

Ammonium–Potassium–Calcium Exchange on Vermiculite and Hydroxy-aluminum Vermiculite

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ABSTRACT

Binary and ternary cation-exchange reactions involving NH_4^+ , K^+ , and Ca^{2+} on vermiculite and hydroxy-Al interlayered vermiculite (HIV) were investigated. In the case of vermiculite, NH_4 -Ca exchange was nearly indistinguishable from the nonpreference isotherm while HIV exhibited preference for NH_4^+ . The presence of K^+ had significant suppressing impact on the apparent NH_4^+ selectivity in NH_4 -Ca exchange in HIV most likely because of retardation of Ca^{2+} diffusion in the interlayer. For vermiculite, the presence of K^+ in the NH_4 -Ca system induced apparent high affinity sites for NH_4^+ most likely because of interlayer collapse. The overall study demonstrated that cation-exchange selectivity coefficients in vermiculite and HIV are dependent on number and type of cations present.

THIS PARTICULAR STUDY deals with NH_4 -K-Ca exchange, a ternary cation-exchange system. Ternary exchange data involving NH_4 -K-Ca to our knowledge are limited but this exchange mode is more representative of agricultural soils than the binary exchange mode, e.g., NH_4 -Ca or K-Ca. Farmers often use NH_4 and K salts as fertilizer sources. Even though applied NH_4^+ has an apparent short life span in agricultural soils (1–4 wk or more depending on rates of nitrification) (Green et al., 1994; Sims and Atkinson, 1974), the NH_4 -K-Ca exchange interactions control distribution of these cations between the exchange and solution phases during that period. Thus, the availability of K^+ and NH_4^+ in the solution phase would be affected by all ions present.

Much research has been reported on soil clay minerals and soils as exchanger surfaces at both theoretical and experimental levels (Vanselow, 1932; Gapon, 1933; Argersinger et al., 1950; Sposito, 1981a,b; Sposito et al., 1983; Sposito et al., 1981; Jardine and Sparks, 1984a,b). These studies and many others (Beckett, 1964; Beckett and Nafady, 1967; Evangelou et al., 1994) consider that soils are two ion-exchange systems. Field soils, however, are multi-ion exchange systems (Curtin and Smillie, 1983; Adams, 1971). It is assumed that data of binary exchange reactions can be employed to predict ternary exchange reactions. In order for this assumption to be valid, one has to accept that binary exchange-selectivity coefficients are independent of exchanger-phase composition. Therefore, there is need for ternary and binary cation-exchange data representing various minerals or soils to demonstrate that binary cation-exchange data can be

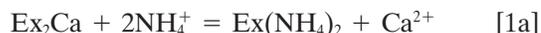
used to predict ternary cation-exchange data. Chu and Sposito (1981) showed at a theoretical level that one couldn't predict exchange-phase solution-phase interactions of a ternary system solely from data obtained from binary exchange. These researchers argued that experimental data obtained from systems with three ions are necessary.

Experimental data of ternary exchange involving NH_4 -Ba-La on montmorillonite were reported by El-prince et al. (1980) who concluded that binary-exchange data described adequately the ternary exchange system. Studies on Na-Ca-Mg exchange reactions by Fletcher et al. (1984b), Sposito et al. (1983), and Sposito and Fletcher (1985) also showed that ternary-exchange data on smectites can be predicted from binary exchange data. Feigenbaum et al. (1991) showed that in the case of K-Mg-Ca exchange on montmorillonitic soils ternary exchange data could be predicted by binary data. However, Sposito et al. (1986) and Sposito and LeVesque (1985) reported that in the case of Na-Mg-Ca exchange on illite the presence of Na^+ did affect the Ca-Mg selectivity coefficient.

It appears that much of the available ternary data deal mostly with freely expanding 2:1 clay minerals, e.g., montmorillonite and bentonite, and some limited ternary data are available for illite. However, to our knowledge no data are available for ternary-exchange reactions on vermiculite or HIV, two clay minerals with some cation-size limitation effects on apparent selectivity (Kozak and Huang, 1971). The objective of this study was to evaluate NH_4 -Ca exchange equilibrium in the presence or absence of added K^+ in vermiculite and HIV.

Theoretical Considerations

A binary-exchange reaction at equilibrium involving NH_4^+ and Ca^{2+} in a soil system can be written as



However, for reasons of consistency and direct comparison with our previous work (Evangelou and Phillips, 1987, 1989) the above exchange expression would be presented as



where Ex denotes an exchanger phase taken to have a charge of negative one (-1) and NH_4^+ and Ca^{2+} denote

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Abbreviations: HIV, hydroxy-Al interlayered vermiculite; HAP, hydroxy-Al polymer; ΣEx_i , sum of exchangeable cations; CEC, cation-exchange capacity; AR_{NH_4} , ammonium activity ratio; CR_{NH_4} , ammonium concentration ratio; AR_{K} , K activity ratio; CR_{K} , K concentration ratio; E_{Ca} , equivalent fraction of Ca on the exchange phase; E_{NH_4} , equivalent fraction of ammonium on the exchange phase; E_{K} , equivalent fraction of K on the exchange phase; d- H_2O , distilled water.

solution species. Note that according to the Vanselow exchange expression (Vanselow, 1932), the difference between the exchange-selectivity coefficients of the above two equations is that the equilibrium expression for [1a] is equal to the equilibrium expression [1b] raised to the second power.

Based on the above, the thermodynamic exchange equilibrium constant K_{eq} for reaction [1b] at room temperature and 1.01 MPa (one atmosphere) pressure can be represented by:

$$K_{eq} = [\alpha_{ExNH_4}/(\alpha_{ExCa})^{1/2}][(\alpha_{Ca})^{1/2}/\alpha_{NH_4}] \quad [2]$$

where α_{Ca} , α_{NH_4} equals the activity of solution phase Ca^{2+} or NH_4^+ and α_{ExNH_4} , α_{ExCa} equals the activity of exchange phase NH_4^+ or Ca^{2+} . Solution activity α_i , is defined by the equation

$$\alpha_i = c_i \gamma_i \quad [3]$$

where c_i equals the concentration of species i and γ_i equals the activity coefficient of species i . To define solution phase α_i , its value is set to 1, hence $\gamma_i = 1$, when solution ionic strength (I) approaches zero. For mixed electrolyte solutions when $I > 0$, the single ion-activity concept introduced by Davies (1962) is employed to estimate α_i which is given below in the *Materials and Methods* section.

The activity component of the adsorbed or solid phase is defined by employing the mole fraction concept (M_i) introduced by Vanselow (1932). According to Vanselow, for a heterovalent binary-exchange reaction such as NH_4 -Ca, assuming that the system obeys ideal solid-solution theory (Evangelou and Phillips, 1987 and references therein), the activity term (α_{Ex_i}) is defined by

$$\alpha_{ExNH_4} \approx M_{NH_4} = \frac{ExNH_4}{ExNH_4 + Ex_2Ca} \quad [4]$$

and

$$\alpha_{Ex_2Ca} \approx M_{Ca} = \frac{Ex_2Ca}{ExNH_4 + Ex_2Ca} \quad [5]$$

where M_{NH_4} or M_{Ca} denote mole fraction of NH_4^+ or Ca^{2+} , respectively. In this study the cation exchange capacity (CEC) of the soil was taken to be $CEC = ExNH_4 + ExCa_{1/2}$ for the binary system and $CEC = ExNH_4 + ExK + ExCa_{1/2}$ for the ternary system where $ExCa_{1/2}$ denotes $cmol_c kg^{-1}$. It was also assumed that any other cation, such as exchangeable H^+ , is present in negligible quantities and does not interfere with NH_4 -Ca exchange, or H^+ is tightly bound to the solid surface giving rise only to pH-dependent charge (Spósito, 1981b).

Based on the above, the Vanselow (1932) exchange selectivity coefficient expression, K_v , for reaction [1b] can be given as

$$K_v = [M_{NH_4}/(M_{Ca})^{1/2}][(\alpha_{Ca})^{1/2}/\alpha_{NH_4}] \quad [6]$$

where $\alpha_{NH_4}/(\alpha_{Ca})^{1/2}$, the inverse of $(\alpha_{Ca})^{1/2}/\alpha_{NH_4}$, is known as the AR_{NH_4} . The magnitude of K_v is taken to represent relative affinity of NH_4^+ with respect to Ca^{2+} by the clay surface (Shainberg et al., 1980; Spósito and LeVesque, 1985). When K_v equals 1 at a given level of

exchangeable NH_4^+ , the exchanger at that level of NH_4^+ load shows no preference for either NH_4^+ or Ca^{2+} . On the other hand, a $K_v > 1$ signifies exchanger preference for NH_4^+ and a $K_v < 1$ signifies exchanger preference for Ca^{2+} .

MATERIALS AND METHODS

The clay sample used in this study was Connecticut Vermiculite obtained from Ward's Natural Science Establishment, Rochester, NY. The $< 2\text{-}\mu\text{m}$ clay fraction of the vermiculite was fractionated by grinding and gravity separation (Carstea et al., 1970; Jackson, 1975) in distilled water ($d\text{-H}_2\text{O}$) suspension. Total elemental analysis of clays was performed using a fusion method employing 1:5 Ca-saturated clay/ $LiBO_2$ flux ratio, fusion at 1050°C , and dissolution of the fused sample by 4% HNO_3 (wt./wt.) (Johnson and Maxwell, 1981). The elements Si, Al, Fe, Mg, Ca, K, and Na were analyzed with atomic absorption spectrophotometry. Based on the total elemental analysis, structural formulae of the clay samples were reconstructed according to the procedures described by Jackson (1975).

To evaluate NH_4 -Ca exchange behavior as affected by hydroxy-Al polymer (HAP), HIV was prepared according to the procedure described by Brydon and Kodama (1966) and Carstea et al. (1970). Briefly, the suspended vermiculite clay in $d\text{-H}_2\text{O}$ was flocculated with 0.33 M $AlCl_3$ and equilibrated twice for 2 d each time with 150 mL of 0.33 M $AlCl_3$. The clay was then washed with $d\text{-H}_2\text{O}$ (six times) until Cl-free before it was vacuum-dried at room temperature. A 5-g sample of Al-saturated vermiculite was placed in a 300-mL beaker and suspended in 250 mL of 0.11 M $AlCl_3$. While being stirred vigorously, the suspension was titrated employing a Radiotitrimer set (TTT 80, ABU 80, PHM 82, Radiometer, Copenhagen) with 0.021 M $Ca(OH)_2$ solution in N_2 atmosphere and at room temperature to a final pH of 5.0. The samples were equilibrated for 6 mo and twice a week they were shaken for 10 min. At the end of the 6-mo period the samples were washed eight times with $d\text{-H}_2\text{O}$ until Cl-free and then air-dried under vacuum at room temperature. Formation of HIV was verified through x-ray diffraction.

Exchange reactions of NH_4 -Ca and NH_4 -K-Ca were carried out employing a batch technique. Clay samples in triplicate of 0.20 g were weighed into preweighed 50-mL test tubes. To each of these test tubes was added 20 mL of a solution composed of various NH_4 -Ca, and NH_4 -K-Ca ratios with a constant Cl concentration at 1 M. After shaking for 11 d, the test tubes were centrifuged at $670 \times g$ for 10 min and the clear supernatants were decanted. To each tube a 20-mL solution of the corresponding NH_4 -Ca, and NH_4 -K-Ca ratio was added at 10 mM Cl concentration. The test tubes were shaken for 3 h, centrifuged at $670 \times g$ for 10 min and the clear supernatants were again decanted. This last treatment was repeated three times; the third time, the test tubes were shaken for 24 h and the supernatants were collected for Ca, K, and NH_4 determinations in the solution phase. Each tube was again weighed to quantify the entrapped solution. The exchangeable NH_4^+ , K^+ , and Ca^{2+} were displaced twice with 20 mL of 0.2 M CsCl. This displacement was derived by trial and error for the purpose of maximizing extractable cations. The soil samples were shaken for 3 h, centrifuged, and the clear supernatants were analyzed for K and Ca by atomic absorption and for NH_4^+ by a Technicon Autoanalyzer (Technion Instruments, Tarrytown, NY) with the phenolphthorite reaction (Knopp and McKee, 1978).

The Vanselow exchange selectivity coefficient (K_v) was cal-

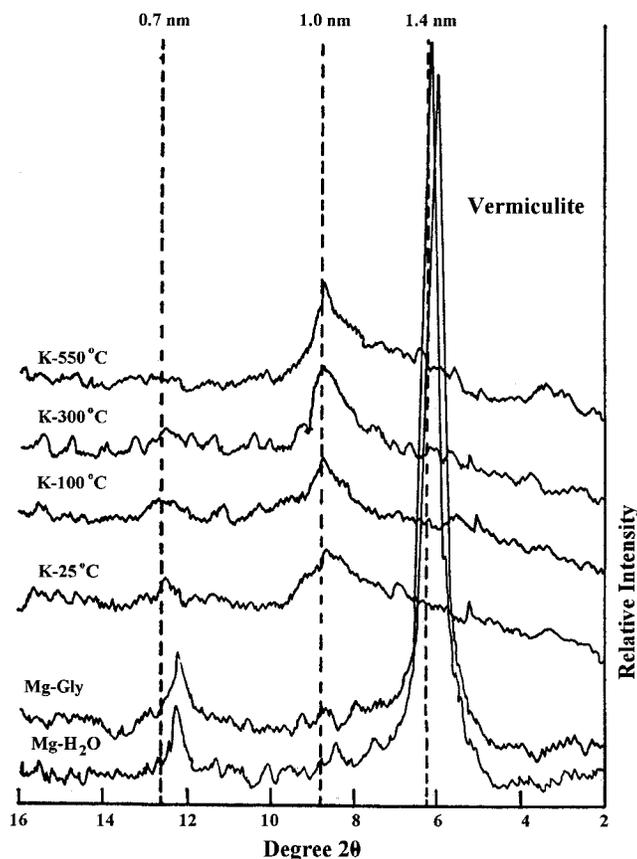


Fig. 1. X-ray diffractograms of vermiculite clay.

culated using Eq. [4], [5], and [6]. Single-ion activity (α) for NH_4^+ , K^+ , and Ca^{2+} employed in Eq. [6] were estimated by the previously described equation:

$$\alpha_{ij} = c_{ij} \gamma_{ij} \quad [7]$$

The values for γ_{ij} were estimated by employing the effective ionic strength (I) equation:

$$I = 1/2 \sum_{b=1}^n C_b Z_b^2 \quad [8]$$

where Z denotes charge of the ionic species b , (b denotes all ionic species in solution), and the Davies equation (Davies, 1962)

$$\log \gamma_i = -AZ_i^2 [I^{1/2} / (1 + I^{1/2}) - 0.3I] \quad [9]$$

Equations [7], [8] and [9] were solved by an ion-association computer model (Evangelou, 1986).

RESULTS AND DISCUSSION

The data in Fig. 1 and 2 show x-ray diffraction patterns of the two clay mineral samples saturated with Mg^{2+} , Mg-glycerol or with K^+ with and without heating. These diffractograms clearly demonstrate the d-spacing behavior of vermiculite. Interlayer expansion (~ 1.4 nm) oc-

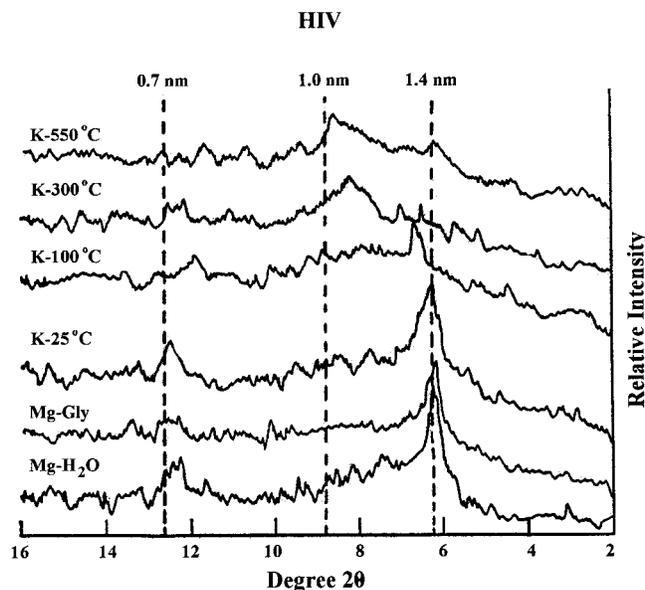


Fig. 2. X-ray diffractograms of hydroxy-Al interlayered vermiculite (HIV).

curred when clays were treated with Mg^{2+} with and without glycerol and collapsed to ~ 1.0 nm when K-saturated with and without heating. In the case of HIV, the peaks remained ~ 1.4 nm by Mg^{2+} or K^+ saturation. Heating of K-saturated vermiculite clay sample did not produce any unique features in the diffractograms except in the case of HIV. In this clay the x-ray diffraction peak near 1.4 nm appeared collapsed and shifted to the left when heated to 100°C (Fig. 2). The instability of the 1.4-nm peak when the K-saturated samples were heated from 25 to 100, 300, and 550°C indicated incomplete filling of the vermiculite interlayer (Barnhisel and Bertsch, 1989).

Based on complete elemental analysis and reconstitution (Table 1), the vermiculite used in this study was trioctahedral. Cation-extractability behavior of the two clay samples is reported in Table 2. These data show that estimated charge based on structural reconstitution was lower on HIV than that of vermiculite. While lacking absolute agreement between experimental and reconstituted charge, we observed there was good agreement in the trends between experimental and reconstituted charge. The poorest agreement was that between total charge determined experimentally by loading the clays with Ca^{2+} and the estimated charge based on reconstitution of HIV (6.51 vs. 39.27 $\text{cmol}_c \text{kg}^{-1}$). The data in Table 2 also show that vermiculite clay, upon introducing HAP, the total charge was reduced by half (79.73 vs. 39.27 $\text{cmol}_c \text{kg}^{-1}$). Furthermore, fixed K^+ decreased by approximately half (65.66 vs. 31.16 $\text{cmol}_c \text{kg}^{-1}$) while fixed ammonium was dramatically suppressed (57.49 vs. 2.88 $\text{cmol}_c \text{kg}^{-1}$). As expected, these data support the

Table 1. Formula of the two clay samples.

Clay	Tetrahedral	Octahedral	Interlayer	Charge [†]
Vermiculite	$[\text{Si}_{5.64} \text{Al}_{2.36}]$	$[\text{Mg}_{4.26} \text{Fe}_{0.44} \text{Al}_{1.30}]$		$\text{O}_{20} (\text{OH})_4 \text{M}_{0.66}^+$
HIV	$[\text{Si}_{5.62} \text{Al}_{2.38}]$	$[\text{Mg}_{4.26} \text{Fe}_{0.44} \text{Al}_{1.30}]$	$[\text{Al}_{1.08} (\text{OH})_{2.94}]$	$\text{O}_{20} (\text{OH})_4 \text{M}_{0.34}^+$

[†] Determined excess negative charge balanced by K and Ca per formula.

Table 2. Exchangeable and non-exchangeable cations of the clay fraction after saturation with K, NH₄, or Ca and formula cation-exchange capacity (CEC).

Clay	Exchangeable [†]			Non-exchangeable [‡]			Total (Exi+Ni)			Formula CEC [§]
	ExK	ExNH ₄	ExCa	NK	NNH ₄	NCa	K	NH ₄	Ca	
	cmol _c kg ⁻¹									
Vermiculite	35.08	20.29	64.91	65.66	57.49	4.72	100.74	77.78	69.91	79.73
HIV	10.90	15.37	4.10	31.16	2.88	2.41	42.06	18.25	6.51	39.27

[†] Exchangeable K and Ca with 0.1 M BaCl₂; NH₄ with 1.0 M KCl.

[‡] Non-exchangeable K, Ca, or NH₄ with 1 M HF:1 M HCl.

[§] Formula CEC is based on a combination of K and Ca.

conclusion that certain surface mechanisms (i.e., steric effect or specific adsorption) were responsible for changes in mineral's ion exchange capacity (Rich and Black, 1964).

Tables 3 through 6 contain exchange data for the binary NH₄-Ca, and ternary NH₄-K-Ca exchange systems for both the vermiculite and HIV clays. At first glance, one can clearly see from these data that ΣEx_i represented only a small fraction of the vermiculite and HIV clays' total charge (Table 2), suggesting that the exchange reactions in the above systems occurred mainly on the clays' external clay surfaces, and possibly some of the interlayer clay surfaces as well (Shainberg et al., 1980). For the vermiculite clay, two important points can be made for the binary and ternary cation-exchange systems: First, we observed a shift in pH (Table 3) as the predominant cation was switched from Ca²⁺ (pH 7.7) to NH₄⁺ (pH 6.9). Secondly, changes in selectivity over different NH₄⁺/Ca²⁺ ratios were marked by changes in exchange capacity (ΣEx_i).

A close examination of pH and ΣEx_i data across the entire isotherm (Table 3) indicates that pH was not significantly influential on magnitude of ΣEx_i. First, the pH variation across the entire isotherm would be considered relatively small, ±0.4 (Table 3). Published data (Fletcher et al., 1984a) did not show large pH dependent charge in 2:1 expanding clay minerals. Secondly, while pH remained relatively constant for a portion of the isotherm (Table 3), ΣEx_i varied from 62.7 to 36.4 cmol_ckg⁻¹. This large variation in ΣEx_i can only be because of variation in NH₄⁺/Ca ratio, thus a cation blocking effect or layer collapse was induced. In the case of the ternary system (Table 4), variation in ΣEx_i

across the entire isotherm was ~5 cmol_ckg⁻¹. However, this variation came about when pH varied from 7.6 to 7.5 whereas solution NH₄⁺ concentration doubled. Therefore, this difference in ΣEx_i cannot be because of a 0.1 unit change in pH but most likely because of change in the composition of the exchange phase. For these two cation-ratio treatments with pH 7.6 and 7.5 exchangeable Ca decreased from 23.6 cmol_ckg⁻¹ to 13.1 cmol_ckg⁻¹, exchangeable NH₄⁺ increased from 0.9 to 3.0 cmol_ckg⁻¹, and exchangeable K⁺ increased from 15.0 to 19.2 cmol_ckg⁻¹. Thus, a blocking effect or partial interlayer collapse was the most likely cause for this decrease in ΣEx_i.

Ideally, pH and ΣEx_i or CEC should be constant across the entire isotherm to generate a cation-exchange isotherm or estimate cation-selectivity coefficients. However, pH or CEC constancy in soil clay minerals is rarely met. For example, in Na-Ca, Na-Mg, and Ca-Mg exchange studies using a montmorillonitic soil (Fletcher et al., 1984a,b), pH across the entire isotherm varied from 6.7 to 7.1 in one case and in another case from 4.4 to 5.0. Additionally, CEC in one case varied from 51 to 60 cmol_ckg⁻¹ and in another case from 64 to 75 cmol_ckg⁻¹. Furthermore, the above soil's CEC in the binary mode was 53 cmol_ckg⁻¹ whereas in the ternary mode was 70 cmol_ckg⁻¹. The latter CEC variation was not attributed to pH because the binary and ternary systems were studied under approximately similar pH. Furthermore, when the exchange data, representing the above soil under three different pH values (pH 4.7, 5.8, and 6.9), were used to calculate CEC (ΣEx_i) the latter varied very little with respect to the three pH values tested. In essence, the so-called pH dependent charge

Table 3. Experimental data on NH₄-Ca exchange at 297 K on vermiculite clay.

pH	°NH ₄ [†]	°Ca	ExNH ₄ [‡]	ExCa	ΣEx _i [§]
	mM		mol _c kg ⁻¹		
7.7	0.13 ± 0.00¶	3.89 ± 0.01	0.002 ± 0.000	0.627 ± 0.005	0.627
7.7	0.33 ± 0.016	3.78 ± 0.03	0.004 ± 0.000	0.542 ± 0.007	0.546
7.7	0.52 ± 0.00	3.65 ± 0.02	0.006 ± 0.000	0.479 ± 0.005	0.485
7.7	0.88 ± 0.00	2.92 ± 0.03	0.009 ± 0.000	0.402 ± 0.005	0.411
7.4	1.56 ± 0.01	2.87 ± 0.03	0.012 ± 0.000	0.352 ± 0.006	0.364
7.2	2.37 ± 0.01	2.77 ± 0.03	0.018 ± 0.001	0.310 ± 0.004	0.328
7.1	4.81 ± 0.00	1.89 ± 0.01	0.020 ± 0.001	0.255 ± 0.007	0.275
7.1	8.24 ± 0.03	0.48 ± 0.01	0.083 ± 0.003	0.185 ± 0.001	0.268
6.9	8.92 ± 0.03	0.25 ± 0.00	0.136 ± 0.001	0.113 ± 0.001	0.219
6.9	9.40 ± 0.04	0.13 ± 0.01	0.190 ± 0.009	0.067 ± 0.001	0.257
6.9	9.49 ± 0.02	0.07 ± 0.00	0.224 ± 0.006	0.043 ± 0.001	0.267
6.9	9.60 ± 0.03	0.03 ± 0.00	0.229 ± 0.003	0.024 ± 0.001	0.253

[†] °i denotes concentration of cation i in solution at equilibrium.

[‡] Exi denotes concentration of adsorbed cation i at equilibrium.

[§] ΣExi denotes total adsorbed cations.

¶ The ± value represents standard deviation.

Table 4. Experimental data on NH₄-K-Ca exchange at 297 K on vermiculite clay.

pH	°NH ₄ †	°Ca	°K	ExNH ₄ ‡	ExCa	ExK	ΣExi§
	mM			mol _c kg ⁻¹			
8.3	0.02 ± 0.00¶	0.90 ± 0.03	6.58 ± 0.07	0.00001 ± 0.000	0.308 ± 0.002	0.103 ± 0.001	0.411
8.3	0.07 ± 0.00	0.89 ± 0.01	6.50 ± 0.18	0.0001 ± 0.000	0.305 ± 0.001	0.103 ± 0.003	0.408
8.4	0.13 ± 0.00	0.81 ± 0.00	6.61 ± 0.08	0.001 ± 0.000	0.301 ± 0.001	0.105 ± 0.002	0.407
8.1	0.26 ± 0.00	0.75 ± 0.02	6.68 ± 0.03	0.002 ± 0.000	0.291 ± 0.002	0.114 ± 0.000	0.407
7.8	0.48 ± 0.00	0.67 ± 0.01	6.60 ± 0.02	0.005 ± 0.000	0.270 ± 0.004	0.131 ± 0.001	0.406
7.6	0.74 ± 0.00	0.58 ± 0.00	6.64 ± 0.04	0.009 ± 0.000	0.236 ± 0.001	0.150 ± 0.001	0.395
7.5	1.46 ± 0.00	0.45 ± 0.01	6.32 ± 0.05	0.030 ± 0.000	0.131 ± 0.000	0.192 ± 0.004	0.353
7.3	2.38 ± 0.01	0.17 ± 0.00	6.12 ± 0.05	0.064 ± 0.001	0.071 ± 0.001	0.225 ± 0.001	0.360
7.3	2.39 ± 0.00	0.08 ± 0.00	6.11 ± 0.05	0.077 ± 0.003	0.050 ± 0.000	0.234 ± 0.002	0.361
7.3	2.72 ± 0.00	0.04 ± 0.00	6.12 ± 0.02	0.083 ± 0.001	0.036 ± 0.001	0.237 ± 0.002	0.356
7.3	2.78 ± 0.01	0.02 ± 0.00	6.07 ± 0.07	0.086 ± 0.001	0.025 ± 0.001	0.241 ± 0.001	0.352
7.3	2.82 ± 0.01	0.01 ± 0.00	6.07 ± 0.05	0.088 ± 0.002	0.019 ± 0.000	0.238 ± 0.001	0.345

† °i denotes concentration of cation i in solution at equilibrium.

‡ Exi denotes concentration of adsorbed cation i at equilibrium.

§ ΣExi denotes total adsorbed cations.

¶ The ± value represents standard deviation.

of a 2:1 shrink/swell clay in the ternary exchange mode, under certain exchangeable cation composition, was basically negligible.

In the present study, the highest ΣEx_i values (Table 3) were associated with the highest Ca²⁺ concentrations added, while the lowest ΣEx_i values corresponded with the highest NH₄⁺ concentrations added. Accordingly, these trends were consistent with the order of exchangeable cations, in terms of magnitude of experimental charge (Table 2), as NH₄⁺ < K⁺ < Ca²⁺. Also, note that this trend was consistent with the order of nonexchangeable cations in vermiculite, Ca²⁺ < NH₄⁺ < K⁺ (Table 2). Based on this information, we propose that vermiculite controlled ion selectivity by acting as a molecular sieve, discriminating among ions based on cation size, charge and hydration energy (Black and Rich, 1964). System pH may also have some role in determining NH₄⁺ selectivity, as we note the decrease in ΣEx_i with decrease in pH (Sposito, 1981b) but in the present study this role may have been small. Based on our data there was no clear consistency in the relationship between pH and CEC. For example, the first four NH₄/Ca treatments in Table 3 exhibited similar pH (pH 7.7) but ΣEx_i varied from ~62.7 to 41.1 cmol_ckg⁻¹. Furthermore, for pH treatments 7.1 and 6.9 ΣEx_i varied from 26.8 to 25.3 cmol_ckg⁻¹. This suggested factors other than pH, e.g., steric factors may have played a role. Note that similar

inconsistencies in ΣEx_i were present in a montmorillonitic soil at pH 6 (Fletcher et al., 1984a,b).

The exchange-isotherm data for both the binary (NH₄-Ca) and ternary (NH₄-K-Ca) exchange systems for the HIV are presented in Tables 5 and 6. In general, ΣEx_i values were lower in HIV than in vermiculite because of Al-hydroxylation which may serve to shield the interlayer surface. Also solution pH was the lowest in the HIV systems, most likely because of hydrolysis of free Al³⁺. Only the data in Table 5 (NH₄-Ca) showed a significant ΣEx_i gradient (~6.0 cmol_ckg⁻¹ for the Ca-rich isotherm vs. ~11.7 cmol_ckg⁻¹ for the NH₄⁺-rich isotherm) in the opposite direction of the data in Table 3. This suggested (i) a potential Ca retardation effect (which would reduce ΣEx_i) because HAP present in the interlayer (Kozak and Huang, 1971) and (ii) perhaps a pH-dependent effect (which would increase ΣEx_i) because of a pH increase (Sposito, 1981b). One could interpret the increase in ΣEx_i at higher NH₄⁺ concentrations as a phenomenon of Ca²⁺ exclusion by the solid phase. It is possible that certain interlayer-exchange sites are accessible to NH₄⁺ and not to Ca²⁺. Unlike the vermiculite system, HIV system is less likely to trap NH₄⁺ via interlayer collapse at higher E_{NH₄}, thus making it accessible to Cs⁺ exchange. In the case of ternary exchange (Table 6), changes in pH and ΣEx_i were negligible. Here, the relatively small pH fluctuation of the

Table 5. Experimental data on NH₄-Ca exchange at 297 K on hydroxy-Al interlayered vermiculite (HIV).

pH	°NH ₄ †	°Ca	ExNH ₄ ‡	ExCa	ΣExi§
	mM		mol _c kg ⁻¹		
4.7	0.05 ± 0.00¶	3.99 ± 0.01	0.002 ± 0.000	0.058 ± 0.001	0.060
4.6	0.26 ± 0.00	3.89 ± 0.01	0.007 ± 0.000	0.057 ± 0.001	0.064
4.7	0.48 ± 0.00	3.84 ± 0.01	0.008 ± 0.000	0.058 ± 0.000	0.066
4.8	0.92 ± 0.00	3.09 ± 0.02	0.015 ± 0.000	0.058 ± 0.000	0.063
5.0	1.62 ± 0.00	3.06 ± 0.02	0.022 ± 0.000	0.058 ± 0.001	0.080
5.0	2.42 ± 0.00	2.95 ± 0.01	0.029 ± 0.000	0.058 ± 0.001	0.087
5.1	5.03 ± 0.01	1.98 ± 0.01	0.048 ± 0.001	0.058 ± 0.001	0.106
5.1	7.93 ± 0.00	0.65 ± 0.00	0.079 ± 0.000	0.041 ± 0.000	0.120
5.2	8.76 ± 0.01	0.35 ± 0.00	0.091 ± 0.000	0.032 ± 0.000	0.122
5.2	9.11 ± 0.01	0.17 ± 0.00	0.100 ± 0.001	0.024 ± 0.000	0.124
5.3	9.31 ± 0.00	0.08 ± 0.00	0.103 ± 0.001	0.017 ± 0.000	0.120
5.4	9.44 ± 0.00	0.03 ± 0.00	0.107 ± 0.000	0.010 ± 0.000	0.117

† °i denotes concentration of cation i in solution at equilibrium.

‡ Exi denotes concentration of adsorbed cation i at equilibrium.

§ ΣExi denotes total adsorbed cations.

¶ The ± value represents standard deviation.

Table 6. Experimental data on NH₄-K-Ca exchange at 297 K on hydroxy-Al interlayered vermiculite (HIV).

pH	°NH ₄ †	°Ca	°K	ExNH ₄ ‡	ExCa	ExK	ΣExi§
	mM			mol _e kg ⁻¹			
5.2	0.04 ± 0.00¶	1.16 ± 0.00	5.95 ± 0.00	0.001 ± 0.000	0.045 ± 0.000	0.069 ± 0.000	0.115
5.2	0.08 ± 0.00	1.15 ± 0.00	5.91 ± 0.01	0.001 ± 0.000	0.045 ± 0.000	0.069 ± 0.000	0.115
5.2	0.16 ± 0.00	1.14 ± 0.00	5.98 ± 0.00	0.002 ± 0.000	0.043 ± 0.000	0.068 ± 0.000	0.113
5.2	0.24 ± 0.00	1.06 ± 0.01	5.92 ± 0.01	0.003 ± 0.000	0.043 ± 0.000	0.068 ± 0.000	0.114
5.2	0.50 ± 0.00	0.95 ± 0.00	5.94 ± 0.02	0.005 ± 0.000	0.043 ± 0.000	0.067 ± 0.000	0.115
5.2	0.75 ± 0.00	0.88 ± 0.01	5.92 ± 0.01	0.009 ± 0.000	0.043 ± 0.000	0.067 ± 0.000	0.119
5.2	1.48 ± 0.00	0.58 ± 0.01	5.90 ± 0.01	0.014 ± 0.000	0.034 ± 0.000	0.067 ± 0.000	0.115
5.2	2.38 ± 0.00	0.19 ± 0.00	5.91 ± 0.01	0.028 ± 0.001	0.021 ± 0.000	0.068 ± 0.000	0.117
5.3	2.58 ± 0.00	0.09 ± 0.00	5.91 ± 0.00	0.033 ± 0.000	0.018 ± 0.000	0.069 ± 0.001	0.110
5.3	2.69 ± 0.00	0.04 ± 0.00	5.92 ± 0.00	0.035 ± 0.000	0.013 ± 0.000	0.069 ± 0.001	0.117
5.3	2.72 ± 0.00	0.02 ± 0.00	5.91 ± 0.00	0.037 ± 0.002	0.009 ± 0.000	0.063 ± 0.004	0.109
5.4	2.76 ± 0.00	0.01 ± 0.00	5.93 ± 0.01	0.040 ± 0.001	0.007 ± 0.000	0.069 ± 0.001	0.116

† i denotes concentration of cation i in solution at equilibrium.
 ‡ Exi denotes concentration of adsorbed cation i at equilibrium.
 § ΣExi denotes total adsorbed cations.
 ¶ The ± value represents standard deviation.

HIV system minimized the potential influence of pH-dependent external sites on exchange, thus, helping elucidate the role of wedge surfaces on binary and ternary exchange.

Variations in CEC (ΣEx_i) and pH do not forbid us from estimating K_v as long as such variations are substantiated by appropriate measurements (Fletcher et al., 1984ab; Zhang and Sparks, 1996). The estimated K_v values represent individual data sets for a particular monovalent cation load and signify the behavior of the clay at that load. In our particular study the data showed that ΣEx_i within a clay mineral was not necessarily related to pH and varied greatly with changes in cation load. The findings suggested that it is difficult to model exchange behavior of vermiculitic clay minerals because CEC and K_v vary as a function of monovalent cation load.

Binary exchange isotherms for both clay samples are presented in Fig. 3. For reference purposes the nonpreference isotherm at 10 mM Cl was included. This nonpreference isotherm was generated by the equation (Sposito, 1981b)

$$E_{NH_4} = \left[1 + \frac{2}{FTN} \left\{ \frac{1}{E'_{NH_4}} - \frac{1}{E'_{Ca}} \right\} \right]^{-1/2} \quad [10]$$

where E_{NH₄} equals the equivalent fraction of NH₄⁺ on exchanger phase, F = γ_{NH₄}²/γ_{Ca}; where γ denotes single-ion activity coefficient, TN represents the total cation normality, and E'_{NH₄} represents equivalent fraction of NH₄⁺ in solution phase. It can be seen from the data in Fig. 3 that vermiculite showed no great preference for either NH₄⁺ or Ca²⁺ while HIV showed NH₄⁺ preference over Ca²⁺. It appeared that HAP shielded internal surfaces and their role in cation exchange was limited. Thus, external clay surfaces were most likely responsible for NH₄⁺ preference behavior. It is well known that external clay surface sites exhibit low charge density (Shainberg et al., 1980). This low surface charge density, because of entropy effects, formed relatively stronger surface complexes with monovalent cations than divalent cations (Shainberg et al., 1980).

The data in Fig. 4 show dependence of K_v on exchangeable loads of monovalent cations. The HIV clay exhibited at least two major classes of exchange sites.

At low exchangeable monovalent cation loads the clay system exhibited extremely high affinity sites (high K_v) for the monovalent cation. These sites were most likely edge sites with highly steric wedge influences or retardation of Ca²⁺ diffusion in the clay interlayer (Kozak and Huang, 1971). At increasing loads of exchangeable monovalent cations, K_v approached 1. On the other hand, vermiculite maintained an approximately constant K_v for NH₄-Ca exchange throughout the exchange isotherm. This suggested nearly constant surface complexation uniformity throughout the entire exchange isotherm.

The influence of a third ion (K at 6.0 mM) on NH₄-Ca exchange on both clay samples are presented in Fig. 5 and 6. Ternary K_v values were calculated by including exchangeable K⁺ in the mole fractions (Sposito and LeVesque, 1985; Sposito et al., 1983). For the HIV mineral, adding K⁺ dramatically suppressed K_v (Fig. 5). In contrast, adding K⁺ to vermiculite enhanced NH₄⁺ selectivity while shifting the maximum K_v to higher E_{NH₄} values (Fig. 6). The mechanism for this apparent reversal in the vermiculite's NH₄⁺ selectivity by the addition of K⁺ is not clear at this time. However,

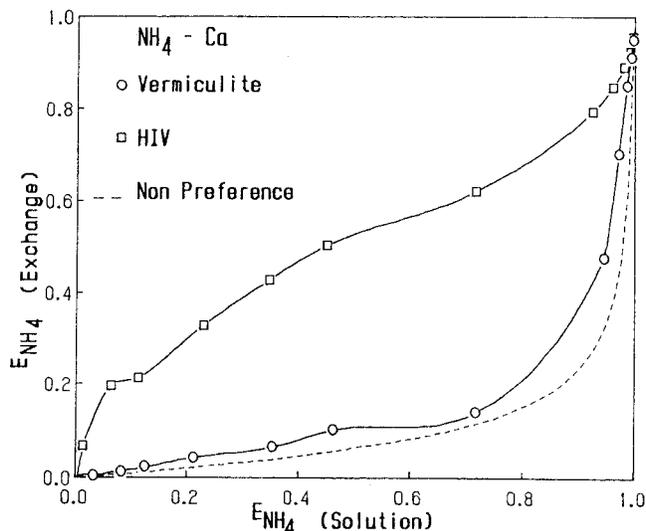


Fig. 3. Exchange isotherms for NH₄-Ca exchange on vermiculite and hydroxy-Al interlayered vermiculite (HIV).

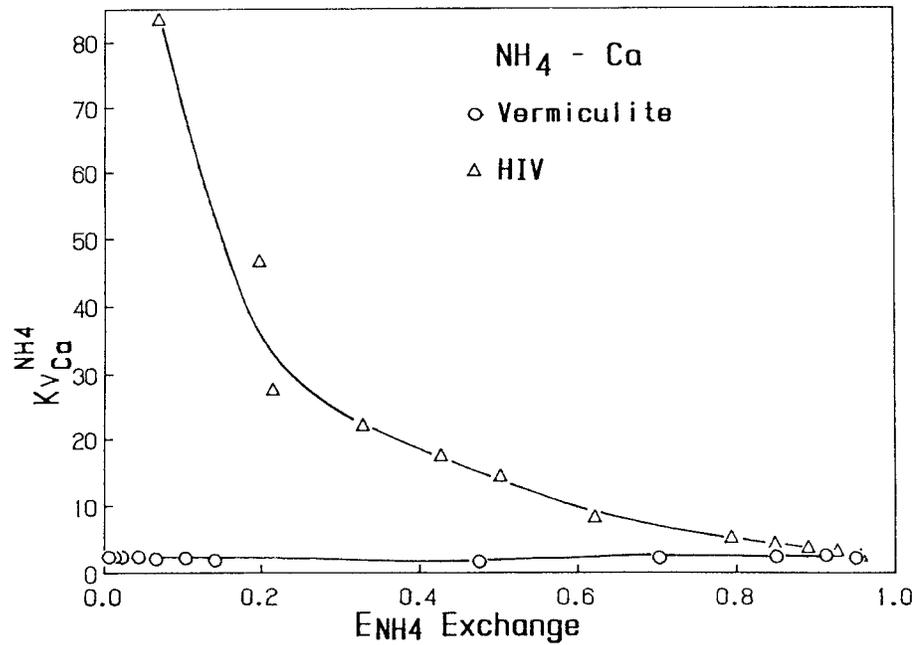


Fig. 4. Vanselow selectivity coefficients of NH_4 -Ca exchange on vermiculite and hydroxy-Al interlayered vermiculite (HIV).

one can hypothesize that in the presence of K^+ the interlayer collapsed (pinching effect) thus preventing Ca^{2+} from exchanging with NH_4^+ (Chappell and Evangelou, 2000 a,b). These results imply that this mechanism is only operable in the absence of HAP. Note also that the decrease in ΣEx_i at high NH_4^+ loading may also suggest that the interlayers of vermiculite are collapsing and thus fixing NH_4^+ and precluding exchange by Cs^+ . This implies that the exchange isotherms maybe biased in that highly selective sites for NH_4^+ are unaccounted for at high mole fractions of NH_4^+ . Accordingly, calcu-

lated K_v values will be low at higher E_{NH_4} making it appear that the solid phase has little preference for NH_4^+ vs. Ca^{2+} .

Direct comparison of the HIV-exchange data to that of vermiculite maybe problematic since the two systems differ in pH. In other words, to a degree the pH difference alone between the two clay mineral systems could explain the difference in exchange behavior. High pH is commonly associated with high surface electrical potential and divalent cations are preferred by the clay surface (Pratt et al., 1962). However, a high clay-surface

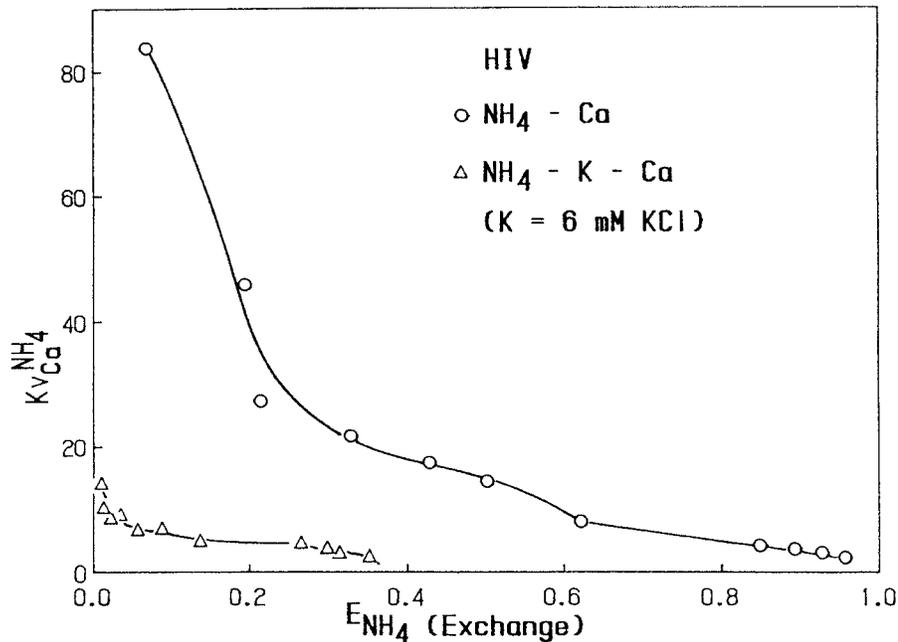


Fig. 5. Vanselow selectivity coefficients for NH_4 -Ca exchange in the presence or absence of K^+ (6.0 mM KCl in solution) on hydroxy-Al interlayered vermiculite (HIV).

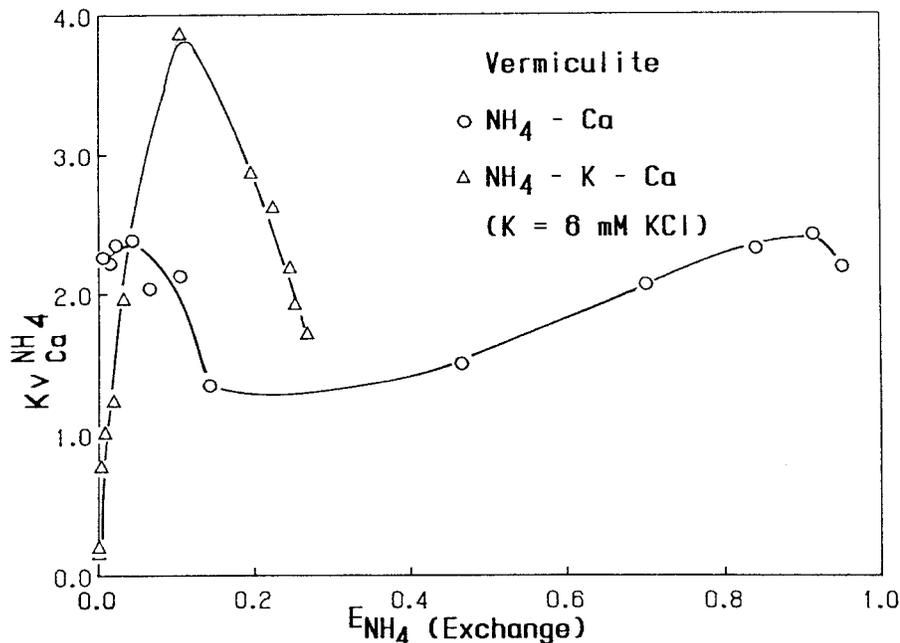


Fig. 6. Vanselow selectivity coefficients for NH₄⁺-Ca exchange in the presence or absence of K⁺ (6.0 mM KCl in solution) on vermiculite.

electrical potential can also be attributed to overlapping clay-interlayer double layers independently of pH (Shainberg et al., 1980). On the other hand, low pH is commonly associated with low clay-surface electrical potential and monovalent cations are preferred. However, clay dispersion may also induce a similar behavior independently of pH (McBride, 1980). One could still argue that the cation-exchange data in Fig. 3 are consistent with the expected cation exchange behavior because of influence of pH. However, the sharp increase in *K_v* at low K⁺ loads in HIV (Fig. 4 and 5) cannot be attributed to pH. This increase in *K_v* (high preference for K⁺) is commonly attributed to an interlayer monovalent cation-sieving effect (Beckett and Nafady, 1967).

In the case of agricultural soils, the most useful portion of a cation-exchange isotherm is that at low monovalent cation loads, e.g., low *E_K* or *E_{NH4}*. For this reason, an analysis of cation-exchange isotherm behavior at low monovalent cation fractional loads was carried out below. For a binary system, e.g., NH₄-Ca exchange, the slope of the isotherm (*CR_{NH4}* vs. *E_{NH4}*) as *CR_{NH4}* approaches zero can be used to estimate magnitude of *K_v* at the low fractional loads. This relationship is given by (Lumbanraja and Evangelou, 1990)

$$\frac{dE_{NH_4}}{dCR_{NH_4}} = (1/2)K_v$$

$$CR_{NH_4} \rightarrow 0 \tag{11}$$

In the case of a ternary exchange system, e.g., NH₄-K-Ca, the solution of *dE_{NH4}/dCR_{NH4}* at a constant *CR_K* as *CR_{NH4}* approaches zero is given by (Lumbanraja and Evangelou, 1990)

$$\frac{dE_{NH_4}}{dCR_{NH_4}} = K_{v1}/[4 + (K_{v2}CR_K)^2]^{1/2}$$

$$CR_{NH_4} \rightarrow 0 \tag{12}$$

where *K_{v1}* is the Vanselow exchange selectivity coefficient for NH₄-Ca exchange with NH₄⁺ as the displacing

cation, and *K_{v2}* is the Vanselow exchange selectivity coefficient for K-Ca exchange with K⁺ as the displacing cation. Note that in Eq. [11] and [12] *CR_{NH4}* was employed instead of *AR_{NH4}* because for the ionic strength tested *CR_{NH4}* and *AR_{NH4}* or *CR_K* and *AR_K* are nearly indistinguishable (Evangelou et al., 1986).

The NH₄-Ca exchange isotherms for vermiculite and HIV are shown in Fig. 7 and 8, respectively. The higher slopes of the isotherms representing the ternary exchange modes as *CR_{NH4}* approached zero suggested that

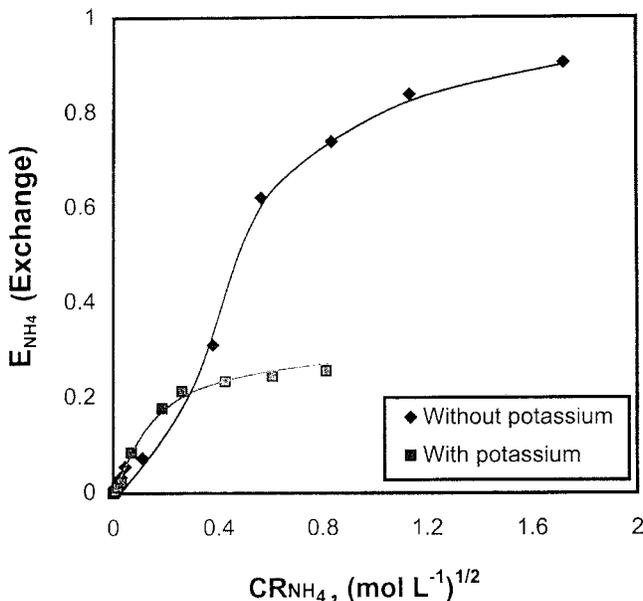


Fig. 7. Relationship between ammonium concentration ratio (*CR_{NH4}*) and equivalent fraction of ammonium on the exchange phase (*E_{NH4}*) on the exchange phase of vermiculite in the presence and absence of K (ternary exchange equivalent fractions were calculated utilizing cation-exchange capacity (CEC) as the sum of all three cations, NH₄⁺, K⁺, and Ca²⁺, on the exchange phase).

the $\text{NH}_4\text{-Ca}$ K_v of the ternary system was greater than the $\text{NH}_4\text{-Ca}$ K_v of the binary system. Note that E_{NH_4} values for the ternary systems were calculated using all three exchangeable cations, e.g., ExK , ExNH_4 , and $\text{ExCa}_{1/2}$. Assuming that the $\text{NH}_4\text{-Ca}$ exchange K_v of the binary and ternary exchange systems were similar, the slope of the ternary plot (as CR_{NH_4} approached zero) in Fig. 7 would be smaller than the slope of the binary plot. This is because $(K_{v1}/2) > (K_{v1}/[4 + (K_{v2}\text{CR}_K)^2]^{1/2})$. On the other hand, if the slope of the ternary plot was slightly greater than the slope of the binary plot as CR_{NH_4} approached zero, then the ternary K_v of $\text{NH}_4^+\text{-Ca}$ exchange would be greater than the binary K_v of the same cation-exchange reaction (see also Fig. 6).

In the case of HIV, the slopes of the binary- and ternary-exchange modes also differ, as CR_{NH_4} approached zero (Fig. 8). The exchange isotherm representing the binary mode reveals a slightly greater slope than the exchange isotherm representing the ternary mode. This implied that $(K_v/2) > K_v/[4 + (K_{v2}\text{CR}_K)^2]^{1/2}$ as CR_{NH_4} approached zero. Furthermore, the K_v representing the binary exchange mode may be equal to or greater than the ternary K_v as CR_{NH_4} approached zero. Support for this conclusion comes from Fig. 5 where the presence of K^+ significantly decreased the K_v of the $\text{NH}_4\text{-Ca}$ exchange at low E_{NH_4} values.

Theoretically, K_v values of ternary exchange systems calculated on the basis of only two exchangeable cations (see Eq. [4], [5], and [6]) should be smaller than the actual binary K_v values (Evangelou and Phillips, 1987). Figures 9 and 10 were plotted based on this reasoning. Note that in Fig. 9 the slope of the ternary mode, with ExK omitted, is greater than the slope of the actual binary mode. However, in the case of HIV the two K_v values are indistinguishable (Fig. 10). Some justification

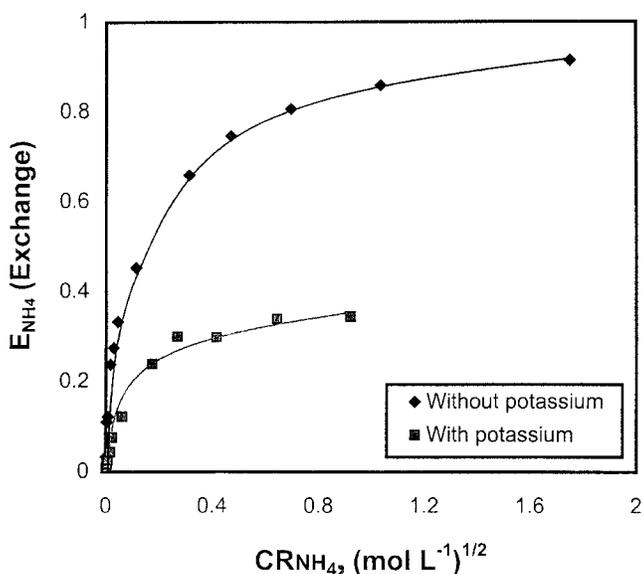


Fig. 8. Relationship between ammonium concentration ratio (CR_{NH_4}) and ammonium on the exchange phase (E_{NH_4}) of hydroxy-Al interlayered vermiculite (HIV) in the presence and absence of K (ternary exchange equivalent fractions were calculated utilizing cation-exchange capacity (CEC) as the sum of all three cations, NH_4^+ , K^+ , and Ca^{2+} , on the exchange phase).

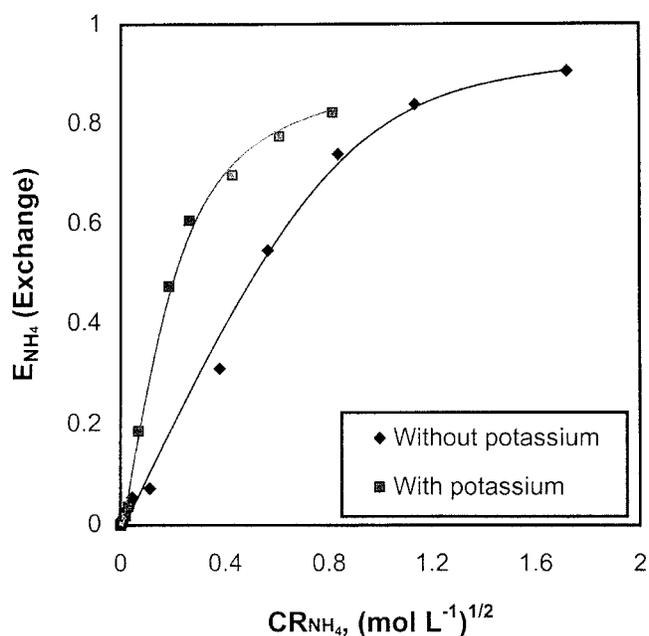


Fig. 9. Relationship between ammonium concentration ratio (CR_{NH_4}) and ammonium on the exchange phase (E_{NH_4}) of vermiculite in the presence and absence of K (ternary exchange equivalent fractions were calculated utilizing cation-exchange capacity [CEC] as the sum of the two cations [NH_4^+ and Ca^{2+}] on the exchange phase).

for treating the HIV ternary system as binary comes from the fact that exchangeable K^+ and solution K^+ remained nearly constant throughout the entire exchange isotherm (Table 6). This is not so for the vermiculite (Table 4) which appeared to behave as a ternary exchange system. The present study's solution K^+ of

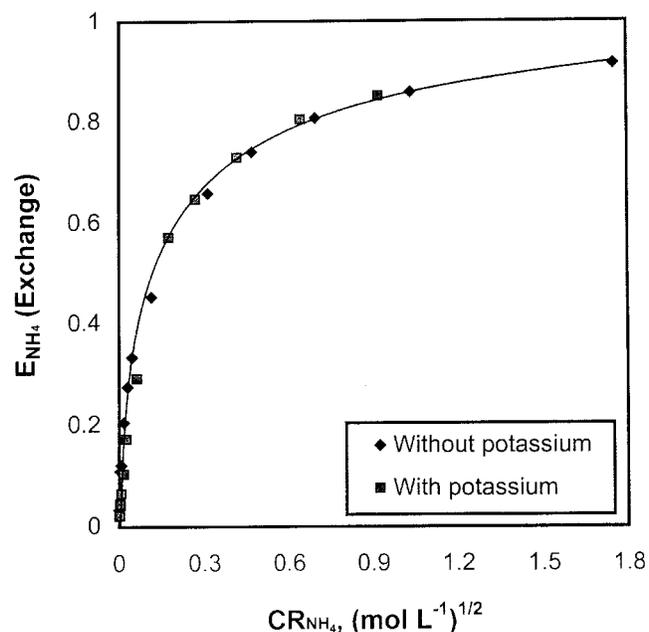


Fig. 10. Relationship between ammonium concentration ratio (CR_{NH_4}) and ammonium on the exchange phase (E_{NH_4}) of hydroxy-Al interlayered vermiculite (HIV) in the presence and absence of K (ternary exchange equivalent fractions were calculated utilizing cation-exchange capacity [CEC] as the sum of the two cations [NH_4^+ and Ca^{2+}] on the exchange phase).

~6 mM (Tables 4 and 6) would be much higher than what one would expect to find in actual soils. However, our previous data (Lumbanraja and Evangelou, 1990) showed that at much lower soil solution K^+ concentration a similar behavior with respect to magnitude of K_v in NH_4^+ -Ca exchange in a vermiculitic soil was observed.

CONCLUSIONS

Formation of HAP in vermiculite increased the mineral's affinity for NH_4^+ while addition of K^+ decreased the vermiculite's affinity for NH_4^+ . On the other hand, in the absence of HAP the presence of K^+ induced high affinity for NH_4^+ at increasing load of NH_4^+ . However, upon continuing to increase NH_4^+ load, NH_4^+ affinity decreased. The findings suggest that in the case of vermiculite, binary exchange data alone may not be able to predict ternary exchange data. However, in the case of HIV, binary data maybe able to predict ternary data as long as the third cation's distribution between exchange and solution phases remains constant across the isotherm.

The findings appear to have important implications in the management of fertilizers in soil systems with vermiculite-like clay minerals with and without HAP. It appears that the clay surface exhibits high specificity for K^+ at low-K fractional loads which cause the vermiculite interlayer to collapse and thus a large proportion of interlayer NH_4^+ most likely becomes fixed. The available-exchange sites appear to have relatively lower affinity for NH_4^+ . Therefore, the data indicate that availability of applied ammonium in vermiculitic soils would depend in the presence or absence of applied K. Applied K would have a tendency to increase NH_4^+ fixation but any remaining exchangeable NH_4^+ would be weakly held by the clay surface.

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Solid State ³¹P Phosphorus Nuclear Magnetic Resonance of Iron-, Manganese-, and Copper-Containing Synthetic Hydroxyapatites

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ABSTRACT

The incorporation of micronutrients into synthetic hydroxyapatite (SHA) is proposed for slow release of these nutrients to crops in the National Aeronautics and Space Administration's (NASA's) Advanced Life Support (ALS) program for Lunar or Martian outposts. Solid state ³¹P nuclear magnetic resonance (NMR) was utilized to examine the paramagnetic effects of Fe³⁺, Mn²⁺, and Cu²⁺ to determine if they were incorporated into the SHA structure. Separate Fe³⁺, Mn²⁺, and Cu²⁺ containing SHA materials along with a transition metal free SHA (pure-SHA) were synthesized using a precipitation method. The proximity (<1 nm) of the transition metals to the ³¹P nuclei of SHA were apparent when comparing the integrated ³¹P signal intensities of the pure-SHA (87 arbitrary units g⁻¹) with the Fe-, Mn-, and Cu-SHA materials (37–71 arbitrary units g⁻¹). The lower integrated ³¹P signal intensities of the Fe-, Mn-, and Cu-SHA materials relative to the pure-SHA suggested that Fe³⁺, Mn²⁺, and Cu²⁺ were incorporated in the SHA structure. Further support for Fe³⁺, Mn²⁺, and Cu²⁺ incorporation was demonstrated by the reduced spin-lattice relaxation constants of the Fe-, Mn-, and Cu-SHA materials (*T*' = 0.075–0.434 s) relative to pure-SHA (*T*₁ = 58.4 s). Inversion recovery spectra indicated that Fe³⁺, Mn²⁺, and Cu²⁺ were not homogeneously distributed about the ³¹P nuclei in the SHA structure. Extraction with diethylenetriamine-penta-acetic acid (DTPA) suggested that between 50 and 80% of the total starting metal concentrations were incorporated in the SHA structure. Iron-, Mn-, and Cu-containing SHA are potential slow release sources of Fe, Mn, and Cu in the ALS cropping system.

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION'S ALS PROGRAM is currently evaluating crop production systems for Lunar or Martian outposts. Crops grown will minimize resupply costs from Earth by providing food and recycling air and water (Averner, 1989; Allen et al., 1995). The ALS program is developing a zeoponic-based plant growth system which is composed of a slow release fertilizer that combines an ammonium (NH₄⁺) and potassium (K⁺) charged clinoptilolite (zeolite) with a nutrient containing SHA [Ca₁₀

(PO₄)₆(OH)₂] (Golden and Ming, 1999; Steinberg et al., 2000). Synthetic hydroxyapatite is produced to contain plant essential nutrients (Mg, Fe, Mn, Cu, Zn, S, Cl, Mo, and B) within the SHA structure. If nutrients can be incorporated into the structure of the sparingly soluble SHA, then slow-nutrient release from SHA at rates suitable for plant growth would be expected. This would be ideal for missions expected to last >1 yr.

Past research using x-ray diffraction (XRD) and infrared (IR) spectroscopy has determined that Fe, Mn, and Cu were substituted into the SHA structure (Tripathy et al., 1989; Golden and Ming, 1999). Golden and Ming (1999) noted that the d[002] spacing of the Fe²⁺, Mn²⁺, and Cu²⁺ substituted SHA was less than the unsubstituted SHA. Substitution of Cu²⁺ into SHA caused the *a* and *c* axes of the Cu²⁺ substituted SHA to be less than the unsubstituted SHA (Tripathy et al., 1989). Tripathy et al. (1989) and Golden and Ming (1999) reported the PO₄-ν₃ absorption wavenumber of the metal substituted SHA to be lower and higher, respectively, than the unsubstituted SHA.

This research examined a lower concentration range of transition metals (7–25 g kg⁻¹) in SHA than were studied by Tripathy et al. (1989, 66–512 g kg⁻¹) and Golden and Ming (1999, 15–50 g kg⁻¹). X-ray analyses of the transition metal containing SHA (metal-SHA) materials of this study did not show any x-ray lines that shifted relative to pure-SHA (Sutter, 2000). The low concentration of metals in SHA did not allow for significant shift of x-ray lines that would indicate incorporation of the metals in SHA. While IR was successful in detecting Fe and Mn incorporation into SHA, IR analyses did not indicate Cu incorporation into SHA (Sutter, 2000). The amount of Cu incorporated into SHA may have been too low for IR to detect. An analytical technique was required that could detect Fe, Mn, as well as Cu incorporation into SHA for the entire metal concentration range of this research. Solid state ³¹P NMR spec-

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Abbreviations: ALS, Advanced Life Support; DTPA, diethylene-tri-amine-penta-acetic acid; IR, infrared; NASA, National Aeronautics and Space Administration; NMR, nuclear magnetic resonance; SHA, synthetic hydroxyapatite; XRD, x-ray diffraction.