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Refinements in a site-mixing model for illites: local electrostatic balance and the quasi-chemical approximation

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Abstract—A quasi-chemical model for illites has been derived, and local electrostatic balance has been added to a random regular solution site-mixing model for illites (STOESSELL, 1979). Each model assumes similar order–disorder conditions for both the end-members micas and the solid solution. Thermodynamic properties of illites predicted by the random, electrostatic, and quasi-chemical models are compared as a function of composition. For natural illite compositions, molar entropies of mixing in the electrostatic model are about 1 entropy unit less than those in the random model. Intermediate values are given by the quasi-chemical model. Each model predicts an increased entropy of mixing in dominantly trioctahedral illites as compared to dioctahedral illites. Each model also predicts destabilization of trioctahedral illites using absolute molar exchange energies greater than $2RT/Z_x$, where Z_x is the number of adjacent cation interactions per site in the Xth site class. The most negative free energies of mixing are predicted by the quasi-chemical model. Intermediate values predicted by the random model are apparently the result of error cancellation due to overestimation of both the entropy and enthalpy of mixing.

NOMENCLATURE

A	Avogadro's number
Al, Fe, K, Mg, Si	Al^{3+}, Fe^{2+}, K^{+}, Mg^{2+}, and Si^{4+} cations
a_j^0	Ideal activity of the jth end-member
ann, mus, phl, pyr	Annite, muscovite, phlogopite, and pyrophyllite end-members
α	Parameter of y, z in eqn (10)
D	Constant in eqn (10)
E	Empty lattice site
$\overline{EX}_{y,z}$	Exchange energy defined by eqn (7) for one mole of y,z adjacent cation interactions
$\epsilon_{X,j}$	Energy due to adjacent cation interactions in the Xth site class of the jth end-member or solution
$\Delta\bar{G}_{mix}$, $\Delta\bar{H}_{mix}$, $\Delta\bar{S}_{mix}$	Free energy, enthalpy, and entropy of mixing one mole of structural units
g_i	Number of distinguishable cation permutations in the ith cation combination of a structural unit
$g_{X,j}$	Number of distinguishable lattice configurations having energy $\epsilon_{X,j}$
I, O, T	Interlayer, octahedral, and tetrahedral site classes
k	Boltzmann's constant
l_X	Number of sites per structural unit in the Xth site class
mX_y	Number of moles of y site occupancies in the Xth site class of the jth end-member or solution
$mX^*_{y,z}$, $mX_{y,z}$	Number of moles of y,z interactions in the Xth site class of the jth end-member or solution in the random and quasi-chemical models, respectively
n	Number of moles of j structural units
$nX_{y,z}$	Number of moles of y,z interactions due to mixing in the Xth site class
P_i	Probability of a structural unit having the ith cation combination
R	Universal gas constant
$\Delta\bar{S}_{is}$, $\Delta\bar{S}_{is,X}$	$\Delta\bar{S}_{mix}$ in an ideal solution and within the Xth site class of an ideal solution, respectively
T	Temperature in degrees Kelvin
$\bar{W}$	Defined in eqn (1)
$\overline{WO1}$, $\overline{WO2}$, $\overline{WO3}$, $\overline{WT1}$	Molar site interaction parameters in the random model defined by STOESSELL (1979) in eqns (28), (29), (30), and (27), respectively
$\overline{WX}_{y,z}$	Energy due to one mole of y,z interactions in the Xth site class
X_j	Mole fraction of the jth end-member
Z_X	Number of adjacent cation interactions per site in the Xth site class
Ω_{mix}	Partition function for mixing in the illite solution defined by eqn (8)
Ω_j	Partition function for mixing in the jth end-member or solution defined by eqn (9).

INTRODUCTION

A RANDOM regular solution site-mixing model for illites was presented in an earlier paper (STOESSELL, 1979). That model contained mica end-members and assumed independent random mixing of cations within several site classes.

The random model did not maintain local electrostatic balance or consider the effects of exchange energies in the mixing process. The constraint of maintaining a local charge balance has been shown to significantly affect cation distributions in site-mixing feldspar models (KERRICK and DARKEN, 1975; ANDERSON and MAZO, 1979). Significant lattice effects in cation exchange in aluminosilicate models due to exchange energies have been derived by BARRER and KLINOWSKI (1977, 1979). The consequences of neglecting these constraints in the random illite model need to be determined.

Two models for illites are presented in this paper, an electrostatic model and a quasi-chemical model. The former maintains local electrostatic balance, and the latter considers exchange energies in computing the numbers of adjacent pairs of cations.

Thermodynamic properties predicted by the random, electrostatic, and quasi-chemical models are compared as a function of composition. The relative significance of assumptions unique to each model are determined, and tentative conclusions are drawn as to each model's validity in geochemical calculations.

THE MODELS

Cations from 4 mica end-members are mixed in a solid solution to simulate an illite. These end-members include 2 dioctahedral micas, muscovite (mus) [$KAl_2AlSi_3O_{10}(OH)_2$] and pyrophyllite (pyr) [$Al_2Si_4O_{10}(OH)_2$], and 2 trioctahedral micas, phlogopite (phl) [$KMg_3AlSi_3O_{10}(OH)_2$] and annite (ann) [$KFe_3AlSi_3O_{10}(OH)_2$]. Cation distributions are constrained by similar mixing rules in both the end-members and the solid solution. Cation mixing takes place over sites within the octahedral (O), tetrahedral (T), and interlayer (I) site classes. Mixing of cations between different site classes is not allowed. Cations of the same species are not distinguishable. In all models the mixing process takes place under constant pressure with an assumed zero volume change, making the enthalpy of mixing equal to the internal energy of mixing and for equivalent Gibbs and Helmholtz free energies of mixing.

Within the quasi-chemical model, the numbers of distinguishable pairs of adjacent cations are subject to a Boltzmann's distribution relative to the appropriate exchange energies. Placement of these pairs on the lattice is done randomly, assuming the pairs are independent. Within the electrostatic model, random mixing of cations is assumed subject to the constraint of electrostatic balance in each structural unit.

The end-member formulas given above have a total cation valence of 22. In this study an illite structural unit will consist of 8 distinguishable lattice sites occupied by cations having this total valence. These sites are arranged on 4 sequential lattice planes parallel to (001). Sites on each plane are limited to only 1 site class. Sequentially, there are 2 T sites, 3 O sites, 2 T sites, and 1 I site on the 4 sheets. The lattice relationships of the cation sites are shown by DEER *et al.* (1976, Fig. 3). Each O site and I site has 6 adjacent sites, and each T site has only 3. An arbitrary division of a lattice into structural units results in 1/3 of the adjacent site interactions in the T and O classes occurring within units. The remaining site interactions occur between units.

Anion mixing is not considered because anions of the same species occupy similar classes of sites in the mica end-members. Mixing of identical anions will not produce distinguishable permutations adding to the configurational entropy. Adjacent anion interactions will not contribute to the enthalpy of mixing (excess enthalpy) because they will cancel out between the solid solution and the mica end-members.

The reader is referred to the earlier paper (STOESSELL, 1979) for a discussion of the bulk compositional differences between the simulated illites and their natural counterparts. The major deficiency is the lack of a ferric mica end-member in the simulated illite.

LOCAL ELECTROSTATIC BALANCE

Entropy of mixing

The electrostatic model is a regular solution with no excess entropy of mixing. The molar entropy of mixing, $\Delta\bar{S}_{\text{mix}}$, is given by Boltzmann's relation for the molar configurational entropy of mixing, $\Delta\bar{S}_{\text{is}}$.

$$\Delta\bar{S}_{\text{mix}} = k \ln \bar{W} \tag{1}$$

where k is Boltzmann's constant and $\bar{W}$ is the ratio of distinguishable lattice configurations in one mole of structural units between the solid solution and the unmixed end-members.

The cation configuration of each structural unit within a solid solution is part of a set of distinguishable cation configurations that are each balanced electrostatically. A much smaller set exists for each of the end-members. $\bar{W}$ becomes the ratio of distinguishable random permutations of one mole of structural units between the solid solution and the end-members.

The different possible combinations of cations in the 3 site classes, which satisfy the electrostatic balance per structural unit, are listed in Table 1. There are 20 possible combinations in the solid solution and 1 for each of the end-members. Additional cation combinations will satisfy the electrostatic balance; however, their presence, from mass balance considerations, would require the existence of other unbalanced combinations. For example, mixing of cations between 4 structural units of muscovite could result in Al occupying all 7 of the T and O sites in one structural unit. However, each of the other 3 structural units will be electrostatically unbalanced.

The distinguishable cation configurations result from permutations of cations within site classes in each cation combination listed in Table 1. There are 223 possible distinguishable cation configurations for a structural unit within the solid solution and 23 in the unmixed end-members.

In the following discussion the subscripts i and j will refer to cation combinations in Table 1 for the solid solution and the end-members, respectively.

Let P_i be the probability that a randomly selected unit structure has the ith cation combination. Then P_i/g_i is the probability that the unit structure has one of the g_i distinguishable cation configurations resulting from permutations in the ith cation combination. X_j/g_j is the corresponding probability in the unmixed end-members where X_j is the mole fraction of the jth end-member. $\bar{W}$ can be written as a multinomial coef-

Table 1. Permissible Structural Units

Solution or end-member	Structural unit cation combinations			Distinguishable permutations	Average site interactions within structural units	
	I	O	T	g	O	T
Solution						
1	E	Al Al E*	Si Si Si Si	3	Al,Al; 2Al,E	2Si,Si
2		Mg Mg Mg		1	3Mg,Mg	
3		Fe Mg Mg		3	Mg,Mg; 2Mg,Fe	
4		Fe Fe Mg		3	Fe,Fe; 2Mg,Fe	
5		Fe Fe Fe		1	3Fe,Fe	
6	K	Al Mg E		6	Al,E; Al,Mg; Mg,E	
7		Al Fe E		6	Al,E; Al,Fe; Fe,E	
8	E	Al Mg Mg	Al Si Si Si	12	Mg,Mg; 2Al,Mg	Al,Si; Si,Si
9		Al Fe Mg		24	Al,Mg; Al,Fe; Mg,Fe	
10		Al Fe Fe		12	Fe,Fe; 2Al,Fe	
11	K	Al Al E		12	Al,Al; 2Al,E	
12		Mg Mg Mg		4	3Mg,Mg	
13		Fe Mg Mg		12	Mg,Mg; 2Mg,Fe	
14		Fe Fe Mg		12	Fe,Fe; 2Mg,Fe	
15		Fe Fe Fe		4	3Fe,Fe	
16	E	Al Al Mg	Al Al Si Si	18	Al,Al; 2Al,Mg	(1/3)Al,Al; (1/3)Si,Si; (4/3)Al,Si
17		Al Al Fe		18	Al,Al; 2Al,Fe	
18	K	Al Mg Mg		18	Mg,Mg; 2Al,Mg	
19		Al Fe Mg		36	Al,Mg; Al,Fe; Mg,Fe	
20		Al Fe Fe		18	Fe,Fe; 2Al,Fe	
End-members						
Muscovite	K	Al Al E	Al Si Si Si	12	Al,Al; 2Al,E	Al,Si; Si,Si
Pyrophyllite	E	Al Al E	Si Si Si Si	3	Al,Al; 2Al,E	2Si,Si
Phlogopite	K	Mg Mg Mg	Al Si Si Si	4	3Mg,Mg	Al,Si; Si,Si
Annite	K	Fe Fe Fe	Al Si Si Si	4	3Fe,Fe	Al,Si; Si,Si

*E signifies an empty site.

ficient with factorial terms containing P_i/g_i and X_j/g_j:

$$\Delta\bar{S}_{\text{mix}} = k\ln\frac{A!}{\prod_i\left(\left(\frac{P_iA}{g_i}\right)!\right)^{g_i}} - k\ln\prod_j\frac{(X_jA)!}{\left(\left(\frac{X_jA}{g_j}\right)!\right)^{g_j}} \qquad (2)$$

where A is Avogadro's number.

Equation (2) can be simplified using Stirling's approximation, the identity $k = R/A$, and these 2 relations:

$$\sum_i P_i = 1 \qquad (3)$$

and

$$\sum_j X_j = 1$$

where R is the universal gas constant. The expression for $\Delta\bar{S}_{\text{mix}}$ becomes:

$$\Delta\bar{S}_{\text{mix}} = -R\left(\sum_i P_i\ln\frac{P_i}{g_i} + \sum_j X_j\ln g_j\right). \qquad (4)$$

g_i and g_j are listed in Table 1. Equation (4) becomes:

$$\Delta\bar{S}_{\text{mix}} = -R\left(\sum_i P_i\ln\frac{P_i}{g_i} + X_{\text{mus}}\ln 12 + X_{\text{pyr}}\ln 3 + X_{\text{phl}}\ln 4 + X_{\text{ann}}\ln 4\right). \qquad (5)$$

The only unknowns in eqn (5) are the probabilities, P_i, in the solid solution. Only 8 of the P_i values for the 20 cation combinations are independent. P_i for a cation combination containing n Fe^{2+} cations must equal

$$\left(\frac{X_{\text{ann}}}{X_{\text{phl}}}\right)^n P_m\left(\frac{g_i}{g_m}\right)$$

where the mth cation combination is identical to the ith combination except for the replacement of n Fe^{2+} cations with n Mg^{2+} cations.

The correct P_i values, for the mixing model, are those that maximize

$$-\sum_i P_i\ln\left(\frac{P_i}{g_i}\right)$$

subject to the constraint of eqn (3) and any 3 independent mass relations that define the bulk composition. In this study the maximization was done using Lagrange multipliers to produce a set of 12 nonlinear equations that were solved with a Newton–Raphson iteration procedure.

Computed P_i probabilities for a few selected bulk illite compositions are listed in Table 2, together with values of $\Delta\bar{S}_{\text{mix}}$ calculated from eqn (5).

$\Delta\bar{S}_{\text{mix}}$ is related to the ideal activity, a_j^0, of the jth end-member by the expression below:

$$\Delta\bar{S}_{\text{mix}} = \Delta\bar{S}_{\text{is}} = -R\sum_j X_j\ln a_j^0$$

where a_j^0 corresponds to the probability of picking at random out of the solid solution, a structural unit of the jth end-member (STOESSELL, 1979). Ideal activity trends will not be discussed in this paper; however, it

Table 2. P_i in solution, $\Delta\bar{S}_{mix}$ in cal/°K/mole, and end-member X_k for selected illite compositions

Cation combinations Table 1	Illites*				
	a	b	c	d	e
P_1	3.16 E-1**	1.66 E-1	1.21 E-1	1.21 E-1	2.47 E-1
P_2	1.14 E-3	3.87 E-3	5.33 E-3	6.67 E-4	1.24 E-3
P_3	3.79 E-4	2.05 E-3	8.00 E-3	4.00 E-3	3.73 E-3
P_4	4.21 E-5	3.61 E-4	4.00 E-3	8.00 E-3	3.73 E-3
P_5	1.56 E-6	2.13 E-5	6.67 E-4	5.33 E-3	1.24 E-3
P_6	1.37 E-1	2.11 E-1	2.04 E-1	1.02 E-1	1.23 E-1
P_7	1.53 E-2	3.72 E-2	1.02 E-1	2.04 E-1	1.23 E-1
P_8	2.15 E-2	4.25 E-2	4.28 E-2	1.07 E-2	1.85 E-2
P_9	4.77 E-3	1.50 E-2	4.28 E-2	4.28 E-2	3.71 E-2
P_{10}	2.65 E-4	1.32 E-3	1.07 E-2	4.28 E-2	1.85 E-2
P_{11}	4.32 E-1	3.86 E-1	2.73 E-1	2.73 E-1	3.06 E-1
P_{12}	1.56 E-3	9.00 E-3	1.20 E-2	1.50 E-3	1.54 E-3
P_{13}	5.18 E-4	4.76 E-3	1.80 E-2	8.98 E-3	4.63 E-3
P_{14}	5.76 E-5	8.41 E-4	8.98 E-3	1.80 E-2	4.63 E-3
P_{15}	2.13 E-6	4.95 E-5	1.50 E-3	1.20 E-2	1.54 E-3
P_{16}	5.06 E-2	5.85 E-2	4.29 E-2	2.14 E-2	3.45 E-2
P_{17}	5.62 E-3	1.03 E-2	2.14 E-2	4.29 E-2	3.45 E-2
P_{18}	1.10 E-2	3.71 E-2	3.60 E-2	9.00 E-3	8.63 E-3
P_{19}	2.45 E-3	1.31 E-2	3.60 E-2	3.60 E-2	1.73 E-2
P_{20}	1.36 E-4	1.16 E-3	9.00 E-3	3.60 E-2	8.63 E-3
$\Delta\bar{S}_{mix}$	3.17	4.20	5.34	5.34	4.62
X_{mus}	0.50	0.50	0.40	0.40	0.40
X_{pyr}	0.40	0.30	0.30	0.30	0.40
X_{phl}	0.09	0.17	0.20	0.10	0.10
X_{ann}	0.01	0.03	0.10	0.20	0.10

*(a) $K_{0.60}(Al_{1.80}Mg_{0.27}Fe_{0.03})Al_{0.60}Si_{3.40}O_{10}(OH)_2$
(b) $K_{0.70}(Al_{1.60}Mg_{0.51}Fe_{0.09})Al_{0.70}Si_{3.30}O_{10}(OH)_2$
(c) $K_{0.70}(Al_{1.40}Mg_{0.60}Fe_{0.30})Al_{0.70}Si_{3.30}O_{10}(OH)_2$
(d) $K_{0.70}(Al_{1.40}Mg_{0.30}Fe_{0.60})Al_{0.70}Si_{3.30}O_{10}(OH)_2$
(e) $K_{0.60}(Al_{1.60}Mg_{0.30}Fe_{0.30})Al_{0.60}Si_{3.40}O_{10}(OH)_2$

**E-X = 10^{-X}

is of interest to note that the ideal activities of pyrophyllite, muscovite, phlogopite, and annite are given by P_1, P_{11}, P_{12}, and P_{15}, respectively, in the electrostatic model (see Table 1).

Enthalpy of mixing

$\Delta\bar{H}_{mix}$, the molar enthalpy of mixing, is assumed to result only from interactions between adjacent sites in the same class. Sixteen distinguishable pairs occur in the solid solution, and 10 in the unmixed end-members. These include all possible y,z pairs of cations and/or empty sites. The number of moles of y,z pairs in the Xth site class due to mixing one mole of structural units is $nX_{y,z}$. Note that $nX_{y,z}$ will be negative if mixing results in a decrease in the number of y,z pairs. The y,z contribution to $\Delta\bar{H}_{mix}$ is the product of $nX_{y,z}$ and the molar interaction parameter, $\overline{WX}_{y,z}$. The sum of the contribution of all 16 distinguishable pairs is equal to $\Delta\bar{H}_{mix}$.

Within the Xth site class, the computation of $nX_{y,z}$ must satisfy two constraints. The total numbers of y and z occupancies and the total number of sites cannot change due to mixing. These constraints dictate some simple relations of the type listed below:

$$nI_{K,E} = -2\,nI_{K,K} = -2\,nI_{E,E}$$

and

$$-2\,nO_{Al,Al} = nO_{Al,E} + nO_{Al,Mg} + nO_{Al,Fe}.$$

Using these constraints an expression for $\Delta\bar{H}_{mix}$ can be written in terms of $\overline{EX}_{y,z}$, the molar exchange energies.

$$\begin{aligned}\Delta\bar{H}_{mix} = {} & nI_{K,E}\overline{EI}_{K,E} + nT_{Al,Si}\overline{ET}_{Al,Si} \\ & + nO_{Al,E}\overline{EO}_{Al,E} + nO_{Al,Mg}\overline{EO}_{Al,Mg} \\ & + nO_{Al,Fe}\overline{EO}_{Al,Fe} + nO_{Mg,E}\overline{EO}_{Mg,E} \\ & + nO_{Fe,E}\overline{EO}_{Fe,E} + nO_{Mg,Fe}\overline{EO}_{Mg,Fe} \qquad (6)\end{aligned}$$

where

$$\overline{EX}_{y,z} = \overline{WX}_{y,z} - \tfrac{1}{2}(\overline{WX}_{y,y} + \overline{WX}_{z,z}). \qquad (7)$$

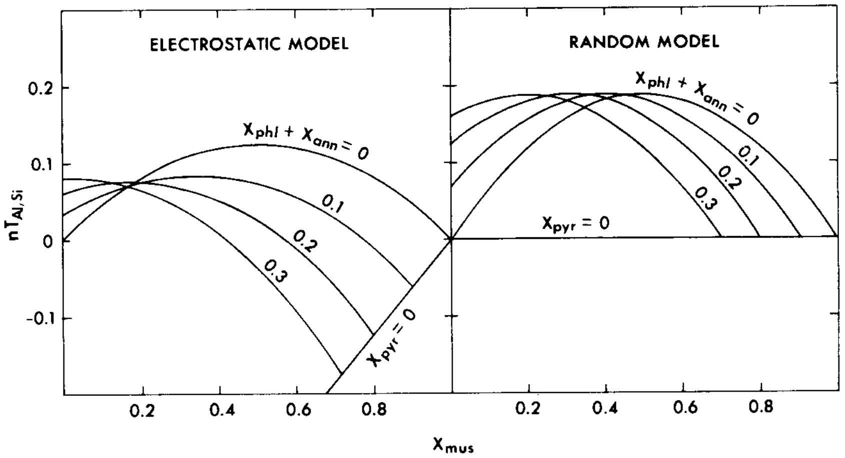

Fig. 1. The compositional dependence of $nT_{Al,Si}$ in the electrostatic and random models.

In the random model $\Delta\overline{H}_{mix}$ was written in terms of 4 molar site interaction parameters (STOESSELL, 1979, eqn (26) for $\Delta\overline{H}_{ex}$). These parameters are related to the molar exchange energies by these relations:

$$\overline{WTI} = 6\,\overline{EI}_{K,E} + 0.75\,\overline{ET}_{Al,Si}$$

$$\overline{WO1} = -4\,\overline{EO}_{Al,E} + 12\overline{EO}_{Al,Mg} + 6\overline{EO}_{Mg,E}$$

$$\overline{WO2} = -4\,\overline{EO}_{Al,E} + 12\overline{EO}_{Al,Fe} + 6\overline{EO}_{Fe,E}$$

and

$$\overline{WO3} = 18\,\overline{EO}_{Mg,Fe}$$

In the electrostatic model, $nX_{y,z}$ is divided into the pairs occurring within electrostatically balanced structural units and the pairs resulting between sites in adjacent units. The number of y,z pairs occurring in a structural unit of each possible cation configuration is listed in Table 1. The number of y,z pairs within the units is computed from the probabilities of occurrence of these cation configurations for the bulk composition. Because the units are distributed randomly, the number of y,z pairs between adjacent units can be calculated within the random model. Two-thirds of the adjacent sites in the O and T site classes and all of them in the Ith site class occur between units. The total number of y,z pairs due to mixing is computed by the random model, multiplied by the appropriate fraction, and then added to the number of such pairs occurring within units to give $nX_{y,z}$.

In illites having compositions corresponding to natural illites, the differences in $nX_{y,z}$ are usually minor between the random and electrostatic models. The major exception is $nT_{Al,Si}$, which is significantly less in the electrostatic model, as shown on Fig. 1.

QUASI-CHEMICAL APPROXIMATION

The canonical partition function is used in the quasi-chemical model. GUGGENHEIM (1952, pp. 42–44) derived the partition function Ω for the quasi-chemical mixing of 2 types of particles over equivalent sites. The extension to the illite solid solution is outlined below.

Ω_{mix}, the partition function for mixing in the illite solution, is a function of the partition functions of the end-members (Ω_{pyr}, Ω_{mus}, Ω_{phl}, Ω_{ann}) and of the solution (Ω_{sol}) which contains one mole of units.

$$\Omega_{mix} = \frac{\Omega_{sol}}{\Omega_{pyr}\Omega_{mus}\Omega_{phl}\Omega_{ann}} \tag{8}$$

where for the jth end-members or solution

$$\Omega_j \doteq g_{I,j}\exp(-\epsilon_{I,j}/kT) \cdot g_{T,j}\exp(-\epsilon_{T,j}/kT)\cdot g_{O,j}\exp(-\epsilon_{O,j}/kT). \tag{9}$$

$g_{X,j}$ is the number of configurations in the Xth site class having energy $\epsilon_{X,j}$ due to interactions between adjacent sites. Each factor, $g_{X,j}\cdot\exp(-\epsilon_{X,j}/kT)$, is the maximum term in a summation over all possible values of $\epsilon_{X,j}$.

For a given composition and temperature, $g_{X,j}$ and $\epsilon_{X,j}$ are functions of the numbers of moles of y,z pairs ($y \neq z$) and of the exchange energies defined by eqn (7). The procedure followed in this study to determine Ω_j was to maximize $g_{X,j}\exp(-\epsilon_{X,j}/kT)$ subject to assumed values of the exchange energies.

Unless otherwise noted, the following discussion concerns the jth end-member or solution. The subscript j has been omitted.

From GUGGENHEIM (1952), it can be shown that

$$k\ln g_X = \Delta S_{is,X} + R\sum_{y,z} mX^*_{y,z}\ln\left(\frac{2mX^*_{y,z}}{\alpha Z_X l_X n}\right) - R\sum_{y,z} mX_{y,z}\ln\left(\frac{2mX_{y,z}}{\alpha Z_X l_X n}\right) \tag{10}$$

where $\alpha = 2$ unless $y = z$, then $\alpha = 1$. $\Delta S_{is,X}$ and $mX^*_{y,z}$ are the configurational entropy and the number of moles of y,z pairs, respectively, in the Xth site class assuming random mixing. Z_X and l_X are the cation coordination number and the number of sites per structural unit, respectively, in the Xth site class. n is the number of moles of j units.

$\Delta S_{\text{is},X}$ and $mX^*_{y,z}$ can be computed from the random model, and mass balance relations of the form

$$mX_{y,y} = \tfrac{1}{2}(Z_X mX_y - \sum_{y,z} (mX_{y,z})_{y \neq z}) \qquad (11)$$

can be used to eliminate $mX_{y,z}(y = z)$ as independent variables in eqn (10). mX_y is the number of moles of y site occupancies in the Xth site class.

By definition

$$\epsilon_X = \sum_{y,z} mX_{y,z} \overline{WX}_{y,z}. \qquad (12)$$

Substitution of exchange energies into eqn (12) yields

$$\epsilon_X = \sum_{y,z} (mX_{y,z} \overline{EX}_{y,z})_{y \neq z} + D \qquad (13)$$

where D is a constant, dependent upon composition, which cancels out in eqn (8).

Values of $mX_{y,z}$ maximizing $g_X \exp(-\epsilon_X/kT)$, in eqn (9), can be determined with eqns (10), (11), and (13). In cases where only $mX_{y,y}$ is possible, g_X is unity. If only one y,z pair occurs such that $y \neq z$, the procedure outlined by GUGGENHEIM (1952) yields an expression for $mX_{y,z}$. Only in the O sites in the solution are different y,z pairs possible such that $y \neq z$. The partial derivatives of $g_O \exp(-\epsilon_O/kT)$ with respect to $mO_{y,z}$ are used to produce a set of nonlinear equations. These are set equal to zero and solved for the solution set of $mO_{y,z}$ using a Newton–Raphson iteration procedure.

Evaluation of Ω_{mix} allows the computation of $\Delta\overline{G}_{\text{mix}}$, the molar free energy of mixing, and $\Delta\overline{S}_{\text{mix}}$.

$$\Delta\overline{G}_{\text{mix}} = -kT \ln \Omega_{\text{mix}} \qquad (14)$$

and

$$\Delta\overline{S}_{\text{mix}} = kT \frac{\partial \ln \Omega_{\text{mix}}}{\partial T} + k \ln \Omega_{\text{mix}} \qquad (15)$$

where the partial of $\ln \Omega_{\text{mix}}$ with respect to T was made using a finite difference approximation.

EXCHANGE ENERGIES

The available precise experimental data for illites (ROUTSON and KITTRICK, 1971) are inadequate to determine $EX_{y,z}$ in ferric iron-free illites. The addition of a ferric mica end-member, when its thermodynamic properties are known, will aid in back-calculating $EX_{y,z}$. Not only experimental data but also assumed equilibrium solubilities obtained from reservoir studies (MERINO and RANSOM, 1981) may be of use in this regard.

Interchange energies used by GUGGENHEIM (1952) are equivalent on a molar basis to $Z_X \overline{E}X_{y,z}$. For binary mixing, GUGGENHEIM (1952) suggests limiting the absolute magnitude of $\overline{EX}_{y,z}$ to $2\,RT/Z_X$ for mixing involving zero excess entropy, e.g. the random and electrostatic models, and $RT \ln(Z_X/(Z_X - 2))$ for quasi-chemical mixing. According to Guggenheim, the latter limit is a minimum value which can be larger, depending on the nature of the phase.

In this paper, assumed values of $\overline{EX}_{y,z}$ will be used to delineate their effects on $\Delta\overline{G}_{\text{mix}}$ in all 3 models. Absolute values greater than $2RT/Z_X$ will be used in the random and electrostatic models for comparison with the quasi-chemical model.

RESULTS AND DISCUSSION

Compositional dependencies of $\Delta\overline{S}_{\text{mix}}$ and $\Delta\overline{G}_{\text{mix}}$, predicted by the three models, are shown on Figs 2–5 for illites composed of 3 end-members. Annite was excluded to reduce the number of exchange energies from 8 to 5. Annite adds ferrous iron to the O sites; however, ferrous iron is a very minor component in natural illites (WEAVER and POLLARD, 1975).

The compositional variations in $\Delta\overline{S}_{\text{mix}}$ shown on Fig. 2 for the random and electrostatic models are independent of the exchange energies. For illites of composition found in nature (predominantly dioctahedral) $\Delta\overline{S}_{\text{mix}}$ in the electrostatic model is about 1 entropy unit less than in the random model. The quasi-chemical model reduces to the random model when the exchange energies are zero. For non-zero energies, $\Delta\overline{S}_{\text{mix}}$ in the quasi-chemical model lies between those of the other two models.

$\Delta\overline{S}_{\text{mix}}$ is largest in all three models in illites having large mole fractions of both the trioctahedral mica

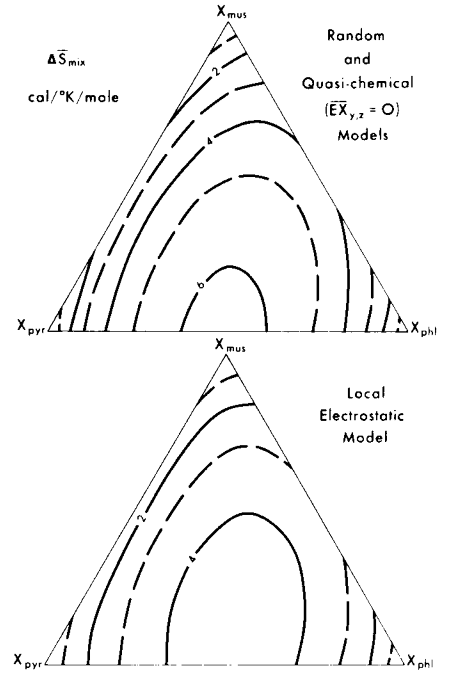

Fig. 2. $\Delta\overline{S}_{\text{mix}}$ compositional dependence in the random, electrostatic, and quasi-chemical ($EX_{y,z} = 0$) models.

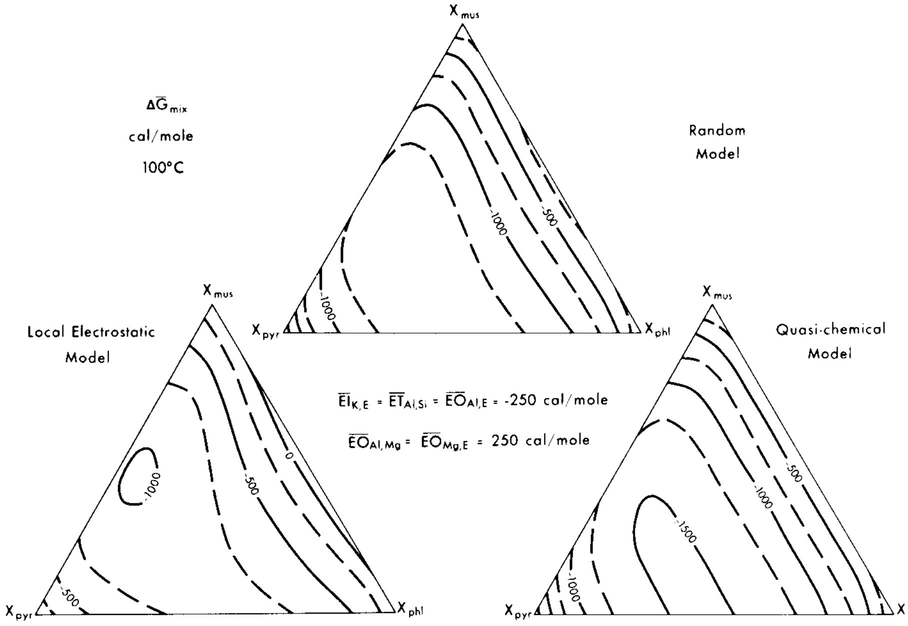

Fig. 3. $\Delta\bar{G}_{\mathrm{mix}}$ compositional dependence at 100°C in the 3 models using $Z_{\mathrm{T}}\ \bar{E}\mathrm{T}_{\mathrm{Al,Si}} = -1.0\,RT$ and $Z_{\mathrm{I}}\ \bar{E}\mathrm{I}_{\mathrm{K,E}} = Z_{\mathrm{O}}\ \bar{E}\mathrm{O}_{\mathrm{Al,E}} = -Z_{\mathrm{O}}\ \bar{E}\mathrm{O}_{\mathrm{Al,Mg}} = -Z_{\mathrm{O}}\ \bar{E}\mathrm{O}_{\mathrm{Mg,E}} = -2.0\,RT$.

phlogopite and the dioctahedral mica pyrophyllite. This is related to the assumption of similar order–disorder states in both the illite and the end-members. Muscovite has the largest configurational entropy of the end-members. Subtraction of this entropy from that present in the illite reduces $\Delta\bar{S}_{\mathrm{mix}}$ in illites having large mole fractions of muscovite.

Negative values of $\bar{E}\mathrm{I}_{\mathrm{K,E}}$, $\bar{E}\mathrm{T}_{\mathrm{Al,Si}}$, and $\bar{E}\mathrm{O}_{\mathrm{Al,E}}$ combined with positive values of $\bar{E}\mathrm{O}_{\mathrm{Al,Mg}}$ and $\bar{E}\mathrm{O}_{\mathrm{Mg,E}}$ help promote the stability of dioctahedral illites relative to trioctahedral illites. Exchange energies having the greatest effect are $\bar{E}\mathrm{I}_{\mathrm{K,E}}$, $\bar{E}\mathrm{O}_{\mathrm{Al,Mg}}$, and $\bar{E}\mathrm{O}_{\mathrm{Mg,E}}$ because of the absence of these y,z pairs in the end-members.

In the quasi-chemical model, negative values of $\bar{E}\mathrm{T}_{\mathrm{Al,Si}}$ and $\bar{E}\mathrm{O}_{\mathrm{Al,E}}$ will increase $m\mathrm{T}_{\mathrm{Al,Si}}$ and $m\mathrm{O}_{\mathrm{Al,E}}$ in both the illite and the end-members, canceling part of

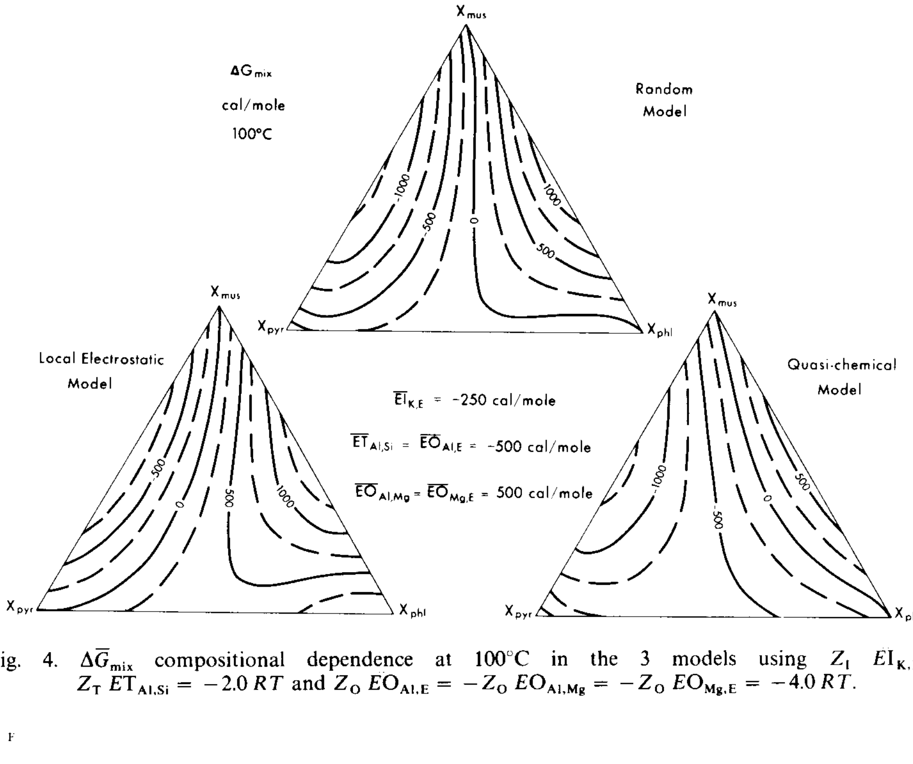

Fig. 4. $\Delta\bar{G}_{\mathrm{mix}}$ compositional dependence at 100°C in the 3 models using $Z_{\mathrm{I}}\ \bar{E}\mathrm{I}_{\mathrm{K,E}} = Z_{\mathrm{T}}\ \bar{E}\mathrm{T}_{\mathrm{Al,Si}} = -2.0\,RT$ and $Z_{\mathrm{O}}\ \bar{E}\mathrm{O}_{\mathrm{Al,E}} = -Z_{\mathrm{O}}\ \bar{E}\mathrm{O}_{\mathrm{Al,Mg}} = -Z_{\mathrm{O}}\ \bar{E}\mathrm{O}_{\mathrm{Mg,E}} = -4.0\,RT$.

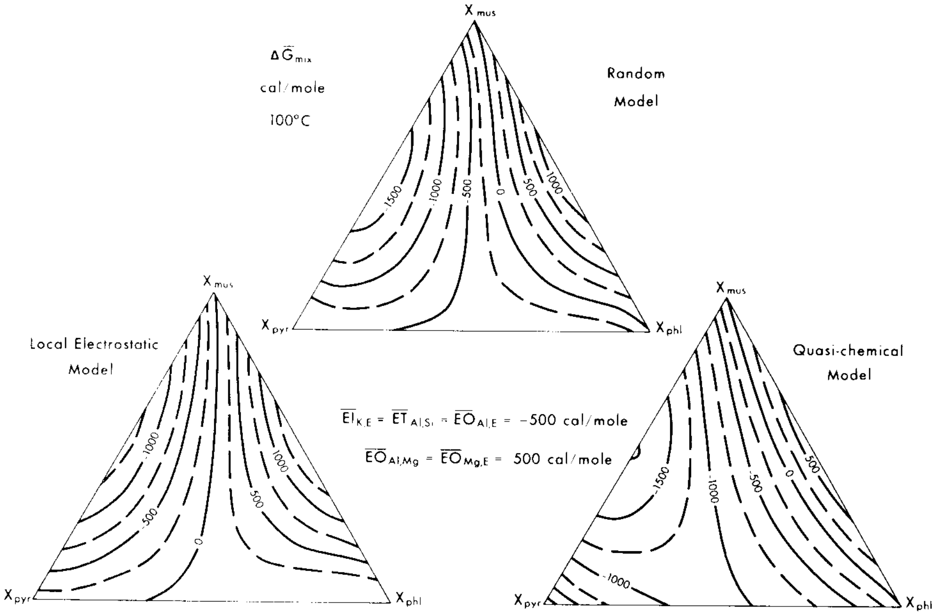

Fig. 5. $\Delta\bar{G}_{mix}$ compositional dependence at 100°C in the 3 models using $Z_T\ \bar{E}T_{Al,Si} = -2.0\,RT$ and $Z_I\ \bar{E}I_{K,E} = Z_O\ \bar{E}O_{Al,E} = -Z_O\ \bar{E}O_{Al,Mg} = -Z_O\ \bar{E}O_{Al,E} = -4.0\,RT$.

the expected decrease in $\Delta\bar{H}_{mix}$. $n\mathrm{T}_{Al,Si}$ ($X_{pyr} \neq 0$) actually becomes less positive with decreasing $\bar{E}\mathrm{T}_{Al,Si}$ because of a larger increase in $m\mathrm{T}_{Al,Si}$ in the end-members relative to the illite solid solution. In all 3 models, $n\mathrm{O}_{Al,E}$ is negative in any illite having a non-zero trioctahedral mole fraction.

The $\Delta\bar{G}_{mix}$ compositional variations in Figs 3–5 are at 100°C. Diagenetic illite is commonly observed in feldspathic reservoirs at approximately this temperature (MERINO and RANSOM, 1981; MICHAEL WILSON, personal communication, 1980).

$\bar{E}\mathrm{X}_{y,z}$ absolute values have been set either to 250 or 500 cal/mol for the $\Delta\bar{G}_{mix}$ computations used in Figs 3–5. The sign of $\bar{E}\mathrm{X}_{y,z}$ was set to maximize stability of predominantly dioctahedral illites relative to trioctahedral illites.

For zero exchange energies, minimum $\Delta\bar{G}_{mix}$ corresponds to maximum $\Delta\bar{S}_{mix}$ in Fig. 2. The $\Delta\bar{G}_{mix}$ minimum is shifted away from the phlogopite corner in Fig. 3; and in Fig. 4, predominantly trioctahedral illites are destabilized in all 3 models. The trend is continued in Fig. 5. Differences between Figs 4 and 5 are due to a decrease of 250 cal/mol in $\bar{E}\mathrm{I}_{K,E}$, reflecting the significances of pair interactions not existing in the end-member micas. Maximum destabilization of trioctahedral illites is predicted by the electrostatic model; however, maximum stability of dioctahedral illites is predicted by the quasi-chemical model. $\Delta\bar{G}_{mix}$ values in the random model fall between those predicted by the other 2 models. Differences in $\Delta\bar{G}_{mix}$ between the random and quasi-chemical models decrease with decreasing mole fraction of phlogopite.

The relative differences in $\Delta\bar{G}_{mix}$ are those expected based on assumptions inherent in each model. In the electrostatic model, the local electrostatic balance per structural unit is probably too restrictive, leading to underestimation of $\Delta\bar{S}_{mix}$. The neglect of exchange energies in determining $n\mathrm{X}_{y,z}$ values causes overestimation of $\Delta\bar{H}_{mix}$. Hence, $\Delta\bar{G}_{mix}$ in the electrostatic model is overestimated. In the quasi-chemical model, the assumption of independence of pairs on the lattice and neglect of local electrostatic balance results in overestimating $\Delta\bar{S}_{mix}$, consequently underestimating $\Delta\bar{G}_{mix}$. Within the random model, random mixing leads to overestimation of both $\Delta\bar{S}_{mix}$ and $\Delta\bar{H}_{mix}$, resulting in 'some' error cancellation in $\Delta\bar{G}_{mix}$.

A quasi-chemical model containing local electrostatic balance would be more accurate than those discussed here. The partition function of this model for illites has not been derived; however, $\Delta\bar{G}_{mix}$ should fall between those predicted by the quasi-chemical and electrostatic models or presumably close to that predicted by the random model. Interestingly, because of error cancellation, the random model may yet prove useful for predicting $\Delta\bar{G}_{mix}$ in geochemical calculations. That use, however, must wait until more information is available on the exchange energies.

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