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## Cation Selectivity in Sodium–Calcium, Sodium–Magnesium, and Calcium–Magnesium Exchange on Wyoming Bentonite at 298 K<sup>1</sup>

GARRISON SPOSITO, KENNETH M. HOLTZCLAW, CLAIRE JOUANY, AND LAURENT CHARLET<sup>2</sup>

### ABSTRACT

Exchange isotherms were prepared for Na<sup>+</sup> in Na<sup>+</sup>–Ca<sup>2+</sup> and Na<sup>+</sup>–Mg<sup>2+</sup> exchange reactions, and for Mg<sup>2+</sup> in Ca<sup>2+</sup>–Mg<sup>2+</sup> exchange reactions, at 298 K on Wyoming bentonite suspended in a 0.05M perchlorate background. These isotherms were essentially congruent with the appropriate thermodynamic nonpreference exchange isotherms. It was concluded from this fact that there is essentially no difference in the affinity of montmorillonite clay for Ca<sup>2+</sup> vs. Mg<sup>2+</sup>. However, exchange isotherms prepared for Na<sup>+</sup> in Na(I)–Ca(II) and Na(I)–Mg(II) exchange, as well as published ones for Mg(II) in Ca(II)–Mg(II) exchange on montmorillonite suspended in a 0.05M chloride background consistently indicate a slight preference on the clay for Ca(II) over Mg(II). This preference for Ca(II) is concluded to be the result of the formation of CaCl<sup>+</sup> complexes, which are more stable thermodynamically and have a greater affinity for the clay than MgCl<sup>+</sup> complexes.

**Additional Index Words:** cation exchange, chloride complexes, saline soils, thermodynamics of cation exchange.

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ONE OF THE CENTRAL PROBLEMS in the chemistry of arid-zone soils is the quantitative characterization of an exchange complex bearing sodium, calcium, and magnesium ions. Rahman and Rowell (1979) and Bresler et al. (1982, part 1) have reviewed this problem recently and have brought into clear focus the two objectives of understanding the patterns of Na–Ca–Mg exchange reactions and of predicting the effect of exchanger composition on soil physical properties. The consensus of the literature is that exchangeable sodium percentage (ESP), electrolyte concentration, and soil mineralogy are the three master chemical variables on which the water-conducting properties of arid-zone soils depend. What remains is to develop a unified, quantitative description of the interrelations among these variables that is of predictive value.

Much of the research on Na–Ca–Mg exchange reactions has involved montmorillonite clay or montmorillonitic soils. In respect to exchange selectivity, the trends that have emerged from the results of published studies are: (i) for a given distribution of Na and bivalent cation in the aqueous solution phase, the resulting ESP on the clay is somewhat higher in Na–Mg exchange than in Na–Ca exchange, and (ii) in Ca–Mg exchange, a small preference for Ca exists on the exchange complex (Schwertmann, 1962; Clark, 1966; Dolcater et al., 1968; Levy and Hillel, 1968; Hunsaker

and Pratt, 1971; Levy and Shainberg, 1972; Levy et al., 1972; van Bladel et al., 1973; Jensen and Babcock, 1973; Gheyi and van Bladel, 1975; Maes and Cremers, 1977; Rahman and Rowell, 1979; Rowell and Shainberg, 1979; van Bladel and Gheyi, 1980; Shainberg et al., 1980). The extent to which Na–Mg exchange results in larger ESP values than Na–Ca exchange is not pronounced, the differences being the order of 3 to 5 in ESP (Rahman and Rowell, 1979). The same is true of the selectivity of montmorillonite for calcium over magnesium. For example, van Bladel and Gheyi (1980) have reported a mean value of  $0.8 \pm 0.1$  for the overall Vanselow selectivity coefficient,

$$K_{TV} = (x_{TMg} Ca_T)/(x_{TCa} Mg_T) \quad [1]$$

which describes the stoichiometric cation exchange reaction:



where  $x_T$  is the mole fraction of all species of a metal in the exchanger phase,  $M_T$  ( $M = Ca$  or  $Mg$ ) is the total molarity of all species of a metal in the aqueous solution phase, and  $X$  refers to 1 mol of negative charge on Camp Berteau montmorillonite clay. This mean value of  $K_{TV}$  is only a little smaller than 1.0, the value that indicates no overall preference for calcium vs. magnesium on the clay.

A common feature in all of the experimental studies cited above [except one, that of Maes and Cremers (1977)] is the use of a chloride background ionic medium in which to carry out the exchange reactions. Sposito et al. (1983) have shown recently that, in chloride media, Na–Ca and Na–Mg exchange reactions on montmorillonite (Wyoming bentonite) actually are ternary cation exchange reactions, involving Na<sup>+</sup>, M<sup>2+</sup>, and the complex, MCl<sup>+</sup> ( $M = Ca$  or  $Mg$ ). According to the data presented by Sposito et al. (1983), as the charge fraction of Ca(II) increases beyond 0.3 in mixed NaCl/CaCl<sub>2</sub> solutions reacting with a Na-montmorillonite, the species of Ca(II) that competes effectively with Na<sup>+</sup> on the external surfaces of the quasicrystals that have formed is the complex, CaCl<sup>+</sup>, not the free cation, Ca<sup>2+</sup>. In the case of Na–Mg exchange, the same process was shown to occur, but to a lesser extent because montmorillonite apparently exhibits a lesser affinity for MgCl<sup>+</sup> than for CaCl<sup>+</sup> (Sposito et al., 1983, Fig. 1).

The significance of the results of Sposito et al. (1983) for cation selectivity in Na–Ca–Mg exchanges on montmorillonite is the possibility that the small overall preference of Ca(II) over Mg(II) that has been observed repeatedly in chloride background media may, in fact, be produced by the greater affinity of the species CaCl<sup>+</sup> for the clay relative to the species MgCl<sup>+</sup>. It is possible that, without the presence of monovalent chloride complexes, montmorillonite would exhibit no differences in Ca(II) vs. Mg(II) selectivity in exchange reactions involving solely the free cations, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>. In this paper, the first measurements of Ca

<sup>1</sup> Contribution from the Dep. of Soil and Environmental Sciences, Univ. of California, Riverside, CA 92521. Received 10 Nov. 1982. Approved 19 Apr. 1983.

<sup>2</sup> Professor of Soil Science, Research Associate IV, Visiting Postdoctoral Fellow, and Graduate Research Assistant, respectively.

→ Mg exchange on montmorillonite in a perchlorate background, where monovalent complexes do not occur, will be presented. Thermodynamic methods will be applied to examine cation selectivity in Na → Ca, Na → Mg, and Ca → Mg exchange reactions on Wyoming bentonite at 298 K in both perchlorate and chloride background media. On the basis of this analysis, the role of the complex,  $MCl^+$  ( $M = Ca$  or  $Mg$ ), will be evaluated in relation to the frequent observation that montmorillonites and montmorillonitic soils adsorb Ca(II) preferentially to Mg(II).

## MATERIALS AND METHODS

### Wyoming Bentonite

Montmorillonite SWy-1, obtained from the Source Clays Repository of the Clay Minerals Society, was used in this study. The unit cell formula for this Crook County, Wyoming, bentonite is (Sposito et al., 1983):

$M_{0.62}^{+}(\text{Si}_{7.80}\text{Al}_{0.20})[\text{Al}_{3.28}\text{Fe(III)}_{0.30}\text{Fe(II)}_{0.04}\text{Mg}_{0.38}]\text{O}_{20}(\text{OH})_4$ , where  $M^+$  refers to 1 mol of monovalent exchangeable cation charge. The procedures employed to purify the clay and prepare it in the sodium-saturated form in either a perchlorate or a chloride background medium have been described in detail by Sposito et al. (1981, 1983). For the exchange experiments involving only calcium and magnesium, the sodium-clay in the perchlorate medium was converted to a calcium-saturated clay by repeated washing (including a 15-min shaking period) and centrifugation with  $2M$   $\text{Ca}(\text{ClO}_4)_2$ .

### Exchange Experiments

Sodium-montmorillonite samples were reacted at  $25.0 \pm 0.3^\circ\text{C}$  with mixed salt solutions of either  $\text{NaClO}_4/\text{Ca}(\text{ClO}_4)_2$ ,  $\text{NaClO}_4/\text{Mg}(\text{ClO}_4)_2$ ,  $\text{NaCl}/\text{CaCl}_2$ , or  $\text{NaCl}/\text{MgCl}_2$ , as described by Sposito et al. (1983). Calcium-montmorillonite samples were reacted at  $25.0 \pm 0.3^\circ\text{C}$  with  $\text{Ca}(\text{ClO}_4)_2/\text{Mg}(\text{ClO}_4)_2$  solutions. The reaction times varied between 24 and 60 h. In the Na-exchange experiments, the anion molarity was maintained at  $0.051 \pm 0.004M$  and the pH value was  $7.0 \pm 0.5$ . In the Ca-Mg exchange experiments, the perchlorate molarity was  $0.048 \pm 0.003M$  and the pH value was  $7.1 \pm 0.3$ . The clay stock suspension concentration was  $23.2 \pm 0.2$  g clay/kg suspension. The methods by which the supernatant solutions and clay slurries were analyzed for Na, Ca, and Mg after the exchange experiments were completed have been described by Sposito et al. (1983).

### Data Analysis

The surface excesses of Na, Ca, and Mg were calculated as described by Sposito et al. (1981):

$$\Gamma_i^{(w)} = n_i - M_w m_i, \quad (i = \text{Na}^+, \text{Ca}^{2+}, \text{or Mg}^{2+}), \quad [3]$$

where  $\Gamma_i^{(w)}$  is the surface excess, in moles per kilogram of clay;  $n_i$  is the total number of moles of metal species  $i$  in the clay slurry per kilogram of clay;  $M_w$  is the mass of water in the clay slurry per kilogram of clay; and  $m_i$  is the molality of metal species  $i$  in the supernatant solution. The quantity  $\Gamma_i^{(w)}$  is the number of excess moles of metal species  $i$ , per kilogram of clay, relative to the number of moles of the metal species present in a bulk aqueous solution of molality  $m_i$  that contains the same mass of water as in the clay slurry.

The adsorbed metal species charge was calculated with the following equation:

$$q_i = Z_i \Gamma_i^{(w)} \quad (i = \text{Na}^+, \text{Ca}^{2+}, \text{etc.}), \quad [4]$$

where  $Z_i$  is the valence of metal species  $i$ . The total adsorbed metal charge,  $Q_o$ , was calculated as the sum of all terms  $q_i$

for the specific metal cation species adsorbed by the clay in a given exchange experiment.

Exchange isotherms for  $\text{Na}^+$  in either the perchlorate or the chloride background medium were prepared after calculating the two charge fractions:

$$E_{\text{Na}} = q_{\text{Na}^+}/Q_o \quad \tilde{E}_{\text{Na}} = [\text{Na}^+]/0.05, \quad [5]$$

where the square brackets refer to a molar concentration. The mean values of  $Q_o$  were 1.03 and  $0.9 \text{ mol}_c \text{ kg}^{-1}$ , for the Na-Ca and Na-Mg exchanges in a  $0.05M$  perchlorate background, and 0.96 and  $1.04 \text{ mol}_c \text{ kg}^{-1}$  for the same two exchanges in a  $0.05M$  chloride background (Sposito et al., 1983). The standard error for all four sets of measurements of  $Q_o$  was  $0.08 \text{ mol}_c \text{ kg}^{-1}$ . Exchange isotherms for  $\text{Mg}^{2+}$  in the Ca-Mg- $\text{ClO}_4$  system were prepared with charge fractions calculated similarly to those in Eq. [5]:

$$E_{\text{Mg}} = q_{\text{Mg}^{2+}}/Q_o \quad \tilde{E}_{\text{Mg}} = 2[\text{Mg}^{2+}]/0.05. \quad [6]$$

Vanselow selectivity coefficients for  $\text{Na}^+ \rightarrow \text{Ca}^{2+}$ ,  $\text{CaCl}^+ \rightarrow \text{Ca}^{2+}$ ,  $\text{Na}^+ \rightarrow \text{CaCl}^+$ ,  $\text{Na}^+ \rightarrow \text{Mg}^{2+}$ ,  $\text{MgCl}^+ \rightarrow \text{Mg}^{2+}$ , and  $\text{Na}^+ \rightarrow \text{MgCl}^+$  exchanges in the  $0.05M$  chloride background were calculated from the data in Tables 4 to 7 of Sposito et al. (1983) with the following equation (Sposito, 1981, Chap. 5; Chu and Sposito, 1981):

$${}^c K_{ij}^T = (x_j^{Z_i(i)Z_i})/(x_i^{Z_j(j)Z_j}), \quad (ij = 1,2,3), \quad [7]$$

where  $x$  is a mole fraction of a metal species in the exchanger phase,  $( )$  refers to an activity of a metal species in the aqueous solution phase, and  $i$  or  $j$  refer to metal species with valence  $Z_i$  or  $Z_j$ . The superscript  $T$  emphasizes the fact that Na-Ca and Na-Mg exchanges in a chloride background medium involve the ternary cation system,  $\text{Na}^+ - \text{M}^{2+} - \text{MCl}^+$  (Sposito et al., 1983). The activities in Eq. [7] were calculated as products of single-ion molar concentrations and single-ion activity coefficients estimated with the Davies equation (Sposito, 1981, Chap. 2). When no confusion results,  ${}^c K_{ij}^T$  will be denoted generically by the symbol  $K_{ij}^T$  (Vanselow coefficient in a ternary exchange system). This selectivity coefficient differs from that in Eq. [1] because it contains species concentrations and mole fractions instead of total concentrations and mole fractions.

## RESULTS AND DISCUSSION

The primary data for  $\text{Ca}^{2+} \rightarrow \text{Mg}^{2+}$  exchange in  $0.05M$  perchlorate are given in Table 1 in terms of  $c$ , the equilibrium molinity (Whitfield, 1979, p. 161) in the aqueous solution phase, and  $q$ , the adsorbed cation charge. The mean value of  $Q_o$  for the Ca-Mg exchange experiments was  $0.96 \pm 0.07 \text{ mol}_c \text{ kg}^{-1}$ , in agreement with the mean value of  $0.97 \pm 0.06 \text{ mol}_c \text{ kg}^{-1}$  reported by Sposito et al. (1983) for Na-Ca and Na-Mg exchanges in  $0.05M$  perchlorate.

Exchange isotherms for  $\text{Na}^+$  on Ca- and Mg-montmorillonite (Wyoming bentonite) are shown in Fig. 1

Table 1—Experimental data on Ca-Mg exchange on Wyoming bentonite in a  $0.05M$  perchlorate background.

$c_{\text{Ca}}$	$c_{\text{Mg}}$	$q_{\text{Ca}}$	$q_{\text{Mg}}$	$Q_o$
mmol $\text{kg}^{-1}$		mol $_c$ $\text{kg}^{-1}$		
$22.90 \pm 0.05$	$<10^{-5}$	$0.98 \pm 0.02$	$<10^{-4}$	0.98
$21.7 \pm 0.1$	$2.45 \pm 0.05$	$0.88 \pm 0.09$	$0.106 \pm 0.027$	0.99
$19.33 \pm 0.03$	$5.04 \pm 0.04$	$0.86 \pm 0.13$	$0.20 \pm 0.07$	1.06
$21.0 \pm 0.1$	$6.60 \pm 0.07$	$0.67 \pm 0.12$	$0.19 \pm 0.05$	0.86
$15.8 \pm 0.1$	$8.03 \pm 0.03$	$0.63 \pm 0.11$	$0.32 \pm 0.05$	0.95
$13.55 \pm 0.04$	$9.87 \pm 0.05$	$0.52 \pm 0.07$	$0.36 \pm 0.04$	0.88
$11.50 \pm 0.03$	$9.15 \pm 0.07$	$0.53 \pm 0.05$	$0.45 \pm 0.07$	0.98
$8.80 \pm 0.05$	$14.86 \pm 0.02$	$0.38 \pm 0.04$	$0.67 \pm 0.11$	1.05
$3.90 \pm 0.04$	$19.5 \pm 0.10$	$0.18 \pm 0.01$	$0.72 \pm 0.04$	0.90
$2.10 \pm 0.02$	$22.3 \pm 0.1$	$0.06 \pm 0.02$	$0.89 \pm 0.16$	0.95

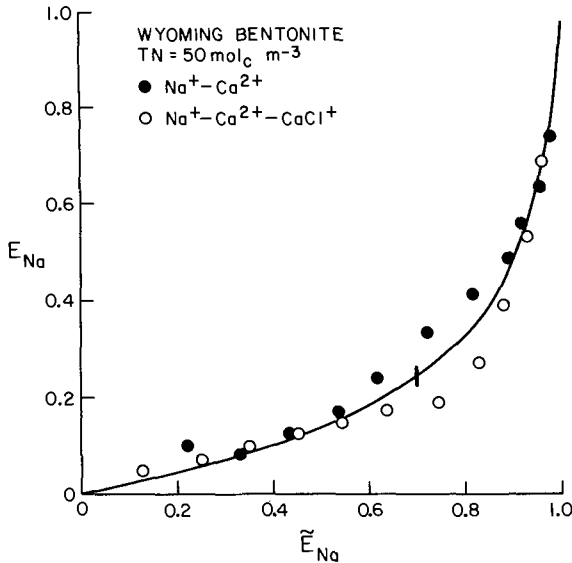


Fig. 1—Exchange isotherms for Na<sup>+</sup> in Na → Ca exchange on Wyoming bentonite in perchlorate (●) and chloride (○) background media. The solid curve is the thermodynamic nonpreference isotherm for monovalent–bivalent cation exchange.

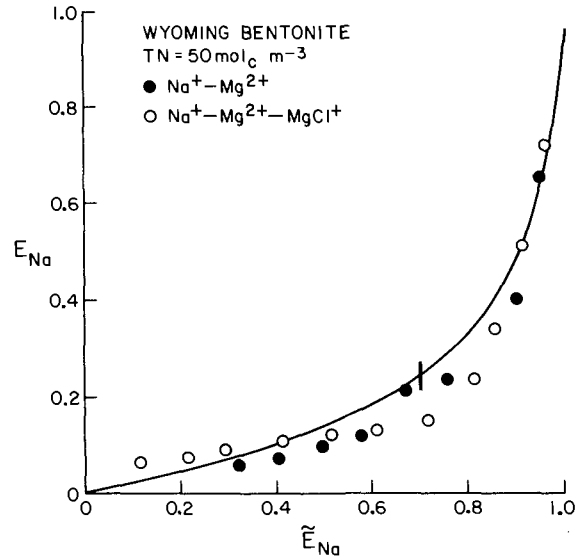


Fig. 2—Exchange isotherms for Na<sup>+</sup> in Na → Mg exchange on Wyoming bentonite in perchlorate (●) and chloride (○) background media. The solid curve is the nonpreference isotherm for monovalent–bivalent cation exchange.

and 2, respectively. The solid curve in each figure is the thermodynamic nonpreference isotherm for a binary monovalent–bivalent cation exchange, calculated with the equation (Sposito, 1981, Chap. 5)

$$E_{Na} = \left[ 1 + \frac{2}{\Gamma TN} \left( \frac{1}{\tilde{E}_{Na}^2} - \frac{1}{\tilde{E}_{Na}} \right) \right]^{-1/2}, \quad [8]$$

where  $\Gamma = \gamma_{Na}^2/\gamma_{Ca}$ ,  $\gamma$  is a single-ion activity coefficient, and TN is the total cation normality (equal to the anion molarity). The thermodynamic nonpreference exchange isotherm is defined by these conditions: (i) that the standard Gibbs energy change for the exchange reaction is zero ( $\Delta G_{ex}^\circ = 0$ ), and (ii) that the exchanger phase activity coefficients have unit value (ideal mixture). Thus, in chemical thermodynamics, cation exchange is said to exhibit no selectivity if the exchange equilibrium constant is equal to 1.0 and the exchanger phase has the properties of an ideal solid solution. The vertical lines through the nonpreference isotherms in Fig. 1 and 2 indicate the standard errors in the measured values of  $E_{Na}$ , which were  $\pm 0.02$  for Na–Ca exchanges and  $\pm 0.03$  for Na–Mg exchanges.

The data in Fig. 1 and 2 indicate that, in the perchlorate background, Wyoming bentonite shows approximately no preference for Na<sup>+</sup> in either Na–Ca or Na–Mg exchange, according to the thermodynamic criterion of nonpreference described above. On a finer scale of examination, the data for the perchlorate medium in Fig. 1 and 2 suggest that Na<sup>+</sup> may be preferred slightly over Ca<sup>2+</sup>, and Mg<sup>2+</sup> may be preferred slightly over Na<sup>+</sup>, when  $0.1 < E_{Na} < 0.4$ .

A Na/Ca- or Na/Mg-montmorillonite suspension with < 30% of the total adsorbed metal charge accounted for by Na<sup>+</sup> comprises fully developed quasicrystals, with bivalent exchangeable cations principally in the interlayer regions and Na<sup>+</sup> relegated to the external surfaces (Shainberg and Otoh, 1968; Bar-On et al., 1970). Exchange reactions involving Na<sup>+</sup> for  $E_{Na} < 0.4$  can, therefore, be expected to occur

principally on external surfaces. On the hypothesis of Sposito et al. (1983), the monovalent complexes, CaCl<sup>+</sup> and MgCl<sup>+</sup>, can compete with Na<sup>+</sup> on the external surfaces more effectively than Ca<sup>2+</sup> or Mg<sup>2+</sup>. This competition, however, is less intense for MgCl<sup>+</sup> than for CaCl<sup>+</sup> because the former complex is less stable thermodynamically and has a lesser affinity for the clay than the latter complex (Sposito et al., 1983, Table 1 and Fig. 1). Perhaps these two characteristics are the cause of the more apparent downward shift of Na<sup>+</sup> selectivity in Na–Ca exchange than in Na–Mg exchange, noted in Fig. 1 and 2, when the background anion is changed from perchlorate to chloride.

Table 2—Vanselow selectivity coefficients and exchanger-phase composition data (mole fractions) for Na<sup>+</sup>–M<sup>2+</sup>–MCl<sup>+</sup> exchange (M = Ca or Mg) on Wyoming bentonite in a 0.05M chloride background.

${}^cK_{12}^T$	${}^cK_{22}^T$	${}^cK_{13}^T$	$x_1$	$x_2$	$x_3$
1 = Na <sup>+</sup> 2 = Ca <sup>2+</sup> 3 = CaCl <sup>+</sup>					
0.989	$5.68 \times 10^{-3}$	13.2	0.806	0.182	0.012
1.10	$1.68 \times 10^{-3}$	25.6	0.684	0.276	0.040
1.33	$1.53 \times 10^{-3}$	29.5	0.542	0.400	0.058
2.05	$9.65 \times 10^{-4}$	46.0	0.410	0.496	0.094
2.08	$5.96 \times 10^{-4}$	59.0	0.293	0.561	0.146
1.23	$4.04 \times 10^{-4}$	55.1	0.263	0.530	0.207
0.971	$3.02 \times 10^{-4}$	56.7	0.222	0.511	0.267
0.788	$2.36 \times 10^{-4}$	57.8	0.183	0.504	0.313
0.596	$1.82 \times 10^{-4}$	57.3	0.147	0.482	0.371
0.473	$1.46 \times 10^{-4}$	56.9	0.108	0.465	0.427
0.292	$1.14 \times 10^{-4}$	50.6	0.064	0.452	0.484
1 = Na <sup>+</sup> 2 = Mg <sup>2+</sup> 3 = MgCl <sup>+</sup>					
0.739	$3.99 \times 10^{-3}$	13.6	0.832	0.157	0.011
0.925	$3.24 \times 10^{-3}$	16.9	0.671	0.304	0.025
1.36	$2.52 \times 10^{-3}$	23.3	0.496	0.462	0.042
2.18	$2.29 \times 10^{-3}$	30.9	0.371	0.569	0.060
2.72	$1.61 \times 10^{-3}$	41.0	0.254	0.651	0.095
2.03	$1.02 \times 10^{-3}$	44.6	0.217	0.656	0.127
1.41	$7.67 \times 10^{-4}$	42.9	0.195	0.647	0.158
0.972	$6.83 \times 10^{-4}$	37.7	0.170	0.640	0.189
0.563	$6.07 \times 10^{-4}$	30.5	0.147	0.635	0.220
0.339	$5.50 \times 10^{-4}$	24.8	0.126	0.622	0.252
0.131	$4.62 \times 10^{-4}$	16.8	0.103	0.617	0.280

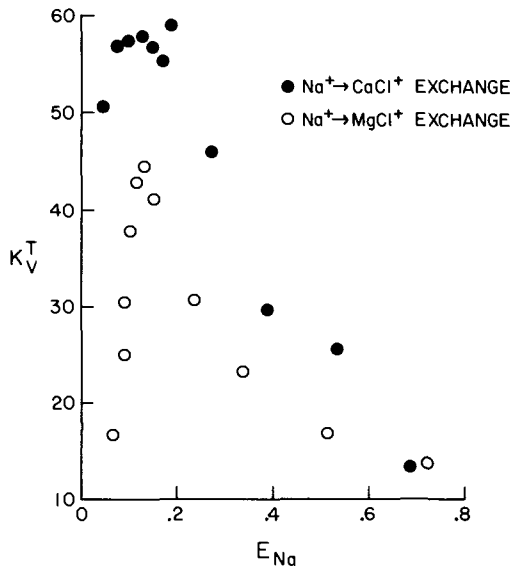


Fig. 3—The Vanselow selectivity coefficient for  $\text{Na}^+ \rightarrow \text{MCl}^+$  exchange ( $\text{M} = \text{Ca}$  or  $\text{Mg}$ ) on Wyoming bentonite as a function of the charge fraction of  $\text{Na}^+$  on the clay.

The differences between Fig. 1 and 2 can be elucidated further through an examination of Table 2. This table lists values for three ternary Vanselow selectivity coefficients along with the mole fractions of  $\text{Na}^+$ ,  $\text{M}^{2+}$ , and  $\text{MCl}^+$  ( $\text{M} = \text{Ca}$  or  $\text{Mg}$ ) on montmorillonite suspended in the chloride background medium. The selectivity coefficients in the first three columns of the table were calculated with Eq. [7] and refer to  $\text{Na}^+ \rightarrow \text{M}^{2+}$ ,  $\text{MCl}^+ \rightarrow \text{M}^{2+}$ , and  $\text{Na}^+ \rightarrow \text{MCl}^+$  exchange, respectively, where  $\text{M} = \text{Ca}$  or  $\text{Mg}$ . The exchanger composition data at a mole fraction of  $\text{Na}^+$  of 0.1 or less indicate that approximately equal numbers of the species,  $\text{Ca}^{2+}$  and  $\text{CaCl}^+$ , are adsorbed. However, only about one-half as many  $\text{MgCl}^+$  are adsorbed as there are  $\text{Mg}^{2+}$  on the clay surface. The calcium distribution, which is equivalent to two-thirds of  $Q_o$  satisfied by  $\text{Ca}^{2+}$  and one-third by  $\text{CaCl}^+$ , is consistent with the concept developed by Sposito et al. (1983), in which a Ca-montmorillonite suspended in a chloride ionic medium consists of quasicrystals having  $\text{Ca}^{2+}$  principally in the interlayer regions and  $\text{CaCl}^+$  principally on the external surfaces. However, in the case of Mg-montmorillonite, only about one-half of the charge on external surfaces evidently is neutralized by adsorbed  $\text{MgCl}^+$ . This smaller adsorption of  $\text{MgCl}^+$  reflects a smaller effect of the complex on  $\text{Na}^+$  selectivity, in agreement with the negligible difference between the isotherms in Fig. 2.

The third column of Table 2 lists values of  $K_V^T$  for the exchanges:  $\text{Na}^+ \rightarrow \text{CaCl}^+$  and  $\text{Na}^+ \rightarrow \text{MgCl}^+$ . These selectivity coefficients are plotted against  $E_{\text{Na}}$  in Fig. 3. Since  $K_V^T \gg 1.0$  for both exchanges, the clay surface is selective for  $\text{CaCl}^+$  and  $\text{MgCl}^+$  over  $\text{Na}^+$ . As  $E_{\text{Na}}$  decreases below 0.4,  $K_V^T$  increases sharply and reaches a maximum value at  $E_{\text{Na}} \approx 0.15$ , thereafter appearing to drop precipitously. The most rapid increase of  $K_V^T$  with decreasing  $E_{\text{Na}}$  occurs after quasicrystal formation, when the remaining exchangeable  $\text{Na}^+$  reside on external surfaces ( $E_{\text{Na}} < 0.4$ ). The reason for this behavior cannot be determined on the

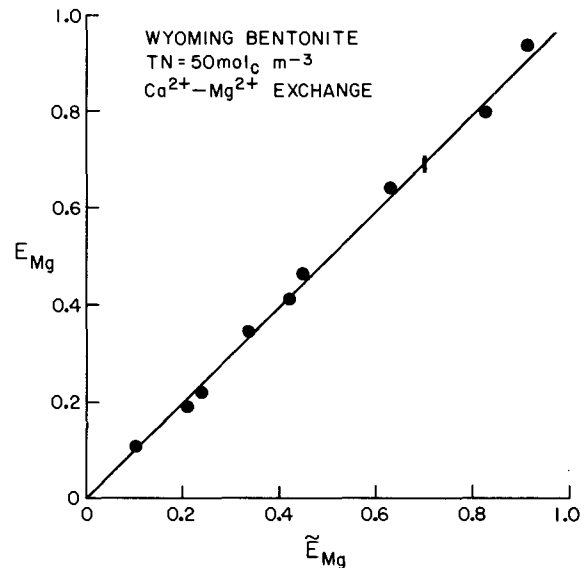


Fig. 4—Exchange isotherm for  $\text{Mg}^{2+}$  in  $\text{Ca} \rightarrow \text{Mg}$  exchange on Wyoming bentonite in 0.05M perchlorate. The solid line is the thermodynamic nonpreference isotherm.

basis of thermodynamic data alone. One possibility is related to the gradual breakdown of quasicrystals that has been observed to begin when  $E_{\text{Na}} \geq 0.15$  on Wyoming bentonite (Shainberg and Otoh, 1968; Banin, 1968; Bar-On et al., 1970; Dufey and Banin, 1979). When  $E_{\text{Na}}$  is very near zero, the quasicrystals remain intact and  $\text{MCl}^+$  is, evidently, increasingly preferred as  $E_{\text{Na}}$  grows larger. When  $E_{\text{Na}} > 0.15$  and the quasicrystals start to disintegrate, the high selectivity for  $\text{MCl}^+$  drops off because  $\text{Na}^+$  now is exchanging on both external and internal surfaces. The combination of these two trends could produce the behavior in Fig. 3.

Figure 4 shows an exchange isotherm, for  $\text{Mg}^{2+}$  in  $\text{Ca}^{2+} \rightarrow \text{Mg}^{2+}$  exchange on Wyoming bentonite, which was constructed with Eq. [6] from the data in Table 1. The thermodynamic nonpreference isotherm in this case is the straight line in the figure that makes a 45-degree angle with both coordinate axes (Sposito, 1981, Chap. 5). The vertical bar indicates the standard error in the measurements of  $E_{\text{Mg}}$ , which was  $\pm 0.01$ . It is apparent that, within the experimental precision, there is no preference for  $\text{Mg}^{2+}$  over  $\text{Ca}^{2+}$  on the clay mineral. A direct computation of the binary Vanselow selectivity coefficient,

$$K_V^B = \frac{x_{\text{Mg}^{2+}}(\text{Ca}^{2+})}{x_{\text{Ca}^{2+}}(\text{Mg}^{2+})}, \quad [9]$$

for each set of exchange data in Table 1 resulted in  $K_V^B = 1.0 \pm 0.2$ , thereby confirming the implication of Fig. 4. Within its experimental precision, this result is not in contradiction with the slight preference of  $\text{Na}^+$  over  $\text{Ca}^{2+}$  in a perchlorate background, indicated in Fig. 1, or the slight preference of  $\text{Mg}^{2+}$  over  $\text{Na}^+$  in a perchlorate background, indicated in Fig. 2. Since  $K_V^B$  in this case is equal to the ratio of the equilibrium constant for  $\text{Na}^+ \rightarrow \text{Mg}^{2+}$  exchange to that for  $\text{Na}^+ \rightarrow \text{Ca}^{2+}$  exchange, the former constant could be as much as 20% larger than the latter constant and still

be consistent with the reported standard deviation of  $\pm 0.2$  for  $K_V^B$ .

The isotherm in Fig. 4 differs from the results of the many studies that have been reported previously for Ca(II)-Mg(II) exchange in chloride background media (Clark, 1966; Hunsaker and Pratt, 1971; Levy et al., 1972; Levy and Shainberg, 1972; Gheyi and van Bladel, 1975; van Bladel and Gheyi, 1980), which imply a slight preference for Ca(II) over Mg(II). The mean values of the overall Vanselow selectivity coefficient for Mg(II)  $\rightarrow$  Ca(II) exchange (the inverse of  $K_{TV}$  in Eq. [1]) that can be calculated from the data reported by Levy and Shainberg (1972) and by van Bladel and Gheyi (1980) are  $1.47 \pm 0.19$  and  $1.26 \pm 0.20$ , respectively. The differences between these two results and the mean  $K_V^B$  determined in this study are concluded to be the result of the greater affinity of the clay for  $\text{CaCl}^+$  vs.  $\text{MgCl}^+$  in a chloride background medium.

### CONCLUSIONS

In a 0.05M perchlorate background at 25°C, the exchange isotherm for  $\text{Na}^+$  competing either with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  on Wyoming bentonite is very nearly congruent with the thermodynamic nonpreference isotherm. When the charge fraction of  $\text{Na}^+$  on the clay lies between 0.1 and 0.4, there is, at most, a slight preference for  $\text{Na}^+$  over  $\text{Ca}^{2+}$  and for  $\text{Mg}^{2+}$  over  $\text{Na}^+$ . The small enhancement in  $\text{Mg}^{2+}$  selectivity may be a result of the fact that about one-third of the permanent charge on the clay originates in the tetrahedral sheet, thus endowing the clay with some "vermiculite-like" character and a slight preference for  $\text{Mg}^{2+}$ .

In a 0.05M chloride background, the exchange isotherm for  $\text{Na}^+$  competing with species of Mg(II) does not appear to be detectably different from the corresponding isotherm in a perchlorate background. The exchange isotherm for  $\text{Na}^+$  competing with species of Ca(II) in a 0.05M chloride background does shift downward, however, to indicate a slight increase in preference for calcium species over  $\text{Na}^+$  when  $E_{\text{Na}}$  drops below 0.4. This shift is caused by the formation of  $\text{CaCl}^+$  complexes which compete strongly with  $\text{Na}^+$  on the external surfaces of quasicrystals.

In a 0.05M perchlorate background at 25°C, the exchange isotherm for  $\text{Mg}^{2+}$  competing with  $\text{Ca}^{2+}$  on Wyoming bentonite is indistinguishable, within experimental precision, from a thermodynamic nonpreference isotherm. Reports of a small preference for Ca(II) over Mg(II) on Wyoming bentonite in chloride background media reflect the greater affinity of the clay for  $\text{CaCl}^+$  vs.  $\text{MgCl}^+$ .

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