# THE POLYMER MODEL OF THERMOCHEMICAL CLAY MINERAL STABILITY

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**Abstract**—The Nriagu polymer model of 2:1 layer type clay minerals develops from the premise that clay minerals are condensation copolymers of solid hydroxides. In the Mattigod-Sposito formulation of the model, standard state chemical potentials (standard Gibbs energies of formation from the elements) of 2:1 clay minerals are predicted quantitatively with a linear correlation equation relating the standard Gibbs energy of the polymerization reaction ($\Delta G^0_r$) to the half-cell layer charge of the clay mineral and to the valence and ionic radius of the exchangeable cation. It is now shown that this correlation equation can be derived from two basic assumptions: (1) that the standard Gibbs energy change for the transfer of a cation in a pure hydroxide solid to a hydroxide component in the tetrahedral or octahedral sheet of a 2:1 clay mineral is independent of the nature of the cation and (2) that the difference between $\Delta G^0_r$ for the polymerization reaction to form a 2:1 clay mineral and $\Delta G^0_r$ for the same reaction to form the zero layer-charge analog of the clay mineral is proportional to the number of interlayer exchangeable cations per unit cell of the clay mineral and to the radius of its exchangeable cation. Both of these assumptions can be tested experimentally, independent of the polymer model.

**Key Words**—Chemical potential, Illite, Layer charge, Polymer model, Smectite, Stability, Vermiculite.

## INTRODUCTION

The clay mineral groups illite, vermiculite, and smectite comprise 2:1 layer type phyllosilicates with the general half-unit-cell chemical formula:

$$C_x[Si_{n1}Al_{4-n1}]$$
$$(Al_{n1+n2-4}Fe(III)_{n3}Fe(II)_{n4}Mg_{n5}M_{n6})O_{10}(OH)_{12}$$
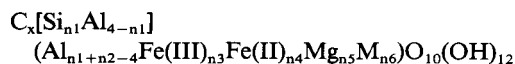
where C represents a cation of valence Z in the interlayer region, [ ] refers to the tetrahedral sheet, ( ) refers to the octahedral sheet, and the $n_i$ values ($i = 1$ to 6) are stoichiometric coefficients subject to the mass and charge balance conditions:

$$\sum_{i=1}^{6} n_i = \begin{cases} 6 \text{ dioctahedral minerals} \\ 7 \text{ trioctahedral minerals} \end{cases} \quad (1)$$

$$x = \begin{cases} 4 - n1 + n4 + n5 \\ \qquad \text{dioctahedral minerals} \\ 2(4 - n1) - n2 - n3 \pm n6 \\ \qquad \text{trioctahedral minerals} \end{cases} \quad (2)$$

where x is the half-cell layer charge and the unspecific trioctahedral sheet cation M is assumed to have either valence 1 (upper sign in Eq. (2)) or 3 (lower sign in Eq. (2)). (If the valence of M is 2, n6 does not appear in Eq. (2).) Typical values of the layer charge x, which is used to define 2:1 layer type clay mineral groups, and of $n_i$ for dioctahedral minerals were compiled by Sposito (1984, Table 1.3). Examples of the trioctahedral minerals include hectorite ($x = 0.33$, $n1 = 4$, $n2 = n3 = n4 = 0$, $n5 = 2.65$, $n6 = 0.33$, $M = Li$) and trioctahedral vermiculite ($x = 0.6$, $n1 = 2.72$, $n2 = 1.5$, $n3 = 0.46$, $n4 = n6 = 0$, $n5 = 1.92$).
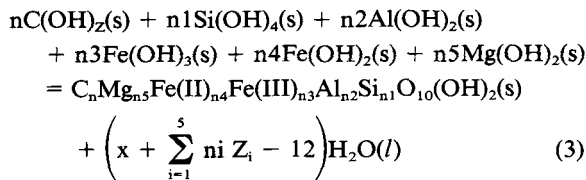
A distinguishing feature of 2:1 clay minerals is the typically fractional values of the stoichiometric coefficients $n_i$ (Weaver and Pollard, 1973). Fractional stoichiometric coefficients imply a solid solution phenomenon with its concomitant problems of thermodynamic metastability and solubility disequilibrium (Gresens, 1981; Lippmann, 1982; Aagaard and Helgeson, 1983). Recognition of this basic fact has prompted a number of recent modeling efforts whose overall objective is to predict the (meta)stability fields of 2:1 clay minerals based on homogeneous mixture models (Stoessell, 1979, 1981; Tardy and Fritz, 1981; Aagaard and Helgeson, 1983). These models have the advantage of being based in a firm theoretical framework, the thermodynamics of mixtures, and of simplicity with respect to the representation of (meta)stability fields in conventional phase diagrams or activity-composition graphs (Stoessell, 1979; Aagaard and Helgeson, 1983). They also face difficulties of a practical kind, however, such as a plethora of end-member components (Tardy and Fritz, 1981) or an intrinsic inability to distinguish beidellites from illites according to site-occupancy statistics (Aagaard and Helgeson, 1983).

The present, incomplete state of modeling of clay mineral stability leaves open the possibility that the polymer approach pioneered by Nriagu (1975) may be useful. This approach does not address the solid solution aspect of 2:1 clay minerals through mixing statistics but nonetheless has heuristic value. Nriagu (1975) proposed that the formation of a 2:1 clay mineral be pictured as polymerization reaction involving solid hydroxide components:

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Table 1. Comparison of experimental standard state chemical potentials (kJ/mole) for dioctahedral smectites with estimates based on the polymer model.

| Smectite | Half-cell chemical formula | $\mu^0_{exp}$[1] | $\mu^0_{calc}$ |
|---|---|---|---|
| Aberdeen, Mississippi | $Mg_{0.2075}(Al_{0.18}Si_{3.82})(Al_{1.29}Fe^{3+}_{0.335}Mg_{0.445})O_{10}(OH)_2$ | −5219 | −5212 |
| Aberdeen, Mississippi | $Al_{0.1383}(Al_{0.18}Si_{3.82})(Al_{1.29}Fe^{3+}_{0.335}Mg_{0.445})O_{10}(OH)_2$ | −5200 | −5196 |
| Belle Fourche, South Dakota | $Mg_{0.1325}(Al_{0.065}Si_{3.935})(Al_{1.515}Fe^{3+}_{0.225}Mg_{0.29})O_{10}(OH)_2$ | −5223 | −5218 |
| Belle Fourche, South Dakota | $Al_{0.0883}(Al_{0.065}Si_{3.935})(Al_{1.515}Fe^{3+}_{0.225}Mg_{0.29})O_{10}(OH)_2$ | −5213 | −5205 |
| Houston, Texas | $Mg_{0.225}(Al_{0.30}Si_{3.70})(Al_{1.345}Fe^{3+}_{0.405}Mg_{0.27})O_{10}(OH)_2$ | −5215 | −5174 |
| Beidellite, Missouri | $Mg_{0.135}Ca_{0.01}Na_{0.07}K_{0.095}(Al_{0.45}Si_{3.55})$ $(Al_{1.41}Fe^{3+}_{0.415}Fe^{2+}_{0.055}Mg_{0.205})O_{10}(OH)_2$ | −5215 | −5223 |
| Beidellite, Missouri | $K_{0.37}Ca_{0.01}Na_{0.07}(Al_{0.45}Si_{3.55})(Al_{1.41}Fe^{3+}_{0.415}Fe^{2+}_{0.055}Mg_{0.205})O_{10}(OH)_2$ | −5262 | −5255 |
| Colony, Wyoming | $Mg_{0.195}(Al_{0.19}Si_{3.81})(Al_{1.52}Fe^{3+}_{0.22}Mg_{0.29})O_{10}(OH)_2$ | −5262 | −5255 |
| Colony, Wyoming | $Mg_{0.185}(Al_{0.19}Si_{3.80})(Al_{1.58}Fe^{3+}_{0.19}Mg_{0.26})O_{10}(OH)_2$ | −5268 | −5268 |
| Colony, Wyoming | $Mg_{0.21}(Al_{0.19}Si_{3.81})(Al_{1.52}Fe^{3+}_{0.21}Mg_{0.29})O_{10}(OH)_2$ | −5262 | −5262 |
| Castle Rock, Colorado | $Mg_{0.21}(Al_{0.32}Si_{3.68})(Al_{1.52}Fe^{3+}_{0.14}Mg_{0.46})O_{10}(OH)_2$ | −5337 | −5333 |
| Upton, Wyoming | $Mg_{0.17}(Al_{0.07}Si_{3.93})(Al_{1.55}Fe^{3+}_{0.20}Mg_{0.24})O_{10}(OH)_2$ | −5218 | −5232 |
| Clay Spur, Wyoming | $Na_{0.27}Ca_{0.01}K_{0.02}(Al_{0.06}Si_{3.94})(Al_{1.52}Fe^{3+}_{0.19}Mg_{0.22})O_{10}(OH)_2$ | −5226 | −5248 |
| Cheto, Arizona | $Ca_{0.185}Na_{0.02}K_{0.02}(Al_{0.07}Si_{3.93})(Al_{1.52}Fe^{3+}_{0.14}Mg_{0.33})O_{10}(OH)_2$ | −5246 | −5276 |

[1] Data compiled by Mattigod and Sposito (1978).

$$nC(OH)_Z(s) + n1Si(OH)_4(s) + n2Al(OH)_2(s)$$
$$+ n3Fe(OH)_3(s) + n4Fe(OH)_2(s) + n5Mg(OH)_2(s)$$
$$= C_nMg_{n5}Fe(II)_{n4}Fe(III)_{n3}Al_{n2}Si_{n1}O_{10}(OH)_2(s)$$
$$+ \left(x + \sum_{i=1}^{5} ni\ Z_i - 12\right)H_2O(l) \qquad (3)$$

where $n = x/Z$, $Z_i$ is the valence of the cation in the hydroxide solid whose stoichiometric coefficient is ni, and n6 has been suppressed to simplify notation. The solid product on the right side of Eq. (3) is a 2:1 clay mineral represented as a condensation copolymer of solid hydroxides, by analogy with biomolecules like proteins, which are condensation copolymers of amino acids, or polysaccharides, which are condensation copolymers of sugars.

The polymer model as introduced by Nriagu (1975) can be used to predict the standard state chemical potentials (standard Gibbs energies of formation from the elements) of montmorillonites, vermiculites, and illites with an inaccuracy of about 40 kJ/mole (Mattigod and Sposito, 1978). Focusing on smectites, Mattigod and Sposito (1978) refined the polymer model proposed by Nriagu (1975) to eliminate its *ad hoc* adjustment of the standard state chemical potentials of metal hydroxides and to elucidate the special role played in the model by interlayer exchangeable cations in determining the stability of a 2:1 clay mineral. Sposito (1985, Appendix) recently gave the polymer model a new mathematical form that relies on only two adjustable parameters. The quantitative accuracy of this reformulated model is illustrated in Table 1 for dioctahedral smectites, based on composition and thermochemical data compiled by Mattigod and Sposito (1978). Experimental and calculated standard state chemical potentials ($\mu^0$) agree closely for specimen montmorillonites (e.g., Belle Fourche, South Dakota), soil montmorillonite (Houston, Texas), and soil bei-

dellites (Saline County, Missouri). The model also predicts a $\mu^0$ value of −5271 kJ/mole for the isostructural zero layer-charge analog pyrophyllite ($Si_4Al_2O_{10}(OH)_2$), in excellent agreement with the experimental value of −5269 ± 4 kJ/mole recommended by Robie *et al.* (1978). The mean absolute difference between $\mu^0_{exp}$ and $\mu^0_{calc}$ for the 14 dioctahedral smectites and pyrophyllite is 11 kJ/mole, which is at the limit of the expected inaccuracy in $\mu^0_{exp}$ derived from solubility data (R. M. Garrels, University of South Florida, St. Petersberg, Florida, personal communication). This degree of quantitative prediction is especially noteworthy for pyrophyllite, whose layer charge ($x = 0$) is well below the minimum value ($x = 0.34$) used in calibrating the two adjustable model parameters. The same kind of predictive quality obtains in the case of $\mu^0$ for trioctahedral vermiculites (Sposito, 1985, Appendix) and for the zero layer-charge analog, talc.

The quantitative success of the polymer model suggests that an inquiry as to its basis in physical chemistry would be worthwhile. In this paper, the version of the model summarized only as a statistical algorithm by Sposito (1985, Appendix) is examined in a physicochemical context and derived with the assistance of concepts in ionic crystal chemistry as discussed by Tardy and Garrels (1974), Chen (1975), Nriagu (1975), Mattigod and Sposito (1978), and Ahrens (1983). The objective of this investigation is to place the polymer model on firmer theoretical grounds and to illustrate its complementary role to the solid solution approach in understanding the stability of 2:1 clay minerals under surface terrestrial conditions (Lippmann, 1981, 1982).

## THE POLYMER MODEL

The polymer model is developed as a predictor of standard state chemical potentials of 2:1 clay minerals

by an analysis of the (negative) standard Gibbs energy change for the reaction in Eq. (3) (Sposito, 1981):

$$\Delta G_r^0 = \mu^0[\text{clay mineral}]$$
$$+ \left(x + \sum_{i=1}^{5} ni\, Z_i - 12\right)\mu^0[H_2O(l)]$$
$$- n\mu^0[C(OH)_z(s)] - \sum_{i=1}^{5} ni\mu_i^0, \quad (4)$$

where $\mu_i^0$ is the standard state chemical potential of the hydroxide solid whose stoichiometric coefficient in Eq. (3) is ni. Equation (4) can be rearranged to provide an expression for $\mu^0[\text{clay mineral}]$:

$$\mu^0[\text{clay mineral}] = n\mu^0[C(OH)_z(s)] + \sum_{i=1}^{5} ni\, \mu_i^0$$
$$- \left(x + \sum_{i=1}^{5} ni\, Z_i - 12\right)\cdot$$
$$\mu^0[H_2O(l)] - |\Delta G_r^0|. \quad (5)$$

Mattigod and Sposito (1978) compiled a set of $\mu^0$ values for $H_2O(l)$, $C(OH)_Z(s)$, and the solid hydroxides in Eq. (3) which they recommended for use on the right side of Eq. (5). Their solid hydroxide data are listed in Table 2 along with corresponding thermochemical data recommended since in the authoritative compilations by Robie *et al.* (1978) and by Wagman *et al.* (1982). The close agreement among the three sets of data suggests that the compilation by Mattigod and Sposito (1978) was adequate in both accuracy and self-consistency. Therefore, its continued use in applications of the polymer model appears warranted.

Given the availability of the $\mu^0$ values on the right side of Eq. (5), there remains only the determination of $\Delta G_r^0$. This can be done by applying Eq. (4) to a calibration set of 2:1 clay minerals for which experimental $\mu^0$ values are known. Absolute values of $\Delta G_r^0$ for 25 homoionic montmorillonites calculated in this way appear in Table 5 of Mattigod and Sposito (1978). These data can be represented mathematically with a linear correlation expression suggested by Sposito (1985, Appendix):

$$|\Delta G_r^0| = A + B\left(\frac{xR}{Z}\right), \quad (6)$$

where A and B are adjustable parameters and R is the crystallographic ionic radius of the interlayer exchangeable cation $C^{z+}$ in Eq. (2). Mattigod and Sposito (1978) used the ionic radii compiled by Pauling (1960) in their more complicated statistical expression for $\Delta G_r^0$, but present consensus is that the compilation by Shannon and Prewitt (1969) is to be preferred. A comparative listing of the two sets of ionic radii is given in Table 3; significant differences exist among the radii for Group IA and IIA metals and Al.

Using the $\Delta G_r^0$ and corresponding x values for the 25 montmorillonites from Mattigod and Sposito (1978) and the Shannon-Prewitt radii, the linear regression equation is:[1]

$$|\Delta G_r^0| = 41.34 + 921.66\left(\frac{xR}{Z}\right) \quad (r^2 = 0.931), \quad (7)$$

where $|\Delta G_r^0|$ is in kilojoules per mole and R is in nanometers. The standard error of estimate for Eq. (7) was 5.0 kJ/mole, and none of the residuals was significant at P = .05. This expression was introduced into Eq. (5) to produce the $\mu^0_{calc}$ data in Table 1. None of the smectite data listed in Table 1 was used to derive Eq. (7).

## ORIGIN OF THE POLYMER MODEL

### Significance of the parameter A

The application of Eq. (4) to the formation of pyrophyllite yields the expression:

$$\Delta G_r^0(\text{pyro.}) = \mu^0[\text{pyrophyllite}] + 10\mu^0[H_2O(l)]$$
$$- 2\mu^0[Al(OH)_3] - 4\mu^0[Si(OH)_4]. \quad (8)$$

Using the $\mu^0$ values in Table 2, $\mu^0[\text{pyrophyllite}] = -5269.4$ kJ/mole, and $\mu^0[H_2O(l)] = -237.14$ kJ/mole (Robie *et al.*, 1978), one calculates $\Delta G_r^0(\text{pyro.}) = -39.4$ kJ/mole. This result is not significantly different (P = .05) from the y-intercept of the linear regression of $\Delta G_r^0$ on (xR/Z) based on Eqs. (6) and (7), i.e., A = -41 ± 5 kJ/mole. Therefore, in keeping with the excellent prediction of $\mu^0[\text{pyrophyllite}]$ by the polymer model, discussed in the Introduction, the parameter A in Eq. (6) can be interpreted as $\Delta G_r^0$ for the formation of a zero layer-charge phyllosilicate from component solid hydroxides. The polymer model implies that this $\Delta G_r^0$ is the same for all isostructural dioctahedral (or, by extension, all trioctahedral) zero layer-charge phyllosilicates.

For the particular example of dioctahedral 2:1 clay minerals, Eqs. (4), (6), and (8) can be combined to produce the expression:

$$\mu^0[\text{clay mineral}] - \mu^0[\text{pyrophyllite}] - n\mu^0[M(OH)_z]$$
$$- n5\mu^0[Mg(OH)_2] - n4\mu^0[Fe(OH)_2]$$
$$- n3\mu^0[Fe(OH)_3] + (2 - n4)\mu^0[Al(OH)_3]$$
$$+ (4 - n5)\mu^0[Si(OH)_4] = -B\left(\frac{xR}{Z}\right), \quad (9)$$

where B = 921 ± 108 (P = .05) kJ/nm·mole according to the statistical analysis leading to Eq. (7). Eq. (9) shows that the polymer model assigns the total con-

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[1] The y-intercept in Eq. (7) differs significantly from that in Eq. (6.1) and Figure 7 of Sposito (1985) because a different set of $\mu^0$ values from those in Table 2 were used by Sposito (1985) to calibrate Eq. (6). No significant differences exist, however, among the $\mu^0_{calc}$ values in Table 1 and those appearing in Table 2 of Sposito (1985).

Table 2. Comparative list compiled of standard state chemical potentials (kJ/mole) for hydroxide solids.

| Solid hydroxide | Mattigod and Sposito (1978) | Robie et al. (1978) | Wagman et al. (1982)[1] |
|---|---|---|---|
| $Al(OH)_3$ | $-1154.9 \pm 1.2$ | $-1154.9 \pm 1.2$ | $-1155.1$ |
| $Ba(OH)_2$ | $-857.2^{2}$ | — | — |
| $Ca(OH)_2$ | $-898.56$ | $-898.4 \pm 1.3$ | $-898.49$ |
| CsOH | $-370.7$ | $-370.7 \pm 0.9$ | — |
| $Fe(OH)_2$ | $-486.6$ | — | $-486.5$ |
| $Fe(OH)_3$ | $-696.4$ | — | $-696.5$ |
| KOH | $-378.9$ | $-378.9 \pm 0.5$ | $-379.08$ |
| LiOH | $-441.4$ | $-438.9 \pm 0.2$ | $-438.95$ |
| $Mg(OH)_2$ | $-833.58$ | $-833.5 \pm 0.4$ | $-833.51$ |
| NaOH | $-379.70$ | $-379.7 \pm 0.1$ | $-379.494$ |
| RbOH | $-364.43$ | — | — |
| $Si(OH)_4$ | $-1322.9$ | — | $-1322.9$ |
| $Sr(OH)_2$ | $-874.8^{2}$ | — | — |

[1] "Overall uncertainty lies between 8 and 80 units of the last (right-most) digit" (Wagman et al., 1982).
[2] Estimated by Mattigod and Sposito (1978).

tribution to the sum of standard state chemical potential differences on the left side solely to the interlayer exchangeable cation, $C^{z+}$.

*Significance of the interlayer cation*

The crystal chemical implications of Eq. (9) can be seen in perhaps the clearest light by adopting a restricted version of the "silication" concept introduced by Tardy and Garrels (1974). Assuming for the sake of discussion that $\mu^0$[clay mineral] in Eq. (4) can be decomposed uniquely into linear combinations of standard state chemical potentials of solid hydroxides and water components in the clay mineral,

$$\mu^0[\text{clay mineral}] \equiv n\mu^0_{CM}[C(OH)_z] + \sum_{i=1}^{5} n_i \mu^0_{iCM}$$
$$+ \left(x + \sum_{i=1}^{5} n_i Z_i - 12\right)\mu^0_{CM}[H_2O],$$
$$\tag{10}$$

where $\mu^0_{CM}$[component] is a standard state chemical potential of a hydroxide or water component *in the clay mineral*. The uniformity assumption introduced by Tardy and Garrels (1974) is applied here only in the restrictive sense that $\mu^0_{CM}$[hydroxide component] is to have the same value in all isostructural 2:1 clay minerals (as opposed to all layer silicates as assumed

Table 3. Comparison of Pauling and Shannon-Prewitt crystallographic ionic radii (nm) of metals.[1]

| Metal | Pauling | Shannon/Prewitt | Metal | Pauling | Shannon/Prewitt |
|---|---|---|---|---|---|
| Li | 0.060 | 0.074 | Mg | 0.065 | 0.072 |
| Na | 0.095 | 0.102 | Ca | 0.099 | 0.100 |
| K | 0.133 | 0.138 | Sr | 0.113 | 0.116 |
| Rb | 0.148 | 0.149 | Ba | 0.135 | 0.136 |
| Cs | 0.169 | 0.170 | Al | 0.050 | 0.053 |

[1] Octahedral coordination.

by Tardy and Garrels (1974)). With this assumption, Eq. (9) can be written in the form:

$$n(\mu^0_{CM}[C(OH)_z] - \mu^0[C(OH)_z])$$
$$+ n5(\mu^0_{CM}[Mg(OH)_2] - \mu^0[Mg(OH)_2])$$
$$+ n4(\mu^0_{CM}[Fe(OH)_2] - \mu^0[Fe(OH)_2])$$
$$+ n3(\mu^0_{CM}[Fe(OH)_3] - \mu^0[Fe(OH)_3])$$
$$+ (n2 - 2)(\mu^0_{CM}[Al(OH)_3] - \mu^0[Al(OH)_3])$$
$$+ (n1 - 4)(\mu^0_{CM}[Si(OH)_4] - \mu^0[Si(OH)_4])$$
$$= -B\left(\frac{xR}{Z}\right) = -nBR. \tag{11}$$

The chemical potential differences in parentheses in Eq. (11) represent standard Gibbs energy changes when a solid hydroxide transforms from a separate hydroxide phase to a hydroxide component in a clay mineral. The weighted sum of these changes on the left side of Eq. (11) may be given the symbol $\delta\Delta G^0_r$ in consonance with the chemical meaning of Eq. (9). Thus, the polymer model states that:

$$\delta\Delta G^0_r = -nBR, \tag{12}$$

where n and R pertain to the interlayer exchangeable cation, $C^{z+}$.

A necessary condition for $\delta\Delta G^0_r$ to be independent of all clay mineral components in Eq. (11) except $C(OH)_z$ is that

$$(\mu^0_{iCM} - \mu^0_i) = \Delta \qquad (i = 1, \ldots, 5), \tag{13}$$

where $\Delta$ is a constant that has the same value for all hydroxide components in the tetrahedral or octahedral sheets of a 2:1 clay mineral. The independence of $\Delta$ from the value of i is a necessary condition imposed by the fact that the ni in Eq. (11) may have arbitrary positive values. The substitution of Eq. (13) into Eq. (11) reduces the latter equation to the expression:

$$n(\mu^0_{CM}[C(OH)_z] - \mu^0[C(OH)_z]) = \delta\Delta G^0_r$$
$$= -nBR, \tag{14}$$

once the mass balance condition in Eq. (2) is imposed. Eq. (14) refers only to the interlayer exchangeable cation on both sides.

Evidence for Eq. (13) with $\Delta = 0$ was adduced by Tardy and Garrels (1974) in their study of the effect of "silication" on hydroxide solids. They argued that cations with electronegativities larger than 1.0 (Pauling scale) should exhibit very small "silication" Gibbs energy differences ($\Delta$). Inasmuch as electronegativity is related closely to ionic potential (Huheey, 1972), this point of view is similar to that expressed by Mattigod and Sposito (1978), who suggested that cations with higher ionic potentials are least perturbed when transferred from a hydroxide solid to a clay mineral matrix. In the polymer model, the thermochemical effect of transferring Mg, Fe(II), Fe(III), Al, and Si from a hydroxide phase to a sheet in a 2:1 clay mineral is assumed to be insensitive to the nature of the cation (which has a relatively high electronegativity), whereas the transfer of a cation from a hydroxide phase to an interlayer exchange site is assumed to depend sensitively on the nature of the cation.

Given Eq. (13), it is evident that $\delta\Delta G^0_r$ can be expressed in general by a product of the stoichiometric coefficient n in Eq. (2) and some positive function f of the atomic structural properties of the interlayer exchangeable cation that relate to crystal chemistry:

$$\delta\Delta G^0_r = -n \; f(\text{properties of } C^{z+}). \qquad (15)$$

Eq. (15) ensures that $\delta\Delta G^0_r$ will vanish for zero layer-charge phyllosilicates. Several choices are possible for the properties of the exchangeable cation on which the function f is to depend. Among them are electronegativity, ionization energy, ionic potential, polarizability, valence, and ionic radius. These properties are not independent. Ahrens (1983) pointed out, for example, that ionization energies can substitute for electronegativities in geochemical correlations. Electronegativities, in turn, are correlated with ionic potentials, as are polarizabilities (Huheey, 1972). Polarizabilities correlate directly with ionic radius, a measure of the extent to which atomic electrons can be spread over adjacent, bonding ligands (Misono *et al.,* 1967). Tardy and Garrels (1974) observed that increasing electronegativity produced decreasing "silication" free energy changes for exchangeable cations in layer silicates. Electronegativity increases with decreasing ionic radius (Huheey, 1972); thus, the left side of Eq. (14) should correlate positively with the ionic radius, a simple crystallographic property of geochemical significance. Thus, Eq. (15) may be epxressed:

$$\delta\Delta G^0_r = -nf(R) \qquad (16)$$

to keep matters uncomplicated. The mathematical form of f(R) is not known, but advantage can be taken of the empirical fact that $\delta\Delta G^0_r$ provides a very small contribution to $\mu^0[\text{clay mineral}]$. (For the smectites list-

ed in Table 1, the mean value of $|\delta\Delta G^0_r|$ is 15 kJ/mole.) Thus, f(R) can be approximated by the first non-vanishing term of its MacLaurin expansion, in which case Eq. (14) results with $B \equiv (df/dR)_{R=0}$.

*Relation to silicate geochemistry*

The left side of Eq. (9), denoted generally with the symbol $\delta\Delta G^0_r$ in this paper, can be interpreted as the standard Gibbs energy change for a reaction in which pyrophyllite combines with solid hydroxides to form a dioctahedral 2:1 clay mineral:

$$\delta\Delta G^0_r = \mu^0[\text{clay mineral}]$$

$$- \sum_{j=0}^{7} nj' \mu^0_j [\text{reactant}], \qquad (17)$$

where $j = 0$ refers to pyrophyllite, $j = 1$ refers to $C(OH)_z(s)$, and the $nj'$ ($j = i + 2$) are stoichiometric coefficients for the other solid hydroxides in Eq. (9). Chen (1975) considered a quantity identical to $\delta\Delta G^0_r$ for a wide variety of silicate formation reactions wherein the product is not necessarily a clay mineral and the reactants need not be the same as those in Eq. (9). His analysis shows that $|\delta\Delta G^0_r|$ can generally be represented mathematically by the expression:

$$|\delta\Delta G^0_r| = a \; \exp(-bk), \qquad (18)$$

where a and b are positive, empirical parameters and k is an index of the "complexity" of the formation reaction. Reactions that feature many reactants of simple structure (e.g., hydroxides) are assigned smaller values of k than those which feature few reactants of complex structure (e.g., layer silicates). Mattigod and Sposito (1978) showed that Eq. (18) could be applied successfully to the formation of Na-montmorillonites, with $b = 0.65 \pm 0.04$ and the value of a increasing with the layer charge. In the present context, the association of Eqs. (12) and (18) implies that:

$$a = nRB \; \exp(bk) = \alpha(xR/Z), \qquad (19)$$

where $\alpha \equiv B \; \exp(bk)$ is a constant. Chen (1975) showed that Eq. (19) is satisfied for a wide variety of silicates containing Na, K, Ca, or Mg (Al and Si are not considered when computing xR/Z), with x representing the structural charge per unit cell. The conclusion drawn by Chen (1975), that Eq. (19) "is probably due to internuclear and interionic repulsion," is consonant with the premises of the polymer model. In this respect, Eq. (12) can be regarded as an example based in the general crystal chemistry of silicate minerals containing Group IA and IIA metals.

## CONCLUSIONS

The foregoing analysis makes it possible to develop a set of physicochemical postulates for the polymer model:

(1) A 2:1 clay mineral can be pictured as a condensation copolymer of solid hydroxides.

(2) The standard Gibbs energy change for the transfer of a cation in a hydroxide solid to a hydroxide component in the tetrahedral or octahedral sheet of a 2:1 clay mineral is independent of the nature of the cation.

(3) The difference between $\Delta G^0_r$ for the reaction to form a 2:1 clay mineral according to postulate (1) and $\Delta G^0_r$ for the same kind of reaction to form the zero layer-charge analog of the clay mineral is proportional to the number of interlayer exchangeable cations per unit cell of the clay mineral and to the radius of the exchangeable cation.

The testing of postulate (2) with precise thermochemical data and the elucidation of postulate (3) in terms of theoretical crystal chemistry certainly is desirable. Another useful line of research would be the exploration of connections between the polymer model and statistical site-mixing models based in solid solution theory. The present discussion will have served its heuristic purpose if it helps to shed light on the foundations of these models and on the thermochemical factors which determine the metastability of 2:1 clay minerals in surface terrestrial environments.

## ACKNOWLEDGMENTS

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