

# Sodium–Calcium Exchange with Anion Exclusion and Weathering Corrections

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## ABSTRACT

In order to accurately model soil reclamation with concentrated electrolytes such as  $\text{CaCl}_2$  or sea water, it must be determined if there is an effect of salinity on the Na–Ca exchange selectivity. A new procedure for determining Na–Ca selectivity in calcareous and gypsiferous soils was used to study the effects of ionic strength and mineralogy on Na–Ca exchange. Four specimen clay minerals and three whole soils were equilibrated with solutions ranging in concentration from 10 to 1000  $\text{mmol L}^{-1}$  and at Na adsorption ratios from 1 to 50 ( $\text{mmol L}^{-1}$ )<sup>1/2</sup>. Exchangeable-cation values were corrected for calcite and gypsum dissolution as well as anion exclusion. The selectivity data were compared with other reported values for Na–Ca exchange in order to determine if there were any trends in selectivity with mineralogy or surface charge density. Generally, Na–Ca selectivity was independent of ionic strength. Vermiculite exhibited near-ideal exchange when compared with the nonpreference isotherm. There was no effect of mineralogy on the Na–Ca selectivity, even though the soils and minerals had various surface charge densities. The Gapon selectivity coefficients ( $K_G$ ) for the calcareous Many Farms soil (a mesic Torrifluent) and the gypsiferous Shiprock soil (a mesic Torriorthent) averaged 0.011 and 0.013 ( $\text{mmol L}^{-1}$ )<sup>-1/2</sup>, respectively. Failure to correct for anion exclusion and min-

eral weathering lowered these average  $K_G$  values to 0.0085 and 0.0064, respectively. The data were compared with the Vanselow ( $K_V = 4.3$ ), nonpreference ( $K_V = 1.0$ ), Gapon ( $K_G = 0.015$ ), and the diffuse double-layer (DDL) models. After the review of the problems associated with the various methods of determining exchangeable cations, we recommend that the alcohol rinse method to remove soluble salts not be used.

MANY SALT-AFFECTED SOILS require the addition of chemical amendments prior to leaching to remove soluble salts and replace adsorbed  $\text{Na}^+$ . In order to calculate the amount of amendment needed to reclaim a sodic soil, knowledge is required of the equilibrium relationship between the solution and exchanger phase composition of the soil. Traditionally, this relationship has been described using the Gapon convention and conveniently expressed by the linear equation

$$\text{ESR} = (K_G \text{ SAR}) + x \quad [1]$$

where ESR (exchangeable sodium ratio) is equal to  $E_{\text{Na}}/E_{(\text{Ca}+\text{Mg})}$ , where  $E_i$  is the equivalent fraction of cation  $i$  on the exchanger phase, SAR is the sodium adsorption ratio of the solution phase defined as  $\text{Na}^+/\sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})}$  with concentrations in  $\text{mmol L}^{-1}$ . Since  $x$  is a small intercept value, often assumed to

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be zero (U.S. Salinity Laboratory Staff, 1954), the value of  $K_G$  can be equated to ESR/SAR and is generally assumed to be a constant over a wide range of soil types, salinity, and exchangeable  $\text{Na}^+$ . The U.S. Salinity Laboratory Staff (1954) reported an average value for  $K_G$  of  $0.015 \text{ (mmol L}^{-1}\text{)}^{-1/2}$  on 59 soil samples from the western USA.

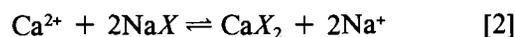
Many workers have reported variations in  $K_G$ , and it is felt by many to be site specific (Levy and Hillel, 1968; Doering and Willis, 1980; Nadler and Magaritz, 1981). Two factors that are known to affect the Na-Ca selectivity relationship are organic-matter content (organic matter tends to increase  $\text{Ca}^{2+}$  preference [Pratt and Grover, 1964; Fletcher et al., 1984b]) and pH (particularly in soils containing large amounts of variable-charge materials [Pratt et al., 1962]). In addition, the DDL theory for cation adsorption predicts an increasing  $\text{Ca}^{2+}$  preference with increasing ionic strength and decreasing exchangeable  $\text{Na}^+$  (Babcock, 1963).

The reported changes in Na-Ca selectivity as a function of salinity and exchanger phase composition have been quite variable. Bower (1959) found that the  $K_G$  of a montmorillonitic clay soil was not significantly affected by solution concentration ( $50\text{--}200 \text{ mmol}_c \text{ L}^{-1}$ ) but increased with increasing exchangeable  $\text{Na}^+$ ; that is,  $\text{Na}^+$  preference increased with increasing  $E_{\text{Na}}$ . Similar results were found by Pratt et al. (1962) on a soil high in amorphous clays and kaolinite and equilibrated with solutions that ranged in concentration from 50 to  $330 \text{ mmol}_c \text{ L}^{-1}$ . They also found that the selectivity coefficient of this soil was strongly pH dependent.

On the other hand, Doering and Willis (1980) reported that the  $K_G$  of a strip-mine spoil material (montmorillonitic) was constant with variations in  $E_{\text{Na}}$  but showed a strong dependence on ionic strength, decreasing from  $0.0163$  to  $0.0085 \text{ (mmol L}^{-1}\text{)}^{-1/2}$  at ionic strengths from  $0.04$  to  $1.06 \text{ mol}_c \text{ L}^{-1}$ , respectively.

Jurinak et al. (1984) reported that  $K_G$  was a constant for a montmorillonitic soil from the Central Valley of California and for a surface overburden material from Montana at all concentrations and SAR values studied ( $0.01\text{--}0.5 \text{ mol}_c \text{ L}^{-1}$  and  $5\text{--}80 \text{ (mmol L}^{-1}\text{)}^{1/2}$ , respectively). On a sample of kaolinitic deep overburden material,  $K_G$  varied from  $0.0138$  to  $0.0047 \text{ (mmol L}^{-1}\text{)}^{-1/2}$  across the concentration range  $0.01$  to  $0.5 \text{ mol}_c \text{ L}^{-1}$ , respectively. They suggested that variations in clay mineralogy were a prime factor determining the ESR-SAR relationship. They also noted that correction for anion exclusion was necessary at concentrations  $> 100 \text{ mmol}_c \text{ L}^{-1}$  for accurate exchangeable- $\text{Na}^+$  values.

Another convention for describing cation exchange was proposed by Vanselow (1932), in which the activity of the exchangeable cations are equated to their mole fraction ( $N_i$ ) on the exchanger and activity is used for ions in solution. This is in contrast to the Gapon convention, in which solution concentration is used. The mass-action expression for Na-Ca exchange and the Vanselow selectivity coefficient ( $K_V$ ) for the reaction are as follows:



$$K_V = \frac{(a_{\text{Na}^+})^2 (N_{\text{Ca}^{2+}})}{(a_{\text{Ca}^{2+}}) (N_{\text{Na}^+})^2} \quad [3]$$

where  $X^-$  refers to an exchange site with a charge of  $-1$ , and  $a_i$  is the activity of the  $i$  ion in solution.

Evaluation of existing data sets must consider the different methods used for determining exchangeable cations. Not all of the methods used account for anion exclusion and it appears that some procedures are preferred to others.

Additional uncertainty is introduced by the lack of correction for mineral weathering (calcite and gypsum dissolution) during the extraction of exchangeable cations.

The following work was done to evaluate the effect of ionic strength and mineralogy on Na-Ca selectivity using a new procedure that accounts for mineral weathering and anion exclusion. These data are compared with results of previous determinations of Na-Ca selectivity of soils and minerals. The various procedures for determining exchangeable cations are discussed and several previously measured selectivities redetermined using the alternative procedure.

## MATERIALS AND METHODS

Three salt-affected soils and four specimen phyllosilicate minerals were chosen for this study. Table 1 lists some general characteristics of the soils and minerals studied. The soils differ mainly in mineralogy. The Imperial Valley clay was sampled in the Imperial Valley of California from an area mapped as Imperial Clay series and classified as a fine, montmorillonitic (calcareous), hyperthermic Vertic Torrifluent. The Shiprock and Many Farms soils were sampled on the Navajo Indian Reservation near the locations of the same name. The Shiprock soil has not been mapped, but appears to be a mesic Torriorthent (possibly Shalet or Fruitland series). The Many Farms soil is also unmapped, but appears to be a mesic Torrifluent (possibly Tours or Navajo series). The surface soils (0-15 cm) were used in these studies.

The phyllosilicate minerals used were Wyoming bentonite (SWy-1) as received from the Source Clays Repository; Silver

Table 1. Characterization of the soils and clay minerals used in this study.

Soil/mineral	Dominant clay mineralogy†	CaCO <sub>3</sub>	Gypsum	Cation-exchange capacity	EGME‡ surface area	Surface charge density
		equiv.		mol <sub>c</sub> kg <sup>-1</sup>	m <sup>2</sup> g <sup>-1</sup>	μmol <sub>c</sub> m <sup>-2</sup>
Imperial Valley clay	S,V,M,K	109	trace	0.30	295	1.02
Shiprock topsoil	V,K,M,C	113	93	0.12	115	1.05
Many Farms topsoil	M,V,S,K	139	0	0.14	121	1.12
Wyoming montmorillonite (SWy-1)	S	trace	N.D.	0.68	753	0.91
Silver Hill illite (IMt-1)	M	0	N.D.	0.14	119	1.14
Utah vermiculite	V	0	N.D.	0.72	173	1.14
South Carolina kaolinite no. 5, Lamar Pit	K	0	N.D.	0.026	N.D.	N.D.

(at pH 7.8)

† Mineralogy key (based on x-ray diffraction peak intensity): S, smectite; V, vermiculite; M, mica (illite); K, kaolinite; C, chlorite.

‡ EGME = ethylene glycol monoethyl ether.

Hill illite, also from the Source Clays Repository, ground and sieved to  $<250 \mu\text{m}$ ; Utah vermiculite, ground to  $<250 \mu\text{m}$  (obtained from J. Rhoades and described by Rhoades, 1967); and kaolinite no. 5 from the Lamar Pit, Bath, SC, also from the Source Clays Repository, ( $<50 \mu\text{m}$ ). These four minerals represent the dominant clay minerals found in arid-land soils.

The samples were weighed (1–5 g) into tared 50-mL polycarbonate centrifuge tubes and equilibrated with solutions of various concentrations and SAR values by repeated shaking, centrifuging, and decanting. The solutions were predominately  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Cl}^-$  with small amounts of  $\text{NaOH}$ ,  $\text{NaHCO}_3$ , or  $\text{HCl}$  added for pH adjustment. The initial solution compositions were 25, 50, 125, 500, and 1000  $\text{mmol}_c \text{L}^{-1}$  with SAR values of 5, 15, 25, and 50 ( $\text{mmol}_c \text{L}^{-1})^{1/2}$ . The kaolinite samples were treated in a similar manner except the solutions used were made to SAR values of 1, 2, 4.2, 15, and 25 ( $\text{mmol}_c \text{L}^{-1})^{1/2}$  and a total concentration of ten  $\text{mmol}_c \text{L}^{-1}$ . These solutions were made with  $\text{NaCl}$ ,  $\text{NaHCO}_3$ , and  $\text{CaCl}_2$  and each solution contained 2  $\text{mmol}_c \text{HCO}_3^- \text{L}^{-1}$  for pH control. All equilibrations were replicated four times. In this study, the solutions were made with Na and Ca (no Mg) and the SAR values are calculated as  $\text{Na}/\sqrt{\text{Ca}}$ , with concentrations in  $\text{mmol}_c \text{L}^{-1}$ .

Following the third or fourth equilibration (depending on the solution concentration) the last decantate was saved and the volume of solution entrained in the centrifuged soil determined by weighing the tube plus the wet soil. The wet soil was then extracted with 0.25 M  $\text{Mg}(\text{NO}_3)_2$  using three sequential rinses and brought to a total volume of 0.10 L. The last decantate and the  $\text{Mg}(\text{NO}_3)_2$  extracting solutions were analyzed for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{SO}_4^{2-}$  using inductively coupled plasma emission spectrometry,  $\text{Cl}^-$  by argentometric titration, and  $\text{HCO}_3^-$  by acid titration to pH 4.40. Methodology and calculations for exchangeable cations are detailed in Amrhein and Suarez (1990) and will be briefly summarized here. Two methods were used to calculate exchangeable cations and anion exclusion based on modifications of the methods outlined in Bolt et al. (1978, p. 59). Method A uses the anions found in the  $\text{Mg}(\text{NO}_3)_2$  extract to calculate the soluble cations and assumes that the equivalent fraction of  $\text{Na}^+$  in the bulk solution (last decant) is equal to the equivalent fraction of  $\text{Na}^+$  in the solution entrained in the wet soil after centrifugation. Method B uses the weight of the wet soil after centrifugation to calculate the entrained solution volume and assumes that the concentration of cations in the bulk solution and in the entrained solution are equal. Anion exclusion can be accounted for in Method B if the anions in the bulk solution and  $\text{Mg}(\text{NO}_3)_2$  extract are measured (but this extra step is usually not done).

Correction for calcite and gypsum dissolution during the  $\text{Mg}(\text{NO}_3)_2$  extracting step was calculated by assuming that the  $\text{SO}_4^{2-}$  in the  $\text{Mg}(\text{NO}_3)_2$  extract was derived from  $\text{SO}_4^{2-}$  in the entrained solution and  $\text{SO}_4^{2-}$  from gypsum dissolution. The quantity of  $\text{SO}_4^{2-}$  from gypsum dissolution was subtracted from the extracted  $\text{Ca}^{2+}$ . Likewise, the quantity of  $\text{HCO}_3^-$  in the  $\text{Mg}(\text{NO}_3)_2$ , in excess of that which was in the entrained solution, was attributed to calcite dissolution and the extracted  $\text{Ca}^{2+}$  corrected accordingly (Amrhein and Suarez, 1990). The reported exchangeable- $\text{Na}^+$  values were determined using this modified Method A, which accounts for anion exclusion and mineral weathering during the equilibrating and extracting steps. Both Methods A and B yield the same cation-exchange capacity (CEC) values when anion exclusion and mineral weathering are properly taken into account (Amrhein and Suarez, 1990). Solution ion activities were calculated using the speciation program WATEQF (Plummer et al., 1976).

## RESULTS AND DISCUSSION

Table 2 gives the solution and exchanger phase data for the four clay minerals and three soils studied. The

value of  $K_G$  was calculated using the total concentration of cations in solution, and the value of  $K_V$  was calculated using the solution ion activities. Utah vermiculite exhibited an increase in  $K_G$  with both increasing concentration and increasing exchangeable  $\text{Na}^+$  (Table 2).

Using the Vanselow expression, the calculated thermodynamic nonpreference isotherms fit the vermiculite exchange data reasonably well (Fig. 1), indicating that Utah vermiculite behaved as an ideal exchanger ( $K_V = 1.0$ ) across all concentrations studied. Also plotted in Fig. 1 are Na–Ca exchange data on Transvaal, South Africa, vermiculite ("World vermiculite," Wild and Keay, 1964) and Utah vermiculite (Rhoades, 1967), which show reasonable agreement with the data of our study. These specimen vermiculites exhibited  $K_G$  values that were much higher than all the other minerals and soils studied (see below). Rhoades (1967) also reported unusually high  $K_G$  values for this specimen vermiculite and found that the  $K_G$  values decreased with increasing temperature while the Na–Ca selectivity on specimen montmorillonites was unaffected by temperature. This suggests that the 1.5-nm c-spacing on vermiculite is strongly affected by temperature but not concentration or SAR values. As the temperature increases, the inner-layer spacing opens, allowing access of the large  $\text{Ca}^{2+}$  ions. The unusually high  $K_G$  values suggest that the large hydrated radius of  $\text{Ca}^{2+}$ , compared with  $\text{Na}^+$ , restricts free access to the inner-layer sites on vermiculite. A similar explanation was proposed by Levy and Shainberg (1972) to explain Ca–Mg selectivity on vermiculite.

The  $K_G$  values for Wyoming montmorillonite tended to increase with increasing exchangeable  $\text{Na}^+$ , particularly at lower concentrations, and decrease with increasing ionic strength (Table 2). This is in contrast to the  $K_V$  values, which tended to increase with increasing ionic strength. That is, the selectivity for  $\text{Ca}^{2+}$  increased

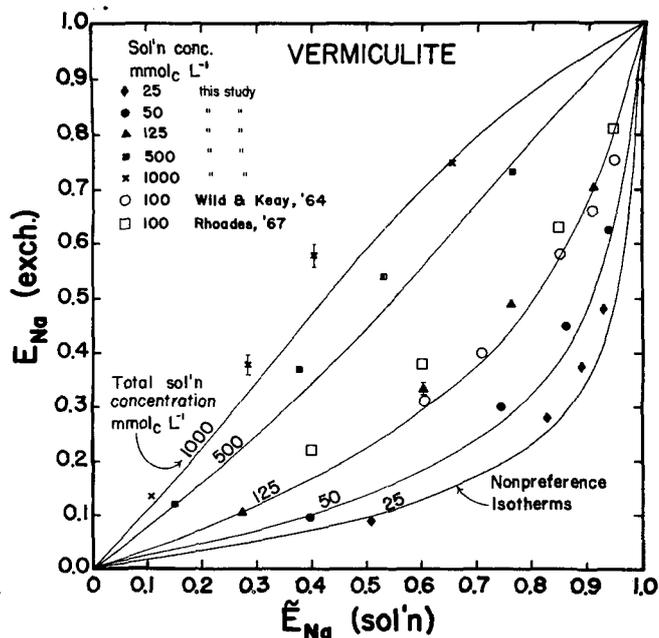


Fig. 1. Equivalent fraction of Na in solution ( $E_{\text{Na}}$ ) vs. equivalent fraction of Na on the exchanger ( $\bar{E}_{\text{Na}}$ ). Standard deviations are shown by vertical bars (often smaller than the symbols and reported only for the data collected in this study).

Table 2. Solution and exchanger compositions and selectivity coefficients for the clay minerals and soils used in this study.

	Initial equilibrating solution		Final Equilibrium Solution				$N_{Na^+} \pm SD\text{\S}$	$K_v \pm SD\text{\ }$	$K_G \pm SD\text{\#}$
	Concentration	SAR†	SAR	pH	$a_{Na^+}\ddagger$	$a_{Ca^{2+}}$			
	mmol <sub>c</sub> L <sup>-1</sup>	(mmol L <sup>-1</sup> ) <sup>1/2</sup>			$\times 10^3$				
Utah vermiculite	25	5	5.1	7.8	10.7	3.26	0.16 ± 0.01	1.09 ± 0.01	0.019 ± 0.000
	50	5	5.1	7.7	16.1	6.66	0.18 ± 0.00	1.04 ± 0.01	0.021 ± 0.000
	125	5	5.0	7.4	24.8	14.8	0.19 ± 0.00	0.93 ± 0.02	0.024 ± 0.000
	500	5	5.1	7.2	52.9	53.0	0.21 ± 0.01	0.91 ± 0.08	0.027 ± 0.002
	1000	5	5.0	7.5	79.3	116.0	0.24 ± 0.00	0.73 ± 0.02	0.031 ± 0.001
	25	15	13.8	7.0	17.2	1.16	0.44 ± 0.00	0.74 ± 0.01	0.028 ± 0.000
	50	15	14.7	7.2	30.2	2.91	0.46 ± 0.00	0.78 ± 0.01	0.030 ± 0.000
	125	15	15.1	7.2	57.1	8.60	0.50 ± 0.01	0.76 ± 0.08	0.033 ± 0.000
	500	15	15.0	7.1	135.0	39.7	0.54 ± 0.00	0.73 ± 0.01	0.039 ± 0.000
	1000	15	15.0	7.1	210.0	92.8	0.55 ± 0.02	0.72 ± 0.09	0.041 ± 0.003
	25	25	19.0	8.3	19.2	0.76	0.55 ± 0.00	0.74 ± 0.02	0.032 ± 0.000
	50	25	23.2	8.4	35.2	1.59	0.62 ± 0.00	0.77 ± 0.00	0.035 ± 0.000
	125	25	24.6	8.3	71.9	5.21	0.66 ± 0.00	0.79 ± 0.01	0.039 ± 0.000
	500	25	24.3	8.0	191.0	30.3	0.70 ± 0.00	0.73 ± 0.02	0.048 ± 0.002
	1000	25	24.8	7.7	308.0	72.6	0.73 ± 0.01	0.66 ± 0.04	0.055 ± 0.003
	25	50	24.7	7.2	19.9	0.48	0.65 ± 0.01	0.68 ± 0.03	0.038 ± 0.001
	50	50	37.8	7.8	37.6	0.68	0.77 ± 0.00	0.80 ± 0.01	0.044 ± 0.001
	125	50	48.0	8.2	85.8	1.96	0.83 ± 0.00	0.95 ± 0.01	0.050 ± 0.000
	500	50	50.0	8.0	277.0	15.4	0.85 ± 0.00	1.07 ± 0.01	0.055 ± 0.000
	1000	50	50.0	7.4	481.0	43.8	0.86 ± 0.00	1.03 ± 0.01	0.060 ± 0.001
Wyoming montmorillonite	25	5	5.2	7.6	11.0	3.18	0.15 ± 0.01	1.4 ± 0.1	0.017 ± 0.001
	50	5	5.2	7.5	16.4	6.65	0.14 ± 0.01	1.9 ± 0.4	0.015 ± 0.001
	125	5	5.0	7.4	26.2	15.2	0.14 ± 0.01	2.1 ± 0.2	0.016 ± 0.001
	500	5	5.1	7.1	53.4	52.8	0.13 ± 0.02	3.0 ± 0.9	0.015 ± 0.002
	1000	5	5.0	7.1	81.3	121.0	0.13 ± 0.02	2.8 ± 0.9	0.016 ± 0.003
	25	15	20.2	7.8	18.9	0.65	0.45 ± 0.00	1.4 ± 0.0	0.021 ± 0.000
	50	15	15.6	7.9	29.9	2.44	0.31 ± 0.02	2.6 ± 0.5	0.015 ± 0.001
	125	15	14.8	7.6	56.3	8.73	0.28 ± 0.01	3.4 ± 0.4	0.013 ± 0.001
	500	15	15.0	7.1	132.0	39.0	0.32 ± 0.00	3.1 ± 0.1	0.015 ± 0.000
	1000	15	15.0	7.2	212.0	93.4	0.28 ± 0.01	4.5 ± 0.4	0.013 ± 0.001
	25	25	36.1	8.9	20.8	0.25	0.66 ± 0.01	1.4 ± 0.1	0.027 ± 0.001
	50	25	27.8	8.5	36.5	1.20	0.54 ± 0.01	1.8 ± 0.1	0.021 ± 0.001
	125	25	24.7	8.0	72.1	5.19	0.45 ± 0.01	2.8 ± 0.1	0.016 ± 0.000
	500	25	24.7	7.3	195.0	30.6	0.43 ± 0.01	3.8 ± 0.2	0.015 ± 0.001
	1000	25	25.0	7.2	326.0	76.8	0.44 ± 0.01	4.0 ± 0.4	0.016 ± 0.001
	25	50	47.4	9.1	21.4	0.15	0.74 ± 0.00	1.5 ± 0.0	0.029 ± 0.001
	50	50	50.7	8.6	39.3	0.41	0.75 ± 0.00	1.6 ± 0.5	0.029 ± 0.001
	125	50	49.3	7.8	86.9	1.90	0.69 ± 0.01	2.6 ± 0.2	0.023 ± 0.001
	500	50	50.0	7.9	277.0	15.3	0.63 ± 0.00	4.8 ± 0.1	0.017 ± 0.000
	1000	50	50.0	7.3	481.9	43.9	0.62 ± 0.01	5.2 ± 0.2	0.016 ± 0.000
Silver Hill illite	25	5	5.3	7.2	11.1	3.26	0.20 ± 0.01	0.8 ± 0.1	0.024 ± 0.001
	50	5	5.0	7.0	15.8	6.72	0.18 ± 0.01	1.0 ± 0.2	0.021 ± 0.002
	125	5	5.0	7.2	25.5	15.4	0.17 ± 0.01	1.2 ± 0.1	0.021 ± 0.001
	500	5	5.0	7.0	52.0	53.6	0.15 ± 0.01	2.1 ± 0.5	0.017 ± 0.002
	1000	5	5.0	6.7	79.5	118.0	0.18 ± 0.01	1.4 ± 0.2	0.022 ± 0.001
	25	15	14.2	8.1	17.9	1.18	0.29 ± 0.01	2.3 ± 0.1	0.015 ± 0.001
	50	15	14.7	8.2	30.5	2.96	0.30 ± 0.00	2.5 ± 0.1	0.015 ± 0.000
	125	15	15.1	7.6	57.1	8.56	0.30 ± 0.00	2.9 ± 0.1	0.014 ± 0.000
	500	15	15.3	7.2	132.0	37.1	0.22 ± 0.02	7.6 ± 2.6	0.009 ± 0.001
	1000	15	15.0	6.7	208.0	90.1	0.31 ± 0.04	3.6 ± 1.2	0.015 ± 0.003
	25	25	24.5	7.1	19.9	0.49	0.41 ± 0.01	2.9 ± 0.1	0.014 ± 0.000
	50	25	29.9	7.3	36.4	1.00	0.46 ± 0.01	3.3 ± 0.1	0.014 ± 0.000
	125	25	24.9	7.2	73.0	5.21	0.43 ± 0.00	3.1 ± 0.1	0.015 ± 0.000
	500	25	25.1	7.0	191.0	29.2	0.38 ± 0.01	5.4 ± 0.5	0.012 ± 0.001
	1000	25	25.1	6.9	303.0	69.2	0.37 ± 0.01	6.0 ± 0.7	0.012 ± 0.001
	25	50	41.6	6.2	20.5	0.18	0.55 ± 0.01	3.4 ± 0.2	0.015 ± 0.000
	50	50	47.8	6.8	39.2	0.47	0.59 ± 0.00	4.0 ± 0.1	0.015 ± 0.000
	125	50	44.4	6.8	101.0	3.06	0.58 ± 0.01	4.1 ± 0.1	0.016 ± 0.000
	500	50	48.2	6.7	252.0	14.0	0.61 ± 0.01	4.8 ± 0.2	0.016 ± 0.001
	1000	50	49.7	7.0	458.0	40.5	0.57 ± 0.02	6.9 ± 1.0	0.013 ± 0.001
South Carolina kaolinite	10	1.0	1.1	7.7	1.86	2.43	0.06 ± 0.01	0.4 ± 0.2	0.030 ± 0.006
	10	2.0	2.3	7.7	3.55	1.86	0.08 ± 0.01	1.1 ± 0.2	0.018 ± 0.002
	10	4.2	4.6	7.8	5.62	1.20	0.09 ± 0.01	2.8 ± 0.1	0.011 ± 0.001
	10	15	16.4	7.8	8.32	0.21	0.28 ± 0.01	3.0 ± 0.3	0.012 ± 0.001
	10	25	35.9	7.8	8.91	0.05	0.47 ± 0.01	3.9 ± 0.1	0.012 ± 0.000

(continued)

† SAR, sodium adsorption ratio =  $Na^+/\sqrt{Ca^{2+}}$  with concentration in mmol/L.

‡  $a_{Na^+}$ ,  $a_{Ca^{2+}}$  are activity of  $Na^+$  and  $Ca^{2+}$ , respectively.

§  $N_{Na^+}$  is the mole fraction of  $Na^+$  on the exchanger.

¶  $K_v$ , Vanselow selectivity coefficient =  $N_{Ca^{2+}}(a_{Na^+})^2/N_{Na^+}(a_{Ca^{2+}})$ .

#  $K_G$ , Gapon selectivity coefficient = exchangeable Na ratio/SAR.

Table 2. (continued).

	Initial equilibrating solution		Final Equilibrium Solution				$N_{Na^+} \pm SD\text{§}$	$K_v \pm SD\text{¶}$	$K_G \pm SD\#$
	Concentration	SAR†	SAR	pH	$a_{Na^+}\ddagger$	$a_{Ca^{2+}}$			
	mmol <sub>e</sub> L <sup>-1</sup>	(mmol L <sup>-1</sup> ) <sup>1/2</sup>			$\times 10^3$				
Imperial Valley clay	25	5	5.4	7.8	11.0	3.05	0.10 ± 0.00	3.5 ± 0.2	0.011 ± 0.000
	50	5	5.1	7.7	15.7	6.48	0.09 ± 0.00	3.8 ± 0.1	0.010 ± 0.000
	125	5	5.0	7.7	25.4	15.2	0.09 ± 0.00	4.4 ± 0.3	0.010 ± 0.000
	500	5	5.0	7.3	50.7	52.1	0.09 ± 0.00	6.0 ± 0.3	0.010 ± 0.000
	1000	5	5.0	7.1	79.5	118.0	0.12 ± 0.02	3.9 ± 1.5	0.013 ± 0.003
	25	15	15.0	7.5	17.9	1.06	0.27 ± 0.00	3.1 ± 0.1	0.012 ± 0.000
	50	15	15.4	7.7	30.8	2.74	0.27 ± 0.00	3.6 ± 0.0	0.012 ± 0.000
	125	15	15.1	6.8	56.9	8.56	0.26 ± 0.01	4.3 ± 0.3	0.011 ± 0.000
	500	15	15.0	7.2	134.0	39.3	0.23 ± 0.01	6.4 ± 0.5	0.010 ± 0.000
	1000	15	15.0	7.1	212.0	93.4	0.25 ± 0.01	5.9 ± 0.8	0.011 ± 0.001
	25	25	20.6	8.3	19.1	0.64	0.33 ± 0.00	3.5 ± 0.1	0.012 ± 0.000
	50	25	24.2	8.4	34.9	1.42	0.37 ± 0.00	3.9 ± 0.0	0.012 ± 0.000
	125	25	24.9	8.0	71.7	5.05	0.38 ± 0.00	4.4 ± 0.2	0.012 ± 0.000
	500	25	24.5	7.7	188.0	29.5	0.33 ± 0.01	7.2 ± 0.8	0.010 ± 0.001
	1000	25	25.0	7.1	314.0	74.4	0.36 ± 0.01	6.7 ± 0.5	0.011 ± 0.000
	25	50	25.5	7.9	20.4	0.47	0.40 ± 0.00	3.3 ± 0.0	0.013 ± 0.000
	50	50	37.7	8.1	39.0	0.74	0.51 ± 0.00	3.8 ± 0.1	0.014 ± 0.000
	125	50	38.1	8.1	86.2	3.11	0.57 ± 0.00	3.2 ± 0.1	0.017 ± 0.000
	500	50	50.0	7.5	268.0	17.0	0.53 ± 0.00	7.3 ± 0.2	0.011 ± 0.000
	1000	50	50.0	7.3	481.0	43.9	0.55 ± 0.00	7.9 ± 0.2	0.012 ± 0.000
Shiprock topsoil	25	5	4.6	8.2	10.7	3.74	0.10 ± 0.00	3.1 ± 0.1	0.011 ± 0.000
	50	5	4.7	7.8	15.5	7.04	0.10 ± 0.01	3.4 ± 0.6	0.011 ± 0.001
	125	5	4.9	8.0	25.3	15.6	0.10 ± 0.00	3.7 ± 0.3	0.011 ± 0.000
	500	5	5.0	7.7	51.8	53.0	0.10 ± 0.00	4.4 ± 0.4	0.011 ± 0.001
	1000	5	4.9	7.7	78.9	119.0	0.12 ± 0.02	3.4 ± 1.7	0.014 ± 0.003
	25	15	11.2	7.4	17.7	1.75	0.22 ± 0.00	3.0 ± 0.1	0.012 ± 0.000
	50	15	13.3	7.3	29.8	3.30	0.23 ± 0.01	3.8 ± 0.3	0.012 ± 0.001
	125	15	14.2	7.1	56.1	9.15	0.26 ± 0.01	3.7 ± 0.4	0.013 ± 0.001
	500	15	14.9	7.6	133.0	39.2	0.14 ± 0.01	16.9 ± 1.6	0.006 ± 0.003
	1000	15	15.0	7.7	211.0	93.1	0.12 ± 0.03	31.8 ± 15.	0.005 ± 0.001
	25	25	15.1	8.4	18.8	1.10	0.25 ± 0.00	4.0 ± 0.1	0.011 ± 0.000
	50	25	20.9	8.3	35.3	1.90	0.31 ± 0.01	4.7 ± 0.3	0.011 ± 0.000
	125	25	24.2	7.9	72.7	5.40	0.35 ± 0.01	5.2 ± 0.7	0.011 ± 0.001
	500	25	24.5	7.8	187.0	29.3	0.27 ± 0.03	12.1 ± 3.0	0.008 ± 0.001
	1000	25	24.9	7.7	316.0	75.9	0.31 ± 0.02	9.4 ± 1.9	0.009 ± 0.001
	25	50	18.3	8.7	20.1	0.85	0.27 ± 0.00	4.6 ± 0.0	0.010 ± 0.000
	50	50	14.9	7.1	37.3	3.51	0.29 ± 0.01	3.4 ± 0.2	0.014 ± 0.000
	125	50	32.0	7.1	84.9	3.96	0.47 ± 0.01	4.3 ± 0.3	0.014 ± 0.001
	500	50	46.3	6.8	267.0	16.8	0.60 ± 0.01	4.8 ± 0.3	0.016 ± 0.001
	1000	50	48.0	6.9	469.0	45.4	0.62 ± 0.00	4.9 ± 0.1	0.017 ± 0.000
Many Farms topsoil	25	5	5.2	8.3	10.9	3.30	0.12 ± 0.01	2.1 ± 0.4	0.014 ± 0.002
	50	5	4.9	8.2	15.6	6.67	0.12 ± 0.01	2.5 ± 0.7	0.013 ± 0.002
	125	5	5.0	8.1	25.6	15.3	0.11 ± 0.01	3.7 ± 0.4	0.012 ± 0.001
	500	5	5.1	7.7	53.0	53.2	0.09 ± 0.02	6.5 ± 3.0	0.010 ± 0.002
	1000	5	5.0	7.7	79.5	118.0	0.13 ± 0.00	2.7 ± 0.1	0.015 ± 0.000
	25	15	14.3	7.6	17.4	1.10	0.26 ± 0.01	3.0 ± 0.3	0.012 ± 0.001
	50	15	14.7	7.5	30.0	2.86	0.26 ± 0.00	3.3 ± 0.1	0.012 ± 0.000
	125	15	14.8	7.3	55.8	8.59	0.26 ± 0.01	4.1 ± 0.3	0.012 ± 0.000
	500	15	15.0	7.1	136.0	40.1	0.26 ± 0.01	5.3 ± 0.2	0.011 ± 0.000
	1000	15	15.0	7.0	211.0	93.4	0.26 ± 0.02	5.4 ± 1.0	0.012 ± 0.001
	25	25	21.6	8.6	19.4	0.60	0.35 ± 0.01	3.3 ± 0.1	0.013 ± 0.000
	50	25	23.8	8.4	34.7	1.47	0.35 ± 0.00	4.3 ± 0.0	0.011 ± 0.000
	125	25	24.6	7.9	70.6	5.01	0.36 ± 0.01	4.9 ± 0.5	0.012 ± 0.001
	500	25	24.0	7.6	181.0	28.2	0.36 ± 0.01	5.7 ± 0.4	0.012 ± 0.000
	1000	25	25.0	7.8	314.0	74.4	0.35 ± 0.05	7.3 ± 3.0	0.011 ± 0.000
	25	50	26.0	8.9	20.7	0.47	0.46 ± 0.00	2.3 ± 0.1	0.017 ± 0.000
	50	50	33.4	8.6	38.7	0.93	0.56 ± 0.00	2.2 ± 0.0	0.019 ± 0.000
	125	50	44.8	8.4	87.9	2.35	0.60 ± 0.00	3.7 ± 0.1	0.017 ± 0.000
	500	50	49.4	7.5	273.0	15.3	0.59 ± 0.01	5.8 ± 0.3	0.015 ± 0.001
	1000	50	49.9	7.6	474.0	43.0	0.55 ± 0.02	7.6 ± 1.0	0.013 ± 0.001

† SAR, sodium adsorption ratio =  $Na^+/\sqrt{Ca^{2+}}$  with concentration in mmol/L.

‡  $a_{Na^+}$ ,  $a_{Ca^{2+}}$  are activity of  $Na^+$  and  $Ca^{2+}$ , respectively.

§  $N_{Na^+}$  is the mole fraction of  $Na^+$  on the exchanger.

¶  $K_v$ , Vanselow selectivity coefficient =  $N_{Ca^{2+}}(a_{Na^+})^2/N_{Na^+}(a_{Ca^{2+}})$ .

#  $K_G$ , Gapon selectivity coefficient = exchangeable Na ratio/SAR.

with increasing total concentration and decreased with increasing exchangeable  $Na^+$ . These trends are in qualitative agreement with DDL theory (Babcock, 1963). Shainberg et al. (1980) modified the DDL theory for

ion demixing and obtained good agreement for Na-Ca exchange on Wyoming montmorillonite.

The Silver Hill illite exhibited a fairly constant  $K_G$  value, except at low SAR values where the preference

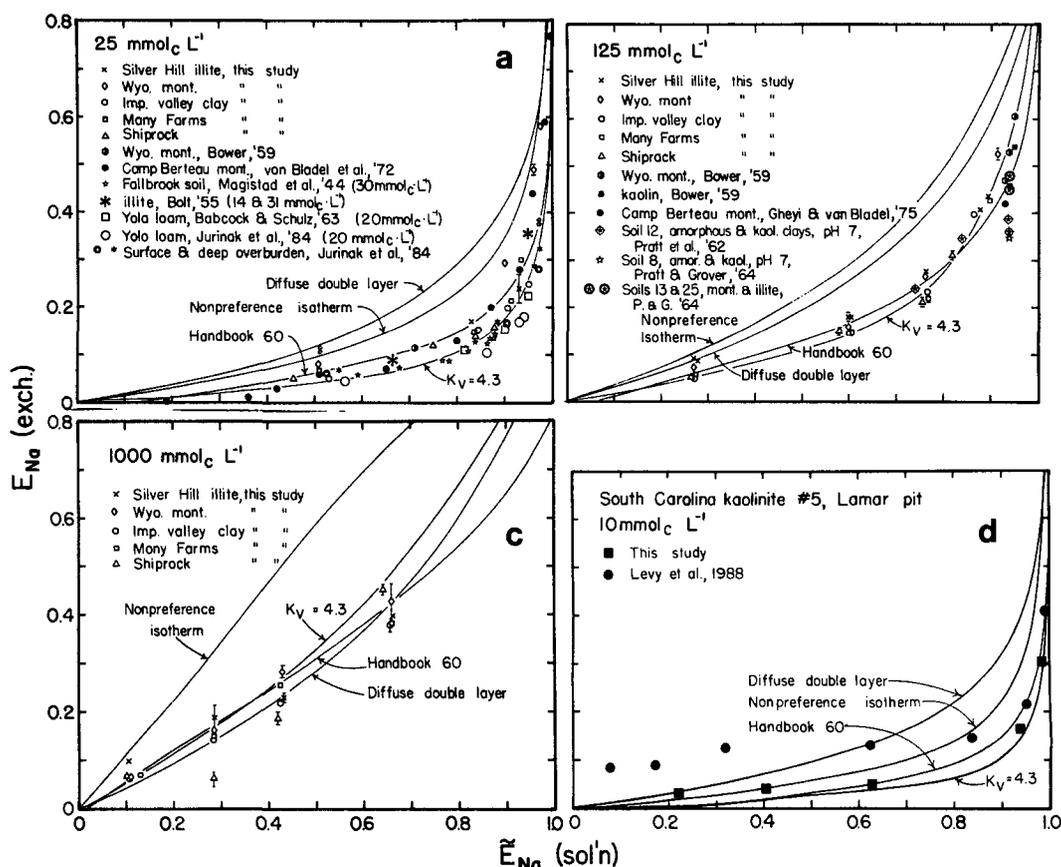


Fig. 2. Equivalent fraction of Na in solution ( $E_{Na}$ ) vs. equivalent fraction of Na on the exchanger ( $E_{Na}^0$ ).  $K_V$  = Vanselow selectivity coefficient. Standard deviations are shown by vertical bars (often smaller than the symbols and reported only for the data collected in this study).

for  $Na^+$  increased ( $K_G$  increased and  $K_V$  was lower). The three soils exhibited little or no trends in  $K_G$  with changes in total concentration or exchangeable  $Na^+$ ; however,  $K_V$  tended to increase with increasing concentration.

Plotted in Fig. 2a, b, and c are some of the exchange data from this study and other studies for comparison (the plots of 5, 10, 50, and 500  $mmol_c L^{-1}$ , which include all available exchange data, can be obtained from the authors). In general, all soils and clay minerals (except vermiculite) exhibited a clear preference for  $Ca^{2+}$  over  $Na^+$  ( $K_V > 1.0$ ) at all concentrations when compared with the thermodynamic nonpreference isotherm. The average  $K_V$  value (excluding the vermiculite data) was 4.3 and the isotherm corresponding to this  $K_V$  value is plotted in each of the figures, as well as the isotherm corresponding to  $K_G = 0.015$  (U.S. Salinity Laboratory Staff, 1954). The calculated DDL isotherms plotted in Fig. 2a, b, and c assumed an average surface charge density of  $1.03 \times 10^{-6} mmol_c m^{-2}$  and tended to predict the measured values only at high concentration. There was no trend in Na–Ca preference as a function of mineralogy, even though the soils and minerals studied represent a wide variety of clay minerals and surface charge densities. This finding is consistent with an earlier study that reported no effect of surface charge density on Na–Ca exchange on four different smectite minerals (Shainberg et al., 1987). Apparently, the effect of pH on Na–Ca selectivity for variable-charge minerals and organic matter can be attributed to spe-

cific competition between  $H^+$  and  $Ca^{2+}$  rather than to a change in surface charge density.

There is no indication that mineralogy affected the Na–Ca selectivity; that is, there was no trend in selectivity in the montmorillonite, illite, and kaolinite data pooled from many sources. There are some specific instances where it appears that one specimen exhibited a higher preference for  $Ca^{2+}$  over  $Na^+$  but, when viewed en masse, these trends are not evident. The soils generally exhibited an increase in  $Ca^{2+}$  preference over the clay minerals and this is attributed to the presence of organic matter in the soils. It is also acknowledged that soils high in variable-charge minerals exhibit an increase in  $Ca^{2+}$  preference with increasing pH (Pratt et al., 1962; Rhue and Mansell, 1988).

There are several techniques for determining exchangeable cations in soils in the presence of soluble cations. The first technique attempts to remove the equilibrating solution (and thus the soluble ions) by washing with water or alcohol mixtures or by dialysis prior to the extracting step. This method has been made popular as the U.S. Salinity Laboratory Staff (1954) procedure for CEC determination and has been used in one form or another by many researchers (Magistad et al., 1944; Lagerwerff and Bolt, 1959; Levy and Hillel, 1968; Paliwal and Gandhi, 1976; Nadler and Magaritz, 1981; Shainberg et al., 1987). After reviewing the literature, we concluded that the use of alcohol washes prior to extraction often gives erroneous exchangeable- $Na^+$  values. For example, the Na–Ca exchange data of Paliwal and Gandhi (1976) exhibit

unusually high  $E_{Na}$  values at low  $\tilde{E}_{Na}$  solution values. Similar results were obtained when water/ethanol washes were used by Levy et al. (1988) on specimen kaolinites and kaolinitic soils.

As a comparison, we determined the Na-Ca exchange isotherm on one of the same kaolinite samples used by Levy et al. (1988) but without rinsing to remove the entrained solution. The exchange data for South Carolina kaolinite no. 5 are presented in Fig. 2d and are in good agreement with selectivities for other clay minerals at this concentration. The data of Levy et al. (1988) are distinctly higher, especially at low  $\tilde{E}_{Na}$  solution values (SAR values <15).

The data of Nadler and Magaritz (1981) demonstrate the extreme  $E_{Na}$  values that can be obtained after washing with ethanol, due to incomplete removal of soluble salts. Amrhein and Suarez (1990) showed that  $Na_2SO_4$ ,  $Na_2CO_3$ , and  $NaHCO_3$  are quite insoluble in ethanol/water mixtures and complete removal of these salts even in repeated washings is unlikely. As a consequence, these salts are incorrectly counted toward the exchangeable  $Na^+$  pool. To avoid the problems associated with removal of the soluble salts, the preferred procedure is to extract the exchangeable and soluble ions and calculate the exchangeable ions by difference. Determination of soluble cations is done by one of two methods, as discussed earlier. Method A uses the anions in the extracting solution to correct for soluble cations and explicitly takes anion exclusion into account and has been used in this study as well as by Bolt (1955), Bower (1959), Pratt et al. (1962), Pratt and Grover (1964), Rao et al. (1968), Rhue and Mansell (1988), Schwertmann (1962), and Suarez and Zahow (1989), among others. Method B uses the volume of entrained solution to estimate the soluble cations and, if the anions in the equilibrating and extracting solution are not measured, it neglects the effect of anion exclusion. Thus, if anion exclusion is neglected (as is most often the case when Method B is used), the sum of the exchangeable cations will not equal the CEC if anion exclusion is significant. Anion exclusion is often significant at high salinity and increases with increasing exchangeable  $Na^+$  (Bower and Goertzen, 1955; Bower and Hatcher, 1962; Jurinak et al., 1984; Amrhein and Suarez, 1990). The following studies employed Method B and did not correct for anion exclusion: Rhoades (1967), Poonia and Talibudeen (1977), Doering and Willis (1980), Sposito et al. (1983a,b,c), Gupta et al. (1984), Fletcher et al. (1984a,b), Sposito and LeVesque (1985), Alperovitch et al. (1986), and Thellier and Sposito (1988). Jurinak et al. (1984) used Method B but corrected the CEC for excluded  $Cl^-$ ; the exact interpretation of ESR values calculated by this procedure is unclear because the sum of exchangeable cations will not necessarily equal the CEC. In our study, anion exclusion was generally < 10% of the CEC, except in the Wyoming bentonite system.

At an ESP of 15, anion exclusion on the Many Farms soil ranged from 0.3 to 18  $mmol_c kg^{-1}$  as the total concentration ranged from 25 to 1000  $mmol_c L^{-1}$ , respectively. Anion exclusion on the Wyoming bentonite at ESP 15 ranged from 25 to 194  $mmol_c kg^{-1}$  through the same concentration range. This is a significant proportion of the CEC (up to 29%) and, if

neglected, could lead to errors in the calculation of ESP, sum of exchangeable cations, and selectivity coefficients. Previous cation-exchange studies on specimen bentonite in which anion exclusion was neglected are, therefore, suspect (Sposito et al., 1983a,b,c).

The potential problem with not removing soluble salts prior to extraction is that the soluble-salt pool can be a significant proportion of the total extracted cations, especially at high concentrations and low CEC values. Thus, the determination of exchangeable cations requires the subtraction of two large numbers to obtain a small number (in this case, the quantity of exchangeable cations).

Failure to correct for mineral dissolution during the extraction step results in erroneously high exchangeable- $Ca^{2+}$  values and thus increases the apparent selectivity of the exchange phase for  $Ca^{2+}$ . Using the previously reported solubility of gypsum and calcite in 0.25  $M Mg(NO_3)_2$  (Amrhein and Suarez, 1990), the maximum possible error that mineral weathering might introduce is 164 and 2390  $mmol_c kg^{-1}$  of apparent exchangeable Ca in a calcareous and a gypsiferous soil, respectively. Errors of this magnitude are not normally measured, because equilibrium with calcite or gypsum is seldom reached during the extracting step. In this study, the weathering correction reduced the exchangeable- $Ca^{2+}$  values from 3 to 20% in the calcareous soils and 30 to 500% in the gypsiferous soil. The mineral-weathering correction became more important as ESP increased. If the anion exclusion and mineral weathering corrections had been neglected, the  $K_G$  values on the Many Farms soil at a total concentration of 25  $mmol_c L^{-1}$  and SAR values of 5, 15, 25, and 50 would have been 0.012, 0.0081, 0.0092, and 0.011  $(mmol L^{-1})^{-1/2}$ , respectively. At 1000  $mmol_c L^{-1}$  total concentration and the same SAR values, the  $K_G$  values would have been 0.0092, 0.0060, 0.0064, and 0.0067  $(mmol L^{-1})^{-1/2}$ , respectively (compare with the  $K_G$  values in Table 2). The weathering correction in the gypsiferous Shiprock soil increased the uncorrected  $K_G$  value up to 3.4-fold. Mineral weathering was also significant during the equilibration step, particularly at low ionic strength and high SAR (Frenkel et al., 1983). This can be seen in Table 2, which shows that, for the Shiprock and Many Farms soils, the final equilibrium SAR was lower than the SAR of the initial equilibrating solution.

An alternative procedure used to determine exchangeable cations employs radioactive tracers. One method assumes a homoionic starting material (Wild and Keay, 1964) and the other method adds the radioactive cations to a system at equilibrium and the equilibrium shift is measured (van Bladel et al., 1972; Gheyi and van Bladel, 1975). This latter method appears to yield good results. However, it requires the additional precautions and counting equipment associated with radio-isotope methods.

## CONCLUSIONS

Sodium-calcium selectivity was determined on three soils and four phyllosilicate minerals at total concentrations from 10 to 1000  $mmol_c L^{-1}$  using a new procedure that corrects for anion exclusion and mineral weathering. Selectivity was generally found to be

independent of total concentration. Specimen vermiculite exhibited near-ideal Na-Ca exchange as defined by the thermodynamic nonpreference isotherm. All of the soils, and the illite, smectite, and kaolinite samples, exhibited  $\text{Ca}^{2+}$  preference over  $\text{Na}^+$  when compared with the thermodynamic nonpreference isotherm. There was no effect on mineralogy on the Na-Ca selectivity, even though the minerals and soils had various surface charge densities. This suggests that the effect of pH on Na-Ca selectivity observed for soils high in organic matter and variable-charge minerals is due to specific  $\text{H}^+$ - $\text{Ca}^{2+}$  competition rather than changes in surface charge density. The traditional relationship for Na-Ca selectivity ( $K_G = 0.015$ ) and the average  $K_V = 4.3$  were found to fit the data reasonably well over all concentrations. The soils exhibited more scatter in Na-Ca selectivity than the pure specimen minerals due to the presence of variable amounts of organic matter, which tends to increase  $\text{Ca}^{2+}$  preference. Mineral weathering also increases the apparent  $\text{Ca}^{2+}$  preference and contributes to variability in the Na-Ca selectivity values previously reported.

Failure to correct for mineral weathering that occurred during the extraction of exchangeable ions increased the apparent exchangeable  $\text{Ca}^{2+}$  from 3 to 20% in the calcareous soils and from 30 to 500% in the gypsiferous soil. On the calcareous Many Farms soil and the gypsiferous Shiprock soil, the corrected  $K_G$  values averaged 1.3 and 2.0 times higher, respectively, than the uncorrected values.

Anion exclusion increased with increasing ESP and increasing salinity but was generally <10% of the CEC, except in the bentonite system where it reached 29% of the CEC at 1000 mmol<sub>c</sub> L<sup>-1</sup>. Determinations of anions in the equilibrating and extracting solutions eliminates the potential errors in determining cation selectivity and CEC, and is preferred over alcohol rinses and estimating soluble cations using the weight of the entrained solution.

Considering the variability of the Na-Ca selectivity determined by different laboratories on the same material and the many different ways of measuring and calculating exchanger phase composition and the inherent errors associated with determining exchangeable-cation composition at high concentration, it would appear that the traditional Gapon expression and selectivity coefficient recommended by the U.S. Salinity Laboratory Staff (1954) are suitable for estimating exchangeable  $\text{Na}^+$ . An average  $K_V$  value of 4.3 can also be used to calculate Na-Ca exchange on soils and clay minerals. The exception to this would be soils dominated by vermiculite (Rhoades, 1967) and soils containing large amounts of organic matter or amorphous clays and having a low pH (Pratt and Grover, 1964).

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