THERMODYNAMIC STUDY OF Na-K-Ca EXCHANGE REACTIONS IN VERMICULITE

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Abstract—The exchange of Na, K, and Ca ions in vermiculite has been studied between 50 and 150°C at a total normality of 0.1. The free energy changes were negative in the Na → K, Ca → K, and Na → Ca exchange reactions, and the cation preference in the vermiculite was Na < Ca < K in the temperature range examined. The enthalpy changes, calculated by application of the van't Hoff equation to the relation between equilibrium constant and temperature, were positive. The cation preference in the vermiculite seems to have been largely controlled by the increase in entropy which was due to the positive values of the entropy change term in the solid for the Na-K and Ca-K exchanges and the positive values of the entropy change in the solution for the Na-Ca exchange. From a thermodynamic analysis of the cation-mixing properties in vermiculite, the observed free energy change in the Na-K exchange was determined solely by the differences of the intrinsic electrostatic binding energy of the cations on the clay surface. That in the Na-Ca exchange was interpreted by taking into account an extra interaction energy of Ca-Ca pairs in addition to the intrinsic energy change. Furthermore, an additional interaction energy between K ions and the clay surface appears to have been added to the free energy change in the Ca-K exchange. In the Na → K and Ca → K exchange reactions a structural modification occurred in the K-equivalent fraction ($\bar{X}_K$) range 0.05–0.6, and a regularly interstratified phase of 15-Å and 10-Å members was formed at $0.05 < \bar{X}_K < 0.4$.

Key Words—Cation exchange, Entropy, Free energy, Interstratification, Thermodynamics, Vermiculite.

INTRODUCTION

The effect of charge density on cation selectivity of smectite has been of interest to clay mineralogists and geologists because the cation selectivity of smectite varies during burial diagenesis and smectite layers gradually prefer K ions and convert to illite layers (Eberl, 1980; Inoue and Utada, 1983). Maes and Cremers (1977, 1978) examined the effect of charge density on homovalent and heterovalent cation-exchange equilibria in smectite but extrapolating their results to the cation selectivity of clays with greater negative layer charge, such as vermiculite, remains uncertain. The present study was undertaken to understand the cation-exchange properties of vermiculite at higher temperatures.

On the other hand, the formation of interstratified phases has been recognized in the cation-exchange of K-bearing vermiculite (Wey *et al.*, 1974; Le Dred *et al.*, 1978; Saehr *et al.*, 1982). These regularly interstratified structures can be detected by long-spacing reflections in their X-ray powder diffraction (XRD) patterns. Saehr *et al.* (1982) related their formation to the existence of two types of cation-exchange sites in vermiculite. There remains some ambiguity in their results, because the samples used appear to have included some initially interstratified material.

The present paper clarifies the cation-mixing properties in vermiculite by applying a statistical thermodynamic theory to cation-exchange equilibria for a solid with a single exchange site.

EXPERIMENTAL

Material

The vermiculite was obtained from Palabora, South Africa, and has the following chemical composition; SiO_2 36.18%, Al_2O_3 9.90%, Fe_2O_3 as total Fe 4.90%, MgO 25.91%, CaO 0.55%, Na_2O 0.06%, K_2O 1.12%, and H_2O 20.64% (Inoue, 1983). It was converted to homoionic forms by repeated treatment with the appropriate chloride solutions. It was washed until no chloride was detected and then dried at room temperature. The cation-exchange capacities (CEC) of the Na-, K-, and Ca-forms were 150, 176, and 175 meq/100 g, respectively. The Na-exchanged vermiculite retained a small amount of Mg ion in the interlayers as evidenced by a slight 15-Å peak of the original vermiculite remaining in the XRD pattern of the Na-exchanged form.

Methods

Approximately 0.1 g of each homoionic vermiculite was shaken at each temperature for at least 2 weeks in a binary chloride mixed solution with various ratios of the two salts. Exchange isotherms were determined at 50°, 70°, 90°, 100°, and 150°C and at a constant total normality (0.1). Runs at 50° and 70°C were carried out in 50-ml polyethylene tubes and runs at 90°, 100°, and 150°C in ~22-ml Teflon vessels. Suspensions at equilibrium were separated, the clay was decomposed by HF and H_2SO_4, and the cation contents in both the

clay and the solution were determined by atomic absorption and emission spectrometers. The equilibrated clays were examined by XRD using oriented specimens at 50–60% RH.

Evaluation of thermodynamic quantities

Applying mass action law to the exchange reaction between a solution cation A^{z_A} and a clay-adsorbed cation B^{z_B}, i.e.,

$$z_B A_s{}^{z_A} + z_A B^{z_B}\text{-vermiculite}$$
$$= z_B A^{z_A}\text{-vermiculite} + z_A B_s{}^{z_B}, \qquad (1)$$
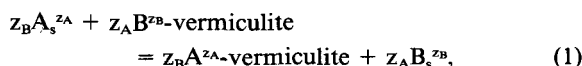
the equilibrium constant K is given by Barrer (1974)

$$K = \frac{\bar{X}_A{}^{z_B} f_A{}^{z_B}}{\bar{X}_B{}^{z_A} f_B{}^{z_A}} \cdot \frac{X_B{}^{z_A} \gamma_B{}^{z_A}}{X_A{}^{z_B} \gamma_A{}^{z_B}} \cdot \frac{1}{Q}$$

$$= K_c \cdot \frac{f_A{}^{z_B}}{f_B{}^{z_A}}, \qquad (2)$$

where

$$Q = z_B{}^{z_A}/[z_A{}^{z_B}(z_A m_A + z_B m_B)^{(z_A - z_B)}].$$

$\bar{X}_i$ and X_j are the equivalent fraction of species i in the solid and the solution, respectively, f_i and γ_i are the activity coefficient of species i in solid and solution, z_i is the charge of species i, and m_i is the molality of species i in solution. Values of the activity coefficients of the ions in solution were computed using the Davies equation (Davies, 1962) and then corrected for the mixing effect of two salt solutions by Guggenheim's method (Guggenheim, 1935). K_c in Eq. (2) is the experimentally determined selectivity coefficient after performing some corrections.

The equilibrium constant K is defined by K_c as shown by Eq. (3) if appropriate standard states are chosen along with application of the Gibbs-Duhem equation (Gaines and Thomas, 1953):

$$\ln K = (z_B - z_A) + \int_0^1 \ln K_c \, d\bar{X}_B. \qquad (3)$$

Here, it is assumed that the changes in the activity of water in clay and solution are negligible. The standard free energy change ΔG^0 for the reaction of Eq. (1) is in turn related to K by the expression (Barrer *et al.*, 1966)

$$\Delta G^0 \text{ (cal/eq)} = -RT \ln K/z_A z_B. \qquad (4)$$

The standard enthalpy change ΔH^0 is evaluated by the van't Hoff equation

$$\Delta H^0 \text{ (cal/eq)} = -\frac{R}{z_A z_B} \cdot \frac{\partial(\ln K)}{\partial(1/T)}. \qquad (5)$$

The standard entropy change ΔS^0 is calculated from the equation

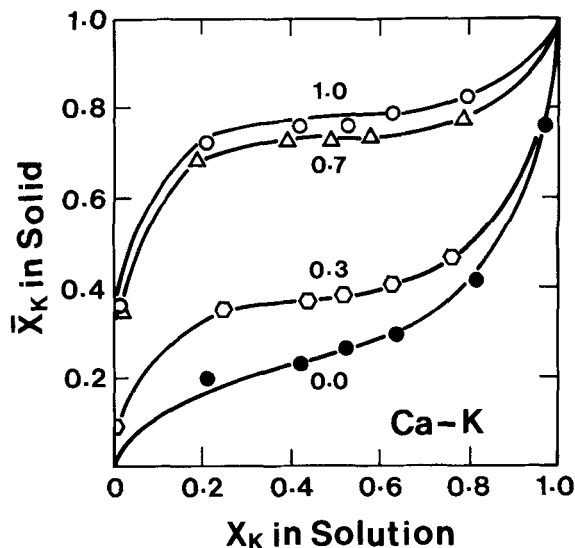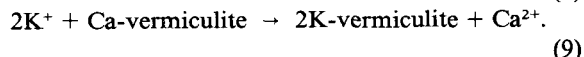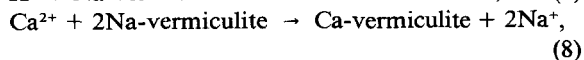$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \qquad (6)$$

Figure 1. Ca-K exchange isotherms at 50°C and 0.1 N obtained with preheated Ca- and K-vermiculites. $\bar{X}_K$ and X_K indicate the K-equivalent fraction in solid and solution, respectively. The numerical values indicate the K-equivalent fractions contained initially in the starting materials.

RESULTS AND DISCUSSION

Isotherms

The Ca-K exchange isotherms obtained by exchange of the preheated K- and Ca-vermiculites are shown in Figure 1. The exchange isotherms exhibited marked hysteresis when the dried K-vermiculite was used as a starting material. A similar hysteresis was observed in the K-Ca exchange of montmorillonite by Inoue and Minato (1979) who concluded that it was caused by the fixation of K ions in the interlayers of clay. To avoid the effect of cation fixation during exchange, reactions were run in the following direction

$$K^+ + \text{Na-vermiculite} \rightarrow \text{K-vermiculite} + Na^+, \qquad (7)$$
$$Ca^{2+} + 2\text{Na-vermiculite} \rightarrow \text{Ca-vermiculite} + 2Na^+, \qquad (8)$$
$$2K^+ + \text{Ca-vermiculite} \rightarrow 2\text{K-vermiculite} + Ca^{2+}. \qquad (9)$$

The smoothed exchange isotherms corresponding to reactions (7), (8), and (9) are shown in Figures 2, 3, and 4, respectively. In the Na-K exchange, the vermiculite showed a marked preference for K over Na (Figure 2). The preference for K increased with increasing temperature. The vermiculite in the Na-Ca exchange showed a preference for Ca over Na; higher temperature favored this preference also (Figure 3). The isotherms for the Ca-K exchange of vermiculite were sigmoidal at the three temperatures (Figure 4); the selectivity for K increased with increasing temperature.
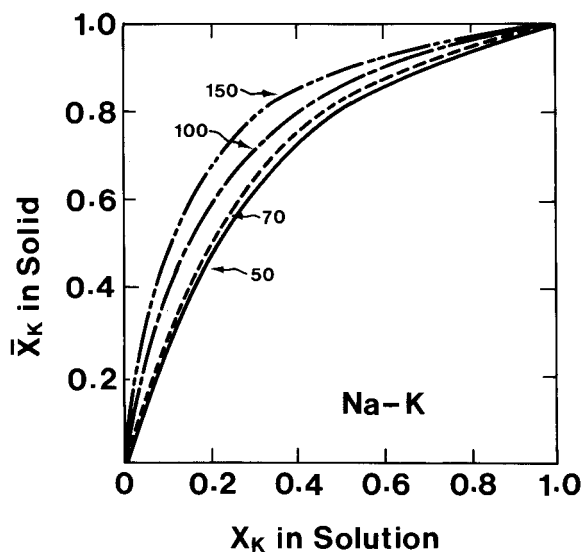
Figure 2.   Na-K exchange isotherms of vermiculite at various temperatures. —— = 50°C, – – – = 70°C, – – – = 100°C, – – – – = 150°C.

Figure 4.   Ca-K exchange isotherms of vermiculite at various temperatures. —— = 50°C, – – – = 90°C, – – – = 150°C.

Thermodynamic quantities

Logarithmic values of the selectivity coefficient K_c at various temperatures are plotted against the equivalent fraction $(\bar{X}_i)$ of each ion in the vermiculite in Figures 5, 6, and 7. The values of ln K were calculated by Eq. (3) from the smoothed curves in Figures 5, 6, and 7. Table 1 gives the standard free energy, enthalpy, and entropy changes in exchange reactions which were calculated from Eqs. (4), (5), and (6). In the calculation of enthalpy change, the relation for ln K vs. 1/T was
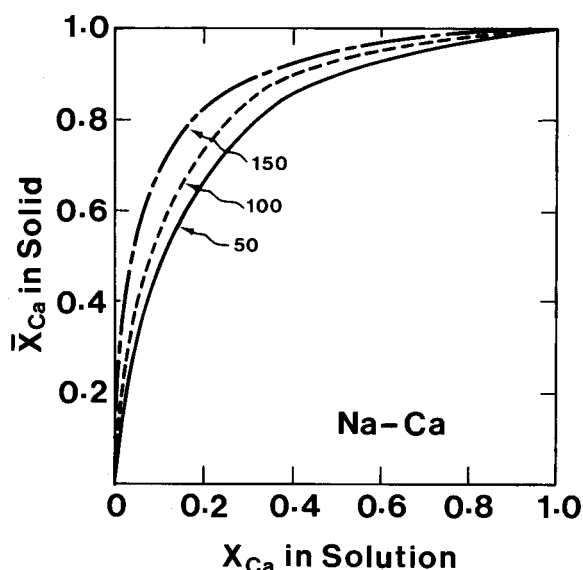
assumed to be linear over the temperature range 50–150°C (Figure 8).

The values for the standard free energy changes suggest that the affinity of the ions for vermiculite follows the order: Na < Ca < K between 50° and 150°C. The

Figure 3.   Na-Ca exchange isotherms of vermiculite at various temperatures. —— = 50°C, – – – = 100°C, – – – = 150°C.

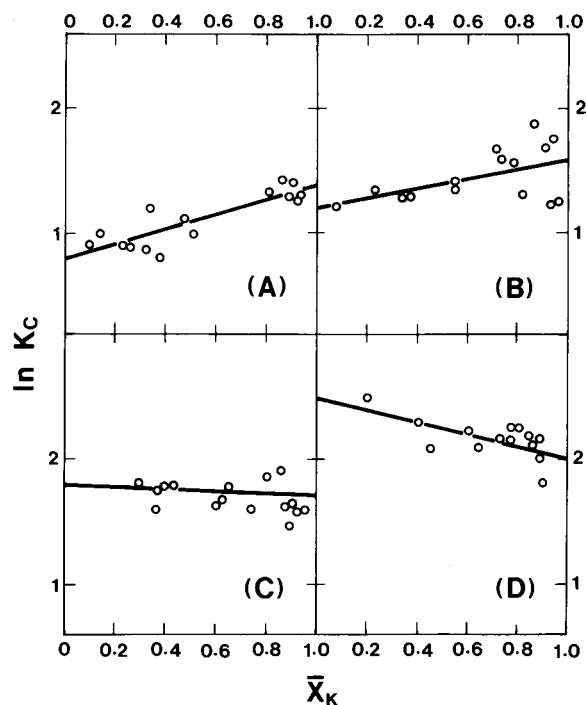Figure 5.   Plots of ln K_c vs. $\bar{X}_K$ for Na-K exchange of vermiculite at (A) 50°C, (B) 70°C, (C) 100°C, and (D) 150°C. The lines are the regression curves at respective temperatures.
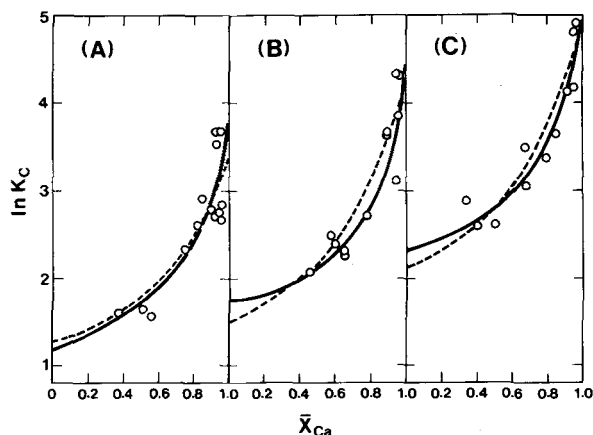
Figure 6. Plots of ln K_c vs. $\bar{X}_{Ca}$ for Na-Ca exchange of vermiculite at (A) 50°C, (B) 100°C, and (C) 150°C. The solid and broken curves are the smoothed observed and calculated curves at respective temperatures (see text).

selectivity sequence for the three cations is different from that for montmorillonite: Na < K < Ca (Inoue and Utada, 1983). The greater preference for K ion in the vermiculite supports the previous concept that increasing negative layer charge can be responsible for the K-enrichment in the interlayers of clay during burial diagenesis, as pointed out previously by Eberl (1980) and Inoue and Utada (1983).

The consistency of the standard free energy change in each cation pair can be checked by the following relation

$$\Delta G^0(Na\text{-}K) - \Delta G^0(2Na\text{-}Ca) = \Delta G^0(Ca\text{-}2K). \quad (10)$$

Using the 50°C data in Table 1, the free energy change in the Ca-K exchange is −90 cal/eq close to the experimental value of −60 cal/eq.

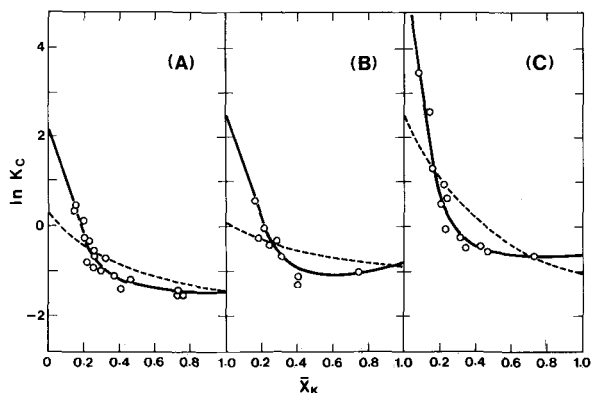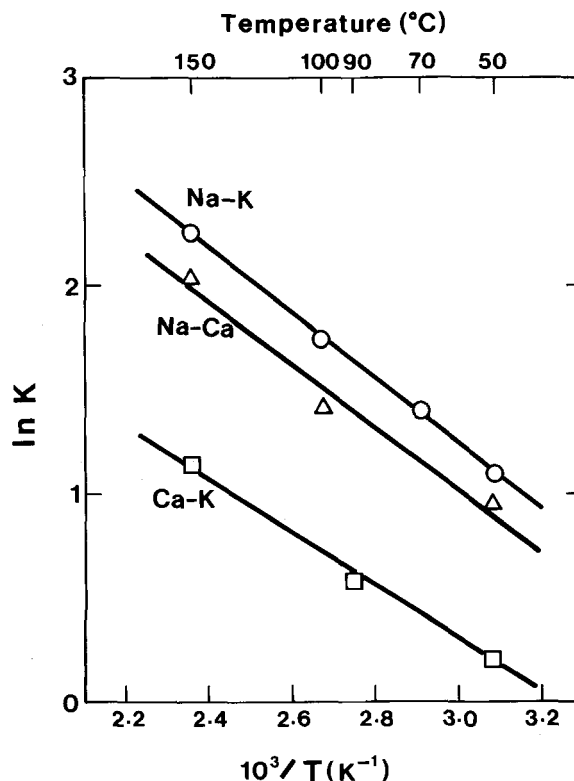The sign of the enthalpy change in Table 1 indicates

Figure 8. Relationship between equilibrium constants and temperature in Na-K, Na-Ca, and Ca-K exchanges of vermiculite.

that the Na-K, Na-Ca, and Ca-K exchange reactions in vermiculite are endothermic. The Na-Ca exchange reaction in smectite is also endothermic (Maes and Cremers, 1977), but the Na-K and Ca-K exchange reactions are exothermic (Inoue and Minato, 1979; Inoue and Utada, 1983). All of the values of entropy change

Figure 7. Plots of ln K_c vs. $\bar{X}_K$ for Ca-K exchange of vermiculite at (A) 50°C, (B) 90°C, and (C) 150°C. The solid and broken curves are the smoothed observed and calculated curves at respective temperatures (see text).

Table 1. Standard free energy (ΔG^0), standard enthalpy (ΔH^0), and standard entropy (ΔS^0) for Na-K, Na-Ca, and Ca-K exchanges of vermiculite.

	Temperature (°C)	ΔG^0 (cal/eq)	ΔH^0 (kcal/eq)	ΔS^0 (cal/eq)
Na-K	50	−700		11.9
	70	−950	3.13	11.9
	100	−1290		11.8
	150	−1890		11.9
			av.	11.9
2Na-Ca	50	−610		6.8
	100	−1040	1.59	7.1
	150	−1740		7.8
			av.	7.2
Ca-2K	50	−60		4.2
	90	−210	1.30	4.2
	150	−480		4.2
			av.	4.2

for the exchange reactions of vermiculite are positive (Table 1). The entropy change of the Na-Ca exchange in smectite is also positive (Maes and Cremers, 1977), but those of the Na-K and Ca-K exchanges in smectite are negative (Maes and Cremers, 1978; Inoue and Minato, 1979).

In Eq. (6), the sign of the free energy change is determined by both enthalpy and entropy change terms. The fact that the free energy change in the vermiculite is negative in spite of positive values of both the enthalpy and entropy changes indicates that the affinity of the ions in the vermiculite is largely determined by the increase in entropy. The total entropy change for the reaction (1) can be written as:

$$\Delta S_{total} = \Delta S_{solid} + \Delta S_{solution}$$
$$= (z_B S_{A\text{-clay}} - z_A S_{B\text{-clay}})$$
$$+ (z_A S_{B\text{-ion}} - z_B S_{A\text{-ion}}). \quad (11)$$

The contribution of the entropies of ions in solution to the observed entropy change for limiting values of ion concentration was evaluated by Goulding and Talibudeen (1980) as follows. Entropies of ions in solution, S_i, at 0.1 N can be calculated by the relationship

$$S_i = S_i^0 - R \ln a_i, \quad (12)$$

where S_i^0 is the entropy of i ion in solution of unit molality, a_i is the activity of i ion, and R is the gas constant. As S_i^0 for Na, K, and Ca ions are 14.4, 25.5, and −13.2 cal/mole (Garrels and Christ, 1965), the entropy changes in the solutions in Eq. (11) are: $\Delta S_{solution}$(Na-K) = −11.1 cal/eq; $\Delta S_{solution}$(Na-Ca) = 22.6 cal/eq; and $\Delta S_{solution}$(Ca-K) = −33.7 cal/eq. Using an average observed ΔS^0 value (Table 1), the entropy changes in the solid are: ΔS_{solid}(Na-K) = 23.0 cal/eq; ΔS_{solid}(Na-Ca) = −15.4 cal/eq; and ΔS_{solid}(Ca-K) = 37.9 cal/eq.

Comparison of ΔS_{solid} and $\Delta S_{solution}$ indicates that the positive values of the observed entropy change are derived from the effect of positive ΔS_{solid} in the Na-K and Ca-K exchanges, and from the effect of positive $\Delta S_{solution}$ in the Na-Ca exchange. The present conclusion that the ΔS_{solid} term of the total entropy change controls the cation preference in K-bearing vermiculite is different from the previously reported conclusion for montmorillonite in which the $\Delta S_{solution}$ is proposed as the predominant control of the cation preference (Hutcheon, 1966; Deist and Talibudeen, 1967; Inoue and Minato, 1979). Moreover, the ΔS_{solid} calculated suggest that replacement of Na by Ca in the vermiculite resulted in a negative entropy change, and, hence, the three-dimensional structure of the vermiculite is more rigid in the Ca-form than in the Na-form. Replacement of Na and Ca by K in the vermiculite, however, resulted in increasing randomness of the structure along the c-axis. The disordering effect by adding K ions in the

vermiculite was more obvious in the Ca-K exchange than in the Na-K exchange.

Cation-mixing properties in vermiculite

Statistic thermodynamic theory for ion mixing in solid was successfully applied to cation-exchange equilibria in zeolites by Barrer and Falconer (1956) and Barrer and Klinowski (1979) and in resins by Harvey *et al.* (1966). A similar theory can be applied to the cation-exchanges in the vermiculite.

In the theory, in A-B exchange on a solid with a single exchange site, no extra energy change occurs for AB or AA pairs, but when two ions of B occupy adjacent sites, an additional energy ω_{BB} exists. The grand partition function for this model is as follows (Barrer and Falconer, 1956):

$$\Omega = g(N_A, N_B)\left[j_A(T)\exp\left(\frac{E_A}{kT}\right)\right]^{N_A}$$
$$\cdot \left[j_B(T)\exp\left(\frac{E_B}{kT}\right)\right]^{N_B} \Omega_c \exp(-E), \quad (13)$$

where N_i, j_i, and E_i are the number, partition function, and intrinsic electrostatic binding energy of species i on the clay surface, Ω_c is the partition function of the clay matrix, E is a function of the energy of interaction of B-B pairs, and $g(N_A, N_B)$ is the statistical weight factor. If it is assumed that the distribution of cations on sites is random, the selectivity coefficient for mono-monovalent cation exchange (A^+-B^+) may be expressed as (Barrer and Falconer, 1956):

$$\ln K_c = K' + C\bar{X}_B, \quad (14)$$

where $C = -\omega_{BB}/kT$, K' is the constant which includes the differences of intrinsic energy of the two cations, and k is the Boltzmann constant.

In mono-divalent cation exchange (A^+-B^{2+}), if it is assumed that the B ions are two charged points rigidly joined to form a dumbbell charge, the selectivity coefficient may be written as (Harvey *et al.*, 1966):

$$\ln K_c = K'' + D\frac{\bar{X}_B(4 - \bar{X}_B)}{(2 - \bar{X}_B)^2}, \quad (15)$$

where $D = \omega_{BB}/kT$, and K'' is the constant which includes the differences of intrinsic energy of the two cations.

In the Na-K exchange of vermiculite (Figure 5) the Kielland plots vary slightly through the entire range of $\bar{X}_K$ in the solid. The interaction energy ω calculated from Eq. (14) = −370 cal/eq at 50°C, −260 cal/eq at 70°C, 60 cal/eq at 100°C, and 420 cal/eq at 150°C. According to Barrer and Falconer (1956), positive values of ω indicate that the cations tend to repel each other, whereas negative values of ω lead the cations to cluster or aggregate. In fact, no immiscibility in solid phase was found in the Na-K exchange isotherms be-
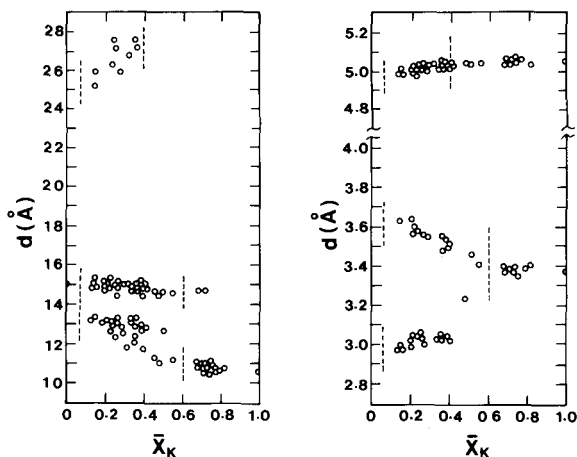
Figure 9. Relationship between d-spacing of basal reflections and $\bar{X}_K$ in (Ca,K)-vermiculite.

Figure 10. Relationship between d-spacing of basal reflections and $\bar{X}_K$ in (Na,K)-vermiculite.

cause of the small values of ω. In the Na-K exchange of vermiculite, the Coulombic forces are the predominant ones acting between the cations and the clay surface, and therefore the observed free energy change appears to be determined solely by the differences of intrinsic electrostatic binding energy between the cations and the clay surface.

By the application of Eq. (15), the fitted curves for the Kielland plots of the Na-Ca exchange of vermiculite by the least-squares method are shown by broken curves in Figure 6. The fits are reasonably good. The free energy, enthalpy, and entropy changes, calculated from the fitted theoretical curves, were in good agreement with the observed data in Table 1. The consistency is an indication that the assumptions used in the calculation of selectivity coefficient on the basis of the statistic thermodynamic theory were correct. The free energy change observed for the Na-Ca exchange of vermiculite may be interpreted by taking into account an extra interaction energy of Ca-Ca pairs in addition to the differences of intrinsic energy of Na and Ca. The interaction energy = -225 cal/eq at 50°C, -340 cal/eq at 100°C, and -395 cal/eq at 150°C.

For the Ca-K exchange of vermiculite, the interaction energy calculated from Eq. (15) were positive at three temperatures, though the fits are not good as shown in Figure 7. The inconsistency of the theory for the experimental data suggests that the observed free energy change consists of another interaction energy between the cations and the clay surface in addition to the intrinsic energy change and the cation-pair interaction energy. According to Barrer and Falconer (1956), positive values of ω may, although not necessarily, lead to sigmoidal isotherms even in the cation-exchange of solid phase with a single exchange site.

Saehr *et al.* (1982) interpreted the sigmoidal isotherms for the Ca-K exchange on the basis of two types of exchange sites in vermiculite. Goulding and Tali-
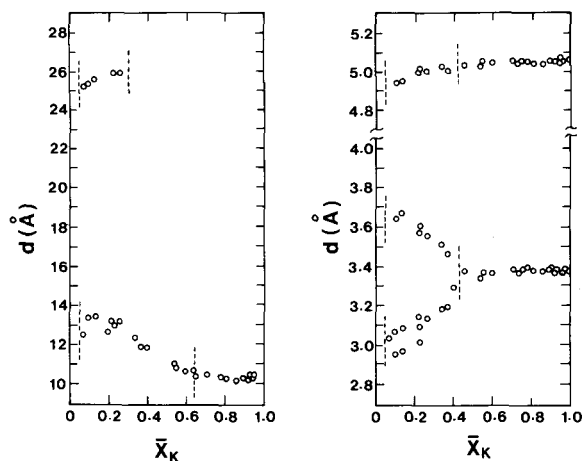
budeen (1980) demonstrated that groups of sites with various exchange enthalpies exist in vermiculite in the Ca $\rightarrow$ K exchange reaction, from the differential enthalpy change measured by microcalorimetry. Accurate mineralogical data for the vermiculites examined are lacking, however, and the evidence that two types of exchange sites exist in vermiculite is uncertain in the present Na-K and Na-Ca exchanges of the vermiculite.

Formation of interstratified phase

The relationships between cation composition in the vermiculite and the peak position of the basal reflections for the Ca-K and Na-K exchanged products are illustrated in Figures 9 and 10, respectively. In the Na-Ca system, the basal spacings of the Ca- and Na-vermiculites were ~ 15 and 12.8 Å, respectively. The basal spacing of 15 Å for the Ca-vermiculite changed little even when more than 70% of Ca was exchanged by Na. The behavior of basal spacing in the (Na,Ca)-vermiculite was different from the previously reported behavior of (Na,Ca)-smectite in which the basal spacing decreased gradually to 12.6 Å as the Na-equivalent fraction approached 60–70% (McAtee, 1956).

In the Ca-K system (Figure 9), structural modification was observed in the range $0.1 < \bar{X}_K < 0.6$ from the variation of some basal reflections in the (Ca,K)-vermiculite. As shown in Figure 11, the (Ca,K)-vermiculites in the compositional range $0.1 < \bar{X}_K < 0.4$ showed a weak long-spacing reflection at 25–27 Å and its second order reflection at 13 Å. These data indicate that a regularly interstratified phase was formed in the range $0.1 < \bar{X}_K < 0.4$ and that the interstratified phase probably consisted of Ca-vermiculite (15 Å) and K-vermiculite (10.6 Å) or K-mica (10 Å) layers. At $\bar{X}_K > 0.7$, the (Ca,K)-vermiculite is nearly all a K-vermiculite, 10-Å structure.

In the Na-K system (Figure 10), structural modification was observable at $0.05 < \bar{X}_K < 0.6$. A weak long-spacing reflection at 23–26 Å corresponding to the first order reflection of a regularly interstratified phase was also observed in the range $0.05 < \bar{X}_K < 0.3$. The 13-Å peak corresponding to the second order reflection of the interstratified phase was not noticeable because of superposition by the 12.8-Å peak of Na-vermiculite.

The relationship between the variation of basal spacing and cation composition mentioned above indicates that in the (Na,K,Ca)-solid solution of vermiculite, structural modification took place at intermediate compositions only when the vermiculite contained K in the interlayers. The structural modification in the vermiculite took place at $0.05 < \bar{X}_K < 0.6$, and a regularly interstratified phase was formed at $0.05 < \bar{X}_K < 0.4$ in the Na-K and the Ca-K systems. Le Dred *et al.* (1978) and Saehr *et al.* (1982) reported that a regularly interstratified phase formed at $0 < \bar{X}_K \le 0.8$ in the Na-K and Ca-K exchanges of vermiculite. The vermiculite used in their experiments included initially a small amount of regularly interstratified material. Therefore, the cation composition range $(0 < \bar{X}_K \le 0.8)$ in which a regularly interstratified phase was formed may be inaccurate.

In the interlayers of vermiculite, K ions usually exist in a dehydrated state, whereas Na and Ca ions hold water molecules tightly. Accordingly, even when the segregation of cations in the Na-Ca exchange of vermiculite occurs in the interlayers, the formation of interstratification does not occur because the hydration states of Na and Ca in the interlayers of vermiculite are similar to each other (MacEwan and Wilson, 1980). On the other hand, dehydrated K ions may interact strongly with the clay surface. Taking into account the cation-mixing properties of vermiculite mentioned above, a large, positive interaction energy including another extra interaction energy between K ions and the clay surface may be responsible for the formation of interstratification in vermiculite as well as the sigmoidal isotherms.

Yoshida (1979) interpreted the formation of an interstratified phase in vermiculite as demixing or segregation of the cations in the interlayers as well as the previously reported behavior of montmorillonite (Glaeser and Mering, 1954; McAtee, 1956; McBride, 1976; Inoue and Minato, 1979) on the basis of another statistic thermodynamic model. The extra interaction energy ω for the isotherms showing segregation of cations must be sufficiently negative as mentioned above. In fact, as shown in Figures 5–7, no immiscibility gap in the solid was found in the isotherms of vermiculite.
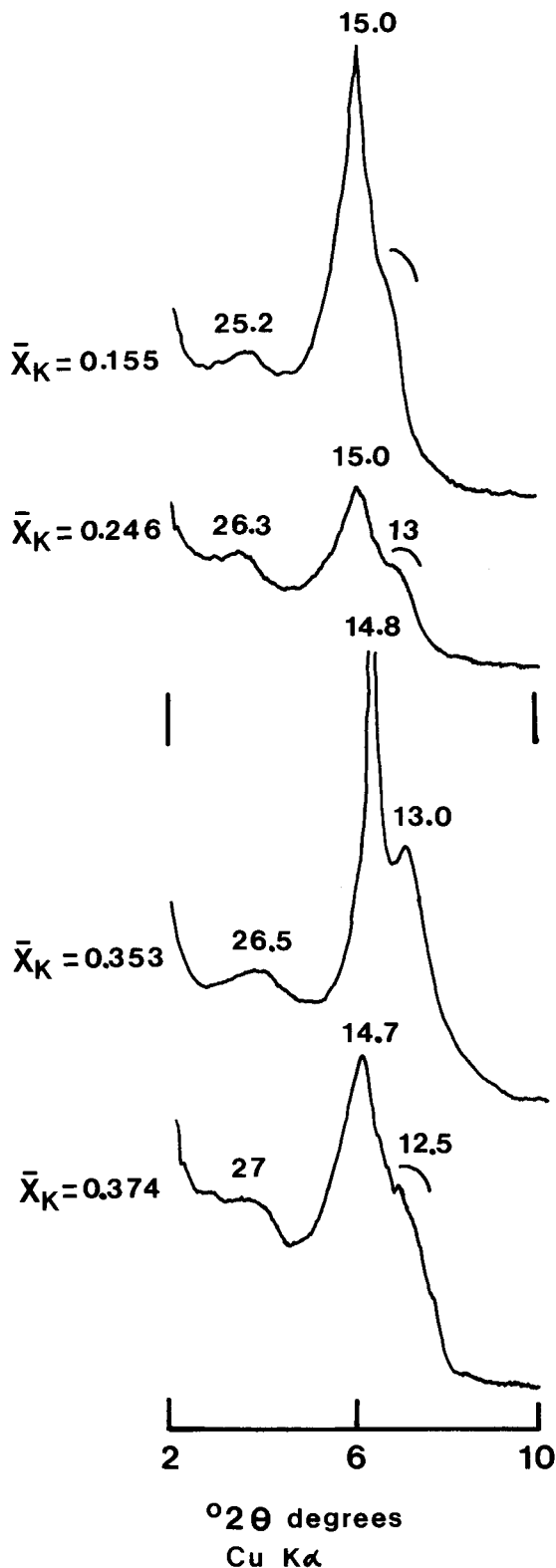
ACKNOWLEDGMENT

Figure 11. X-ray powder diffraction patterns of (Ca,K)-vermiculites with various K-equivalent fractions. The $\bar{X}_K$ values are the K-equivalent fractions in the specimens.

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Резюме—Исследовался обмен ионов Na, K, и Ca в вермикулите при температурах от 50° до 150°C при полной нормальности 0,1. Изменения свободной энергии были отрицательными для реакции Na → K и Na → Ca, а предпочтительный порядок обмена катионов для вермикулита в исследованном диапазоне температур был Na < Ca < K. Изменения энтальпии, рассчитанные при использовании формулы Вант-Гоффа для зависимости между постоянной равновесия и температурой, были положительными. Предпочтительный порядок обмена катионов для вермикулита кажется быть контролированным сильно увеличением энтропии, которое было результатом положительных значений изменения энтропии в твердом теле для обменов Na → K и Ca → K, а также положительных значений изменения энтропии в растворе для обмена Na → Ca. Из термодинамического анализа свойств катионов в вермикулите, наблюдаемое изменение свободной энергии во время обмена Na → K определялось исключительно как разницы между величинами внутренней энергии электростатической связи катионов на поверхности глины. В случае обмена Na → Ca изменение свободной энергии было интерпретировано, принимая во внимание дополнительную энергию взаимодействия пар Ca-Ca в дополнение к величине изменения внутренной энергии. Более того казалось, что дополнительная энергия взаимодействия между ионами K и поверхностью глины как бы прибавлялась к изменению свободной энергии в случае обмена Ca → K. В реакциях обмена Na → K и Ca → K происходило структурное видоизменение в диапазоне 0,05–0,6 K-квивалентной фракции ($\bar{x}_K$) и регулярно переслаивающаяся фаза членов 15-Å и 10-Å формировалась при $0,05 < x_K < 0,4$. [E.G.]

Resümee—Es wurde der Austausch von Na-, K-, und Ca-Ionen in Vermiculit zwischen 50° und 150°C bei einer Gesamtnormalität von 0,1 untersucht. Die Veränderungen der freien Energie waren in den Na → K-, Ca → K- und Na → Ca-Austauschreaktionen negativ. Die Kationenbevorzugung in Vermiculit war im untersuchten Temperaturbereich Na < Ca < K. Die Enthalpieveränderungen, die unter Anwendung der van't Hoff'schen Gleichung für die Beziehung zwischen Gleichgewichtskonstanze und Temperatur berechnet wurden, waren positiv. Die Kationenbevorzugung in Vermiculit scheint sehr stark durch die Entropiezunahme kontrolliert zu werden, die von den positiven Werten des Entropieänderungsterms für die Na-K- and Ca-K-Austauschreaktionen in der festen Phase und von den positiven Werten der Entropieänderung für den Na-Ca-Austausch in der Flüssigphase herrühren. Aus einer thermodynamischen Analyse der Kationenmischungseigenschaften in Vermiculit wurden die beobachteten Änderungen der freien Energie beim Na-K-Austausch nur durch die Differenzen der intrinsischen elektrostatischen Bildungsenergie der Kationen an die Tonoberfläche bestimmt. Die Veränderungen der freien Energie beim Na-Ca-Austausch wurde interpretiert, indem eine zusätzliche Wechselwirkungsenergie von Ca-Ca-Paaren zusätzlich zu der intrinsischen Energieänderung berücksichtigt wurde. Darüberhinaus scheint man eine zusätzliche Wechselwirkungsenergie zwischen K-Ionen und der Tonoberfläche zu der Veränderung der freien Energie beim Ca-K-Austausch hinzufügen zu müssen. Bei den Na → K- und Ca → K-Austauschreaktionen tritt eine Modifikation im K-äquivalenten Fraktionsbereich ($\bar{X}_K$) 0,05–0,6 ein, und eine regelmäßige Wechsellagerungsphase aus 15-Å and 10-Å Gliedern bildete sich bei 0,05 < $\bar{X}_K$ < 0,4. [U.W.]

Résumé—L'échange d'ions Na, K, et Ca dans la vermiculite a été étudiée entre 50° et 150°C à une normalité totale de 0,01. Les changements d'energie libre étaient négatifs dans les réactions d'échange Na → K, Ca → K, et Na → Ca et sur la gamme de températures étudiée la préférence de cations dans la vermiculite était Na < Ca < K. Les changements d'enthalpie, calculés par l'application de l'équation de van't Hoff à la relation entre la constante d'équilibre et la température, étaient positifs. La préférence de cations dans la vermiculite semble être contrôlée en grande partie par l'augmentation d'entropie, qui était due aux valeurs positives du terme de changement d'entropie dans le solide pour les échanges Na-K et Ca-K, et les valeurs positives du changement d'entropie dans la solution pour l'échange Na-Ca. A partir d'une analyse thermodynamique des propriétés de mélange de cations dans la vermiculite, on a déterminé que le changement observé d'énergie libre dans l'échange Na-K était déterminé uniquement par les différences de l'énergie intrinsèque de liaison électrostatique des cations sur les surfaces argileuses. Cela a été interpreté, dans l'échange Na-Ca en tenant compte d'une énergie d'interaction supplémentaire de paires Ca-Ca en plus du changement intrinsèque d'énergie. De plus, une énergie d'interaction additionnelle entre les ions K et la surface argile semble avoir été ajoutée au changement d'energie libre dans l'échange Ca-K. Dans les réactions d'échange Na → K, et Ca → K, une modification structurale s'est produite sur la gamme de fraction K-equivalente ($\bar{X}_K$) 0,05–0,6, et une phase régulièrement interstratifiée de membres 15 Å et 10 Å s'est formee à 0,05 < $\bar{X}_K$ < 0,4. [D.J.]