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RELATIONSHIP BETWEEN CATION EXCHANGE SELECTIVITY AND CRYSTALLINE SWELLING IN EXPANDING 2:1 PHYLLOSILICATES

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Abstract—A theoretical model describing the interaction between crystalline swelling and cation exchange selectivity is proposed for expanding 2:1 phyllosilicates. The model is based on the assumption that changes in basal spacing of a clay are phase changes, and that each phase of a clay has a different selectivity constant for a particular cation exchange reaction. Energy barriers stabilize the various phases over a limited range of interlayer ionic composition. These energy barriers cause hysteresis in crystalline swelling, which in turn causes hysteresis in cation exchange. Results are presented for an experiment involving Ba-Mg exchange on a synthetic fluoro-hectorite. The results demonstrate key aspects of the proposed model, including a correlation between measured selectivity coefficients and basal spacings (R^2 = 0.85), an abrupt change in basal spacing that corresponds with an abrupt change in selectivity and corresponding hysteresis in crystalline swelling and cation exchange selectivity. The results also demonstrate increased selectivity for the preferred cation (Ba) at high solution mole fraction of the preferred cation. This trend is opposite of that observed for heterogeneous natural smectites but consistent with predictions of the model for a homogeneous smectite.

Key Words—Cation Exchange Selectivity, Crystalline Swelling, Demixing, Fixation, Ion Exchange Hysteresis, Layer Charge, Smectite.

INTRODUCTION

Cation exchange selectivity is one of the most important properties of 2:1 phyllosilicates; however, the mechanisms which control this property are poorly understood. Historically, 3 general classes of models have been invoked for explaining exchange selectivity: nonmechanistic models derived using principles of mass action and thermodynamics, mechanistic models based on diffuse double layer theory and mechanistic models derived from the energetics of hydration and electrostatic interactions.

Calculation of mass action selectivity coefficients from measured ion exchange data is perhaps the most common treatment of cation exchange selectivity. Ideally, such coefficients estimate thermodynamic equilibrium constants (K_e). This treatment of ion exchange does not distinguish between the solid and liquid phases and therefore requires that activities be determined for adsorbed ions. Vanselow (1932) suggested that activities of adsorbed ions are closely approximated by mole fractions of the ions adsorbed onto the solid. Measured Vanselow coefficients (K_v), however, often vary with the ionic composition of the exchanger and the total ionic strength of the equilibration solution (Laudelout et al. 1968). Gaines and Thomas (1953) proposed integration of measured selectivity coefficients over the full compositional range as a means of estimating thermodynamic equilibrium constants. Under the Gaines–Thomas approach, variations in measured selectivity coefficients with the ionic composition of the exchanger are arbitrarily attributed to variations in activities of the adsorbed ions. The Gaines–Thomas approach explicitly includes changes in chemical potential for water that may occur during an ion exchange reaction.

The thermodynamic treatment of cation exchange selectivity has 2 fundamental problems: 1) Hysteresis is sometimes observed in ion exchange reactions involving 2:1 phyllosilicates (Verburg and Baveye 1994), and when hysteresis is observed the thermodynamic treatment of ion exchange is invalid, because reversibility is a requirement of equilibrium. 2) The standard thermodynamic approach is inherently nonmechanistic: one may predict the outcome of an ion exchange reaction, but one will never know the cause of ion exchange selectivity.

Eriksson (1952) proposed a mechanistic model for cation exchange selectivity that is based on diffuse double layer (DDL) theory. With various modifications, the Eriksson model has been shown to estimate selectivity coefficients for heterovalent exchange reactions that are within an order of magnitude of measured coefficients (Laudelout et al. 1968; Maes and Cremers 1977; Barak 1989). The Eriksson model considers only electrostatic interactions and treats all cations as point charges; therefore, it does not distinguish selectivities for exchange reactions involving cations of like charge. Several authors have proposed modifications of the Eriksson model in an effort to overcome this problem. Neal and Cooper (1983), for ex-

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ample, assumed that an ion could come no closer to a charged surface than its hydrated radius, and Nir (1986) used specific binding coefficients to account for differences in selectivity for cations of like charge. For a given clay, the Eriksson model can be adjusted to fit measured data. However, no amount of adjustment will change the fundamental prediction of the Eriksson model that higher charged cations will be increasingly preferred as layer charge of the clay increases. Although this relationship has been qualitatively demonstrated for Na-Ca exchange (Maes and Cremers 1977), the opposite relationship is observed for K-Ca exchange (Sawhney 1969; Shainberg et al. 1987). Failure of the Eriksson model to account for the relationship between layer charge and selectivity in K-Ca exchange reactions suggests a major flaw in the Eriksson model.

On a more fundamental level, the validity of the Eriksson model for describing the ion exchange selectivity exhibited by smectites may be questioned because the Eriksson model is based on DDL theory. In aqueous systems, smectites exist as quasicrystals. Each quasicrystal consists of 1 to several hundred lamellae stacked with parallel c axes but randomly oriented a and b axes. Diffuse double layers may form in the bulk solution adjacent to external surfaces of the quasicrystals; however, DDLs do not form between lamellae within a quasicrystal. Within a quasicrystal, the lamellae are separated by 4 or fewer discrete layers of water molecules, and anions are excluded from the interlayer spaces (Posner and Quirk 1964). Assuming that an average quasicrystal consists of 10 coordinated lamellae with layer charge distributed uniformly over all surfaces, then 90% of the exchangeable cations are retained on internal surfaces and only 10% are retained on external surfaces. Diffuse double layer theory and the Eriksson model are relevant for describing selectivity exhibited by the 10% of cations sorbed on the external surfaces, but have no bearing on selectivity for the 90% of cations retained on internal surfaces.

Another approach to understanding cation exchange selectivity is based on Eisenman's (1962) theory, which was developed to explain the behavior of ion-selective electrodes. Eisenman argued that the molar free energy of exchange ($\overline{\Delta G}_{ex}$) is determined by the net change in Coulombic and hydration energies for the exchanging cations. Eberl (1980) applied Eisenman's theory to 2:1 phyllosilicates for exchange reactions between Cs and other alkali cations. To do so, he assumed that Cs was unhydrated both in solution and when adsorbed onto a clay. However, he was unable to use the Eisenman approach for partially hydrated 2:1 clays, because the hydration states of partially hydrated interlayer cations were unknown. Instead, he assumed that the interlayer water in a 2:1 clay was analogous to water in a concentrated alkali halide solution. With this assumption, he was able to estimate $\overline{\Delta G}_{ex}$ as a function of both interlayer molarity and layer charge. Consistent with experimental data, the analysis indicated that preference for the lesser hydrated cation increases as interlayer water decreases and as layer charge density increases. Thus, Eberl (1980) suggested a link between the extent of interlayer hydration and exchange selectivity.

Several authors (van Bladel and Laudelout 1967; Banin 1968; McBride 1980; Saehr et al. 1982) have suggested that clay microstructure may influence cation exchange and selectivity relationships. Indeed, evidence for demixing (Shainberg and Otoh 1968; Fink et al. 1971) suggests that internal surfaces of quasicrystals have different selectivities than external surfaces. Saehr et al. (1982) presented evidence that K-vermiculite ($d(001)$ = 10 Å), Ca-vermiculite ($d(001)$ = 15 Å), and regularly interstratified K/Ca-vermiculite ($d(001)$ = 25 Å) have distinctly different selectivity coefficients for the K-Ca exchange reaction.

In the present paper, we present a conceptual model and a series of equations describing the interaction between crystalline swelling and cation exchange selectivity. The model was originally proposed in 1987 (as part of a Ph.D. dissertation; Laird 1987). However, further work on the model was delayed until 1993. Since then we have published 3 papers that offer background for the present work. Shang et al. (1995) described an analytical technique for measuring basal spacings of smectites dispersed in electrolyte solutions. Laird et al. (1995) demonstrated that hysteresis is inherent to crystalline swelling of 2:1 phyllosilicates. And most recently, Laird (1996) described a macroscopic energy balance model for predicting the extent of crystalline swelling of 2:1 phyllosilicates. Also presented in this paper are results of an ion exchange experiment that was designed and conducted to test several aspects of the proposed model.

MODEL

Crystalline swelling is a process whereby 2:1 phyllosilicates intercalate 0, 1, 2, 3 or 4 discrete layers of water molecules (Norrish 1954). In the proposed model, each of these layer hydrates is assumed to be a separate phase and transitions from 1 layer hydrate to another (both expansion and collapse) are phase transitions. The various phases of 2:1 phyllosilicates are stabilized over a limited range of conditions (such as temperature, pressure and interlayer ionic composition) by energy barriers which also cause hysteresis in crystalline swelling (Laird et al. 1995; Laird 1996). The processes controlling crystalline swelling and cation exchange selectivity are hypothesized to be linked through a feedback loop (Figure 1), such that the extent of crystalline swelling influences selectivity (because each phase has a different value of K_e), selectivity influences the interlayer ionic composition and the interlayer ionic composition influences the extent of

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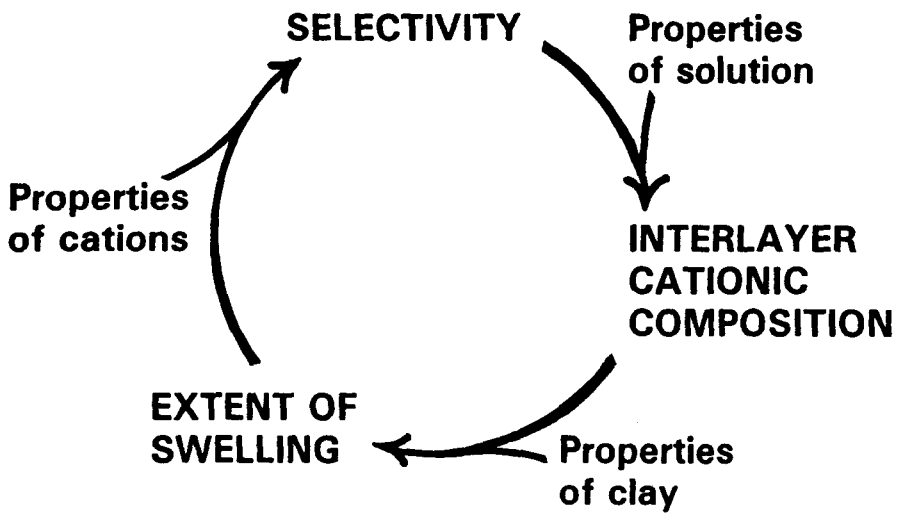


Figure 1. Conceptual model for the feedback interaction between crystalline swelling and cation exchange selectivity in 2:1 phyllosilicates.

crystalline swelling (because different cations have different hydration energies which influences the swelling pressure).

Previous models describing ion exchange phenomena have been based on the assumption that instability of measured selectivity coefficients (such as K_v) with changes in the solution chemistry are due to changes in the activity of the cations adsorbed on the solid. The proposed model is a radical departure from this concept. We assume that K_v is a relative accurate measure of K_e and that changes in K_v are due to phase changes that occur during an ion exchange reaction because each phase has different intrinsic selectivities. The proposed model is specific for expanding 2:1 phyllosilicates and does not describe ion exchange reactions involving other types of clay.

Traditionally, the extent of crystalline swelling for 2:1 phyllosilicates has been attributed to a balance between strong electrostatic-attraction (G_{at}) and hydration-repulsion (G_{rp}) potential energies (Norrish 1954; Kittrick 1969; Parker 1986). Recently, a new term for the potential energy due to mechanical resistance (G_{rs}) has been introduced into the energy balance equation for crystalline swelling (Laird 1987; Laird et al. 1995). For a static system, the potential energy balance is:

$$G_{rp} = G_{at} + G_{rs} \quad [1]$$

By Equation [1], G_{rs} is defined as positive when mechanical resistance contributes to the potential energy of attraction and negative when it contributes to the potential energy of repulsion. For a dynamic system, changes in these potential energies (due to factors such as infinitesimal changes in relative humidity or interlayer ionic composition) are described by:

$$\Delta G_{rp} = \Delta G_{at} + \Delta G_{rs} \quad [2]$$

Equation [2] describes reversible energy changes that may occur within a closed system as long as the basal spacing of the clay does not change. A change in basal spacing, however, indicates a phase transition and energy changes occurring during a phase transition are irreversible. During expansion, water is transferred from the solution to the interlayers, the layers move apart, and water in the surrounding solution is displaced to accommodate the expanding layers. During collapse, water is transferred from the interlayers to the solution, the layers move closer together and water molecules from the solution move in to fill the void left by the retreating layers. Irreversible work is required for each of these mass transfers. The energy needed for irreversible work is a barrier that stabilizes the various layer hydrates (phases) over a limited range of temperature, pressure and interlayer ionic composition. This energy barrier causes intrinsic hysteresis in crystalline swelling (Laird et al. 1995).

In the present model, Equation [1] is used to describe the potential energy balance for 2:1 phyllosilicates in "apparent equilibrium" (a system in thermal and mechanical equilibrium but not necessarily in material equilibrium) with solutions containing 2 competing cations. For such a system, G_{at} may be expressed as:

$$G_{at} = X''_A G_{c(A)} + X''_B G_{c(B)} + G_v \quad [3]$$

where X''_A and X''_B are interlayer equivalent fractions of cations A and B, $G_{c(A)}$ and $G_{c(B)}$ are the electrostatic attraction energies between the interlayer cations and the negative surface charge sites (attraction due to cation bridging) and G_v is the van der Waals attraction energy between 2 adjacent layers. The G_{rp} for the same clay may be expressed as:

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$$G_{rp} = X''_A G_{h(A)} + X''_B G_{h(B)} + G_{h(S)} + G_b \quad [4]$$

where $G_{h(A)}$ and $G_{h(B)}$ are potential energies of hydration for the interlayer cations, and $G_{h(S)}$ is the potential energy of hydration for the interlayer charge sites. Quantitatively $G_{h(i)}$ (where i = A, B or S) is equal to the difference between the hydration energy of the cation or charge site in the interlayers and the hydration energy of the same cation or charge site in the equilibrating solution. The Born repulsion energy (G_b) prevents the clay from collapsing below 10 Å (Laird 1996) but otherwise does not contribute significantly to the energy balance.

Recognizing that $X''_B = 1 - X''_A$ for a binary cation exchange system, Equations [1], [3] and [4] may be combined and solved for X''_A:

$$X''_A = \frac{G_{h(B)} - G_{c(B)} + G_{h(S)} + G_b - G_v - G_{rs}}{(G_{c(A)} - G_{c(B)}) - (G_{h(A)} - G_{h(B)})} \quad [5]$$

Equation [5] describes the relationship between the interlayer ionic composition of a binary cation–clay system and the various potential energies that control crystalline swelling of 2:1 phyllosilicates.

We take the Eisenman model (Eisenman 1962) as a starting point for quantifying $\overline{\Delta G}_{ex}$:

$$\overline{\Delta G}_{ex} = [(\bar{G}_{c(A)} - \bar{G}_{c(B)}) - (\bar{G}_{h(A)} - \bar{G}_{h(B)})] \quad [6]$$

The potential energy terms in the Eisenman model are typically estimated from electrostatic considerations only. This approach neglects the contribution of entropy due to the mixing of cations which must be included for a rigorous solution. The bars above the energy terms in Equation [6] indicate a molar scale (J/mol), whereas all of the energy terms in Equations [1] through [5] are relative to surface area of the clay (J/m^2). Other than unit differences, the electrostatic and hydration potential energies in Eisenman's equation are the same as those that control crystalline swelling in binary cation–clay systems (Equations [3] through [5].)

The $\overline{\Delta G}_{ex}$ for a homovalent-binary exchange on 2:1 phyllosilicates is obtained by combining Equations [5] and [6]:

$$\overline{\Delta G}_{ex} = (G_{h(B)} - G_{c(B)} + G_{h(S)} + G_b - G_v - G_{rs}) \times \frac{Nez}{\sigma X''_A} \quad [7]$$

where N is Avogadro's number, e is the charge on a proton, σ is the surface charge density of the clay and z is the cation valence. The $\overline{\Delta G}_{ex}$ for a heterovalent–binary exchange reaction is:

$$\overline{\Delta G}_{ex} = (G_{h(B)} - G_{c(B)} + G_{h(S)} + G_b - G_v - G_{rs}) \times \frac{Nez_A z_B}{\sigma X''_A} \quad [8]$$

where z_A and z_B are the valences of cations A and B, respectively. Finally, the free energy of exchange is related to the equilibrium constant for the exchange reaction by:

$$\overline{\Delta G}_{ex} = -RT \ln(K_e) \quad [9]$$

where R is the gas constant and T is the absolute temperature.

The final terms in Equations [7] and [8] account for unit differences of the various energy terms and for stoichiometry differences between homovalent and heterovalent exchange reactions. At first glance, the presence of X''_A in the denominator of the final term of Equations [7] and [8] may seem unreasonable, because it implies that $\overline{\Delta G}_{ex}$ is a variable that depends on the extent of an exchange reaction, whereas by definition $\overline{\Delta G}_{ex}$ is a constant. The apparent contradiction is resolved, however, by appreciating the role of G_{rs} in crystalline swelling (Laird 1996) and cation exchange selectivity. During a cation exchange reaction, G_{rs} changes in direct response to stress on the clay water system (analogous to the resistance offered by a table as more or less weight is placed on the table). Therefore, as long as the basal spacing of the clay remains constant (no phase change), any change in X''_A will be exactly balanced by a change in G_{rs} such that $\overline{\Delta G}_{ex}$ remains constant. However, if enough stress is placed on the clay water system, the clay may undergo a phase transition. As mentioned previously, energy changes during phase transitions are irreversible; therefore, Equations [5] through [9] are valid only for systems with stable basal spacings.

EXPERIMENTAL

Materials

The synthetic fluoro-hectorite (Corning[1] 118 EUA fluoro-hectorite material) used for this experiment was provided by Corning. Structural interpretation of chemical analyses for Ba- and Mg-saturated portions of the synthetic fluoro-hectorite yielded the following formulae:

$$Ba_{0.28}(Si_{4.03})(Mg_{2.29}Li_{0.66}Al_{0.01}Fe^{III}_{0.01})O_{10}F_2 \quad \text{and}$$

$$Mg_{0.28}(Si_{4.01})(Mg_{2.31}Li_{0.66}Al_{0.01}Fe^{III}_{0.01})O_{10}F_2$$

respectively. The structural formulae were calculated assuming a total anionic charge of −22 (that is, exactly 10 oxygen and 2 fluorine atoms per formula unit) and a total of 7.00 structural cations per formula unit. Structural Si for both formulae exceeds the theoretical maximum of 4.00. This discrepancy may be caused by contamination, analytical error or errors in the assumptions used for calculating the structural formulae. The discrepancy, however, is small and therefore the formulae are believed to provide a reasonable representation of the fluoro-hectorite chemistry.

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Preparation of Ba- and Mg-Clays

Bulk samples of Ba- and Mg-saturated synthetic fluoro-hectorite were prepared. To do so, two 10-g samples of the original fluoro-hectorite were placed in separate 250-mL centrifuge bottles along with 200 mL of 0.5 *M* $BaCl_2$ or $MgCl_2$. The samples were stirred with a Teflon rod (to break up any clay clumps), sonicated for 2 min and then shaken for 24 h on an orbital shaker. The samples were centrifuged (8000 rpm for 10 min) to settle the clay and decanted. Using the above procedure, the samples were washed a total of 4 times in their respective salt solutions. Excess salt was removed by washing the samples 10 times, using DI water for the initial wash and grading to 80% ethanol for the final 4 washes. Electrical conductivity of the supernatant was reduced to 1.5 μS/cm for both samples after the 10th wash. The samples were freeze-dried and stored in sealed containers.

Dialysis Equilibration Technique

A dialysis technique was used to equilibrate the prepared clay samples with various mixed 0.01 *M* $BaCl_2$/$MgCl_2$ solutions. Eleven stock solutions containing concentrated mixtures of $BaCl_2$ and $MgCl_2$ in the appropriate ratios (X'_{Ba} = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0) were prepared. The stock solutions were diluted (10 mL to 500 mL) to prepare the appropriate mixed 0.01 *M* $BaCl_2$/$MgCl_2$ solutions for all subsequent procedures. Sections of dialysis tubing (Spectra/Por 3) were presoaked in the appropriate mixed salt solution. One end of the dialysis tubing was tied off using monofilament nylon line (4-lb test fishing line). Then 0.20 g of either Ba- or Mg-saturated fluoro-hectorite along with 20 mL of the appropriate mixed salt solution were placed in the dialysis tubing and the upper end of the dialysis tubing was tied off. The dialysis tubes were placed in 250-mL-wide mouth polyethylene bottles along with 200 mL of the appropriate mixed salt solution. By this procedure, 22 samples were prepared for equilibration using the Ba- and Mg-saturated fluoro-hectorite samples with each of the 11 mixed 0.01 *M* $BaCl_2$/$MgCl_2$ solutions. The samples were equilibrated at room temperature for 80 d during which the equilibration solutions were refreshed a total of 20 times.

After the equilibration was complete, the contents of the dialysis tubes were transferred to 50-mL centrifuge tubes. The centrifuge tubes were sealed and shaken well; then a small amount of the clay suspension was withdrawn using a syringe for XRD analyses. The remaining clay suspensions were centrifuged and the supernatant decanted. The samples were washed (stirred, sonicated, centrifuged and decanted) with 50% ethanol until the electrical conductivity of the supernatant was below 1.0 μS/cm. The samples were dried (24 h at 60 °C), crushed in an agate mortar, transferred to glass vials, dried for 5 more d at 60 °C and then cooled and stored in a desiccator.

ICP Analysis

The samples were analyzed for Ba and Mg concentrations. To do so, duplicate portions of each of the ethanol-washed samples were decomposed in sealed acid digestion vessels using 48% HF following the procedure of Bain and Smith (1987). Barium and Mg concentrations were determined simultaneously using a Thermo Jarrell Ash ICAP 61E inductively coupled plasma (ICP) atomic emission spectrometer.

Calculations of Adsorbed Mole Fraction Ba

A ratio technique was used to calculate the mole fraction of Ba retained on each sample. Measured elemental concentrations (mg L^{-1}) for the sample digests were first divided by their respective atomic weights to express the concentrations as mmol L^{-1}. Then, for each sample, the concentration of Ba was divided by the sum of the Ba and Mg concentrations. Finally, the Ba/(Ba + Mg) ratio for each sample was divided by the Ba/(Ba + Mg) ratio for a sample that was 100% Ba-saturated (this last step is needed to account for structural Mg). By using this ratio technique to calculate adsorbed mole fractions, errors inherent to the measurement of sample weights (due to differences in both the residual water content of samples and the atomic weights of Ba and Mg) and errors occurring during the ICP analysis (due to factors such as fluctuations in plasma conditions or rates of sample introduction) were eliminated. Using the ratio technique, replicate determinations of adsorbed Ba mole fraction agreed to 2 and, in most cases, 3 significant figures, whereas, using a standard approach for calculating the adsorbed Ba mole fractions, the replicate determinations generally agreed to only the 1st significant figure.

X-ray Diffraction (XRD) Analysis of Clay Suspensions

Basal spacings of the fluoro-hectorite in suspensions at equilibrium with the various mixed Ba/Mg solutions were determined by XRD using symmetrical transmission geometry with a liquid sample cell as described by Shang et al. (1995). Briefly, the clay suspensions were injected into a thin (18-mm-diameter by 1-mm-thick) sample cell fitted with Mylar windows on both sides. The sample cell was mounted perpendicularly to both the zero plane of the goniometer and the plane of the goniometer circle, permitting diffraction patterns to be recorded using X-radiation that passed through the suspension in the cell. The XRD analyses were conducted using Cu*K*α radiation from a Siemens D5000 X-ray diffractometer operated in θ-θ mode and equipped with a solid state Li(Si) detector.

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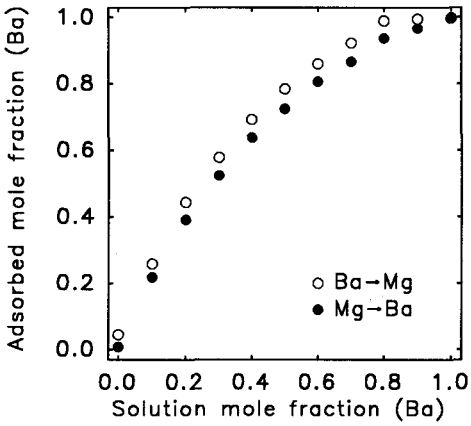


Figure 2. Forward and reverse isotherms for Ba-Mg exchange on synthetic fluoro-hectorite.

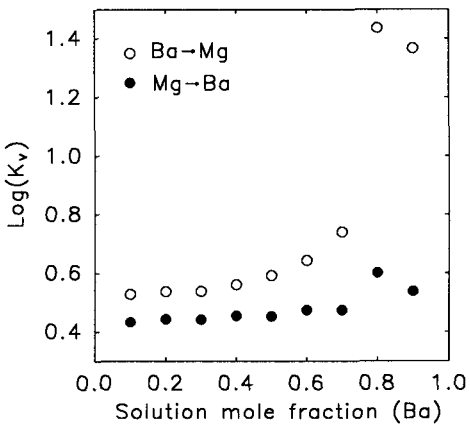


Figure 3. Relationship between log of the Vanselow selectivity coefficient and solution mole fraction Ba for the Ba-Mg exchange reaction on synthetic fluoro-hectorite.

Vanselow Selectivity Coefficient

In this study, we consider the forward reaction to be the replacement of Mg adsorbed onto the clay by Ba from solution:

$$BaCl_2(aq) + Mg\,X_2(s) = MgCl_2(aq) + Ba\,X_2(s) \quad [10]$$

Conversely, the replacement of adsorbed Ba by Mg from the solution is considered the reverse reaction. The equilibrium constant for the reaction is approximated by the Vanselow selectivity coefficient:

$$K_c \approx K_v = \frac{\gamma_{Mg}(Mg)X''_{Ba}}{\gamma_{Ba}(Ba)X''_{Mg}} \quad [11]$$

where γ indicates single ion activity coefficients, parentheses indicate molar concentrations in solution and X'' indicates adsorbed mole fraction for the subscripted cations. Activity coefficients were calculated using the Debye–Huckel model.

RESULTS

The relationships between adsorbed mole fraction Ba (X''_{Ba}) and solution mole fraction Ba (X'_{Ba}) for both the forward and reverse reactions are shown in Figure 2. Standard deviations for the replicate determinations of X''_{Ba} were less than 0.003 for all samples, hence, error bars are smaller than the symbols for the data points in Figure 2. The convex nature of the isotherms indicates that Ba is preferred over Mg. Hysteresis in the cation exchange reaction is evidenced by the difference in the isotherms for the forward and reverse reactions.

The relationship between Log(K_v) and X'_{Ba} is presented in Figure 3. For the forward reaction, there is a slight increase in preference for Ba (increase in Log(K_v)) with increasing X'_{Ba}. For the reverse reaction, there is a substantial increase in preference for Ba with increasing X'_{Ba}.

The relationship between X'_{Ba} and basal spacing of the synthetic fluoro-hectorite at equilibrium with the various mixed $BaCl_2/MgCl_2$ solutions is shown in Figure 4. Basal spacings were nearly constant (18.5 to 18 Å) during the forward reaction, indicating that the fluoro-hectorite dominantly contained 3 layers of interlayer water molecules. For the forward reaction, both broadening and loss in intensity of the 001 XRD peaks were observed with increasing X'_{Ba}, indicating increasing interstratification. The results for the reverse reaction clearly demonstrate a transition from a 2-layer hydrate (16 Å basal spacing) to a 3-layer hydrate (18.5 Å basal spacing) with decreasing X'_{Ba}.

Figure 5 presents the relationship between Log(K_v) and basal spacing of the synthetic fluoro-hectorite. Regression analysis indicated a correlation coefficient of 0.85 ($P > F < 0.001$) for the relationship between Log(K_v) and basal spacing.

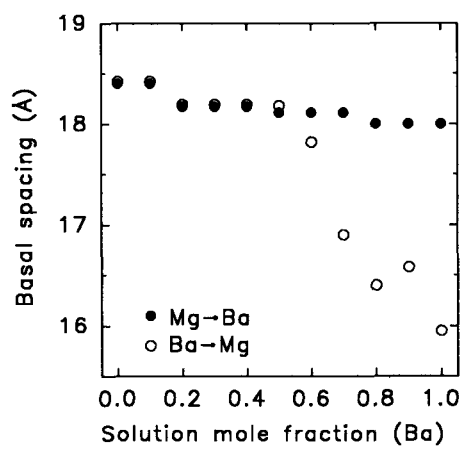


Figure 4. Relationship between basal spacing of the synthetic fluoro-hectorite and solution mole fraction Ba.

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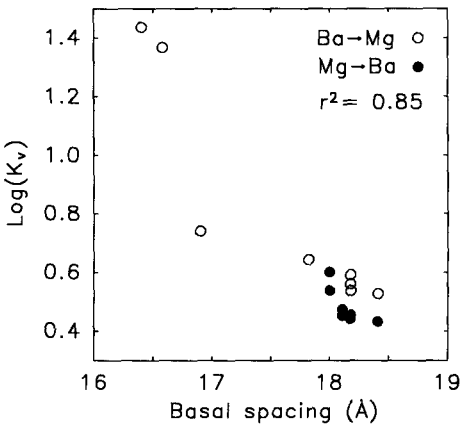


Figure 5. Relationship between log of the Vanselow selectivity coefficient and basal spacing for the Ba-Mg exchange reaction on synthetic fluoro-hectorite.

DISCUSSION

A thermodynamic equilibrium constant for an ion exchange reaction, by definition, must be independent of the extent to which the reaction has proceeded. However, 2 phases of the same substance may have different K_e values for the same ion exchange reaction. Thus the observed change in K_v with X'_{Ba} for the reverse reaction (Figure 3) indicates that either K_v is a poor approximation of K_e or else that a phase change occurred during the course of the exchange reaction. The correlation between Log(K_v) and basal spacing (Figure 5) and coincidence of abrupt changes in basal spacing and Log(K_v) values (Figures 3 and 4) strongly supports interpretation of the 16-Å fluoro-hectorite and 18.5-Å fluoro-hectorite as 2 distinct phases with unique K_e values.

Evidence of an energy barrier that inhibits both expansion and collapse is obtained by comparing the results for the 2 samples that were equilibrated in 0.01 *M* $BaCl_2$. The sample that was Ba-saturated, dialyzed, freeze-dried and then equilibrated for 80 d with 0.01 *M* $BaCl_2$ exhibited a basal spacing of 15.95 Å. By contrast, the sample that was Mg-saturated, dialyzed, freeze-dried and then equilibrated for 80 d with 0.01 *M* $BaCl_2$ (solution refreshed 20 times) exhibited a basal spacing of 18.00 Å (Figure 4). Chemical analysis indicated that both samples were 100% Ba-saturated at the time of the XRD analysis. These results demonstrate that both the 16- and 18.5-Å phases of Ba-fluoro-hectorite are stable in 0.01 *M* $BaCl_2$. Such stability is clear evidence for an energy barrier that inhibits both expansion and collapse of smectites. Apparently, when the dry Mg-saturated samples were first placed in the various 0.01 *M* $BaCl_2$/$MgCl_2$ solutions, the interlayer Mg provided enough swelling pressure to expand the clay to 18 Å. Although ion exchange began immediately, it proceeded at a slower rate than swelling and did not proceed to completion until the equilibration solutions had been refreshed several times. These samples remained at 18 Å even when Ba-saturated because there was not enough electrostatic attraction pressure to overcome the 16–18.5 Å energy barrier. By contrast, the samples that were originally Ba-saturated expanded to only 16 Å when first placed in the various 0.01 *M* $BaCl_2$/$MgCl_2$ solutions, because the low hydration energy of Ba did not provide enough swelling pressure to expand the clay over the 16–18.5 Å energy barrier. Later, as ion exchange proceeded, enough Mg entered the interlayers of samples in the low X'_{Ba} solutions for the clay to expand over the energy barrier. The samples in high X'_{Ba} solutions did not take up enough interlayer Mg to overcome the energy barrier and therefore remained at 16 Å.

Under the proposed model, phase changes allow a clay to adapt to changes in solution chemistry, such that selectivity for a particular cation should be highest when a homogeneous clay is nearly saturated with that cation. This phenomenon has never before been observed but is demonstrated by the results for the Ba-Mg-exchange experiment. Selectivity for Ba is highest when the clay is nearly saturated with Ba (Figure 3). By contrast, in most cation exchange systems, selectivity for the preferred cation is highest at low-solution mole fractions of the preferred cation (Gast 1972; McBride 1979). This trend is attributed to site heterogeneity, whereby highly selective sites fill up with the preferred cation first (Peigneur et al. 1975; McBride 1976). The fluoro-hectorite was selected for the Ba-Mg exchange experiment in part because, as a synthetic clay, it ought to be nearly homogeneous, thus eliminating confounding effects due to heterogeneity. For natural clays, clearly both heterogeneity and crystalline swelling effects contribute to observed non-ideal exchange behavior.

Heterogeneity in surface properties of 2:1 phyllosilicates introduces another level of complexity to the interaction between crystalline swelling and ion exchange selectivity. Because of heterogeneity, the conditions that induce a phase transition in one domain may not cause a phase transition in another domain of the same sample. Thus K_v changes gradually with X'_A, because phase transitions occur at different values of X'_A for each domain. Furthermore, when a phase change occurs in one domain, the accompanying change in selectivity will be followed by a change in the composition of the interlayer cations for that domain and a balancing change in the chemistry of the equilibrating solution. The change in solution chemistry will inhibit phase changes in other domains. Thus phase changes in response to changing solution chemistry are self-quenching. Within the proposed model, effects of layer charge heterogeneity can be modeled by calculating weighted average solutions for Equation [7] or [8] relative to the distribution of layer charge densities in a sample.

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The model predicts hysteresis in cation exchange reactions any time there is a phase change in the clay. Vanselow (1932) may have anticipated this explanation for hysteresis when he stated: "This phenomenon of hysteresis may possibly be related to some phase of the crystal structures of the base-exchange substances." Newman (1970) recognized a connection between crystalline swelling and exchange hysteresis when he stated: "hysteresis may be expected whenever there is a change in the number of layers in interlayer water. . .". A small amount of hysteresis was observed in the Ba-Mg exchange isotherms (Figure 2). Coincident with the observed hysteresis is a transition from a 2-layer hydrate to the 3-layer hydrate for the reverse reaction (Figure 4).

Verburg and Baveye (1994, 1995a, 1995b) and Verburg et al. (1995) have recently attributed hysteresis in cation exchange reactions to the combined effects of hysteresis in crystalline swelling and hysteresis in quasicrystal formation and destruction. In the present model, the formation and destruction of quasicrystals may be regarded as a phase transition whereby the clay expands or contracts from the crystalline swelling range to the double layer swelling range. An energy barrier undoubtedly inhibits this phase transition in the same manner as the energy barriers that inhibit phase transitions within the crystalline swelling range.

The proposed model readily explains why selectivity for Ca increases with the layer charge of smectites for Na-Ca exchange (Maes and Cremers 1977) and decreases with layer charge for K-Ca exchange (Sawhney 1969; Shainberg et al. 1987). Both Na and Ca are strongly hydrated cations that support expanded smectite interlayers (~19 Å) regardless of layer charge; therefore, no phase change occurs (if the salt concentration is high enough to prevent dispersion) during a Na-Ca exchange reaction and the divalent cation (Ca) is increasingly preferred as layer charge increases. By contrast, K is a weakly hydrated cation that induces collapse in high charge density smectites but not in low charge density smectites. In the proposed model, layer collapse causes a substantial increase in selectivity for the weakly hydrated cation (that is, K). Thus with K-Ca exchange, the effects of layer collapse dominate over the effects of valence to cause an increase in preference for K with increasing layer charge.

Demixing is an obvious consequence of the interaction between crystalline swelling and cation exchange selectivity. Because of the energy barriers that inhibit phase transitions, 2 or more phases of the same clay may coexist in the same system. These phases will have distinctly different selectivities and therefore different interlayer ionic compositions. In the Ba/Mg exchange experiment, the 16-Å phase has nearly an order of magnitude higher selectivity for Ba than does the 18.5-Å phase (Figure 3). Furthermore, external surfaces of quasicrystals may be regarded as a separate phase with unique selectivities dictated by conditions at the interface between the bulk solution and the clay. Because cations adsorbed on external surfaces are less constrained than those in the interlayers, the external surfaces should be more accommodating to strongly hydrated cations. Alternatively, large distances separating charge sites on external surfaces should favor monovalent cations. Therefore, evidence for demixing where Na and Li are found on external surfaces (Shainberg and Otoh 1968; Fink et al. 1971) is a logical consequence of selectivity relationships.

Fixation of K, NH_4, Rb and Cs in the interlayers of collapsed 2:1 phyllosilicates has traditionally been treated differently from ion exchange and selectivity. However, in the proposed model, fixation is simply an extreme case, wherein the clay has collapsed to 10 Å and, as a consequence, selectivity for weakly hydrated cations increases by several orders of magnitude. However, fixation is distinguished from other ion exchange reactions by slow kinetics and steric restrictions.

CONCLUSIONS

A model is presented for the interaction between crystalline swelling and cation exchange selectivity. The model provides a unifying framework for understanding the effect of cation valence and cation hydration energy on selectivity, the effect of layer charge on selectivity, non-ideal exchange behavior, hysteresis, demixing and fixation phenomena. The results of an experiment involving Ba-Mg exchange on a synthetic fluoro-hectorite demonstrate many of the relationships predicted by the model, including correlation between measured selectivity coefficients and basal spacings, an abrupt change in basal spacing that correspond with an abrupt change in selectivity and corresponding hysteresis in crystalline swelling and cation exchange selectivity. The experimental results also demonstrate a new phenomenon, increased selectivity for the preferred cation (Ba) at high solution mole fraction of the preferred cation. This trend is exactly opposite of that observed with natural (heterogeneous) smectites but is predicted by the proposed model for homogeneous smectites such as the synthetic fluoro-hectorite used in the study.

[1] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that might also be suitable.

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