Clays and Clay Minerals, Vol. 28, No. 3, pp. 161–172, 1980.

ALKALI CATION SELECTIVITY AND FIXATION BY CLAY MINERALS

DENNIS D. EBERL

Department of Geology, University of Illinois, Urbana, Illinois 61801

Abstract—Two variables must be considered when calculating exchange free energies (ΔG^0ex) for 2:1 clays: (1) anionic field strength, as expressed by equivalent anionic radius (r_a), and (2) interlayer water content, as expressed by interlayer molality. For smectites that are in a state of high hydration, interlayer molality is determined by the cations undergoing exchange. Thus ΔG^0ex for an exchanging cation pair can be calculated solely from measurements of r_a. r_a is related to layer charge per half unit cell (C) and *ab* unit cell area (A) by: $r_a = (-A/8\pi C)^{1/2}$. The layer charge necessary for cation fixation can be predicted by calculating the r_a at which cation exchange with an illite structure expresses a ΔG^0ex equal to that of exchange with a smectite structure. The theory can also be applied qualitatively to understand the high selectivity of illite for Cs^+, the fixation of K^+ rather than Na^+ in shales during diagenesis, the stability of illite over muscovite in the weathering environment, and cation segregation in smectite.

Key Words—Cation exchange, Cation fixation, Cation selectivity, Equivalent anionic radius, Free energy of exchange, Illite, Smectite.

INTRODUCTION

One would like to predict the sorptive properties of a clay for all ions simply by characterizing the clay. This goal requires a fundamental understanding of both the exchange process and the influence of clay crystal chemistry on this process. Previous studies have emphasized the exchange process and have led to a largely empirical understanding. The present study looks at cation exchange from the standpoint of the clay structure.

The exchange reaction for a 2:1 clay involving alkali cations A^+ and B^+ can be represented by the law of mass action:

$$AX + B^+ \rightleftarrows BX + A^+,$$

where X is the negatively charged clay surfaces. The equilibrium exchange constant (K_e) for this reaction is:

$$K_e = \frac{[BX][A^+]}{[AX][B^+]},$$

where $[A^+]$ and $[B^+]$ refer to cation activities in solution, and [BX] and [AX] refer to their activities on the clay surfaces. The activities of cations in solution can be calculated from measured concentrations by an expression such as $(A^+)\gamma = [A^+]$, where the parenthesis refers to the concentration of A^+ in solution and γ is the activity coefficient of A^+. γ can be calculated from the ionic strength of a dilute solution with the Debye-Hückel equation (Garrels and Christ, 1965). Unfortunately the Debye-Hückel equation is not applicable for calculating activity coefficients for cations held on clay surfaces, and the experimental values usually reported are concentrations, expressed in terms of the selectivity coefficient (K_c):

$$K_c = \frac{(BX)[A^+]}{(AX)[B^+]},$$

where (BX) and (AX) refer to concentrations of B^+ and A^+ on the clay surfaces. K_c has been empirically related to K_e by:

$$K_e = \left(\frac{(BX)}{(AX)}\right)^n \frac{[A^+]}{[B^+]}, \qquad (1)$$

where n is an empirical exponent measured for a particular clay. This equation is not valid in the vicinity of end-member compositions (Garrels and Christ, 1965). The selectivity coefficient equals the equilibrium constant when $n = 1$.

The equilibrium constant can be calculated from measured values of the selectivity coefficient by the Gaines-Thomas equation (Gaines and Thomas, 1953). This equation for univalent ions is:

$$\ln K_e \approx (n_2 - n_1) \ln P/P^0 + \int_0^1 \ln K_c \, dN_A, \qquad (2)$$

where n_1 and n_2 are the moles of water in the interlayer (for a smectite-like clay) when pure B^+ or A^+ are exchanged, P is the vapor pressure of the solution, P^0 is the vapor pressure of pure water, and N_A is the mole fraction of A^+ in the clay interlayer. The experimental strategy is to assume that $n_1 = n_2$, in which case Eq. (2) reduces to:

$$\ln K_e = \int_0^1 \ln K_c dN_A. \qquad (3)$$

K_c is then measured for a range of N_A. Values of $\ln K_c$ are plotted against N_A, and the area under the curve is measured to find $\ln K_e$. The exchange free energy (ΔG^0ex) can then be calculated:

Copyright © 1980, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

$$\Delta G^0ex = -RT \ln K_e. \quad (4)$$

Experimentalists often give few details concerning the clay used in their experiments, other than reporting, for example, that it was a bentonite from Texas, and sometimes giving its cation-exchange capacity (CEC). Because K_e has been found to vary from smectite to smectite, such a description is insufficient to understand how the clay influences K_e. Furthermore, CEC is a measurement which is difficult to relate precisely to the underlying clay structure (i.e., layer charge) because it depends on the method used to measure it, on the formula weight of the clay (which is usually not given), on crystallite size, and on whether or not the clay is a mixed-layered species.

The question thus arises, what are the fundamental properties of a clay which determine K_e for an exchanging ion pair? The calculations presented here suggest that K_e (and therefore ΔG^0ex) is a function of a clay's electric field strength, as represented by equivalent anionic radius, and its interlayer water content, as represented by interlayer molality.

METHODS FOR CALCULATING ΔG^0ex

The calculations generally follow those developed by Eisenman (1961, 1962) for cation-selective electrodes. All exchange free energies are calculated relative to Cs^+ because Cs^+ is considered to be unhydrated both in solution and in the clay interlayer. Cation exchange between a Cs-saturated, 2:1 clay (CsX) and a hydrated alkali cation in dilute solution $J^+(aq)$ can be represented by:

$$CsX + J^+(aq) \rightleftharpoons JX + Cs^+(aq).$$

The 2:1 clay in the above reaction can exist in two end-member states. It can be dry, a state in which interlayer cations are not hydrated and are fixed (illite-like or mica-like structure); or the clay can be water swollen, a state in which interlayer cations are hydrated and float between the 2:1 layers (smectite or vermiculite structure). The mixed-layer structure is intermediate and contains both types of interlayers.

ΔG^0ex for a dry interlayer

The free energy of exchange (ΔG^0ex) for an illite-like structure in the above reaction is the energy required to remove Cs^+ from the clay interlayer to a hydrated state in solution, plus the energy required to dehydrate a cation from solution and fix it to the clay interlayer; or:

$$\Delta G^0ex = (\Delta G^0Cs^+(aq) - \Delta G^0CsX) + (\Delta G^0JX - \Delta G^0J^+(aq)). \quad (5)$$

$\Delta G^0J^+(aq)$ is equal to the hydration free energy (ΔG^0hyd) of the cation, a value which can be calculated from thermochemical data presented in Rossini *et al.* (1952). Various formulations of hydration free energy for alkali cations are given in Table 1. Column B gives the energies as they are usually presented (e.g., Friedman and Krishnan, 1973). The values chosen for convenience in the present calculations are those in column C in which ΔG^0hyd for Cs^+ is assumed to be zero. The free energy of interlayer surface fixation for the cation-clay species (CsX and JX) can be estimated by calculating the electrostatic energy of attraction between the cation and the clay's interlayer surfaces. Such a calculation for a system at one atmosphere gives the enthalpy of the clay–cation bond for interlayer cations bound between basal oxygen planes. This enthalpy can be assumed to equal the bond's free energy if the small entropy difference between various monovalent cations fixed on the interlayer surfaces is ignored (Eisenman, 1962; Gast and Klobe, 1971). This energy will differ from the energy of a cation bound in hexagonal holes, a situation which will be discussed below.

Table 1. Hydration free energies in kcal/mole (calculated from Rossini *et al.*, 1952) and ionic radii for alkali cations.

J^+	(A) ΔG^0 hyd J^+ (2) (absolute hydration energy)	(B) ΔG^0 hyd J^+ (1) referred to gaseous Cs^+)	(C) ΔG^0 hyd J^+ (assumes ΔG^0 hyd Cs^+ = 0)	(D) Ionic radius J^+ (Å)
H^+	−363.574	−260.095	−192.685	−0.4
Li^+	−225.196	−121.717	−54.307	0.78
Na^+	−201.295	−97.816	−30.406	0.98
K^+	−183.650	−80.171	−12.761	1.33
Rb^+	−178.583	−75.104	−7.694	1.48
Cs^+	−170.889	−67.410	0	1.69

(A) ΔG^0 hyd J^+ (2) = ΔG^0 fJ^+ (aq) − [ΔH^0 fJ^+ (g) − T(S^0 J(g) − S^0 J(c))].
(B) ΔG^0 hyd J^+ (1) = ΔG^0 hyd J^+ (2) − [ΔH^0 fCs^+ (g) − T(S^0 Cs(g) − S^0 Cs(c))].
(C) ΔG^0 hyd J^+ = ΔG^0 hyd J^+ (1) − ΔG^0 hyd Cs^+ (1).
(D) Values (in Å) from Goldschmidt and Pauling are those used by Eisenman (1962).

The energy of interlayer surface fixation is a function of the radius and charge of the cation, and the anionic field strength (E) of the clay. E is a function of the clay's *ab* unit cell area and its layer charge, and can be expressed most conveniently as an "equivalent anionic radius" (r_a). This value is the radius of a sphere of unit negative charge that has the same electrostatic energy of interaction for the interlayer cation as do the basal oxygen planes which bound the interlayer cation. The equivalent anionic radius (in Å) for the interlayer of a 2:1 clay can be calculated from:

$$r_a = (-A/8\pi C)^{1/2} \quad (6)$$

where C is the layer charge in equivalents per $O_{10}(OH)_2$ (or per half unit cell) and A is the *ab* area in $Å^2$. This relationship, which is derived in Figure 1, does not take into account an effect for charge location. r_a has been calculated for a range of layer charges based on the muscovite *ab* area, and is given in Figure 2.

Once r_a for a particular clay has been calculated, the potential energy (P.E.) expressed by the cation and the clay's interlayer surfaces can be treated as an attraction between two spheres using Coulomb's law:

$$P.E.JX = \Delta H^0JX = [332q_1q_2/(r_a + r_c)] \approx \Delta G^0JX \quad (7)$$

where ΔH^0JX is the enthalpy of fixation in kcal/mole, q_1 and q_2 are the charge of the cation (+1) and the equivalent anion (−1), and r_c is the radius of J^+, the fixed alkali cation (see Table 1). The exchange free energy can now be calculated for an alkali cation that substitutes for Cs^+ in a dry interlayer from Eq. (5).

ΔG^0ex for a wet interlayer

Electrostatic calculations can not be used to find exchange free energies for water-swollen clay because the location and hydration state of absorbed cations are unknown. Following

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

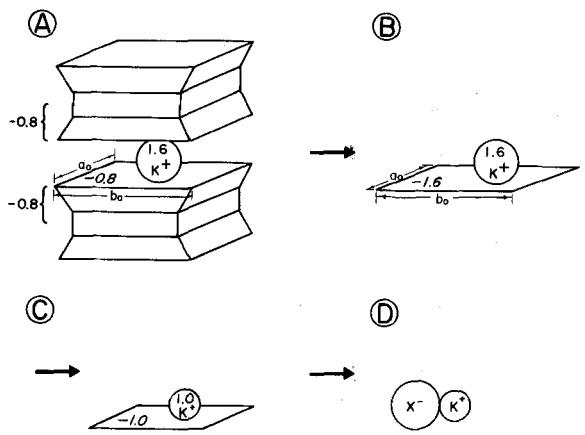


Figure 1. Derivation of Eq. (6) for an illite-like example (depicted in **A**) which has a layer charge (C) of −0.8 equivalents per $O_{10}(OH)_2$ and an *ab* unit cell area on each interlayer surface of **A**. In **B** the upper interlayer surface in **A** has been superimposed on the lower surface, yielding a plane with half the surface area of the two planes in **A**, but with twice the charge of an *ab* plane. This situation is energetically equivalent to that shown in **A** because energy is a scalar quantity. In **C** the surface areas of the plane and cation are adjusted proportionately until the charge on each is −1 and +1 respectively. The new area (A′) of the plane equals −A/2C. In **D** the negative plane has been transformed into an electrically equivalent sphere. The electric field strength (E) of a surface is given by $E = 4\pi\sigma k$, where σ is the surface charge density (charge/surface area) and k is the constant of proportionality (Sears and Zemansky, 1955). Thus, for the sphere in **D**, $E_s = qk/r^2$, where q is the charge and r the radius. For the plane in **C**, $E_p = 4\pi kq/A'$. Setting E_p equal to E_s and solving, $r = (A'/4\pi)^{1/2}$. Substituting in the relationship for A′ given above yields the radius of the equivalent anion, $r_a = (-A/8\pi C)^{1/2}$.

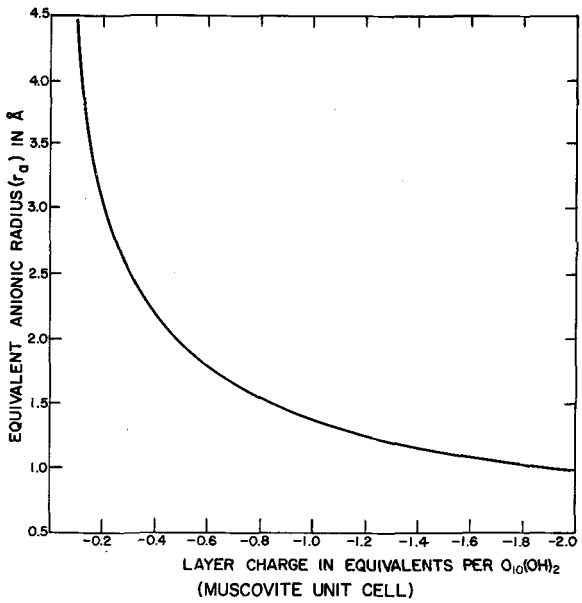


Figure 2. Relationship between equivalent anionic radius (r_a) and layer charge (using *ab* area of muscovite).

the example of Eisenman (1961, 1962), the cation–clay–interlayer water system is treated as an alkali halide–interlayer water solution of a given molality, where clay of a specific r_a is represented by a halide ion with the same anionic radius. Using this model, the free energy for alkali exchange can be calculated with a formula presented by Cruickshank and Meares (1957):

$$\Delta G^0ex = 2RT(\Phi - \ln \gamma\pm\ m\pm)_{CsX} - 2RT(\Phi - \ln \gamma\pm\ m\pm)_{JX} \quad (8)$$

where Φ, m±, and γ± are the osmotic coefficient, mean ionic molality and mean ionic activity coefficient for the subscripted species. This equation is similar to Eq. (5) in that ln γ± m± is a function of the free energy change undergone by the interlayer cation going from interlayer space to infinite dilution. In addition, Φ expresses a similar change for interlayer water. The molality in Eq. (8) is assumed to be equal for both the CsX reference "solution" and the JX "solution." In this equation "X" represents a clay with a r_a equal to the radius of a halide anion, either Cl^- (1.81 Å), Br^- (1.95 Å) or I^- (2.16 Å).

Φ and γ± have been measured for various metal halides, and are tabulated by molality in Robinson and Stokes (1959). Thus exchange free energies for smectites and vermiculites with r_a equal to the radii of the halides can be calculated readily and then extrapolated to fit other anionic radii.

DEPENDENCE OF ΔG^0ex ON r_a AND INTERLAYER WATER CONTENT

Plots of ΔG^0ex versus r_a for "dry" clay are given in the steep curves on the right side of Figure 3 for the reaction of alkali cations relative to Cs^+ (Eq. (5)). Curves for water swollen clay for an arbitrarily chosen molality (m) of 3 are the more gently sloping curves to the left (Eq. (8)). This molality corresponds to about 18 water molecules per interlayer cation. (The number of interlayer water molecules per cation is given by 55.56/m.) In this and all subsequent figures, the lowest curve for a given r_a indicates the cation that is most preferred by the clay, and the distance between curves is a measure of how much it is preferred. As mentioned above, it is assumed that Cs^+ in a wet interlayer is unhydrated (see Norrish, 1954, for experimental evidence). Therefore, Cs^+ has approximately the same free energy for a given r_a in a wet interlayer as in a dry interlayer. This simplification yields one straight baseline in Figure 3 for the Cs^+ reference.

With increasing layer charge (decreasing r_a) in Figure 3, the "wet" curve for each cation intersects the "dry" curve. Because these curves represent reactions that differ only in the state of hydration of the JX clay, their intersection (at the inflection point) represents the layer charge at which the free energy of the wet interlayer equals that of the dry interlayer. To the left of this intersection cation exchange with a water-swollen clay expresses the least free energy, and exchange with a

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

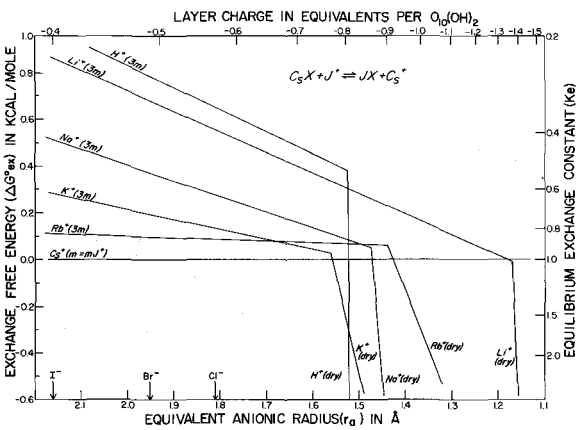


Figure 3. Change in exchange free energy (ΔG^0ex) with r_a for the reaction indicated, where J^+ is an alkali cation. Calculations for smectite curves made for a 3 molal interlayer solution. The lowest curve is for the cation that is most preferred by the clay, and the separation between curves is a measure of how much it is preferred.

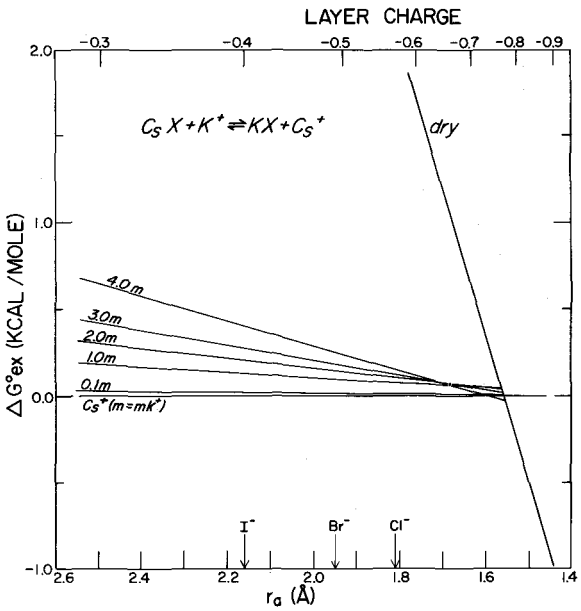


Figure 5. Change in ΔG^0ex with r_a for the Cs–K reaction indicated for several interlayer water contents.

smectite or vermiculite is preferred over that with an illite structure. To the right of this intersection exchange with a dry interlayer is preferred.

Curves relating ΔG^0ex to r_a for clays with interlayer molalities other than 3 are given in Figures 4 and 5, using Na^+ and K^+ as examples. As the water content of the interlayer decreases (molality increasing), the curves steepen and rotate clockwise to approach the "dry" curves, thereby revealing a greater change in selectivity with layer charge for the drier clays.

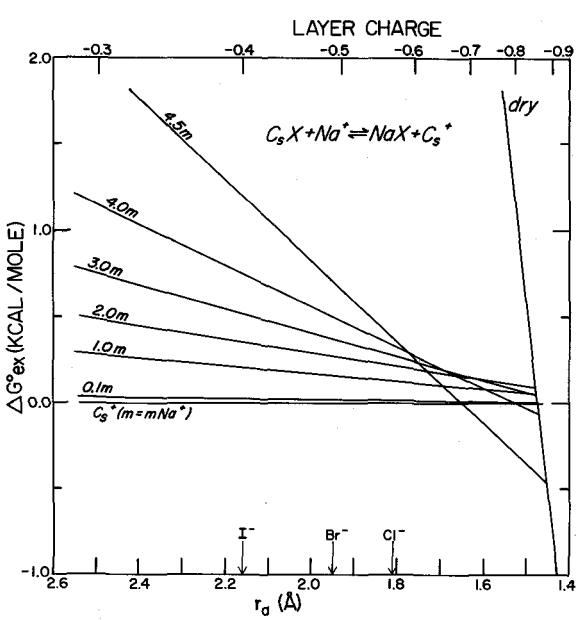


Figure 4. Change in ΔG^0ex with r_a for the Cs–Na reaction indicated for several interlayer water contents.

A comparison of Figures 4 and 5 shows that changes in water content affect Na-selectivity more than K-selectivity for the molalities shown. The general pattern for the magnitude of this effect is $H^+ > Li^+ > Na^+ > K^+ > Rb^+$. Eisenman (1962) further showed that for any molality, the relative selectivity sequence for a given r_a will not change, but only the magnitude of the selectivity. For example, montmorillonite with an r_a of 2.16 Å (layer charge = −0.4 for a muscovite unit-cell area), the selectivity sequence is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ > H^+$ no matter what the interlayer molality, *provided the reactions are compared at the same interlayer molality*. If the reactions are compared at different interlayer molalities, then the selectivity sequence can apparently be altered. For example, in Figure 6 a 3-m clay with an r_a of 2.16 Å gives a ΔG^0ex of 0.28 kcal/mole for the reaction $CsX + K^+ \rightleftharpoons KX + Cs^+$ and a ΔG^0ex of 0.51 kcal/mole for the reaction $CsX + Na^+ \rightleftharpoons NaX + Cs^+$. By subtraction, K^+ is preferred over Na^+ on the clay by 0.23 kcal/mole. But if the reaction involving Na^+ and Cs^+ occurs at 1 m, then Na^+ will apparently be preferred over K^+ by 0.07 kcal/mole. Actually K^+ will always be preferred over Na^+ in a clay with this r_a if they are allowed to compete directly because both cations will experience the same interlayer water content. The problem arises in adding exchange reactions which have a common ion to find ΔG^0ex for the unreacted pair (the method of additivity).

Figures 3–6 have another interesting aspect. Although a change in interlayer water content can affect the magnitude of the selectivity of clay for various cat-

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

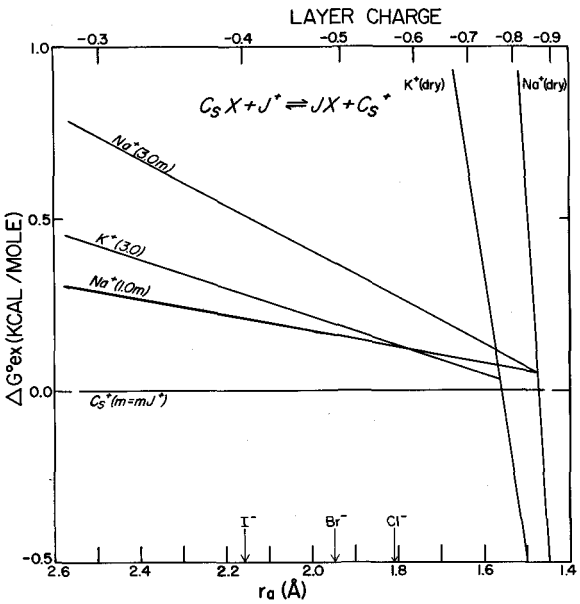


Figure 6. A comparison between Cs–K exchange at 3 molal and Cs–Na exchange at 3 molal and 1 molal.

ions, it does not significantly affect the layer charge (or r_a) at which the wet and dry curves intersect.

COMPARISON BETWEEN CALCULATED AND MEASURED ΔG^0ex

Measured and predicted ΔG^0ex for several reactions are compared in Table 2. These values were measured using Eq. (3) by the authors indicated, and are predicted in the present paper using Eqs. (5) and (8). If two "bad" values for the high-charge smectites (Plymouth and Chambers) are omitted (omission to be justified below), predicted and measured values differ on the average by 85 cal/mole, a value which lies within the experimental error. Gast (1969), for example, considers his error to be 50 to 100 cal/mole, based on a comparison between measured values and those calculated by additivity. His error may be smaller than this, however, because, as was pointed out, additivity disregards the effect of interlayer water content on ΔG^0ex.

Layer charges for the Wyoming and Chambers montmorillonites in Table 2 are from Grim and Güven (1978), and that for the Bayard montmorillonite is from Eliason (1966). Charges for the Plymouth (CEC = 124 meq/100

Table 2. A comparison between predicted and measured exchange free energies (ΔG^0ex).

Clay (X)	Layer charge per $O_{10}(OH)_2$	Assumed interlayer molality	ΔG^0 ex predicted (kcal/mole)	ΔG^0 ex measured (kcal/mole)	Source
		$LiX + Na^+ \rightleftarrows NaX + Li^+$			
Montmorillonite (Colony, Wyoming)	−0.35	0.1	−0.04	−0.036	Tabikh *et al.* (1960)
Montmorillonite (Wyoming)	−0.38	0.1	−0.04	−0.048	Gast and Klobe (1971)
Montmorillonite (Chambers, Arizona)	−0.46	0.1	−0.02	−0.08	Gast and Klobe (1971)
Leached vermiculite (Transvaal)	−0.94	0.1	−1.4	−1.444	Gast and Klobe (1971)
		$LiX + K^+ \rightleftarrows KX + Li^+$			
Montmorillonite (Wyoming)	−0.38	2.0	−0.42	−0.49	Gast (1969)
		$NaX + K^+ \rightleftarrows KX + Na^+$			
Montmorillonite (Colony, Wyoming)	−0.35	3.5	−0.38	−0.335	Tabikh *et al.* (1960)
Montmorillonite (Wyoming)	−0.38	3.5	−0.34	−0.306	Gast (1969)
Montmorillonite (Belle Fourche, South Dakota)	−0.40	3.5	−0.32	−0.481	Tabikh *et al.* (1960)
Montmorillonite (Plymouth, Utah)	−0.46	3.5	−0.25	−0.685	Tabikh *et al.* (1960)
		$NaX + Rb^+ \rightleftarrows RbX + Na^+$			
Montmorillonite (Wyoming)	−0.38	4.0	−0.74	−0.711	Gast (1969)
		$NaX + Cs^+ \rightleftarrows CsX + Na^+$			
Montmorillonite (Bayard, New Mexico)	−0.30	4.5	−1.98	−2.278	Eliason (1966)
Montmorillonite (Wyoming)	−0.38	4.5	−1.32	−1.15	Gast (1969)
Montmorillonite (Chambers, Arizona)	−0.46	4.5	−0.85	−2.035	Eliason (1966)
		$KX + Cs^+ \rightleftarrows CsX + K^+$			
Montmorillonite (Chambers, Arizona)	−0.46	high	none[1]	−1.524	Faucher and Thomas (1954)
		$RbX + Cs^+ \rightleftarrows CsX + Rb^+$			
Montmorillonite	−0.38	high	none[1]	−0.575	Gast (1969)

[1] Molality too high for prediction based on experimental values for Φ and $\gamma\pm$.

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

g), Colony (CEC = 95 meq/100 g), and Belle Fourche (CEC = 108 meq/100 g) montmorillonites were calculated from their CEC by assuming the same formula weight as the Wyoming montmorillonite (373 amu). That for the leached Transvaal sample was calculated from its CEC (214 meq/100 g) assuming a formula weight halfway between phlogopite and annite (417 amu) and a trioctahedral *ab* area of 49.29 Å^2.

Some of the error in predicted values in Table 2 may result from inhomogeneous layer charge distribution (Lagaly and Weiss, 1976). The tabulated layer charge is an average for all layers in, for example, a smectite crystal. Hence ΔG^0ex is also an average. The error in calculated values will be small provided the highest layer charge is below the charge necessary for dehydration of one of the exchanging cations. If this charge is exceeded, however, then the dehydrated cation will be favored over the predicted value. This effect is expected for inhomogeneous high-charge smectites undergoing exchange with cations of low hydration energy. Such interlayer dehydration has been confirmed by X-ray diffraction for K-saturated Chambers montmorillonite (Faucher and Thomas, 1954).

Molalities in Table 2 used to calculate predicted free energies from Eq. (8) were chosen to give the best fit with measured free energies. It is assumed that each cation pair undergoing exchange has a constant average interlayer molality regardless of the clay's layer charge, unless the charge is sufficient to dehydrate one of the cations. This assumption implies either that hydration of the negative clay interlayer surfaces does not change with layer charge, in which case the molalities in Table 2 give a true indication of interlayer water content (ignoring water that is associated with neither clay surface nor cation); or that although hydration of the surfaces may change with layer charge, the only water that need be considered in these calculations is that which hydrates the cations, in which case the molalities in Table 2 are "effective molalities" and refer only to water associated with interlayer cations. In favor of the first alternative, the presence of unhydrated basal oxygen planes would be consistent with evidence that big anions such as Cl^-, Br^-, and I^- are largely unhydrated (Bernal and Fowler, 1933; Stokes and Robinson, 1948). As r_a decreases, however, interlayer surface hydration may become increasingly important because small anions are strongly hydrated.

The molalities in Table 2 may seem at first to be arbitrary choices: Figures 4 and 5 show that calculated ΔG^0ex can be made to fit a wide range of experimental ΔG^0ex simply by changing the molality, although such a manipulation is made more difficult by the added constraint of constant average molality for an exchanging cation pair. Figure 7, however, suggests that the choices are not arbitrary. Such an inverse correlation between cation hydration energy and molality is expected if interlayer water content (or effective interlayer water content) results mainly from cation hydration: the larger the cation's hydration energy, the larger the shell of water molecules it will carry into the interlayer, the lower the molality (or the effective molality) of the interlayer.

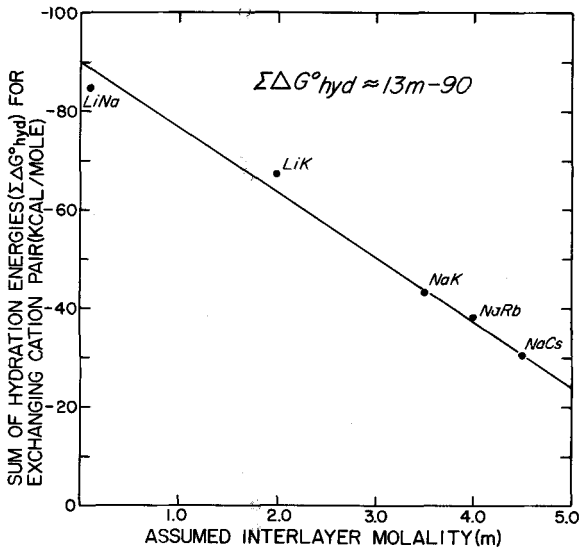


Figure 7. Sum of hydration energies for cations undergoing exchange plotted against "best fit" interlayer molalities from Table 2.

Figure 7 should be viewed with caution. It is based on scanty data. Secondly, the interlayer water content will also depend on the past history of a clay. Tabikh *et al.* (1960), for example, showed that drying a clay before it is used in exchange studies may lead to a marked change in ΔG^0ex. Their explanation appeals to a change in water content. Clay that is kept in a highly hydrated state may be a different system from clay that has been dried because the previously dried clay may contain a different amount of interlayer water as cations assume new and varying adsorption sites. Variation in interlayer water content may also explain why different values of K_e for reversed reactions are sometimes calculated from the Gaines-Thomas equation (Eq. (3)). Interlayer water content may be path-dependent.

The preceding discussion suggests that interlayer water content is not fixed when adsorption isotherms are measured, but varies with the mole fraction of each cation on the clay. Thus, the molalities in Table 2 and Figure 7 are average molalities over the range of integration from $N_A = 0$ to $N_A = 1$. Therefore, if possible, it would be better to use the full Gaines-Thomas equation (Eq. (2)) when measuring K_e rather than the experimentally convenient Eq. (3). Eq. (1) is valid only for roughly equal amounts of A^+ and B^+ on the exchanger because this compositional range yields an average interlayer molality. Variations in K_c as a function

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

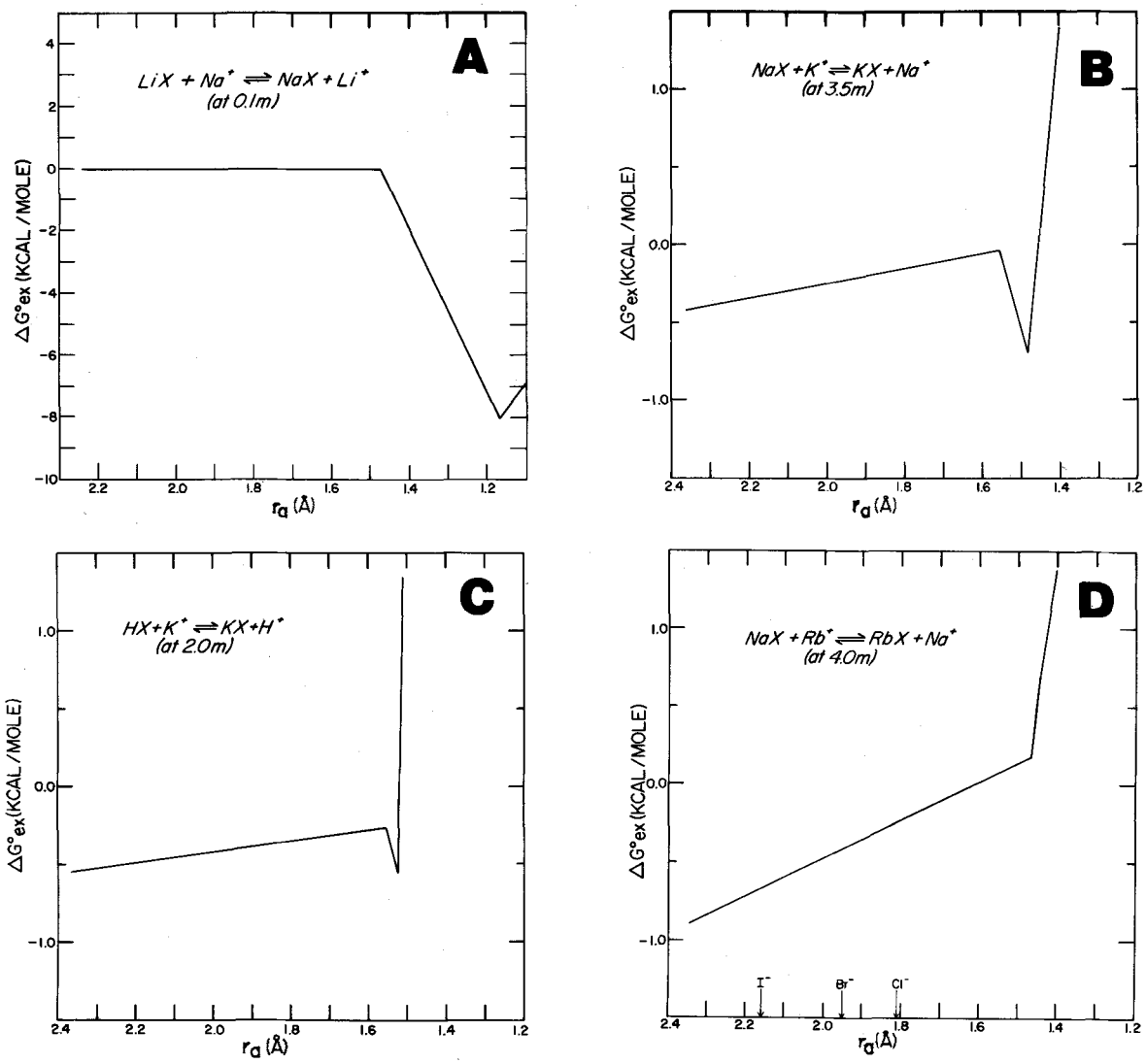


Figure 8. Calculated change in ΔG^0ex with r_a for four exchange reactions. Molalities for **A**, **B**, and **D** are "best fit" molalities from Table 2. Molality for **C** was chosen arbitrarily.

of N_A may at least partly result from changes in interlayer water content.

Assuming that Figure 7 is correct for highly hydrated 2:1 clays in general, curves relating ΔG^0ex to r_a can be plotted for particular alkali exchange reactions at molalities read from the figure. Sample plots are given in Figure 8. With decreasing r_a the first and second breaks in slope correspond to cation dehydration. As an example of how these curves work, the Li–Na data in Table 2 can be compared with Figure 8A. For the Colony, Wyoming, and Chambers montmorillonites (r_a = 2.30 Å, 2.22 Å, and 2.01 Å), there is little preference for either cation; but for the leached Transvaal vermiculite (r_a = 1.40 Å), ΔG^0ex is strongly negative because interlayer Na^+ dehydrates. A negative free energy moves the reaction written in Figure 8A to the right, and Na^+ is preferred on the clay. At an even smaller r_a, Li dehydrates and then becomes preferred, but this stage is probably never realized in clays.

Exchange data presented for H^+-saturated clays by Truesdell and Christ (1968) and Blackmon (1958) cannot be fitted to theoretical values: such a fit would require improbably high molalities. Exchange sites in their clays may not have been occupied by H^+, since it is well known that interlayer H^+ readily exchanges with octahedral aluminum (e.g., Banin and Ravikovitch, 1966).

CATION FIXATION

Hower and Mowatt (1966) have demonstrated that illite has a layer charge less than that of muscovite.

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

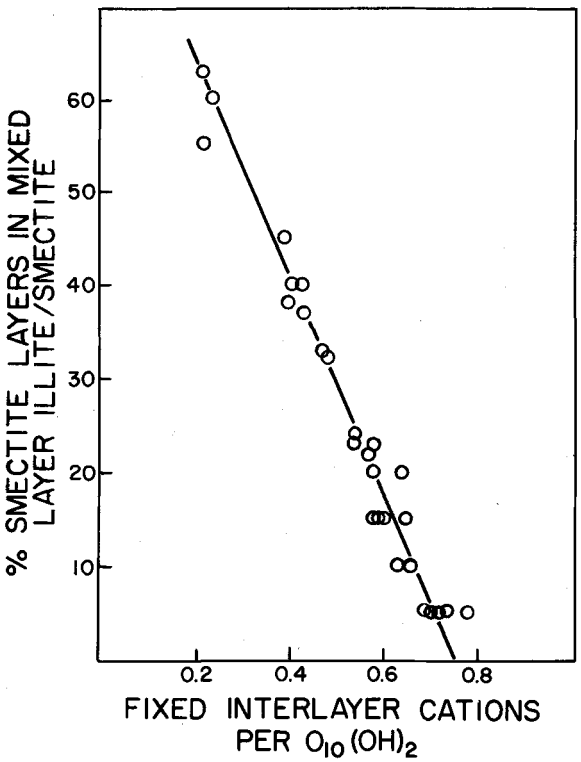


Figure 9. Percent smectite layers in mixed-layer illite/smectite vs. number of fixed cations in illite layers (from Hower and Mowatt, 1966).

Their evidence is presented in Figure 9; here a plot of fixed interlayer cations vs. percent smectite layers in mixed-layer illite/smectite extrapolates to a layer charge of -0.75 per $O_{10}(OH)_2$ for no expanding layers (illite). Their chemical analyses show that cations in the collapsed interlayers are almost entirely potassium. The question thus arises, why do illites have a charge of -0.75 rather than a full mica charge of -1.0?

Illite layers can develop from the dehydration of smectite by a gradual increase in layer charge (Perry and Hower, 1970; Hower *et al.*, 1976; Weaver and Beck, 1971; Eberl and Hower, 1976). Figure 3 predicts that illite formed by this mechanism will have a layer charge of -0.77, which agrees with the measured value.

Figure 3 also predicts that Na-illite (brammallite) will have a charge of -0.86. Accurate chemical analyses of well-characterized brammallite do not exist, but Kodama (1966) found a charge of -0.9 for Na-illite layers in rectorite from Baluchistan, and Brown and Weir (1965) found charges of -0.86 and -0.82 for such layers in rectorite from Dagestan and Arkansas. Hydrothermal experiments have shown that Na-rectorite, like illite, can develop from smectite by reactions which increase layer charge, and that the charge on the brammallite interlayers is greater than that found on illite (Eberl and Hower, 1977).

Table 3. Theoretical equivalent anionic radius (r_a) and layer charge (C) required for cation fixation.

Cation	Equivalent anionic radius (Å)	Layer charge (equivalents/$O_{10}(OH)_2$, muscovite unit cell)
K^+	1.558	−0.77
H^+	1.523	−0.80
Na^+	1.473	−0.86
Rb^+	1.437	−0.90
Li^+	1.167	−1.37

Layer charges predicted from Figure 3 for the fixation of other alkalis (Table 3) cannot be checked against natural samples. Rb-vermiculite, however, will absorb one water layer (Tarasevich *et al.*, 1971), suggesting that the position of Rb^+ relative to K^+ in Table 3 is correct. Two observations, however, do not fit these predictions: the ability of sodium tetraphenylboron to expand mica layers (Scott and Smith, 1966), and the ability of paragonite to expand when finely ground in water (Barshad, 1950). According to Figure 3, interlayer Na^+ should not hydrate against a -1.0 charge; and, indeed, the brammallite layers in rectorite do not hydrate. The inconsistency may be explained by appealing to hydration of the basal oxygen surfaces, an effect which should become increasingly important as layer charge increases. The r_a of paragonite and muscovite (1.37 Å) is similar to that of F^- (1.34 Å), an anion which is strongly hydrated. Thus the combined hydration energy of interlayer Na^+ and the basal oxygen planes may be sufficient to expand a mica once the interlayer has been disrupted by grinding or cation exchange.

As mentioned above, the "dry" curves in Figures 3–6 describe selectivity for cations dehydrated on basal oxygen planes rather than for cations held in hexagonal holes. The physical meaning of the dry curves and their inflection points can be brought into sharper focus if fixation is viewed as a two-step process: (1) a cation is first dehydrated by the negatively charged interlayer surfaces; and (2) it then migrates into hexagonal holes in the surfaces. The inflection points in Figure 3 indicate the layer charge required for the first step, and thus represent energies which must be exceeded in order for cations to be fixed in the holes. Cations will be held in the holes by an energy greater than that calculated by Eq. (7) for a given r_a because fixation in the holes allows the cation to approach more closely the seat of the negative charge.

Cations may be fixed at a layer charge lower than that predicted by the inflection points in Figure 3 if the clay is oven-dried; by this process, step 1 is by-passed, and cations may migrate directly into the holes which represent energy wells. This migration may take time and added energy, however, because holes on either side

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

Table 4. Sorption of Cs by clays after 90 hr from 6 M $NaNO_3$ waste solutions (summarized from Tamura and Jacobs, 1960).

Clay	CEC	mg Cs/g of clay	meq Cs/meq of exchange
Illite	15	0.165	1.103
Montmorillonite	100	0.141	0.141
Biotite/vermiculite	57	0.043	0.033
Kaolinite	8.7	0.029	0.334

of the interlayer space must line up. The formation of illite interlayers by the alternate wetting and drying of K-smectite (Gaultier and Mamy, 1979) can be understood in this light.

QUALITATIVE APPLICATIONS OF THE THEORY

Sorption of Cs^+ by clays

The need to dispose of radioactive wastes has led to research on the sorption of Cs^+ by clays. About 75% of the activity of liquid supernatant in intermediate level wastes is due to radiocesium, after radiostrontium has been removed by soda-lime softening. Tamura and Jacobs (1960) studied the ability of illite, montmorillonite, mixed-layer biotite/vermiculite, and kaolinite to remove Cs^+ from simulated effluents. Their data are summarized in Table 4. The experiments used 6 M $NaNO_3$ solutions with Cs^+ concentrations on the order of 0.2–8.0 $\times$ 10^{-4} M to approximate actual conditions. One would expect that illite and kaolinite would be poor adsorbers of Cs^+ under these conditions based on the law of mass action and their CECs. Table 4, however, shows that *all* of illite's exchange sites are occupied by Cs^+, and that it adsorbs more Cs^+ by weight than the other clays. Although the effectiveness of kaolinite based on weight is low, it is quite effective based on its CEC. Tamura and Jacobs (1960, 1961) further discovered that the Cs-selectivities of vermiculite, montmorillonite, and illite were improved by collapsing them to 10 Å, insofar as was possible, by K-saturation and dry heating prior to exchange, and that a synthetic Na-fluorophlogopite (CEC = 5.6 meq/100 g) was more highly selective for Cs^+ than was a synthetic K-fluorophlogopite (CEC = 13.8 meq/100 g).

Their data can be understood if edge exchange sites (which dominate the CEC of illite and kaolinite) can be treated as surfaces of uniform charge density. This model is reasonable if some edge CEC results from charge imbalance within the crystal (Brindley and MacEwan, 1953). The r_a value for the surface of illite can then be calculated in a manner similar to that carried out for the interlayer:

$$r_a = [10^5 A_s/(CEC)4\pi)]^{1/2} \quad (9)$$

where A_s is the external surface area in m^2/g. The surface area of an illite is 97.1 m^2/g (data of Nelson and Hendricks listed in Grim, 1968). Assuming the charge is distributed over the entire illite surface, r_a is greater than 200 meters. This value is ridiculously high. Nevertheless, it indicates that r_a for the illite surface will lie very far off the graph to the left in Figure 3, yielding an enormous preference of the clay for Cs^+ over other alkali cations, even if these cations are present in high concentrations. With an r_a of montmorillonite or vermiculite, however, Figure 3 shows a small preference or no preference for Cs^+ (although preference for Cs^+ will be somewhat greater than that shown in Figure 3 if fixation in hexagonal holes is considered), and the exchange sites are swamped by the concentrated Na^+ in solution.

Kaolinite is expected to behave similarly to illite, except that kaolinite's larger particle size yields about 1/6 of the surface area of illite. Eq. (9) gives kaolinite about half of the r_a of illite. Thus, kaolinite should adsorb Cs^+ less strongly than illite, as the data indicate. Collapsed vermiculite and montmorillonite should adsorb Cs^+ more strongly than expanded phases because unsatisfied charges within the crystal can not be balanced by cations close to the source of the charge. The experiments of Tamura and Jacobs (1960, 1961) demonstrate this effect. The inverse relationship found between CEC and Cs-selectivity for their synthetic fluorophlogopites is also explained by Eq. (9).

The mechanism for cesium selectivity proposed here differs from the "frayed edge" theory (Jackson, 1963; Gaudette *et al.*, 1966; Sawhney, 1972). Frayed edges which expose the interlayer region will have a low r_a and therefore will not be highly selective for Cs^+ when other cations are present in high concentrations. Exchange sites which result from broken bonds at crystal edges will probably also have a low r_a. Paradoxically, it is the regions of low surface-charge density which are most selective for Cs^+. The strong attraction for unhydrated Cs^+ results from bonds that are so weak that the other water-insulated cations are not attracted. This "weak force" fixation can be understood in terms of Eisenman's elegant principle of atomistic asymmetry, with the realization that illite behaves like a Cs^+-selected electrode.

Burial diagenesis and the fixation of K^+ in shales

A second application of the theory concerns burial diagenesis in subsiding basins such as the Gulf of Mexico. The layer charge on smectite increases with increasing burial depth in response to increasing temperature (Perry and Hower, 1970; Hower *et al.*, 1976; Weaver and Beck, 1971). Thus, moving from left to right in Figures 3 and 8B, the curves, which were calculated for 25°C and 1 atmosphere and for cation fixa-

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

tion to interlayer surfaces rather than into hexagonal holes, describe qualitatively the change in alkali selectivity of smectite undergoing diagenesis.

The analyses of Weaver and Beck (1971) and Hower *et al.* (1976) showed that although smectite reacts in a pore solution rich in sodium, the cation that is fixed is almost entirely potassium. This potassium probably comes from decomposition of detrital potassium feldspar (Hower *et al.*, 1976). Figures 3 and 8B suggest a crystal chemical reason why potassium is fixed in these shales rather than sodium. Figure 3 shows that with increasing layer charge potassium is the first cation to dehydrate. Until a layer charge of -0.77 is reached, selectivity of the interlayer for K^+ is only slightly greater than that for Na^+. But with potassium dehydration, selectivity for K^+ increases rapidly. The selectivity of Na^+ between layer charges of -0.77 and -0.86 is described by the gently sloping curve for a water-swollen clay in Figure 2, whereas K^+ is described by the steep curve for a dry clay. At these charges potassium is thereby dehydrated, concentrated, and fixed in the smectite interlayer, forming illite, while Na^+ and interlayer water are expelled to the pore solution. If K-fixation in hexagonal holes is considered rather than interlayer surface fixation, the selectivity of the clay for dehydrated K^+ over hydrated Na^+ would be much greater than that shown in Figure 3.

Stability of illite in the weathering environment

Figures 3 and 8C show that K^+ is preferred over H^+ in illite-like interlayer (r_a = 1.55 Å), but that preference for H^+ increases dramatically for a muscovite-like interlayer (r_a = 1.37 Å) because H^+ dehydrates. This effect may partly explain the greater stability of illite over muscovite in the weathering environment, and the experimental evidence that total interlayer K^+ in illite is less susceptible to H^+ and Na^+ attack (Scott and Smith, 1966; Scott, 1968; Norrish, 1973; Garrels and Howard (1959) measured a K_e of $10^{7.4}$ for muscovite–H^+-exchange). One might first think that muscovite would be less subject to vermiculitization than illite because its interlayer K^+ is bound with greater energy. But this view is one-sided. The attraction of other ions in solution for the interlayer sites must also be considered. In addition, the attraction of water for the interlayer planes in muscovite will be greater than that in illite, thereby also tending to make muscovite less stable.

Cation segregation in smectite

The theory suggests an explanation for cation segregation in smectite. Mering and Glaeser (1953) and McAtee (1956) showed that Na^+ and Ca^{2+} will segregate into separate interlayers in some smectites. The alkylammonium method shows that many smectites are not homogeneous, but that their layer charge is distributed between high and low-charge interlayers (Lagaly and Weiss, 1976). If cation selectivity is a function of layer charge, as is proposed here, and if the change in selectivity as a function of layer charge differs for Ca^{2+} and Na^+, as is reasonable considering their large differences in hydration energy and valence, cation segregation may be expected for smectites which have an inhomogeneous layer charge distribution. Once segregation is initiated, then differences in water content between sodium and calcium interlayers may further accentuate segregation by leading to an even greater difference in selectivity.

SUMMARY

Cation selectivity and cation fixation in clay both result from an interplay of two competing forces: (1) the force of attraction of a cation for its hydration shell; and (2) the force of attraction of the cation for clay surfaces. Selectivity arises because these forces differ for different cations. Fixation occurs when the second force exceeds the first. Fixation must be considered in a description of selectivity because selectivity increases dramatically for cations that dehydrate. A third force, the attraction of water for interlayer surfaces, may become important as r_a decreases.

The crystal chemistry of a clay, especially its interlayer water content and layer charge, will strongly influence these forces. The key to describing this influence is to treat the clay as a spherical anion which has an electric field equivalent to that of the clay. Exchange free energies for wet and dry interlayers can then be calculated by treating the interlayer either as a concentrated alkali-halide solution or as an electrostatic attraction between two spheres.

ACKNOWLEDGMENTS

The author thanks R. M. Garrels for telling him that clays behave like ion-selective electrodes; R. Couture, R. M. Garrels, B. F. Jones, J. W. Stucki, and J. L. White for their comments on the manuscript; and Mrs. P. Buschman for her help. This research was supported by the Earth Sciences Section, National Science Foundation, NSF Grant EAR76-13368 A01.

REFERENCES

Banin, A. and Ravikovitch, S. (1966) Kinetics of reactions in the conversion of Na- or Ca-saturated clay to H-Al clay: *Clays & Clay Minerals* **14,** 193–204.

Barshad, I. (1950) The effect of the interlayer cations on the expansion of the mica type of crystal lattice: *Amer. Mineral.* **35,** 225–238.

Bernal, J. D. and Fowler, R. H. (1933) A theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions: *J. Chem. Phys.* **1,** 515–548.

Blackmon, P. D. (1958) Neutralization curves and the formulation of monovalent cation exchange properties of clay minerals: *Amer. J. Sci.* **256,** 733–743.

Brindley, G. W. and MacEwan, D. M. C. (1953) Structural

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

aspects of the mineralogy of clays: in *Ceramics—A Symposium,* The British Ceramic Society, Stoke-on-Trent, 15–59.

Brown, G. and Weir, A. H. (1965) An addition to the paper "The identity of rectorite and allevardite": *Proc. Internat. Clay Conf.* **2,** Stockholm, 87–90.

Cruickshank, E. H. and Meares, P. (1957) The thermodynamics of cation exchange. Part 2: Comparison between resins and concentrated choride solutions: *Trans. Faraday Soc.* **53,** 1299–1308.

Eberl, D. D. and Hower, J. (1976) Kinetics of illite formation: *Geol. Soc. Amer. Bull.* **87,** 1326–1330.

Eberl, D. D. and Hower, J. (1977) The hydrothermal transformation of sodium and potassium smectite into mixed-layer clay: *Clays & Clay Minerals* **25,** 215–228.

Eisenman, G. (1961) On the elementary origin of equilibrium ionic specificity: in *Symposium on Membrane Transport and Metabolism,* A. Kleinzeller and A. Kotyk, eds., Academic Press, New York, 163–179.

Eisenman, G. (1962) Cation selective glass electrodes and their mode of operation: *Biophys. J.* **2,** pt. 2 (supplement), 259–323.

Eliason, J. R. (1966) Montmorillonite exchange equilibria with strontium–sodium–cesium: *Amer. Mineral.* **51,** 324–335.

Faucher, J. A. and Thomas, H. C. (1954) Adsorption studies on clay minerals. IV. The system montmorillonite–cesium–potassium: *J. Chem. Phys.* **22,** 258–261.

Friedman, H. L. and Krishnan, C. V. (1973) Thermodynamics of ionic hydration: in *Water, A Comprehensive Treatise 3,* F. Franks, ed., Plenum Press, New York, 1–118.

Gaines, G. L. and Thomas, H. C. (1953) Adsorption studies on clay minerals. III. A formulation of the thermodynamics of exchange adsorption: *J. Chem. Phys.* **21,** 714–718.

Garrels, R. M. and Christ, C. L. (1965) *Solutions, Minerals and Equilibria:* Harper and Row, Inc., New York, 450 pp.

Garrels, R. M. and Howard, P. (1959) Reactions of feldspar and mica with water at low temperature and pressure: *Clays & Clay Minerals* **6,** 68–88.

Gast, R. G. (1969) Standard free energies of exchange for alkali metal cations on Wyoming bentonite: *Soil Sci. Soc. Amer. Proc.* **33,** 37–41.

Gast, R. G. and Klobe, W. D. (1971) Sodium-lithium exchange equilibria on vermiculite at 25°C and 50°C: *Clays & Clay Minerals* **19,** 311–319.

Gaudette, H. E., Grim, R. E., and Metzger, C. F. (1966) Illite: a model based on sorption behavior of cesium: *Amer. Mineral.* **51,** 1649–1656.

Gaultier, J. P. and Mamy, J. (1979) Evolution of exchange properties and crystallographic characteristics of biionic K-Ca montmorillonite submitted to alternate wetting and drying: *Internat. Clay Conf. 1978,* M. M. Mortland and V. C. Farmer, eds., Elsevier, Amsterdam, 167–175.

Grim, R. E. (1968) *Clay Mineralogy* (2nd ed.): McGraw-Hill, New York, 596 pp.

Grim, R. E. and Güven, N. (1978) *Bentonites:* Elsevier, Amsterdam, 256 pp.

Hower, J. and Mowatt, T. C. (1966) Mineralogy of the illite–illite/montmorillonite group: *Amer. Mineral.* **51,** 821–854.

Hower, J., Eslinger, E. V., Hower, M. E., and Perry, E. A. (1976) Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence: *Geol. Soc. Amer. Bull.* **87,** 725–737.

Jackson, M. L. (1963) Interlayering of expansible layer silicates in soils by chemical weathering: *Clays & Clay Minerals* **11,** 29–46.

Kodama, H. (1966) The nature of the component layers of rectorite: *Amer. Mineral.* **51,** 1035–1055.

Lagaly, G. and Weiss, A. (1976) The layer charge of smectitic layer silicates: *Proc. Internat. Clay Conf., 1975, Mexico City,* S. W. Bailey, ed., Applied Publishing Ltd., Wilmette, Illinois, 157–172.

McAtee, J. L. (1956) Random interstratification in montmorillonite: *Amer. Mineral.* **41,** 627–631.

Méring, J. and Glaeser, R. (1953) Cations échangeables dans montmorillonite: *Bull. Groupe Fr. Argiles* **5,** 61–72.

Norrish, K. (1954) The swelling of montmorillonite: *Discuss. Faraday Soc.* **18,** 120–134.

Norrish, K. (1973) Factors in the weathering of mica to vermiculite: *Proc. Internat. Clay Conf. 1972, Madrid, Spain,* J. M. Serratosa, ed., 417–432.

Perry, E. A. and Hower, J. (1970) Burial diagenesis in Gulf Coast pelitic sediments: *Clays & Clay Minerals* **18,** 165–178.

Robinson, R. A. and Stokes, R. H. (1959) *Electrolyte Solutions* (2nd ed.): Butterworths Scientific Publications, London, 559 pp.

Rossini, F. D., Wagman, D. D., Evans, W. D., Levine, S., and Jaffe, I. (1952) Selected values of chemical thermodynamic properties: *Nat. Bur. Stand. Circ.* **500,** U.S. Gov. Printing Office, Washington, D.C., 1268 pp.

Sawhney, B. L. (1972) Selective sorption and fixation of cations by clay minerals: a review: *Clays & Clay Minerals* **20,** 93–100.

Sears, F. W. and Zemansky, M. W. (1955) *University Physics* (2nd ed.): Addison-Wesley, Reading, Massachusetts, 1031 pp.

Scott, A. D. (1968) Effect of particle size on interlayer potassium exchange in micas: *Trans. 9th Int. Congr. Soil Sci.* **2,** 649–660.

Scott, A. D. and Smith, S. J. (1966) Susceptibility of interlayer potassium in micas to exchange with sodium: *Clays & Clay Minerals* **14,** 69–81.

Stokes, R. H. and Robinson, R. A. (1948) Ionic hydration and activity in electrolyte solutions: *J. Amer. Chem. Soc.* **70,** 1870–1878.

Tabikh, A. A., Barshad, I., and Overstreet, R. (1960) Cation exchange histeresis in clay minerals: *Soil Sci.* **90,** 219–226.

Tamura, T. and Jacobs, D. G. (1960) Structural implications in cesium sorption: *Health Phys.* **2,** 391–398.

Tamura, T. and Jacobs, D. G. (1961) Improving cesium selectivity of bentonites by heat treatment: *Health Phys.* **5,** 149–154.

Tarasevich, Y. I., Orazmuradov, A. O., and Ovcharenko, F. D. (1971) Heat of adsorption of water on cation-substituted vermiculite: *Colloid J. USSR* **33,** 496–500 (Eng. Transl.).

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

Weaver, C. E. and Beck, K. C. (1971) Clay water diagenesis during burial: How mud becomes gneiss: *U.S. Geol. Surv. Prof. Pap.* **134,** 1–78.

(Received 18 September 1979; accepted 19 January 1980)

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press

Резюме—При вычислении свободных энергий обмена (ΔG^0ex) для глин 2:1 необходимо рассматривать две переменненные (1) силу анионного поля, выраженную в виде эквивалентного анионного радиуса (r_a), и (2) содержание межслойной воды, вырвженное в виде межслойной мольности. Для смективов, которые находятся в состоянии высокой гидротации, межслойная мольность обуславлевается катионами, повергающимися обмену. Таким образом, ΔG^0ex для пары обмениваемых катионов может быть вычислена исключительно по данным измерений r_a. Величина r_a связана с зарядом слоя на половину элементарной ячейки, (C), и с площадью (A) элементарной ячейки *ab* соотношением $r_a = (-A/8\pi C)^{1/2}$. Заряд слоя, необходимого для фиксации катиона, может быть предсказан вычислением r_a при котором катионный обмен с иллитовой структурой выражает ΔG^0ex равный ΔG^0ex обмена со смектитовой структурой. Эту теорию можно также применить качественно, чтобы понять высокую селективность иллита для Cs^+, фиксацию K^+ вместо Na^+ в сланцах во время диагенеза, устойчивость иллита по сравнению с мусковитом в среде выветривания и сегрегацию катионов в смектите. [N.R.]

Resümee—Zwei Variable müssen bei der Berechnung der freien Austauschenergie (ΔG^0ex) bei 2:1 Tonen berücksichtigt werden: (1) die Anionenfeldstärke, wie sie durch den äquivalenten Anionenradius (r_a) ausgedrückt wird und (2) der Zwischenschichtwassergehalt, wie er durch die Zwischenschichtmolalität gegeben ist. Bei Smektiten, die sich in einem Stadium großer Hydratation befinden, wird die Zwischenschichtmolalität durch die austauschbaren Kationen bestimmt. Daher kann ΔG^0ex für ein Austauschkationenpaar nur durch die Bestimmung von r_a berechnet werden. Der Wert von r_a steht in Beziehung zur Schichtladung pro halber Einheitszelle (C) und *ab* Einheitszellenbereich (A) durch: $r_a = (-A/8\pi C)^{1/2}$. Die Ladungsdichte, die für die Kationenfixierung notwendig ist, kann vorausgesagt werden, indem der r_a berechnet wird, bei dem der Kationenaustausch mit einer Illitstruktur ein ΔG^0ex gleich dem eines Kationenaustausches mit einer Smektitstruktur ausdrückt. Diese Theorie kann auch qualitativ verwendet werden, um die große Selektivität des Illit für Cs^+ zu verstehen, die Fixierung von K^+ vor Na^+ in Schiefertonen während der Diagenese, die Stabilität des Illits gegenüber Muskovit unter Verwitterungsbedingungen und die Kationenentmischung in Smektit. [U.W.]

Résumé—Deux variables doivent être considérées lorsqu'on calcule l'échange d'énergies libres ΔG^0ex des argiles 2:1: (1) la force de champ anionique, exprimée par le rayon équivalent r_a, et (2) la teneur en eau interfeuillet, exprimée par la molalité interfeuillet. Pour les smectites qui sont dans un état d'hydratation élevée, la molalité interfeuillet est determinée par les cations subissant l'échange. De cette manière, ΔG^0ex pour une paire de cations échangeants ne peut être calculé qu'à partir de la mesure de r_a. La valeur r_a est apparentée à la charge de feuillet par ½ maille (C) et par surface de maille *ab* (A) par $r_a = (-A/8\pi C)^{1/2}$. La charge de feuillet nécessaire pour la fixation de cation peut être prédite en calculant la valeur r_a à laquelle l'échange de cation avec une structure illite exprime une valeur ΔG^0ex égale à celle de l'échange avec une structure smectite. La théorie peut aussi être appliquée qualitativement pour comprendre la haute sélectivité de l'illite pour Cs^+, la fixation de K^+ plutôt que Na^+ dans les roches argileuses pendant la diagénèse, la plus grande stabilité de l'illite que de la muscovite dans un environement d'altération, et la ségrégation de cations dans la smectite. [D.J.]

https://doi.org/10.1346/CCMN.1980.0280301 Published online by Cambridge University Press