FAR INFRARED ANALYSIS OF THE STRUCTURAL ENVIRONMENT OF INTERLAYER K$^+$, NH$_4^+$, Rb$^+$ AND Cs$^+$ SELECTIVELY RETAINED BY VERMICULITE

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Abstract—To get a better understanding of the mechanisms of selective retention of cations by clay minerals, we have studied the physicochemical state and the location of immobilized cations. The approach developed is based on the concomitant study of the exchange isotherms and the compensating cations/clay structure interactions, using far infrared (FIR) spectroscopy. For that, cations are used as spectroscopic probes to characterize the selective sites.

Exchanged K,Rb-, K,Cs-, K,NH$_4$- and NH$_4$,Cs-Llano vermiculite samples were prepared. The exchange isotherms illustrate the higher selectivity of Llano vermiculite in the following order: K$^+$ < Rb$^+$ < Cs$^+$. Desorption experiments show that a 2 N MgCl$_2$ solution can extract a small fraction of immobilized Cs$^+$. The concomitant analyses of the exchange phenomena at microscopic (X-ray diffraction) and molecular (far and middle IR spectroscopy) levels show that: (1) only ~65% of the interlamellar hydrated Mg^{2+} of Llano vermiculite is exchanged; (2) cations are randomly distributed in the interlamellar spaces; and (3) retention is strongly related to the distance between compensating cations and oxygen atoms of the ditrigonal cavity.

The low hydration energy of selectively retained cations induces strong cation/clay interactions, which give FIR absorption bands of compensating cations. The FIR absorption bands of smaller cations shift towards lower wavenumbers when the proportion of the larger cations increases, whereas the wavenumber of the larger ones is constant. This reproducible scenario shows that larger cations act as wedges and expand layers, thus increasing the distance between the smaller cations and the layers. Calculation of the distances $d_{M-O\ inner}$ and $d_{M-O\ outer}$ shows that selectively-retained cations are six-coordinated in these dehydrated systems. The decrease of the difference between $d_{M-O\ outer}$ and $d_{M-O\ inner}$ from K$^+$ to Cs$^+$ may explain the observed selectivity of Llano vermiculite.

Key Words—Cation/Clay Interactions, Far Infrared Spectroscopy, Retention, Selectivity, Vermiculite.

INTRODUCTION

The selective retention of cations by clay minerals is a well-known phenomenon, important to soil science. The assessment of K$^+$ adsorbed onto and fixed into the clay fraction of soils is of particular importance to agronomists because it can help predict the bioavailability of K$^+$ amendments in fertilizers. K$^+$ selectivity by clay minerals has traditionally been studied by way of isotherm exchange data, often plotted as a function of the cations sorbed by the minerals and the relative concentration of cations in solution (see *e.g.* Fripiat *et al.*, 1971). The mechanism of K$^+$ retention by clay mineral surfaces and interlayer sites, however, is still not well understood, particularly in light of other potentially toxic elements and compounds that are known to occur in the soil environment and compete with K$^+$ for site occupancy. To gain a better understanding of the reaction mechanisms responsible for cation behavior, a new method is offered herein to examine the retention phenomenon at the molecular and site scale. The purpose of this study is to use far infrared (FIR) spectroscopy as a technique to measure directly the selectively-retained cations as they are bonded to the O atoms within the ditrigonal sites of clay minerals.
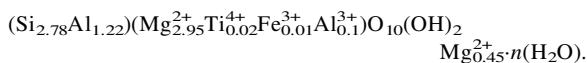
The application of FIR spectroscopy to the study of compensating cations in clay minerals was first shown to be feasible by Fripiat (1981). Laperche (1991) and Schroeder (1992) demonstrated independently that cations with low hydration energy, such as K$^+$, NH$_4^+$, Rb$^+$ and Cs$^+$ in clay minerals give characteristic FIR signals. It has also been long known that these cations are selectively retained by vermiculite (Sawhney, 1972). However, the selective retention of these cations by vermiculite has not been studied by FIR. A more specific aim of this work is to use the classic cation/clay selectivity of vermiculite and examine it by FIR spectroscopy, so as to develop a more complete picture of the mechanism for selective cation retention in soil environments.

MATERIALS AND METHODS

All exchange experiments were conducted with the <140 μm and the <2 μm fractions of Llano vermiculite. The respective size-fractions were obtained by sedimentation after grinding in water. The crystal chemical properties of the Llano vermiculite have been described

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by De La Calle and Suquet (1988). The general structural formula is given as:

$$(Si_{2.78}Al_{1.22})(Mg^{2+}_{2.95}Ti^{4+}_{0.02}Fe^{3+}_{0.01}Al^{3+}_{0.1})O_{10}(OH)_2$$
$$Mg^{2+}_{0.45} \cdot n(H_2O).$$

The cation exchange capacity (CEC) of the Llano vermiculite is reported as 229 meq/100 g of dehydrated clay (300°C), (Rausell-Colom *et al.*, 1980).

All exchange reactions were conducted by saturation with chloride solution repeated four times. The total initial cation content corresponded to 30 times the CEC. Each suspension was stirred for 24 h at 80°C. Maximum exchange was assumed to have occurred after the fourth contact with the chloride solution. Dual cation saturation experiments were also conducted. Natural Llano vermiculite was used as the starting material. Mixed solutions of KCl-RbCl, KCl-CsCl, KCl-NH$_4$Cl, and NH$_4$Cl-CsCl were prepared and contact times with the vermiculite were conducted in the same way as the single cation experiments (*i.e.* stirred for 24 h at 80°C). The proportions of cations in the bulk solution and retained by vermiculite are noted as follow: $\frac{Cs}{Cs\ \ K}$ is the fraction of Cs$^+$ (*vs.* Cs$^+$+K$^+$) in the bulk solution and $\frac{\overline{Cs}}{\overline{Cs}\ \ \overline{K}}$ is the fraction of Cs$^+$ retained by vermiculite. Vermiculite suspensions were subsequently centrifuged and washed with distilled water to remove free salts.

The mass of cations retained on the vermiculite was determined by subsequent HF digestion of the dried sample and measurement by X-ray fluorescence (XRF) spectroscopy. Chemical analyses were not performed on K,NH$_4$- and NH$_4$,Cs-vermiculites because of insufficient sample quantity.

Desorption experiments were conducted using Cs-vermiculite in contact with: (1) dual ionic solutions of K$^+$ and Cs$^+$ chlorides with progressively decreasing Cs$^+$ concentration ranging from 0 to 100 relative percent; (2) 0.2 N-MgCl$_2$ and 0.2 N-CaCl$_2$ solutions; and (3) 2 N-MgCl$_2$ solution. These experiments were performed separately at both 20°C and 80°C.

The FIR spectra were collected under vacuum with a Bruker IFS 113V spectrometer. Samples of the <2 μm fraction were deposited onto Millipore filters (0.45 μm pore-size) using 10 mg of sample mass. The mid-IR spectra were collected for the <140 μm fraction using KBr pellets. Pellets were heated overnight at 250°C.

X-ray diffraction (XRD) patterns were recorded with a SIEMENS D5000 diffractometer (CoKα Fe-filtered radiation, λ = 1.7890 Å) equipped with a cell that allows control of relative humidity, vacuum and heating (Diaz, 1999). Samples for XRD study were prepared both as randomly-oriented powders and as oriented aggregates on glass slides. Samples always remained under vacuum during heating, cooling and data recording.

RESULTS

Chemical data

Exchange isotherms for Llano vermiculite in contact with varied proportions of K$^+$ and Rb$^+$ or K$^+$ and Cs$^+$ are shown in Figure 1. The high selectivity of Llano vermiculite for both Cs$^+$ and Rb$^+$ is readily seen. Also noted is the higher selectivity of Cs$^+$ over that of Rb$^+$. These results agree with those of Klobe and Gast (1970) and Sawhney (1972). Chemical concentration data for
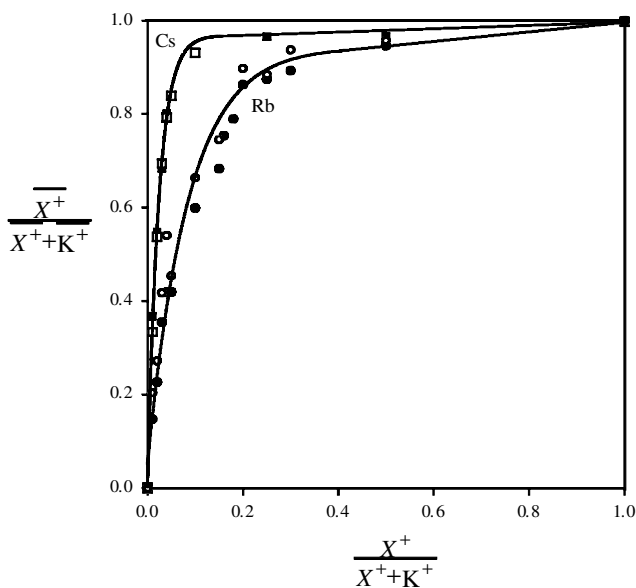

Figure 1. Llano vermiculite exchange isotherms for Cs$^+$ and Rb$^+$. K$^+$ and X^+ (Cs$^+$ or Rb$^+$) and $\overline{K}$ and $\overline{X}$ ($\overline{Cs}$ or $\overline{Rb}$) are ions in solutions and ions retained by vermiculite, respectively. ■: Cs chemical analysis; □: Cs XRF analysis; ●: Rb chemical analysis; ○: Rb XRF analysis.

Table 1. Chemical analysis of K^+, Rb^+ and Cs^+ in exchanged Llano vermiculite, in meq/100 g.

$\frac{Rb}{Rb\ K}$ in the bulk solution	$\overline{Rb}$ (meq/100 g)	$\overline{K}$ (meq/100 g)	$\overline{K}\ \overline{Rb}$ (meq)	% CEC	$\frac{Cs}{Cs\ K}$ in the bulk solution	$\overline{Cs}$ (meq/100 g)	$\overline{K}$ (meq/100 g)	$\overline{K}\ \overline{Cs}$ (meq)	% CEC
0.00	0	152	152	66	0.00	0	166	166	73
0.01	11	141	152	66	0.01	22	129	152	66
0.02	16	123	139	61	0.02	41	115	156	68
0.03	31	124	155	68	0.03	63	99	162	71
0.04	39	118	157	69	0.04	77	65	141	62
0.05	36	108	143	62	0.05	91	59	150	66
0.10	63	93	156	68	0.10	110	27	136	59
0.15	78	79	156	68	0.25	121	15	136	59
0.16	82	59	141	62	0.50	126	15	141	62
0.18	97	57	153	67	1.00	127	0	127	56
0.20	119	41	160	70					
0.25	114	36	150	66					
0.30	136	36	172	75					
0.50	140	17	157	69					
1.00	134	0	134	59					

both solution species and adsorbed species are reported in Table 1. These data further reveal that the amount of cations retained is less than the CEC of the clay. The range of proportions for $Rb^+ + K^+$ and $Cs^+ + K^+$ retained is 130–160 meq/100 g of dried sample. The CEC is 229 meq/100 g of dehydrated material, indicating that ~65% of the interlamellar Mg^{2+} is exchanged.

Desorption experiments show that Cs^+ is not removed from the Cs-vermiculite upon contact with the various proportions of K,CsCl solution. This includes the lowest concentration Cs^+ solution with 1% Cs^+ relative to K^+. $CaCl_2$ and $MgCl_2$ (0.2 N) solutions also did not lead to Cs^+ exchange (Table 2). Only the 2 N $MgCl_2$ solution resulted in extraction of Cs^+. The exchange appears limited and ~37% of the Cs^+ remains in the interlamellar spaces of the vermiculite.

XRD data

The XRD data obtained for the <140 µm size-fraction of K-, Rb- and Cs-samples, heated for 24 h at 250°C, under vacuum give d_{001} values of 10.11, 10.32 and 10.66 Å, respectively. Figure 2 shows the XRD patterns of the dual ionic K,Rb- and K,Cs-vermiculites. These two examples correspond to the <140 µm size-fraction heated at 250°C with $\frac{Rb}{Rb\ K}$ = 0.33 and $\frac{Cs}{Cs\ K}$ = 0.68. Several orders of the reflection 00l are visible on these diagrams.

Table 2. Cs^+ content (meq/100 g) in Llano vermiculite after desorption experiments.

Exchange solution	Temperature (°C)	Cs^+ remaining in vermiculite (meq/100 g)
$CaCl_2$ (0.2 N)	20	133
$CaCl_2$ (0.2 N)	80	132
$MgCl_2$ (0.2 N)	20	134
$MgCl_2$ (0.2 N)	80	125
$MgCl_2$ (2 N)	80	84

The d_{001} values obtained for K- and Rb-, and for K- and Cs-vermiculites are $d_{001,\ 002,\ 003,\ 004,\ 005}$ = 10.35, 5.08, 3.40, 2.54, 2.02 Å and $d_{001,\ 002,\ 003,\ 004,\ 005}$ = 10.58, 5.14, 3.44, 2.66, 2.03 Å, respectively. The d-spacing orders give an average value of d_{001} of 10.19 Å for $K_{0.65}$,$Rb_{0.35}$-vermiculite and 10.39 Å for $K_{0.32}$,$Cs_{0.68}$-vermiculite. Using the coefficient of variation (CV) criteria of Bailey (1982), the CV for the d_{001} K-Rb and K-Cs series are 0.9% and 2.0%, respectively. These values are greater than the recommended limit of 0.75% that constitutes a rational series of reflections. The CV values therefore indicate that the stuctures are sufficiently aperiodic to be considered mixed layered. In other words, the K,Rb- and K,Cs-vermiculite samples are randomly interstratified. Sawhney (1969) observed similar mixed-layer XRD properties with K-exchanged Llano vermiculite.

The XRD analyses indicate that the distribution of the interlayer types are random. However, the XRD method cannot provide insights into the near-neighbor distribution of cations in the interlamellar spaces. It is possible that the two different types of cations can be mixed in all interlamellar spaces or segregated into separate homoionic interlayers. The latter scenario leads to the stacking of interlamellar spaces filled by one or the other cation which in turn produces an interstratified system.

MIR data

Figure 3 shows the MIR stretching range for the structural OH groups in the K-, Rb- and Cs-vermiculite. The wavenumber of the structural OH group changes with the octahedral sheet composition and the occupancy of the interlamellar spaces (Farmer, 1974). In Llano vermiculite, OH groups are linked to three octahedral Mg^{2+} and are directed to either interlamellar hydrated Mg^{2+} (unperturbed OH groups) or a compensating cation, K^+, Rb^+ or Cs^+ (perturbed OH groups). Unperturbed OH groups give an absorption band at
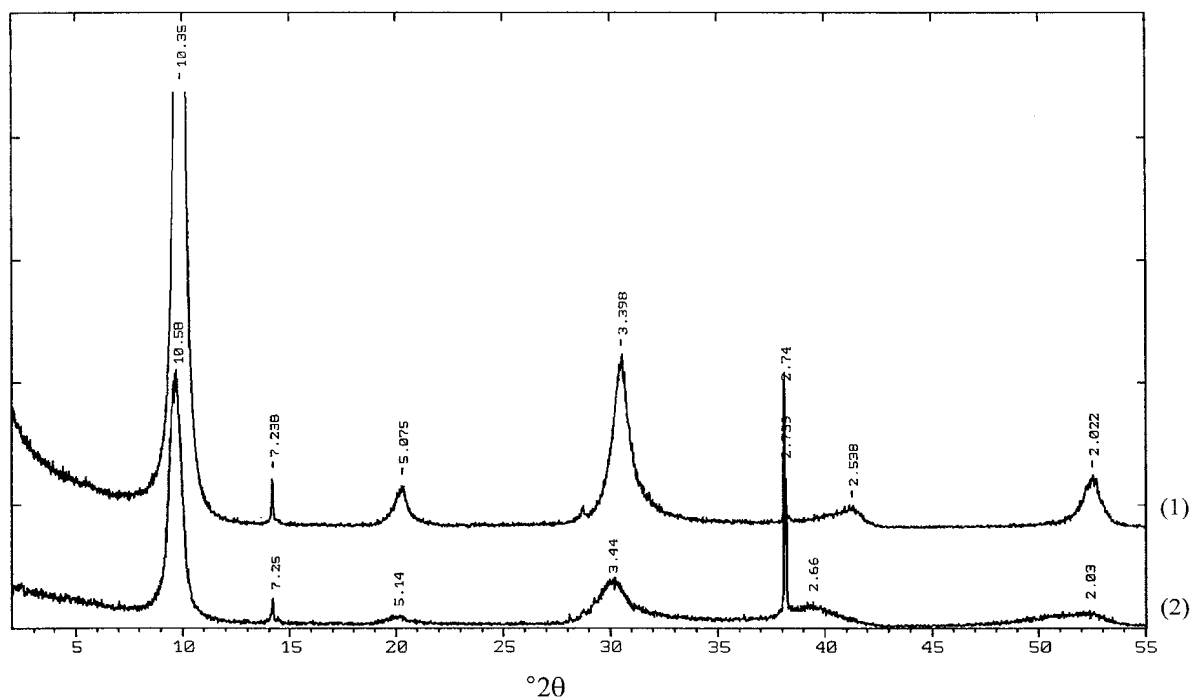
Figure 2. XRD patterns of (K$_{0.65}$,Rb$_{0.35}$)-vermiculite (1) and (K$_{0.32}$,Cs$_{0.68}$)-vermiculite (2) (<140 μm size-fraction, heated at 250°C, under vacuum).
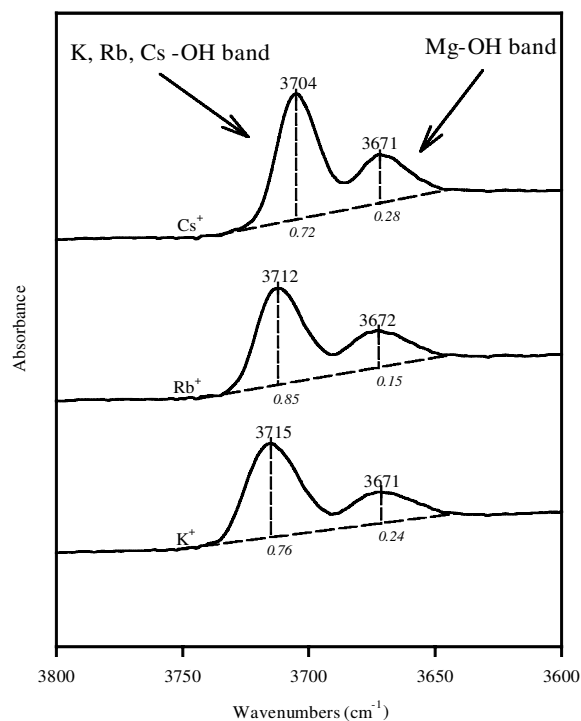

Figure 3. Stretching vibration bands of OH groups in K-, Rb- and Cs-vermiculite (<10 μm size-fraction, heated at 250°C). Numbers in italics correspond to the relative intensity of each perturbed and unperturbed OH-group band.

3671 cm^{-1} (Figure 3). When interlamellar Mg^{2+} of vermiculite is exchanged with K$^+$, Rb$^+$ and Cs$^+$, the repulsive interactions between cations and protons induce a shift from 3671 cm^{-1} to 3715, 3712 and 3704 cm^{-1}, respectively. The ionic radii for K$^+$, NH$_4^+$, Rb$^+$ and Cs$^+$ in six-fold coordination with oxygen are 1.38, 1.43, 1.52 and 1.67 Å, respectively (Shannon, 1976). As the size of the cations increases, there is a decrease in the repulsive interactions between compensating cations and protons. The increase in the distance between compensating cations and protons of structural OH groups is supported by the observed increase of average d_{001} going from K-vermiculite to Rb-vermiculite and to Cs-vermiculite.

If we consider that the absorption coefficient is the same for each configuration of OH groups in the 3715 to 3670 cm^{-1} region, then it is possible to link the intensity of the absorption band of both perturbed and unperturbed OH groups and their relative occurrence. The spectral band intensities in Figure 3 indicate that ~20% of hydrated Mg^{2+} remains in the interlamellar spaces. This assessment is lower than those ascertained by chemical analysis. The discrepancy can be explained by several factors, including: (1) the effects of sloping linear baseline position; (2) the presence of the vibration bands of remaining water molecules ($\approx$3600 cm^{-1}) that would minimize the 3671 cm^{-1} band intensity; and (3) an incorrect assumption of equal linear absorption coefficients for the two bands.

FIR data

Hydrated cations do not give an absorption band in the FIR range because of the presence of water molecules between the compensating cations and the oxygen atoms of the layer (Laperche, 1991; Schroeder, 1992). Therefore, FIR spectrometry gives a signal only for cations with a low hydration energy. This creates an advantage for studying selectively-retained cations K^+, Rb^+ and Cs^+ by vermiculite.

The FIR spectra of K,Rb-vermiculites are given in Figure 4. The absorption bands around $67\ cm^{-1}$ and $81\ cm^{-1}$ correspond to the in-plane vibration modes of Rb^+ and K^+ in Rb- and K-vermiculite, respectively (Laperche, 1991). The very small shift of the $67\ cm^{-1}$ band towards higher wavenumber, as the Rb^+ content decreases, is probably due to the overlapping of both the Rb^+ and K^+ bands. The $81\ cm^{-1}$ band shifts to lower wavenumbers as the proportion of K^+ decreases (*e.g.* $74\ cm^{-1}$ at 71% $\overline{Rb}$).

Figure 5 shows the FIR spectra of K,Cs-vermiculite series. The absorption bands around 60 and $81\ cm^{-1}$ correspond to the in-plane modes of Cs^+ and K^+, respectively, in the vermiculite. Similar to the K,Rb-vermiculite series, the $81\ cm^{-1}$ K^+ band shifts to a lower wavenumber as the proportion of K^+ decreases (*e.g.* $73\ cm^{-1}$ at 84% $\overline{Cs}$). Also notable is the development of a lower wavenumber band in the region of $54\ cm^{-1}$ for the vermiculites with intermediate dual Cs^+-K^+ saturation states.

DISCUSSION

To understand the mechanisms of selective retention of cations in vermiculite, we will consider the location and the interactions between compensating cations and oxygen atoms of the ditrigonal cavity. This will be done taking into account data obtained using XRD and FIR. In particular, the interactions between cations selectively retained and the clay structure will be analyzed through the relative distance between compensating cations and the oxygen atoms of the ditrigonal cavity.

Distribution of the exchanged cations between interlamellar spaces

Several authors have shown that exchange experiments performed on vermiculites lead to the formation of regularly interstratified layers (Klobe and Gast, 1970; Le Dred *et al.*, 1979; Martin de Vidales *et al.*, 1990). In our experiments, XRD patterns show that no regular interstratification occurs during the exchange process and the probability of sequence for Cs^+-, Rb^+- or K^+-layer type is random. This gives rise to the question as to whether or not the individual ditrigonal sites are randomly occupied throughout the vermiculite. The continuous shift of the K^+ absorption band to lower wavenumbers, as the proportion of Rb^+ or Cs^+ increases, suggests that both types of monovalent cations are randomly distributed in the interlamellar spaces. Indeed, if the interlamellar spaces were occupied by only K^+, without near Rb^+ or Cs^+ neighbors, then the band would remain at $81\ cm^{-1}$.
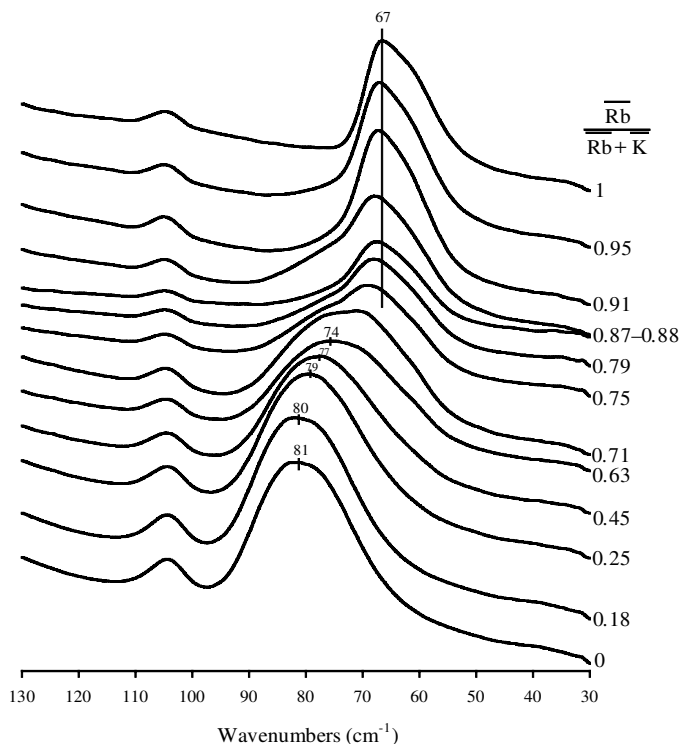

Figure 4. FIR spectra of (K,Rb)-vermiculite. $\frac{\overline{Rb}}{Rb+K}$ is the proportion of Rb^+ retained in vermiculite.
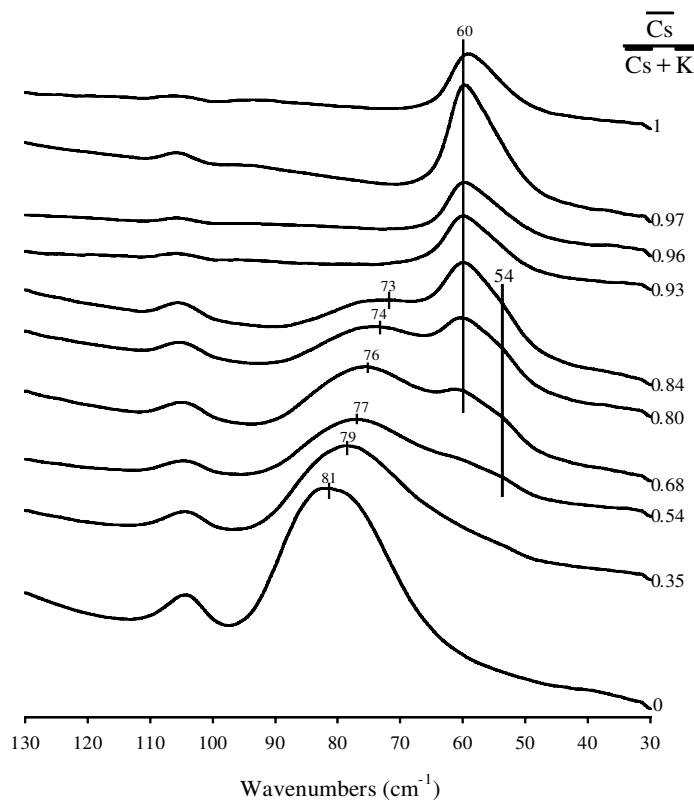
Figure 5. FIR spectra of (K,Cs)-vermiculite. $\frac{\overline{Cs}}{Cs\ K}$ is the proportion of Cs$^+$ retained in vermiculite.

Location of the exchanged cations in the interlamellar spaces

The selective retention of cations by clays is based on both crystal-chemistry of clays and physicochemical properties of cations. Diaz (1999) showed that cation retention is related to the distance between compensating cations and the nearest oxygen atoms of the ditrigonal cavity, as well as the hydration energy of the cations. Selectivity increases as the hydration energy of cations decreases and their size increases.

One explanation for the band shift is to have larger cations act as wedges to expand the layers (Figure 6). The band shift observed for K$^+$, when the amount of Cs$^+$ or Rb$^+$ in exchange sites increases, is probably due to the fact that K$^+$ is more loosely coordinated in these intermediate domains. The shift of the absorption band

of K$^+$ to lower wavenumbers can be related to an increase of the distance between K$^+$ and the nearest oxygen atoms ($d_{K-O\ inner}$). This is in agreement with the XRD data which show an increase of d_{001}. Tateyama *et al*. (1977) showed a negative linear relationship between the wavenumber of the FIR absorption band of K$^+$ in micas and the distance between K$^+$ and the nearest O atoms of the double ditrigonal cavity. Distortion of cavity is a consequence of tetrahedral sheet rotation (McCauley and Newnham, 1971), thus resulting in sets of inner and outer basal oxygen atoms bonded with K$^+$. Tateyama *et al*. (1977) gave the following relationship for distance between the K$^+$ and inner oxygen atoms ($d_{K-O\ inner}$) as a function of the observed interlayer vibrational mode wavenumber v_i:
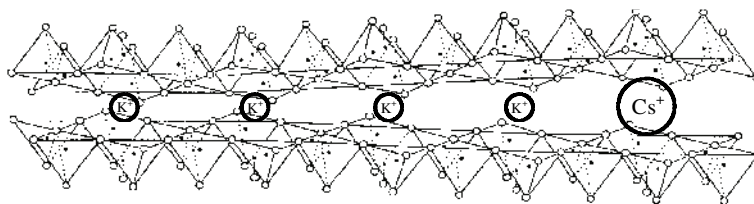

Figure 6. Schematic representation of retained cations located in the interlamellar spaces of vermiculite. The M^+-O distance is shortest in fully collapsed areas. It increases for smaller cations located in more expanded domains.

$$d_{K-O \text{ inner}} \text{ (Å)} = 3.676 - 0.0076 \, v_i \text{ (cm}^{-1}) \qquad (1)$$

Schroeder (1990) examined this relationship by studying a wide range of K-micas and concluded that calculation of $d_{K-O \text{ inner}}$ using only v_i is more complex. In a wide range of K-micas, the influence of F substitution must also be considered. However, it is reasonable to assume the Tetayama *et al.* (1977) relationship in our study, because the same intralayer structure is present and F is absent. The equation predicts that $d_{K-O \text{ inner}}$ should increase when the bands shifts from 81 to 73 cm^{-1} and the proportion of larger cations retained, Rb$^+$ or Cs$^+$, increases. If this hypothesis is correct, then the absorption band of K$^+$ should shift to a lower wavenumber with a K,NH$_4$-vermiculite. The radius of NH$_4^+$ is larger (1.43 Å) than the radius of K$^+$ (1.38 Å). Likewise, with a NH$_4$,Cs-vermiculite, where the radius of NH$_4^+$ is smaller (1.43 Å) than the radius of Cs$^+$ (1.67 Å), a band shift to lower wavenumber for NH$_4^+$ should be seen.

Figure 7 shows the FIR spectra of the K,NH$_4$-vermiculite series. The mass of NH$_4^+$ is smaller than the mass of K$^+$, therefore its absorption band appears at higher wavenumber (126 cm^{-1}). The wavenumber of the band from the larger NH$_4^+$ does not shift, while the band of the smaller K$^+$ shifts from 81 to 71 cm^{-1}. The decrease of the K$^+$ band intensity is more readily
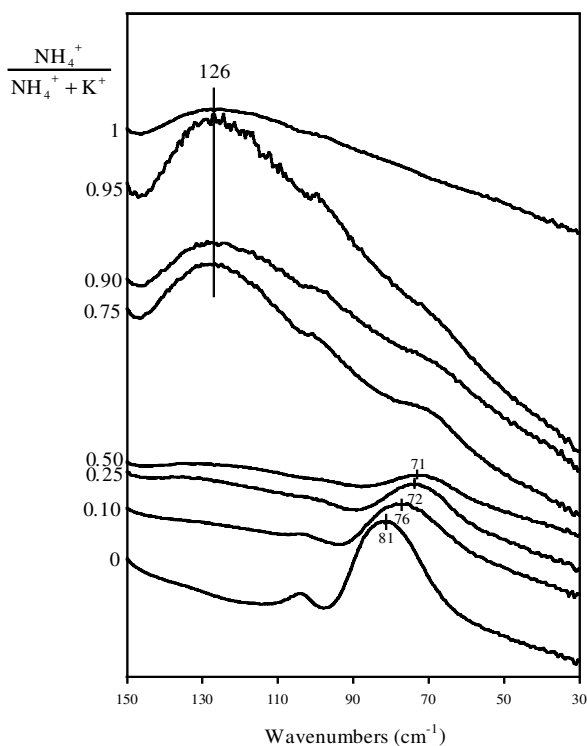
observed, when compared to the other dual cation series because of the greater difference in the mode wavenumbers. In contrast, the NH$_4^+$ band seen in the FIR spectra of the NH$_4$,Cs-vermiculites series (Figure 8) shows a shift from 126 cm^{-1} to lower wavenumbers. The intensity of the absorption band of NH$_4^+$ also decreases with increasing Cs$^+$ content.

In all cases, it appears that the larger cations act to wedge and expand layers, thus inducing a low-wavenumber shift of the FIR absorption band of smaller cations, while the band positions of the larger cations remain constant. This wedge mechanism can be extended to structural changes induced by the unexchanged hydrated Mg^{2+}. At 0% relative humidity the d_{001} spacing of Llano vermiculite is 11.6 Å (De La Calle *et al.*, 1985). This spacing is larger than the 10.66 Å observed for dehydrated Cs$^+$. This reflects the fact that Mg^{2+} remains in the interlayer site as a hydrated complex. The wedge effect of hydrated Mg^{2+} cations increases the $d_{Cs-O \text{ inner}}$ for the fraction of exchanged Cs$^+$ cations. These Cs$^+$ cations are probably the origin of the shoulder observed at ~54 cm^{-1} (Figure 5). The same behavior is observed for Rb$^+$. These FIR data show that retention of cations, randomly distributed in the interlamellar spaces of Llano vermiculite, is strongly related to the distance between the O atoms of the ditrigonal cavity.
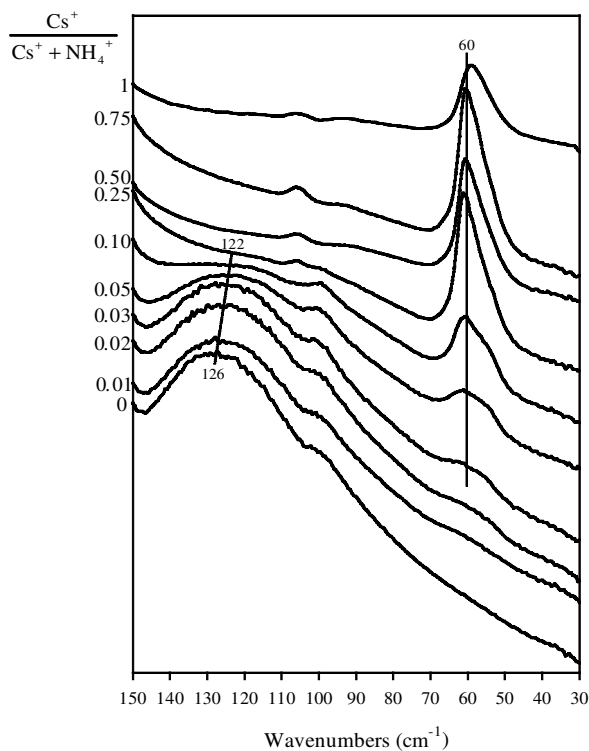
Figure 7. FIR spectra of (K,NH$_4$)-vermiculite. $\frac{NH_4}{NH_4 + K}$ is the proportion of NH$_4^+$ in the bulk solution.

Figure 8. FIR spectra of (NH$_4$,Cs)-vermiculite. $\frac{Cs}{Cs + NH_4}$ is the proportion of Cs$^+$ in the bulk solution.

Table 3. X-ray powder diffraction data (<2 µm size-fraction, heated at 250°C), α and d_{M-O} calculations for K-, Rb- and Cs-Llano vermiculite.

X-vermiculite	X-ray powder diffraction data		Calculations			
	d_{001} (Å)	b (Å)	α (°) (equation 4)	$d_{M-O\ inner}$ (Å) (equation 2)	$d_{M-O\ outer}$ (Å) (equation 3)	$d_{M-O\ outer} - d_{M-O\ inner}$
K^+	10.26	9.204	10.91	2.941	3.427	0.486
Rb^+	10.58	9.240	9.68	3.073	3.494	0.421
Cs^+	10.95	9.264	8.76	3.217	3.585	0.368

Effect of $d_{M-O\ inner}$ and $d_{M-O\ outer}$ on the 'trapping' of selectively-retained cations

Schroeder (1992) observed that Rb^+ and Cs^+ FIR bands are not detected on the exchangeable (*i.e.* lower charge) sites of Rb- and Cs-saturated illite. The FIR absorption bands therefore, probably result only from the interactions between compensating cations and oxygen atoms of the ditrigonal cavity. As a consequence, it is possible to relate the FIR vibration mode of compensating cations in vermiculite with the compensating cation M^+–O atom bond length, d_{M-O}. Theoretical calculation
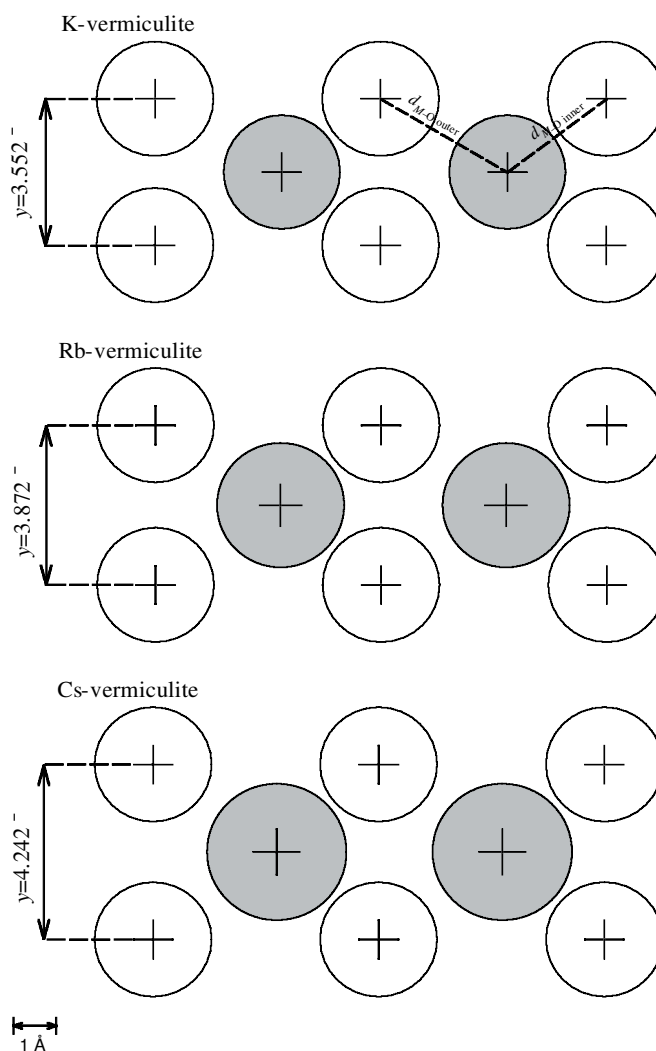

Figure 9. Schematic representation of retained cations located in the interlamellar spaces of exchanged vermiculite. Gray circles are compensating cations (K^+, Rb^+ or Cs^+) and open circles correspond to oxygen atoms O_V. The distance between two oxygen atoms O_V on the x axis is equal to 5.349 Å (Shirozu and Bailey, 1966).

of the d_{M-O} values for K^+-, Rb^+- and Cs^+-vermiculites allows for a comparison with the interlayer structure of Llano vermiculite and give indications on the mechanisms of selective retention.

Using the ideal ditrigonal model of McCauley and Newnham (1971), the compensating cation-oxygen bond lengths are given by:

$$d_{M-O\ inner} \supset \sqrt{\left[2H \sin(60-\alpha)/\sqrt{3}\right]^2 \quad 0.25y^2} \quad (2)$$

$$d_{M-O\ outer} \supset \sqrt{\left[2H \sin(60 \quad \alpha)/\sqrt{3}\right]^2 \quad 0.25y^2} \quad (3)$$

where H, α and y are the tetrahedral $O_{basal}-O_{basal}$ bond length, the tetrahedral rotation angle and the interlayer distance, respectively. Shirozu and Bailey (1966) have shown that the mean tetrahedral $O_{basal}-O_{basal}$ distance, H, is equal to 2.686 Å. Starting from atomic positions calculated by Shirozu and Bailey (1966), the y value, corresponding to the interplanar O_V-O_V distance, may be calculated, in Llano vermiculite, by

$$y = d_{001} - 6.708 \quad (4)$$

The tetrahedral rotation angle, α, is calculated from the Donnay *et al.* (1964) formula:

$$\cos\alpha \supset \frac{b}{4\sqrt{2}d_t} \quad (5)$$

with d_t the mean tetrahedral cation–oxygen bond length, $d_t = \overline{T-O} = 1.657$ Å (Shirozu and Bailey, 1966). The experimental data used in the calculation of the compensating cation-oxygen distance, the basal spacing d_{001} and the b parameter are summarized in Table 3. The calculations resulting from equations 2 and 3 show an increase of $d_{M-O\ inner}$ and $d_{M-O\ outer}$ with the size of compensating cations (*i.e.* $d_{K-O\ inner} < d_{Rb-O\ inner} < d_{Cs-O\ inner}$). The calculated d_{M-O} values also suggest that the compensating cations are in six-fold coordination. This is supported by the observation that the $d_{M-O\ inner}$ is less than the sum of the various ionic radii in 12-fold coordination (*i.e.* 1.64, 1.72 and 1.88 Å for K^+, Rb^+ and Cs^+, respectively, from Shannon, 1976) and O atoms (assuming the radius of O^{2-} = 1.40 Å). Also notable is that the differences between $d_{K-O\ inner}$, $d_{Rb-O\ inner}$ and $d_{Cs-O\ inner}$ are close to the differences between the ionic radius of the corresponding cations.

Figure 9 represents a schematic diagram of the interlamellar space of K-, Rb- and Cs-vermiculites. The cations are placed with respect to the position of O atoms and the calculated $d_{M-O\ inner}$ values from Table 3. This view corresponds to the (x,z) plane of Figure 2 from Shirozu and Bailey (1966, p. 1134). The distance between two oxygen atoms, O_V, on the x axis is equal to the a parameter of Mg-vermiculite (5.349 Å). It is assumed that the a parameter is very little affected by the hydration state of vermiculite. The distance between

two oxygen atoms O_V on the z axis corresponds to the interlamellar spacing (y) calculated from equation 4. The compensating cations are located with respect to calculated $d_{M-O\ inner}$ in the middle of the interlamellar space and then placed in a position of body-centered symmetry within the interlayer. A comparison reveals that the $d_{M-O\ outer}$ values measured on Figure 9 match well with the calculated values (Table 3). This affirms that the selectively retained cations are well placed in the ditrigonal cavities and they are in contact with the six nearest oxygen atoms of the ditrigonal tetrahedral ring. A decrease in the difference ($d_{M-O\ outer} - d_{M-O\ inner}$) from K^+, to Rb^+ and to Cs^+ is also shown in this schematic figure. The shorter distances should induce an affinity between Cs^+ and the outer O atoms of the ditrigonal cavity, that is stronger than that with Rb^+ and K^+. This helps to explain the increasing selectivity of $K^+ < Rb^+ < Cs^+$ in vermiculite.

CONCLUSIONS

Exchange experiments using K^+, NH_4^+, Rb^+ and Cs^+ in Llano vermiculite reveal that cations are randomly distributed throughout all the interlamellar spaces. Segregation or demixing of compensating cations into regularly-ordered sites is not observed. The selective retention of cations by vermiculite is related to the match between the geometry of the ditrigonal cavities in silica tetrahedral sheets and the physicochemical properties of the cations. Selectivity of vermiculite for K^+, NH_4^+, Rb^+ and Cs^+ increases with increasing ionic size. During the exchange process, K^+, NH_4^+, Rb^+ and Cs^+ in solution are losing their hydration water molecules as they key into ditrigonal sites. The exchange induces a collapse of the layers trapping the cations. It is proposed that this process extends from the edges to the center of particles. This explains why only one third of the Mg^{2+} of Llano vermiculite remains fixed in the interlamellar sites.

Geometric calculations show that $d_{K-O\ inner} < d_{Rb-O\ inner} < d_{Cs-O\ inner}$. The increase of $d_{M-O\ inner}$ corresponds to the difference between the size of cations. This suggests that K^+, Rb^+ and Cs^+ are in contact with the six nearest O atoms of the ditrigonal cavity. The model, as shown in Figure 9, shows the location of K^+, Rb^+ and Cs^+ in the interlamellar spaces of Llano vermiculite. For steric reasons, only hexacoordinated Cs^+ can occupy the available volume. This agrees with the fact that $d_{Cs-O\ inner} < d_{Cs-O\ outer}$, suggesting again that Cs^+ is in contact with the six nearest O atoms of the ditrigonal cavity. The increasing selectivity of Llano vermiculite for monovalent cations according to the order $K^+ < Rb^+ < Cs^+$ may be related to the decreasing difference between $d_{M-O\ inner}$ and $d_{M-O\ outer}$ when K^+ is replaced by Rb^+ and Cs^+. The mid-IR data suggest a lower repulsive effect of the proton, which belongs to the structural OH groups, with Cs^+ rather than Rb^+ and with K^+. That may

also be related to the higher selectivity of vermiculite for Cs^+ than for Rb^+ and for K^+.

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REFERENCES

Bailey, S.W. (1982) Nomenclature for regular interstratifications. *American Mineralogist,* **67**, 394–398.

De La Calle, C. and Suquet, H. (1988) Vermiculite. Pp. 455–496 in: *Hydrous Silicates* (S.W. Bailey, editor). Reviews in Mineralogy, **19**. Mineralogical Society of America, Washington D.C.

De La Calle, C., Suquet, H. and Pezerat, H. (1985) Vermiculites hydratées à une couche. *Clay Minerals,* **20**, 221–230.

Diaz, M. (1999) Etude des interactions cations compensateurs/feuillets dans les argiles: contribution à la connaissance des mécanismes de rétention sélective. PhD thesis, Univ. Orléans, Orléans, France, 135 p.

Donnay, G., Donnay, J.D.H. and Takeda, H. (1964) Trioctahedral one-layer micas. II. Prediction of the structure from composition and cell dimensions. *Acta Crystallographica,* **17**, 1374–1381.

Farmer, V.C. (1974) The layer silicates. Pp. 331–338 in: *The Infrared Spectra of Minerals* (V.C. Farmer, editor). Monograph, **4**. Mineralogical Society, London.

Fripiat, J.J. (1981) Application of far infrared spectroscopy to the study of clay minerals and zeolites. Pp. 191–210 in: *Advanced Techniques for Clay Minerals Analysis* (J.J. Fripiat, editor). Elsevier, Amsterdam.

Fripiat, J.J., Chaussidon, J. and Jelli, A. (1971) *Chimie-physique des Phénomènes de Surface. Applications aux Oxydes et aux Silicates.* Masson, Paris, 387 p.

Klobe, W.D. and Gast, R.G. (1970) Conditions affecting cesium retention and sodium entrapment in hydrobiotite and vermiculite. *Soil Science Society of America Proceedings,* **34**, 746–750.

Laperche, V. (1991) Etude de l'état et la localisation des cations compensateurs dans les phyllosilicates par des méthodes spectrométriques. PhD thesis, Univ. Paris VII, Paris, France, 100 p.

Le Dred, R., Saehr, D. and Baron, J. (1979) Préparation de vermiculite-interstratifiée-(Na,Rb) et -(Na,Cs) de type 1/1 par échange de cations. *Compte-Rendu de l'Académie des Sciences de Paris,* **289**, 47–50.

Martin de Vidales, J.-L., Vila, E., Ruiz-Amil, A., de La Calle, C. and Pons, C.-H. (1990) Interstratification in Malawi vermiculite: effect of bi-ionic K-Mg solutions. *Clays and Clay Minerals,* **38**, 513–521.

McCauley, J.M. and Newnham, R.E. (1971) Origin and prediction of ditrigonal distortions in micas. *American Mineralogist,* **56**, 1626–1638.

Rausell-Colom, J.A., Fernandez, M., Serratosa, J.M., Alcover, J.F. and Gatineau, L. (1980) Organisation de l'espace interlamellaire dans les vermiculites monocouches et anhydres. *Clay Minerals,* **15**, 37–58.

Sawhney, B.L. (1969) Regularity of interstratification as affected by charge density in layer silicates. *Soil Science Society of America Proceedings,* **33**, 42–46.

Sawhney, B.L. (1972) Selective sorption and fixation of cations by clay minerals: a review. *Clays and Clay Minerals,* **20**, 93–100.

Schroeder, P.A. (1990) Far infrared, X-ray powder diffraction, and chemical investigation of potassium micas. *American Mineralogist,* **75**, 983–991.

Schroeder, P.A. (1992) Far infrared study of interlayer torsional vibrational mode of mixed-layer illite/smectite. *Clays and Clay Minerals,* **40**, 81–91.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica,* **A32**, 751–767.

Shirozu, H. and Bailey, S.W. (1966) Crystal structure of a two layer Mg-vermiculite. *American Mineralogist,* **51**, 1124–1143.

Tateyama, H., Shimoda, S. and Sudo, T. (1977) Estimation of K–O distance and tetrahedral rotation angle of K-micas from far infrared absorption spectral data. *American Mineralogist,* **62**, 534–539.