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A regular solution site-mixing model for illites

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Abstract—The dependence on the composition of the thermodynamic stability of an illite can be treated in terms of a regular solution site-mixing model. Four end-member micas (muscovite, pyrophyllite, phlogopite, and annite) were mixed to simulate an illite in this study. In the model, random mixing of cations was assumed over each given class of cation sites. Mixing over cation sites between different classes of cation sites was not allowed. The resulting free energy and chemical potential equations contain four site interaction parameters: three for octahedral site interactions and one for interlayer and tetrahedral site interactions. These parameters cannot presently be evaluated because of a lack of experimental data on Fe^{3+}-free illites. The model does imply that the octahedral site interaction parameters must be significantly more positive than the interlayer and tetrahedral site interaction parameter to account for the dominant dioctahedral nature of most natural illites. This constraint is necessary to balance out the increase in stability due to the configurational entropy of an illite having a major trioctahedral component.

The model can be extended to cover a wider range of illite compositions by the inclusion of an end-member mica containing Fe^{3+} ions in the octahedral sites. At present the thermodynamic properties of such an end-member are unknown.

INTRODUCTION

THE THERMODYNAMIC stabilities of most clay minerals are particularly difficult to evaluate because of their complex and variable compositions. TARDY and GARRELS (1974) presented a novel and useful approach for estimating the free energies of formation of such minerals using an empirical additive scheme of the 'silicated' free energies of formation of oxides and hydroxides.

This report presents a regular solution site-mixing model for illites which may prove useful in delineating illite stability relations in sediment diagenesis. The need for such a model arose from an examination of the application of the Tardy and Garrels scheme to illites at 25°C and 1 bar. TARDY and GARRELS (1974) estimated the free energies of formation for several illites for which experimental values have been obtained by ROUTSON and KITTRICK (1971). Their estimated values were in good agreement with recalculated values of the original free energies reported by Routson and Kittrick. However, this agreement was apparently due to their assumption (in the recalculations) of an increased stability of 3.5 kcal per mol (-116 to -119.5) in the free energy of aqueous Al^{3+}. This correction was an overcorrection of 2 kcal per mol as indicated by the recently published value from HEMMINGWAY and ROBIE (1977).

The general validity of applying a regular solution site-mixing model to illites has to be determined by comparison between predicted and experimental results. Presently, there are not enough experimental data on illites to test such a hypothesis. It is hoped, however, that this paper will stimulate experimentalists to determine more free energies for illites of varying composition and over a range of pressures and temperatures.

ILLITE END-MEMBERS

In this study an illite is simulated by mixing various mica end-members in a solid solution. The mixing is done over available octahedral, tetrahedral, and interlayer cation sites. Four end-members were used to generate an illite: two dioctahedral micas, muscovite [$KAl_2AlSi_3O_{10}(OH)_2$] and pyrophyllite [$Al_2Si_4O_{10}(OH)_2$]; and two trioctahedral micas, phlogopite [$KMg_3AlSi_3O_{10}(OH)_2$] and annite [$KFe_3AlSi_3O_{10}(OH)_2$]. The resulting illite has an interlayer cation K^+ to balance the charge deficiency caused by the substitution of Al^{3+} for Si^{4+} in the tetrahedral sites. The octahedral cations are Al^{3+}, Mg^{2+}, and Fe^{2+}.

The major differences between the simulated illites and natural illites are the absence of Fe^{3+} in the octahedral sites and the lack of an octahedral charge deficiency. An end-member mica containing octahedral Fe^{3+} ions and having an octahedral charge deficiency is needed. At present the thermodynamic properties of such a mica are not available.

WEAVER and POLLARD (1975) list the structural formulas of 29 different illites. In general these illites are primarily dioctahedral and are characterized by K^+ in the interlayer sites, Si^{4+} and Al^{3+} in the tetrahedral sites, and Al^{3+} in the octahedral sites together with minor amounts of Mg^{2+} and Fe^{3+} and very minor amounts of Fe^{2+}. The interlayer

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charge is dominantly due to a tetrahedral charge deficiency rather than an octahedral charge deficiency, although the latter is frequently significant.

REGULAR SOLUTIONS

A regular solution is a solution having zero excess entropy of mixing (HILDEBRAND *et al.*, 1970). By definition, an ideal solution is a regular solution having zero excess enthalpy of mixing. As shown below, the thermodynamic properties of a regular solution are expressed in terms of the standard state chemical potentials of the end-members, the configurational entropy of mixing, and the excess enthalpy of mixing. Table 1 contains a list and explanation of all symbols used in the following discussions.

The free energy of formation of a solution, ΔG_s, at a given pressure and temperature is related to its thermodynamic components by:

$$\Delta G_s = \sum_i n_i \mu_i \qquad (1)$$

where n_i and μ_i are the number of moles and the chemical potential of the i-th component, respectively. The chemical potential is defined by:

$$\mu_i = \mu_i^\circ + RT \ln a_i \qquad (2)$$

where μ_i° is the standard state chemical potential, a_i is the thermodynamic activity, R is the universal gas constant, and T is the absolute temperature in degrees Kelvin.

a_i is defined as:

$$a_i = a_i^\circ \lambda_i \qquad (3)$$

Table 1. Symbols used in the text

A	Avogadro's number
a, a°	Activity and activity in an ideal solution, respectively
ΔE	Internal energy of formation
ΔG	Free energy of formation
ΔH	Enthalpy of formation
k	Boltzmann's constant
λ	Activity coefficient
μ, μ°	Chemical potential and standard state chemical potential, respectively
N, N	Number of molecules, cations, etc., as defined in the text
n	Moles of molecules, cations, etc., as defined in the text
P	Pressure in bars
P	Probability as defined in text
R	Universal gas constant
ΔS	Entropy of formation
T	Temperature in degrees Kelvin
W	Increase in number of distinguishable configurations resulting from random mixing in a solution
W_s, w	Number of distinguishable configurations resulting from random mixing in a solution and end-member, respectively
$\overline{WO}1$, $\overline{WO}2$, $\overline{WO}3$, $\overline{WTI}$	Regular solution site interaction parameters defined by eqns (28), (29), (30), and (27), respectively
$WX_{y,z}$	Contribution to ΔH_{ex} for the interaction on adjacent lattice sites of a pair of y and z cations in the X-th cation site class
X	Mole fraction
z	Average number of adjacent sites
Subscripts	
Al, Fe, K, Mg, Si	Al^{3+}, Fe^{2+}, K^+, Mg^{2+}, Si^{4+} cations occupying lattice sites
ann	Annite
E	Signifies an empty lattice site
ex	Excess
I	Interlayer cation sites
i, j, c, y, z	Defined in text
ill	Illite
is	Ideal solution
mix	Mixing for ΔE_{mix} and mixture for N_{mix}
mm	Mechanical mixture
mus	Muscovite
O	Octahedral cation sites
phl	Phlogopite
pyr	Pyrophyllite
s	Solution
T	Tetrahedral cation sites
Superscripts	
$\overline{\quad}$	Molal or molar quantity, as defined in text
$^\circ$	Standard state or ideal solution property, as defined in text

where a_i° is the activity in an ideal solution and λ_i is the activity coefficient. An ideal solution is defined as a solution in which the total free energy of mixing results from the configurational entropy of mixing. This implies zero enthalpy of mixing.

The configurational entropy of mixing in an ideal solution, ΔS_{is}, is described by:

$$\Delta S_{is} = k \ln W. \qquad (4)$$

Where k is Boltzmann's constant and W is the increase in total number of distinguishable configurations resulting from random mixing. In this study a configuration will represent a particular distribution of groups of cations on distinguishable sites within a lattice framework.

Combining eqns (1), (2), and (3) yields:

$$\Delta G_s = \sum_i n_i \mu_i^\circ + RT \sum_i n_i \ln a_i^\circ + RT \sum_i n_i \ln \lambda_i. \quad (5)$$

ΔG_s can also be expressed as the sum of contributions due to a mechanical mixture, an ideal solution, and the non-ideal deviation from an ideal solution. The latter is commonly called the 'excess' contribution to ΔG_s:

$$\Delta G_s = \Delta G_{mm} + \Delta G_{is} + \Delta G_{ex}. \qquad (6)$$

The corresponding terms between eqns (5) and (6) are equivalent and we can write:

$$\Delta G_{is} = RT \sum_i n_i \ln a_i^\circ, \qquad (7)$$

and

$$\Delta G_{ex} = RT \sum_i n_i \ln \lambda_i. \qquad (8)$$

Differentiating eqn (8) at constant T and P and applying the Gibbs–Duhem equation gives:

$$\left(\frac{\partial \Delta G_{ex}}{\partial n_i}\right)_{T,P,n_j} = RT \ln \lambda_i. \qquad (9)$$

ΔG_{is} and ΔG_{ex} are also defined by eqns (10) and (11), respectively.

$$\Delta G_{is} = -T\Delta S_{is}, \qquad (10)$$

and

$$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}. \qquad (11)$$

ΔS_{is} was defined by eqn (4). Combining eqns (4), (7), and (10) yields:

$$R \sum_i n_i \ln a_i^\circ = -k \ln W. \qquad (12)$$

ΔH_{ex} is the total enthalpy of mixing and ΔS_{ex} is the difference between the total entropy of mixing and ΔS_{is}. For a regular solution, ΔS_{ex} is defined to be zero (Hildebrand *et al.*, 1970). Substituting this property of a regular solution into eqn (11) and combining with eqn (9) yields:

$$RT \ln \lambda_i = \left(\frac{\partial \Delta H_{ex}}{\partial n_i}\right)_{T,P,n_j}. \qquad (13)$$

Using the above relations, eqn (6) for a regular solution can be restated as:

$$\Delta G_s = \sum_i n_i \mu_i^\circ - T\Delta S_{is} + \Delta H_{ex}. \qquad (14)$$

CONFIGURATIONAL ENTROPY OF MIXING WITHIN AN ILLITE

The general procedure outlined by Temkin (1945) was used to compute the configurational entropy for the mixing of the four end-member micas. The configurational entropy of mixing is the total increase in site configurations resulting from the random mixing of groups of cations over distinguishable cation sites. Mixing over anion sites will not produce distinguishable permutations. This is because identical anions occupy similar classes of sites in each mica end-member, and as discussed below, mixing was not allowed between different classes of sites.

The structural formula of the simulated illite can be written as:

$$[K_{0-1}][Al_{0-2}, Mg_{0-3}, Fe_{0-3}][Al_{0-1}, Si_{3-4}]O_{10}(OH)_2$$

where the cation subscripts show the possible ranges due to variations in the mole fractions of the end-member micas. From left to right the brackets enclose cations occupying interlayer (I), octahedral (O), and tetrahedral (T) sites, respectively. For a discussion of these three classes of cation sites, the reader is referred to any standard text on clay mineralogy such as that by Grim (1968). Briefly, the site classes correspond to lattice layers within a general mica or illite structure. These layers are parallel to the ab crystallographic plane and are characterized by cations having a common coordination number which could be either octahedral, tetrahedral, or 12-fold (interlayer). The repeat pattern of the layers is TOTI. There are four T sites, three O sites, and one I site per structural formula of the mica end-members. The cation site occupancies for the four end-member micas (per structural formula) are shown in Table 2.

One basic assumption has to be made to allow computation of the number of distinguishable permutations. Random mixing of cations was assumed over each class of cation sites; however, mixing of cations between sites of different classes was not allowed. Random mixing implies electrical neutrality will not necessarily be maintained over the smallest integer structural formula, because cations of different valences are being mixed on each class of cation sites.

The configurational entropy of mixing was defined

Table 2. Cation site occupancies in the four end-member micas*

Mica	I	O	T
Muscovite	K^+	$2Al^{3+}$, E	$3Si^{4+}$, Al^{3+}
Pyrophyllite	E	$2Al^{3+}$, E	$4Si^{4+}$
Phlogopite	K^+	$3Mg^{2+}$	$3Si^{4+}$, Al^{3+}
Annite	K^+	$3Fe^{2+}$	$3Si^{4+}$, Al^{3+}

* I, O, and T refer to interlayer, octahedral, and tetrahedral sites, respectively. E indicates an empty site. The occupancies are per structural formula.

by eqn (4) in terms of W which is the total number of distinguishable site permutations resulting from the mixing of the end-members. W is calculated by computing the number of such permutations in the solution, W_s, divided by the number of such permutations present in a mechanical mixture of the end-members, $\Pi_i w_i$:

$$W = W_s \div \prod_i w_i. \tag{15}$$

W_s and $\Pi_i w_i$ can be computed from the multiplication of the appropriate multinomial coefficients (McQuarrie, 1973). These coefficients, the bracketed terms in eqns (16) and (17), are of the form:

$$\left(\frac{(l\mathrm{N})!}{\Pi_i(N_i!)}\right)_{c,j}$$

where the subscripts c and j refer to the class of cation sites and the end-member or mixture, respectively. l is the number of c cation sites per structural formula and N is the number of j molecules. N_i is the total number of c cation sites in j molecules occupied by the i-th cation. If i = E, then the sites are empty. For each multinomial coefficient, $l\mathrm{N} = \Sigma_i N_i$,

$$W_s = \left(\frac{\mathrm{N}!}{N_K!N_E!}\right)_{\mathrm{I,mix}} \cdot \left(\frac{(3\mathrm{N})!}{N_{Al}!N_E!N_{Mg}!N_{Fe}!}\right)_{\mathrm{O,mix}} \times \left(\frac{(4\mathrm{N})!}{N_{Al}!N_{Si}!}\right)_{\mathrm{T,mix}}, \tag{16}$$

and

$$\prod_i w_i = \left(\frac{(3\mathrm{N})!}{N_{Al}!N_E!}\right)_{\mathrm{O,mus}} \cdot \left(\frac{(4\mathrm{N})!}{N_{Si}!N_{Al}!}\right)_{\mathrm{T,mus}} \times \left(\frac{(3\mathrm{N})!}{N_{Al}!N_E!}\right)_{\mathrm{O,pyr}} \cdot \left(\frac{(4\mathrm{N})!}{N_{Si}!N_{Al}!}\right)_{\mathrm{T,phl}} \times \left(\frac{(4\mathrm{N})!}{N_{Si}!N_{Al}!}\right)_{\mathrm{T,ann}} \tag{17}$$

Equations (16) and (17) can be substituted into eqn (15) and simplified using Stirling's approximation together with stoichiometric relations of the mixture and end-members. These relations are of the form:

$$N_{\mathrm{K,I,mix}} = \mathrm{N}_{mus} + \mathrm{N}_{phl} + \mathrm{N}_{ann}$$

and

$$N_{\mathrm{Al,O,mus}} = 2\mathrm{N}_{mus}. \tag{18}$$

Finally, the simplified equation can be substituted into eqn (4) and k can be replaced by R/A where A is Avogadro's number. The resulting equation is:

$$\begin{aligned}\Delta S_{is} = -R\Big[&(n_{mus} + n_{phl} + n_{ann})\ln(1 - X_{pyr}) \\ &+ n_{pyr}\ln X_{pyr} + 3(n_{mus} + n_{pyr}) \\ &\times \ln(X_{mus} + X_{pyr}) + 3n_{phl}\ln X_{phl} \\ &+ 3n_{ann}\ln X_{ann} + (n_{mus} + n_{phl} + n_{ann}) \\ &\times \ln(1 - X_{pyr}) + 4n_{pyr}\ln\left(\frac{3 + X_{pyr}}{4}\right) \\ &+ 3(n_{mus} + n_{phl} + n_{ann})\ln\left(1 + \frac{X_{pyr}}{3}\right)\Big]\end{aligned} \tag{19}$$

where n_i and X_i refer to the number of mols and the mole fraction of the i-th end-member in the mixture, respectively. If any X_i goes to unity then n_j and X_j will go to zero. Note that ΔS_{is} goes to zero if any X_i goes to unity. The first two terms in eqn (19) refer to mixing on the interlayer sites; the next three terms describe mixing on the octahedral sites; and the remaining three terms relate to mixing on the tetrahedral sites.

Equating eqns (4) and (12) yields:

$$\Delta S_{is} = -R\sum_i n_i \ln a_i^\circ. \tag{20}$$

Equation (19) can be rewritten in the form of eqn (20) which allows isolation of the equations for a_i° for the four end-members. This procedure follows that outlined by TEMKIN (1945). The equations are:

$$a_{mus}^\circ = (1 - X_{pyr})(X_{mus} + X_{pyr})^3(1 - X_{pyr})\left(1 + \frac{X_{pyr}}{3}\right)^3 \tag{21}$$

$$a_{pyr}^\circ = (X_{pyr})(X_{mus} + X_{pyr})^3\left(\frac{3 + X_{pyr}}{4}\right)^4 \tag{22}$$

$$a_{phl}^\circ = (1 - X_{pyr})(X_{phl})^3(1 - X_{pyr})\left(1 + \frac{X_{pyr}}{3}\right)^3 \tag{23}$$

$$a_{ann}^\circ = (1 - X_{pyr})(X_{ann})^3(1 - X_{pyr})\left(1 + \frac{X_{pyr}}{3}\right)^3. \tag{24}$$

In each of the four equations above, the first and second terms result from mixing on the interlayer and octahedral sites, respectively. The remaining terms are for mixing on the tetrahedral sites. Note that a_i° goes to 1 as X_i goes to unity.

The physical significance of an ideal activity becomes apparent if we consider the probability, P_i, of picking at random out of the solution all the structural units, N_i, of a given end-member. For example, let us compute $\ln P_{pyr}$, the natural log of the probability of picking the N_{pyr} structural units of pyrophyllite from the solution. P_{pyr} corresponds to picking N_{pyr} empty interlayer sites, $2N_{pyr}$ aluminum occupied octahedral sites, N_{pyr} empty octahedral sites, and $4N_{pyr}$ silicon occupied tetrahedral sites. In terms of mole fractions and using the stoichiometries of the end-members, we can write:

$$\ln P_{pyr} = \ln\left[X_{pyr}^{N_{pyr}} \left(\frac{2(X_{mus} + X_{pyr})}{3}\right)^{2N_{pyr}} \times \left(\frac{X_{mus} + X_{pyr}}{3}\right)^{N_{pyr}} \left(\frac{(3N_{pyr})!}{(2N_{pyr})!N_{pyr}!}\right) \times \left(\frac{3 + X_{pyr}}{4}\right)^{4N_{pyr}} \right]$$

where the first term corresponds to picking the empty interlayer sites; the second term, the aluminum occupied octahedral sites; the third term, the empty octahedral sites; the fourth term, the number of distinguishable permutations of octahedral site occupancies; and the fifth term, the silicon occupied tetrahedral sites. The use of Stirling's approximation reduces the fourth term:

$$\ln \frac{(3N_{pyr})!}{(2N_{pyr})!N_{pyr}!} \doteq N_{pyr} \ln \frac{27}{4}.$$

Substituting this simplified term into the above expression gives:

$$\ln P_{pyr} = N_{pyr} \ln X_{pyr}(X_{mus} + X_{pyr})^3 \left(\frac{3 + X_{pyr}}{4}\right)^4.$$

A comparison with this expression and eqn (22) shows:

$$P_{pyr} = (a_{pyr}^\circ)^{N_{pyr}}$$

and for each of the ideal activity expressions, we can write:

$$P_i = a_i^{\circ N_i}.$$

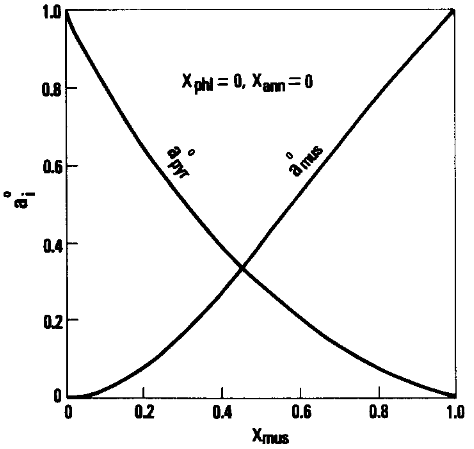

Fig. 1. The ranges of the ideal solution activities of muscovite, a_{mus}°, and pyrophyllite, a_{pyr}°, in a binary solid solution as computed from eqn (21) and (22).

The ideal activity approximates the probability of picking at random one structural unit of an end-member out of solution. It only approximates because of the use of Stirling's approximation in the derivation of the configurational entropy. One interesting point is that an end-member whose composition overlaps completely with the other end-members will not have a zero ideal activity when its mole fraction is zero. This follows because the probability of picking at random a structural unit of that end-member would not be zero. An example of this in the illite model is muscovite. A solution of pyrophyllite with phlogopite and/or annite would have a zero mole fraction of muscovite and a non-zero a_{mus}° as predicted from eqn (21).

A decrease in a_i° represents an increase in the stability of the i-th end-member in an ideal solution. The ranges of a_i° predicted from eqns (21) to (24) are shown on Figs. 1–5. The corresponding entropies predicted from eqn (19) range from 0 to 9 cal/mol/deg. The maximum value corresponds to trioctahedral illites with only minor amounts of dioctahedral components. This implies that natural illites should have a major trioctahedral component if they can be represented by the ideal solution model developed here. This is not the case in natural illites; they have only a minor trioctahedral component. For this reason

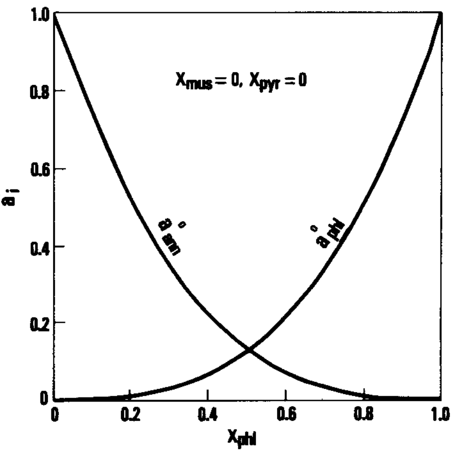

Fig. 2. The ranges of the ideal solution activities of phlogopite, a_{phl}°, and annite, a_{ann}°, in a binary solid solution as computed from eqns (23) and (24).

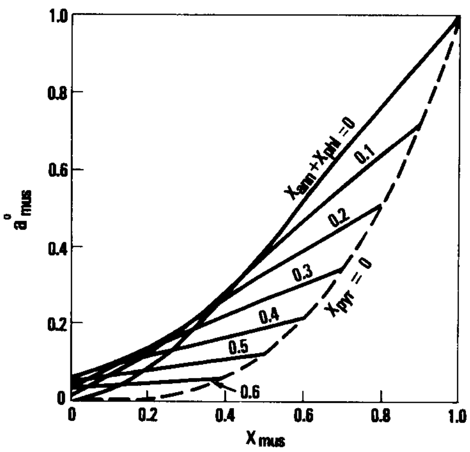

Fig. 3. The range of the ideal solution activity of muscovite, a°_{mus}, in a quaternary solid solution as computed from eqn (21).

a regular solution contribution of excess enthalpy was added to the solid solution model.

EXCESS ENTHALPY OF MIXING WITHIN AN ILLITE

The general procedure outlined by DENBIGH (1971, pp. 432–435) was followed to formulate an expression for the excess enthalpy of mixing, ΔH_{ex}. Random mixing is assumed over lattice sites within each site class; thus ΔS_{ex} is zero. The internal energy of mixing, ΔE_{mix}, is assumed to result only from interactions between ions on adjacent sites. Because the mixing takes place at constant pressure, the change in volume with mixing is assumed negligible and ΔH_{ex} becomes equivalent to ΔE_{mix}.

The computation of ΔH_{ex} is tedious but fairly simple. The number of site interactions within a given site class is derived (from simple probability theory using a random cation distribution) for a particular interaction of ions, i.e. Si^{4+}–Al^{3+} interactions in the tetrahedral site class. The number of such interactions due to mixing is equal to the total number of such interactions within the solution minus the sum of such interactions in the end-members. The resulting number is then multiplied by a parameter describing the contributions to ΔH_{ex} per interaction. The process is repeated for each of the other particular interactions of ions in the site class, i.e. Si^{4+}–Si^{4+} and Al^{3+}–Al^{3+} interactions in the tetrahedral class. The summation of the results of this procedure for each cation site class is equal to ΔH_{ex}. As was the case for ΔS_{is}, anion sites are not considered. This follows because identical anions occupy similar classes of sites in each end-member and therefore also in the mixture. The resulting contributions to ΔH_{ex} from the anion site interactions will cancel out between the mixture and the end-members.

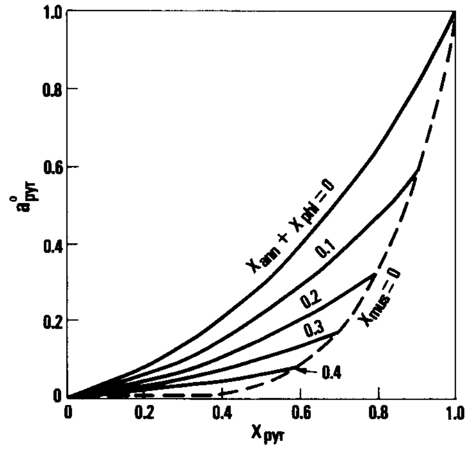

Fig. 4. The range of the ideal solution activity of pyrophyllite, a°_{pyr}, in a quaternary solid solution as computed from eqn (22).

The number of site interactions for each particular interaction of cations within each cation site class is listed in Table 3. Each symbol used to denote the contribution to ΔH_{ex} per interaction is also given in Table 3. An expression for ΔH_{ex} can be written by summing the terms in Table 3 according to the procedure described above. The expression can then be simplified using the following relations:

$$\sum_{i} X_i = 1$$

$$N_i = n_i A$$

and

$$WX_{y,z} = \overline{WX}_{y,z}/A.$$

$WX_{y,z}$ is the contribution per interaction to ΔH_{ex} for the site interaction of the y, z cations within the X-th

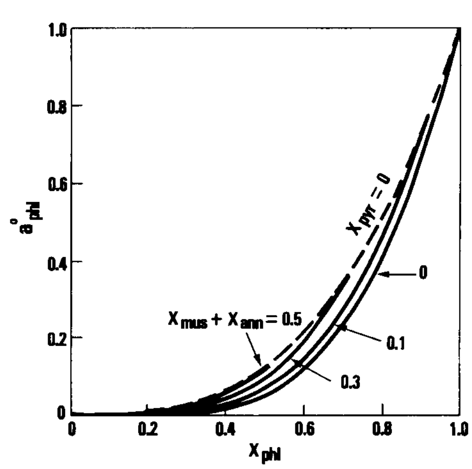

Fig. 5. The range of the ideal solution activity of phlogopite, a°_{phl}, in a quaternary solid solution as computed from eqn (23). The range of the ideal solution activity of annite, a°_{ann}, in a quaternary solid solution as computed from eqn (24) is shown on Fig. 5 if the subscripts phl and ann are interchanged.

Table 3. The number of pairs of adjacent lattice sites having x, y occupancies, $N_{x,y}$, in the solution and in the end-members*

Solution or end-member	Site class	x, y	ΔH_{ex} per interaction	$N_{x,y}$
Solution	T	Al^{3+}, Si^{4+}	$WT_{Al,Si}$	$z_T(N_{mus} + N_{phl} + N_{ann}) \times (3N_{mus} + 3N_{phl} + 3N_{ann} + 4N_{pyr}) \div 4N_{mix}$
	T	Al^{3+}, Al^{3+}	$WT_{Al,Al}$	$z_T(N_{mus} + N_{phl} + N_{ann})^2 \div 8N_{mix}$
	T	Si^{4+}, Si^{4+}	$WT_{Si,Si}$	$z_T(3N_{mus} + 3N_{phl} + 3N_{ann} + 4N_{pyr})^2 \div 8N_{mix}$
	O	Mg^{2+}, Al^{3+}	$WO_{Mg,Al}$	$z_O2(N_{mus} + N_{pyr})(N_{phl}) \div N_{mix}$
	O	Fe^{2+}, Al^{3+}	$WO_{Fe,Al}$	$z_O2(N_{mus} + N_{pyr})(N_{ann}) \div N_{mix}$
	O	Mg^{2+}, Fe^{2+}	$WO_{Mg,Fe}$	$z_O3(N_{phl})(N_{ann}) \div N_{mix}$
	O	Mg^{2+}, E	$WO_{Mg,E}$	$z_O(N_{phl})(N_{mus} + N_{pyr}) \div N_{mix}$
	O	Fe^{2+}, E	$WO_{Fe,E}$	$z_O(N_{ann})(N_{mus} + N_{pyr}) \div N_{mix}$
	O	Al^{3+}, E	$WO_{Al,E}$	$z_O2(N_{mus} + N_{pyr})^2 \div 3N_{mix}$
	O	E, E	$WO_{E,E}$	$z_O(N_{mus} + N_{pyr})^2 \div 6N_{mix}$
	O	Al^{3+}, Al^{3+}	$WO_{Al,Al}$	$z_O2(N_{mus} + N_{pyr})^2 \div 3N_{mix}$
	O	Mg^{2+}, Mg^{2+}	$WO_{Mg,Mg}$	$z_O3(N_{phl})^2 \div 2N_{mix}$
	O	Fe^{2+}, Fe^{2+}	$WO_{Fe,Fe}$	$z_O3(N_{ann})^2 \div 2N_{mix}$
	I	K^+, E	$WI_{K,E}$	$z_I(N_{mus} + N_{phl} + N_{ann})(N_{pyr}) \div N_{mix}$
	I	K^+, K^+	$WI_{K,K}$	$z_I(N_{mus} + N_{phl} + N_{ann})^2 \div 2N_{mix}$
	I	E, E	$WI_{E,E}$	$z_I(N_{pyr})^2 \div 2N_{mix}$
Muscovite	T	Al^{3+}, Si^{4+}	$WT_{Al,Si}$	$z_T3N_{mus} \div 4$
	T	Al^{3+}, Al^{3+}	$WT_{Al,Al}$	$z_TN_{mus} \div 8$
	T	Si^{4+}, Si^{4+}	$WT_{Si,Si}$	$z_T9N_{mus} \div 8$
	O	Al^{3+}, E	$WO_{Al,E}$	$z_O2N_{mus} \div 3$
	O	E, E	$WO_{E,E}$	$z_ON_{mus} \div 6$
	O	Al^{3+}, Al^{3+}	$WO_{Al,Al}$	$z_O2N_{mus} \div 3$
	I	K^+, K^+	$WI_{K,K}$	$z_IN_{mus} \div 2$
Pyrophyllite	T	Si^{4+}, Si^{4+}	$WT_{Si,Si}$	z_T2N_{pyr}
	O	Al^{3+}, E	$WO_{Al,E}$	$z_O2N_{pyr} \div 3$
	O	E, E	$WO_{E,E}$	$z_ON_{pyr} \div 6$
	O	Al^{3+}, Al^{3+}	$WO_{Al,Al}$	$z_O2N_{pyr} \div 3$
	I	E, E	$WI_{E,E}$	$z_IN_{pyr} \div 2$
Phlogopite	T	Al^{3+}, Si^{4+}	$WT_{Al,Si}$	$z_T3N_{phl} \div 4$
	T	Al^{3+}, Al^{3+}	$WT_{Al,Al}$	$z_TN_{phl} \div 8$
	T	Si^{4+}, Si^{4+}	$WT_{Si,Si}$	$z_T9N_{phl} \div 8$
	O	Mg^{2+}, Mg^{2+}	$WO_{Mg,Mg}$	$z_O3N_{phl} \div 2$
	I	K^+, K^+	$WI_{K,K}$	$z_IN_{phl} \div 2$
Annite	T	Al^{3+}, Si^{4+}	$WT_{Al,Si}$	$z_T3N_{ann} \div 4$
	T	Al^{3+}, Al^{3+}	$WT_{Al,Al}$	$z_TN_{ann} \div 8$
	T	Si^{4+}, Si^{4+}	$WT_{Si,Si}$	$z_T9N_{ann} \div 8$
	O	Fe^{2+}, Fe^{2+}	$WO_{Fe,Fe}$	$z_O3N_{ann} \div 2$
	I	K^+, K^+	$WI_{K,K}$	$z_IN_{ann} \div 2$

* N_{mus}, N_{pyr}, N_{phl}, and N_{ann} refer to the number of molecules from the muscovite, pyrophyllite, phlogopite, and annite components, respectively, and N_{mix} is the sum total of molecules from all 4 components. A molecule refers to a structural formula unit as defined in the text.

cation site class, and $\overline{WX}_{y,z}$ is the corresponding molar quantity. The simplified expression for ΔH_{ex} is given below:

$$\begin{aligned}
\Delta H_{ex} = & \left[(n_{mus} + n_{phl} + n_{ann})X_{pyr}z_T \times \left(\frac{\overline{WT}_{Al,Si}}{4} - \frac{\overline{WT}_{Al,Al}}{8} - \frac{\overline{WT}_{Si,Si}}{8}\right)\right] \\
& + \left[(n_{mus} + n_{pyr})X_{phl}z_O \times \left(2\overline{WO}_{Mg,Al} + \overline{WO}_{Mg,E} - \tfrac{2}{3}\overline{WO}_{Al,E} - \frac{\overline{WO}_{E,E}}{6} - \tfrac{2}{3}\overline{WO}_{Al,Al} - \tfrac{3}{2}\overline{WO}_{Mg,Mg}\right)\right] \\
& + \left[(n_{mus} + n_{pyr})X_{ann}z_O \times \left(2\overline{WO}_{Fe,Al} + \overline{WO}_{Fe,E} - \tfrac{2}{3}\overline{WO}_{Al,E} - \frac{\overline{WO}_{E,E}}{6} - \tfrac{2}{3}\overline{WO}_{Al,Al} - \tfrac{3}{2}\overline{WO}_{Fe,Fe}\right)\right] \\
& + \left[n_{ann}X_{phl}z_O\left(3\overline{WO}_{Mg,Fe} - \tfrac{3}{2}\overline{WO}_{Mg,Mg} - \tfrac{3}{2}\overline{WO}_{Fe,Fe}\right)\right] + \left[(n_{mus} + n_{phl} + n_{ann}) \times X_{pyr}z_I\left(\overline{WI}_{K,E} - \frac{\overline{WI}_{K,K}}{2} - \frac{\overline{WI}_{E,E}}{2}\right)\right].
\end{aligned} \tag{25}$$

The first and last bracketed terms in eqn (25) represent tetrahedral and interlayer site interactions, respectively, between pyrophyllite and the other three end-member components. The second and third bracketed terms describe the octahedral site interactions between the two dioctahedral end-member components and the phlogopite and annite components, respectively. The fourth such term gives the octahedral site interactions between the two trioctahedral end-member components. Equation (25) can be further simplified by combining the $\overline{WX}_{y,z}$ terms, resulting in the following expression:

$$\begin{aligned}\Delta H_{ex} = {} & (n_{mus} + n_{phl} + n_{ann})X_{pyr}\,\overline{WT1} \\ & + (n_{mus} + n_{pyr})(X_{phl}\,\overline{WO1} + X_{ann}\,\overline{WO2}) \\ & + X_{phl}n_{ann}\,\overline{WO3}\end{aligned} \tag{26}$$

where

$$\begin{aligned}\overline{WT1} = {} & z_T\left(\frac{\overline{WT}_{Al,Si}}{4} - \frac{\overline{WT}_{Al,Al}}{8} - \frac{\overline{WT}_{Si,Si}}{8}\right) \\ & + z_I\left(\overline{WI}_{K,E} - \frac{\overline{WI}_{K,K}}{2} - \frac{\overline{WI}_{E,E}}{2}\right)\end{aligned} \tag{27}$$

$$\begin{aligned}\overline{WO1} = {} & z_O\left(2\,\overline{WO}_{Mg,Al} + \overline{WO}_{Mg,E} - \tfrac{2}{3}\,\overline{WO}_{Al,E}\right. \\ & \left. - \frac{\overline{WO}_{E,E}}{6} - \tfrac{2}{3}\,\overline{WO}_{Al,Al} - \tfrac{3}{2}\,\overline{WO}_{Mg,Mg}\right)\end{aligned} \tag{28}$$

$$\begin{aligned}\overline{WO2} = {} & z_O\left(2\,\overline{WO}_{Fe,Al} + \overline{WO}_{Fe,E} - \tfrac{2}{3}\,\overline{WO}_{Al,E}\right. \\ & \left. - \frac{\overline{WO}_{E,E}}{6} - \tfrac{2}{3}\,\overline{WO}_{Al,Al} - \tfrac{3}{2}\,\overline{WO}_{Fe,Fe}\right)\end{aligned} \tag{29}$$

and

$$\overline{WO3} = z_O\left(3\,\overline{WO}_{Mg,Fe} - \tfrac{3}{2}\,\overline{WO}_{Mg,Mg} - \tfrac{3}{2}\,\overline{WO}_{Fe,Fe}\right). \tag{30}$$

Expressions for $\ln \lambda_i$ can be determined by taking the partial derivative of eqn (26) with respect to n_i and applying eqn (13). The resulting eqns are given below.

$$\begin{aligned}\ln \lambda_{mus} = {} & (X^2_{pyr}\,\overline{WT1} - X_{phl}X_{ann}(\overline{WO3} - \overline{WO1} \\ & - \overline{WO2}) + X^2_{phl}\,\overline{WO1} + X^2_{ann}\,\overline{WO2})/RT\end{aligned} \tag{31}$$

$$\begin{aligned}\ln \lambda_{pyr} = {} & ((1 - X_{pyr})^2\,\overline{WT1} - X_{phl}X_{ann} \\ & \times (\overline{WO3} - \overline{WO1} - \overline{WO2}) \\ & + X^2_{phl}\,\overline{WO1} + X^2_{ann}\,\overline{WO2})/RT\end{aligned} \tag{32}$$

$$\begin{aligned}\ln \lambda_{phl} = {} & (X^2_{pyr}\,\overline{WT1} + X_{ann}(1 - X_{phl}) \\ & \times (\overline{WO3} - \overline{WO1} - \overline{WO2}) \\ & + (1 - X_{phl})^2\,\overline{WO1} + X^2_{ann}\,\overline{WO2})/RT\end{aligned} \tag{33}$$

and

$$\begin{aligned}\ln \lambda_{ann} = {} & (X^2_{pyr}\,\overline{WT1} + (1 - X_{ann})X_{phl} \\ & \times (\overline{WO3} - \overline{WO1} - \overline{WO2}) \\ & + X^2_{phl}\,\overline{WO1} + (1 - X_{ann})^2\,\overline{WO2})/RT.\end{aligned} \tag{34}$$

In eqns (31) to (34), as $X_i \Rightarrow 1$ then $\lambda_i \Rightarrow 1$ and the eqns for $\ln \lambda_j$, where $j \neq i$, give the limiting values for λ_j when $X_j \Rightarrow 0$.

SITE INTERACTION PARAMETERS

Experimental thermodynamic data for illites, whose compositions can be approximated by the model, are needed to evaluate the four site interaction parameters ($\overline{WT1}$, $\overline{WO1}$, $\overline{WO2}$, and $\overline{WO3}$). These data could be free energies of formation determined from equilibrium solubility studies or heats of solution measured by calorimetry. These parameters need to be evaluated at several different temperatures (of diagenetic interest) to determine their temperature dependence. At present, the only reliable experimental data are at 25°C and 1 atm for illites containing significant amounts of ferric iron (ROUTSON and KITTRICK, 1971), but the lack of a ferric mica end-member precludes the use of this data.

The evaluation of the site interaction parameters will have to wait until more experimental data are available. In terms of the model, the dominant dioctahedral nature of most illites places some restrictions on the relative values of these parameters. As shown previously, maximum configurational entropy occurs in trioctahedral illites. This increased stability will have to be balanced out by decreased stability resulting from site interactions between octahedral sites. In the model, this implies $\overline{WO1}$, $\overline{WO2}$, and $\overline{WO3}$ are significantly more positive than $\overline{WT1}$.

The number of site interaction parameters can be reduced if ferrous iron, a very minor component in illites, is neglected. The mole fraction of annite would then become zero, resulting in $\overline{WO2}$ and $\overline{WO3}$ dropping out of the free energy expressions, leaving only $\overline{WT1}$ and $\overline{WO1}$ to be evaluated.

FREE ENERGY EXPRESSIONS

An expression for the molar free energy of formation of an illite, $\Delta\overline{G}_{ill}$, is obtained by substituting eqns (19) and (26) into eqn (14) and replacing the mols of end-members by their respective mol fractions:

$$\begin{aligned}\Delta\overline{G}_{ill} = {} & \sum_i X_i\mu^\circ_i + RT\left[(1 - X_{pyr})\left(2\ln(1 - X_{pyr})\right.\right. \\ & \left.\left. + 3\ln\left(1 + \frac{X_{pyr}}{3}\right)\right) + X_{pyr}\left(\ln X_{pyr}\right.\right.\end{aligned}$$

$$
\begin{aligned}
&+ 4\ln\left(\frac{3 + X_{\mathrm{pyr}}}{4}\right)\Bigg)\Bigg) + 3(X_{\mathrm{mus}} + X_{\mathrm{pyr}}) \\
&\times \ln(X_{\mathrm{mus}} + X_{\mathrm{pyr}}) + 3X_{\mathrm{phl}}\ln X_{\mathrm{phl}} \\
&+ 3X_{\mathrm{ann}}\ln X_{\mathrm{ann}}\Bigg] + (1 - X_{\mathrm{pyr}})X_{\mathrm{pyr}}\,\overline{WT1} \\
&+ (X_{\mathrm{mus}} + X_{\mathrm{pyr}})(X_{\mathrm{phl}}\,\overline{WO1} \\
&+ X_{\mathrm{ann}}\,\overline{WO2}) + X_{\mathrm{phl}}X_{\mathrm{ann}}\,\overline{WO3}. \qquad (35)
\end{aligned}
$$

Equations (21) to (24) and (31) to (34) define a_i° and $\ln \lambda_i$ for each end-member. Expressions for the chemical potentials of the end-members are defined by substituting the appropriate equations for a_i° and $\ln \lambda_i$ into eqn (3) which is then substituted into eqn (2):

$$
\begin{aligned}
\mu_{\mathrm{mus}} = \mu_{\mathrm{mus}}^\circ + RT\ln\Bigg[&(1 - X_{\mathrm{pyr}})^2(X_{\mathrm{mus}} + X_{\mathrm{pyr}})^3 \\
&\times\left(\frac{3 + X_{\mathrm{pyr}}}{3}\right)^3\Bigg] + X_{\mathrm{pyr}}^2\,\overline{WT1} - X_{\mathrm{phl}}X_{\mathrm{ann}} \\
&\times(\overline{WO3} - \overline{WO1} - \overline{WO2}) + X_{\mathrm{phl}}^2\,\overline{WO1} \\
&+ X_{\mathrm{ann}}^2\,\overline{WO2} \qquad (36)
\end{aligned}
$$

$$
\begin{aligned}
\mu_{\mathrm{pyr}} = \mu_{\mathrm{pyr}}^\circ + RT\ln\Bigg[&X_{\mathrm{pyr}}(X_{\mathrm{mus}} + X_{\mathrm{pyr}})^3 \\
&\times\left(\frac{3 + X_{\mathrm{pyr}}}{4}\right)^4\Bigg] + (1 - X_{\mathrm{pyr}})^2\,\overline{WT1} \\
&- X_{\mathrm{phl}}X_{\mathrm{ann}}(\overline{WO3} - \overline{WO1} - \overline{WO2}) \\
&+ X_{\mathrm{phl}}^2\,\overline{WO1} + X_{\mathrm{ann}}^2\,\overline{WO2} \qquad (37)
\end{aligned}
$$

$$
\begin{aligned}
\mu_{\mathrm{phl}} = \mu_{\mathrm{phl}}^\circ + RT\ln\Bigg[&(1 - X_{\mathrm{pyr}})^2X_{\mathrm{phl}}^3 \\
&\times\left(\frac{3 + X_{\mathrm{pyr}}}{3}\right)^3\Bigg] + X_{\mathrm{pyr}}^2\,\overline{WT1} \\
&+ X_{\mathrm{ann}}(1 - X_{\mathrm{phl}})(\overline{WO3} - \overline{WO1} - \overline{WO2}) \\
&+ (1 - X_{\mathrm{phl}})^2\,\overline{WO1} + X_{\mathrm{ann}}^2\,\overline{WO2} \qquad (38)
\end{aligned}
$$

$$
\begin{aligned}
\mu_{\mathrm{ann}} = \mu_{\mathrm{ann}}^\circ + RT\ln\Bigg[&(1 - X_{\mathrm{pyr}})^2X_{\mathrm{ann}}^3 \\
&\times\left(\frac{3 + X_{\mathrm{pyr}}}{3}\right)^3\Bigg] + X_{\mathrm{pyr}}^2\,\overline{WT1} \\
&+ (1 - X_{\mathrm{ann}})X_{\mathrm{phl}}(\overline{WO3} - \overline{WO1} - \overline{WO2}) \\
&+ X_{\mathrm{phl}}^2\,\overline{WO1} + (1 - X_{\mathrm{ann}})^2\,\overline{WO2}. \qquad (39)
\end{aligned}
$$

SUMMARY

Expressions describing the compositional dependence of the thermodynamic stability of an illite have been derived in terms of a regular solution site-mixing model. Four end-member micas (muscovite, pyrophyllite, phlogopite, and annite) were used to simulate an illite. A ferric mica end-member is needed to extend the model to illites containing ferric iron. At present the thermodynamic properties of such an end-member are unknown; however, when they become known, the end-member can be added following the procedure outlined in this report.

The model should prove useful in delineating illite stability relations in sediment diagenesis, but this application must wait until experimental data are available to evaluate the site interaction parameters. Only two parameters need be evaluated to apply the model to iron-free illites.

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