978) Improved method for estimating the standard free energies of formation of smectites. *Geochim. Cosmochim. Acta* **42**, 1753–1762.

MAY H. M., KINNINBURGH D. G., HELMKE P. A., and JACKSON M. L. (1986) Aqueous dissolution, solubilities and thermodynamic stabilities of common aluminosilicate clay minerals: Kaolinite and smectite. *Geochim. Cosmochim. Acta* **50**, 1667–1677.

MERING J. (1975) Smectites. In *Soil Components 2: Inorganic Components* (ed. J. E. GIESEKING), pp. 97–119. Springer-Verlag.

MERINO E. and RANSOM B. (1982) Free energies of formation of illite solid solutions and their compositional dependence. *Clays Clay Mineral.* **30**, 29–39.

MOONEY R. W., KEENAN A. G., and WOOD L. A. (1952) Adsorption of water vapor by montmorillonite. *J. Amer. Chem. Soc.* **74**, 1367–1374.

NRIAGU J. (1975) Thermochemical approximations for clay minerals. *Amer. Mineral.* **60**, 834–839.

OVCHARENKO F. D., TARASEVICH Y. S., VALITSKAYA U. M., and POLYANOV V. E. (1967) Adsorption of water vapor on cation-substituted vermiculite. *Kolloidnyi Zh.* **29**, 565–568.

PAULING L. (1960) *The Nature of the Chemical Bond.* Cornell Univ. Press.

PERRY E. A. and HOWER J. (1972) Late stage dehydration in deeply buried pelitic sediments. *Bull. AAPG* **56**, 2013–2100.

PONS C. H. (1980) Mise en évidence des relations entre la texture et la structure dans les systèmes eau-smectites par diffusion aux petits angles du rayonnement X synchrotron. Thesis, Univ. Orléans.

PONS C. H., TCHOUBAR C., and TCHOUBAR D. (1980) Organisation des molécules d'eau à la surface des feuillets dans un gel de montmorillonite Na. *Bull. Mineral.* **103**, 452–456.

PONS C. H., ROUSSEAUX F., and TCHOUBAR D. (1981a) Utilisation du rayonnement synchrotron en diffusion aux petits angles pour l'étude du gonflement des smectites: I. Etude du système eau-montmorillonite Na en fonction de la température. *Clay Minerals* **16**, 23–42.

PONS C. H., TESSIER D., BEN RHAIEM H., and TCHOUBAR D. (1981b) A comparison between X-Ray studies and electron microscopy observations of smectite fabric. In *Developments in Sedimentology* (ed. H. VAN OLPHEN and F. VENIALE) Vol. 35, pp. 165–186. Elsevier.

PONS C. H., ROUSSEAUX F., and TCHOUBAR D. (1982) Utilisation du rayonnement synchrotron en diffusion aux petits angles pour l'étude du gonflement des smectites: II. Etude des différents systèmes eau-smectites en fonction de la température. *Clay Minerals* **17**, 327–338.

POWERS M. C. (1967) Fluid release mechanisms in compacting marine mudrocks and their importance in oil exploration. *AAPG Bull.* **51**, 1240–1254.

PROST R. (1975) Etude de l'hydratation des argiles: Interaction eau-mineral et mécanismes de la rétention d'eau. *Ann. Agron.* **26**, 463–535.

QUIRK J. P. (1968) Particle interaction and soil swelling. *Israel J. Chem.* **6**, 213–234.

ROBIE R. A. and WALDBAUM D. R. (1968) Thermodynamic properties of minerals and related substances at 298,15°K (25°C) and one atmosphere (1.013 bars) pressure and at higher temperature. *Geol. Surv. Bull.* **1259**, 1–256.

ROBIE R. A., HEMINGWAY B. S., and FISHER J. R. (1978) Thermodynamic properties of minerals and related substances at 298,15°K and 1 bar (10^5 Pascals) pressure and at higher temperatures. *USGS Bull.* **1452**, 1–456.

SPOSITO G. (1986) On the polymer model of thermochemical clay mineral stability. *Clays Clay Mineral.* **34**, 198–203.

STOESSEL R. K. (1979) A regular solution site mixing model for illites. *Geochim. Cosmochim. Acta* **43**, 1151–1159.

STOESSEL R. K. (1981) Refinements in a site mixing model for illites: Local electrostatic balance at the quasi chemical approximation. *Geochim. Cosmochim. Acta* **45**, 1733–1741.

SUQUET H. (1978) Propriétés de gonflement et structure de la saponite. Comparaison avec la vermiculite. Thesis, Univ. Pierre et Marie Curie, Paris.

TARASEVICH I., VALITSKAYA V. M., and OVCHARENKO T. D. (1968) Adsorption of water vapor on cation-substituted montmorillonite. *Kolloidnyi Zh.* **6**, 889–896.

TARDY Y. (1978) Relationships among Gibbs free energies of formation of compounds. *Amer. J. Sci.* **279**, 217–224.

TARDY Y. (1982) Kaolinite and smectite stability in weathering conditions. *Estudios Geologicos* **38**, 295–312.

TARDY Y. and FRITZ B. (1981) An ideal solid solution model for calculating solubility of clay minerals. *Clay Minerals* **16**, 361–373.

TARDY Y. and GARRELS R. M. (1974) A method of estimating the Gibbs energy of formation of layer silicates. *Geochim. Cosmochim. Acta* **38**, 1101–1116.

TARDY Y. and GARRELS R. M. (1976) Prediction of Gibbs energies of formation: I. Relationship among Gibbs energies of formation of hydroxides, oxides and aqueous ions. *Geochim. Cosmochim. Acta* **40**, 1051–1056.

TARDY Y. and GARRELS R. M. (1977) Prediction of Gibbs energies of formation: II. Monovalent and divalent metal silicates. *Geochim. Cosmochim. Acta* **41**, 87–92.

TARDY Y. and TOURET O. (1987) Hydration energies of smectites: A model for glauconite, illite, and corrensite formation. In *Proc. Intl. Clay Conf., Denver, 1985* (ed. L. G. SCHULTZ, H. VAN OLPHEN, and F. A. MUMPTON), pp. 46–52.

TARDY Y., LESNIAK P., DUPLAY J., and PROST R. (1980) Energie d'hydratation de l'hectorite. *Bull. Mineral.* **103**, 217–223.

TARDY Y., DUPLAY J., and FRITZ B. (1987) Stability fields of smectites and illites as a function of temperature and chemical composition. *Proc. Intl. Mtg. on Geochemistry of the Earth Surface and Processes of Mineral Formation, Granada, 1986,* pp. 461–494.

TESSIER D. (1984) Etude expérimentale de l'organisation des matériaux argileux. Thesis, Univ. Paris.

TESSIER D. and BERRIER J. (1978) Observations d'argiles hydratées en microscopie électronique à balayage, importance et choix de la technique de préparation. In *Proc. 5th Intl. Working Mtg. Soil Micromorphology, Granada,* pp. 117–135.

TESSIER D. and QUIRK J. P. (1979) Sur l'aspect de la microscopie électronique dans la connaissance du gonflement des matériaux argileux. *C. R. Acad. Sci.* **288D**, 1375–1378.

THORSTENSON D. C. and PLUMMER L. N. (1977) Equilibrium criteria for two-component solid reacting with fixed composition in aqueous phase. Example: The magnesian calcites. *Amer. J. Sci.* **277**, 1203–1223.

TOURET O. (1988) Structure des argiles hydratées. Thermodynamique de la deshydratation et de la compaction des smectites. Thesis, Univ. Strasbourg.

TRUESDELL A. H. and CHRIST C. L. (1968) Cation exchange in clays interpreted by regular solution theory. *Amer. J. Sci.* **266**, 402–412.

TURKI F. (1987) Hydratation des matériaux argileux gonflants. Thesis, Univ. Strasbourg.

VAN OLPHEN H. (1965) Thermodynamic of interlayer adsorption of water in clays. *J. Colloid Sci.* **20**, 822–857.

VAN OLPHEN H. (1977) *An Introduction to Clay Colloid Chemistry.* Interscience Publ.

VIEILLARD P. and TARDY Y. (1988a) Estimation of enthalpies of formation of minerals based on their refined crystal structures. *Amer. J. Sci.* **288**, 997–1040.

VIEILLARD P. and TARDY Y. (1988b) Une nouvelle échelle d'électronégativité des ions dans les cristaux. Principe et méthode de calcul. *C. R. Acad. Sci.* **306**, 423–428.

VIEILLARD P. and TARDY Y. (1989) Une nouvelle échelle d'électronégativité dans les oxydes et les hydroxydes. *C. R. Acad. Sci.* **308**, 1539–1545.

WAGMAN D. D., EVANS W. H., PARKER V. B., SCHUMM R. H., HALOW I., BAILEY S. M., CHUNRY K. L., and NUTTALL R. L. (1982) The NBS tables of thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic substances in S1 Units. *J. Phys. Chem.; Ref. Data* **2** (suppl 2.), 1–392.