LAYER-CHARGE AND CATION-EXCHANGE CHARACTERISTICS OF VERMICULITE (WEATHERED BIOTITE) ISOLATED FROM A GRAY LUVISOL IN NORTHEASTERN SASKATCHEWAN[1]

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Abstract—Layer charge and cation-exchange characteristics of weathered biotite isolated from a Gray Luvisol in Saskatchewan showed that this product was a high-charge vermiculite. Cation-exchange capacity (CEC) of the sand-size (100–250 μm) weathered biotite particles from different horizons, as determined by a 30-min Ca/Mg exchange, was low (23–71 meq/100 g). Increasing the exchange period to 24 hr increased the CEC to 33–95 meq/100 g for samples from the solum horizons and to 155–163 meq/100 g for samples from C horizons. The free oxide coatings on the mineral particles in the solum horizon samples apparently prevented the exchange cations from entering the interlayers. Removal of free oxides followed by 24-hr exchange sharply increased the CEC of these samples to 105–155 meq/100 g. Oxidation and loss of structural iron resulted in lower octahedral-cation occupancy (2.4–2.6 per half unit cell), suggesting a transition of the trioctahedral biotite to dioctahedral vermiculite. X-ray powder diffraction and high-resolution transmission electron microscopic analyses of alkylammonium-exchanged samples from the sand fractions of all horizons and magnetic separates of the coarse clays showed a linear increase in the d-value of the vermiculite with increasing chain length of the cations. The linear relationships suggest a paraffin-type arrangement having a uniform and high layer charge (0.70–0.76 per half unit cell in the sand-size particles; 0.80–0.84 in the clay fraction). The empirical relationship between tilt angle (α) and the layer charge density for paraffin-type structures, as suggested by Lagaly and Weiss, cannot be used for accurate layer-charge determination. Based on experimental evidence, a straight line relationship between the tilt angle and layer charge is suggested. The layer charge values show no marked variation within the profile and agree well with those calculated from the chemical composition. The repotassified layers of vermiculite in the sand-size weathered biotite particles did not respond to the Ca/Mg exchange, but were expanded by the alkylammonium cations; in contrast, a pure biotite standard (Bancroft, Ontario) of same particle size was unaffected by either treatment.

Key Words—Alkylammonium, Biotite, Cation exchange, Layer charge, Tilt angle, Transmission electron microscopy, Vermiculite, X-ray powder diffraction.

INTRODUCTION

Biotite weathering significantly affects the exchange reactions in soil. The hydration, oxidation, and loss of potassium and structural iron from biotite lead to its transformation to vermiculite (Farmer *et al.,* 1971). In this process, the layer charge density is reduced. To understand the reactivity of the alteration products, the layer charge density of these materials must be determined. Lagaly and Weiss (1969), Lagaly *et al.* (1976), and Lagaly (1982) described a method to determine the layer charge based on the measurement of basal spacings after exchange with alkylammonium cations of varying chain lengths. The distinct arrangement of these organic cations in the interlayers of expandable 2:1 phyllosilicates is controlled by the layer charge density and the chain length, and has been described by several workers (Brindley and Hofman, 1962;

Brindley and Ray, 1964; Brindley, 1965; Johns and Sen Gupta, 1967; Lagaly and Weiss, 1969, 1970, 1971; Lagaly *et al.,* (1976). Calculation of layer charge by the alkylammonium technique is simple and straightforward; however, our studies have shown that the standard curve suggested by Lagaly and Weiss (1969) to calculate layer charge for high-charge clays does not agree with that calculated from the chemical composition of purified materials. Tilt angles measured for some of our clays were less than 54°, and angles for the Llano vermiculite, measured by Lagaly (1982), were 50°–51°. These cannot be plotted on the curve published by Lagaly and Weiss (1969).

The present study was undertaken to determine the layer-charge and cation-exchange characteristics of weathered biotite isolated from the sand fractions and its counterpart from the clays of a Gray Luvisol profile. The results reported here add to our recent attempts (Ghabru *et al.,* 1987a, 1987b, 1987c, 1988) to increase our understanding of the weathering of soil biotite. In addition, the study attempted to clarify the relationship between tilt angle and layer charge when using the alkylammonium exchange technique.

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Table 1. Chemical composition[1] (wt. %) of the Ca-saturated, sand-size (100–250 μm) vermiculite (weathered biotite) isolated from the Gray Luvisol after dithionite-citrate-bicarbonate treatment.

Horizon	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	K_2O	H_2O	Total
Ae1	36.39	2.23	16.25	12.97	2.91	0.09	9.21	1.25	5.07	9.11	95.48
Ae2	35.65	2.18	15.91	15.89	1.95	0.13	10.08	1.24	4.97	10.42	98.42
BA	36.54	1.85	19.60	16.38	1.16	0.07	7.10	2.20	3.25	11.71	99.86
Bt	34.33	1.86	16.12	18.29	0.83	0.10	9.51	2.49	2.99	12.96	99.48
Ccaj	34.50	2.00	15.55	16.45	1.86	0.14	10.33	2.57	2.39	13.20	98.99
Ck1	33.51	2.19	15.31	16.14	2.50	0.09	10.90	2.68	2.41	12.88	98.61
Ck2	33.37	2.10	15.51	16.62	2.18	0.12	10.70	2.70	2.79	12.88	98.97
Biotite[2]	35.63	3.30	16.77	0.95	16.75	0.20	10.52	—	9.48	3.95	97.55

[1] Corrected for free Fe, Al, Si, and Mn.
[2] Biotite standard (100–250 μm), Bancroft, Ontario.

MATERIALS AND METHODS

Sand-size (100–250 μm) weathered biotite grains isolated from different horizons of a Gray Luvisol in Saskatchewan using a liquid magnetic separation (LMS) technique (Ghabru et al., 1987c) with no chemical pretreatments were used in this study. Coarse clay (2–0.2 μm) samples from different horizons were also separated into different fractions using high-gradient magnetic separation (HGMS) procedures at various levels of magnetic flux density (Ghabru et al., 1988). The LMS technique (Ghabru et al., 1987a, 1987c) provides an excellent means of separating minerals in the sand fraction of soils; HGMS permits similar isolation for clay-size minerals. Characterization of pure minerals isolated from the soil system avoids approximations in pedogenetic interpretations arising from the use of pure geologic mineral standards. Chemical pretreatment during the separation was avoided to preclude the production of any artifacts which might result from such treatment. The sand-size weathered biotite grains were dominantly composed of vermiculite as established previously by X-ray powder diffraction (XRD), with a very small amount of biotite/vermiculite mixed-layers (12 Å) and a trace of mica (10-Å component) (Ghabru et al., 1987a); in the Ae horizon, however, the greater amount of the 10-Å component is due to the repotassification of vermiculite.

Total chemical composition was obtained by the Lim and Jackson (1982) procedure. Ferrous iron content was determined by the modified Pratt method (Johnson and Maxwell, 1981). A vermiculite and a pure biotite sample (Bancroft, Ontario, Canada), obtained from Ward's Natural Science Establishment, Rochester, New York, were cut to 100–250 μm particles and used as a standards.

The alkylammonium chlorides of various chain lengths, prepared according to the procedure described by Rühlicke and Kohler (1981) and Rühlicke and Niederbudde (1985), were used as aqueous solutions of the following concentrations: 0.5 N for n_c = 8–9; 0.1 N for n_c = 10–14; and 0.05 N for n_c = 16. The samples were treated for 24 hr at 65°C, in the same manner as described in the above-mentioned procedure. Sections cut from the alkylammonium-exchanged samples after they were impregnated by epoxy resin, were examined by high-resolution transmission electron microscopy (HRTEM). XRD patterns were recorded for oriented aggregate specimens of clays and spinner powder mounts of sand-size samples on a Philips X-ray diffractometer using Mn-filtered FeKα radiation at a 0.5°/min scanning speed and a 600-mm/hr chart speed. Measured d(001) values were plotted against the chain length (n_c) to examine the homogeneity of layer charge. Tilt angles were calculated as suggested by Lagaly and Weiss (1969) to determine the amount of layer charge.

Table 2. Cation occupancy and layer charge per half unit cell calculated from chemical composition of the Ca-saturated, sand-size (100–250 μm) vermiculite (weathered biotite) isolated from the Gray Luvisol.

| Horizon/ sample	Tetrahedral cations		Octahedral cations							Charge per half unit cell	Interlayer cations	
	Si	Al	Fe^{3+}	Al	Fe^{2+}	Ti	Mn	Mg	Total		K^+	Ca^{2+}
Ae1	2.85	1.15	0.76	0.35	0.19	0.13	0.01	1.07	2.51	0.76	0.51	0.11
Ae2	2.76	1.24	0.93	0.21	0.12	0.13	0.01	1.17	2.57	0.70	0.50	0.10
BA	2.77	1.23	0.94	0.52	0.07	0.10	—	0.80	2.43	0.71	0.32	0.18
Bt	2.70	1.30	1.08	0.19	0.06	0.10	0.01	1.11	2.55	0.73	0.30	0.21
Ccaj	2.72	1.28	0.97	0.16	0.12	0.12	0.01	1.21	2.59	0.73	0.24	0.22
Ck1	2.66	1.34	0.96	0.09	0.16	0.13	0.01	1.29	2.64	0.75	0.25	0.23
Ck2	2.65	1.35	0.99	0.10	0.15	0.12	0.01	1.27	2.64	0.74	0.28	0.23
Biotite[1]	2.74	1.26	0.06	0.26	1.08	0.19	0.01	1.21	2.81	0.94	0.93	—

[1] Biotite standard (100–250 μm), Bancroft, Ontario.
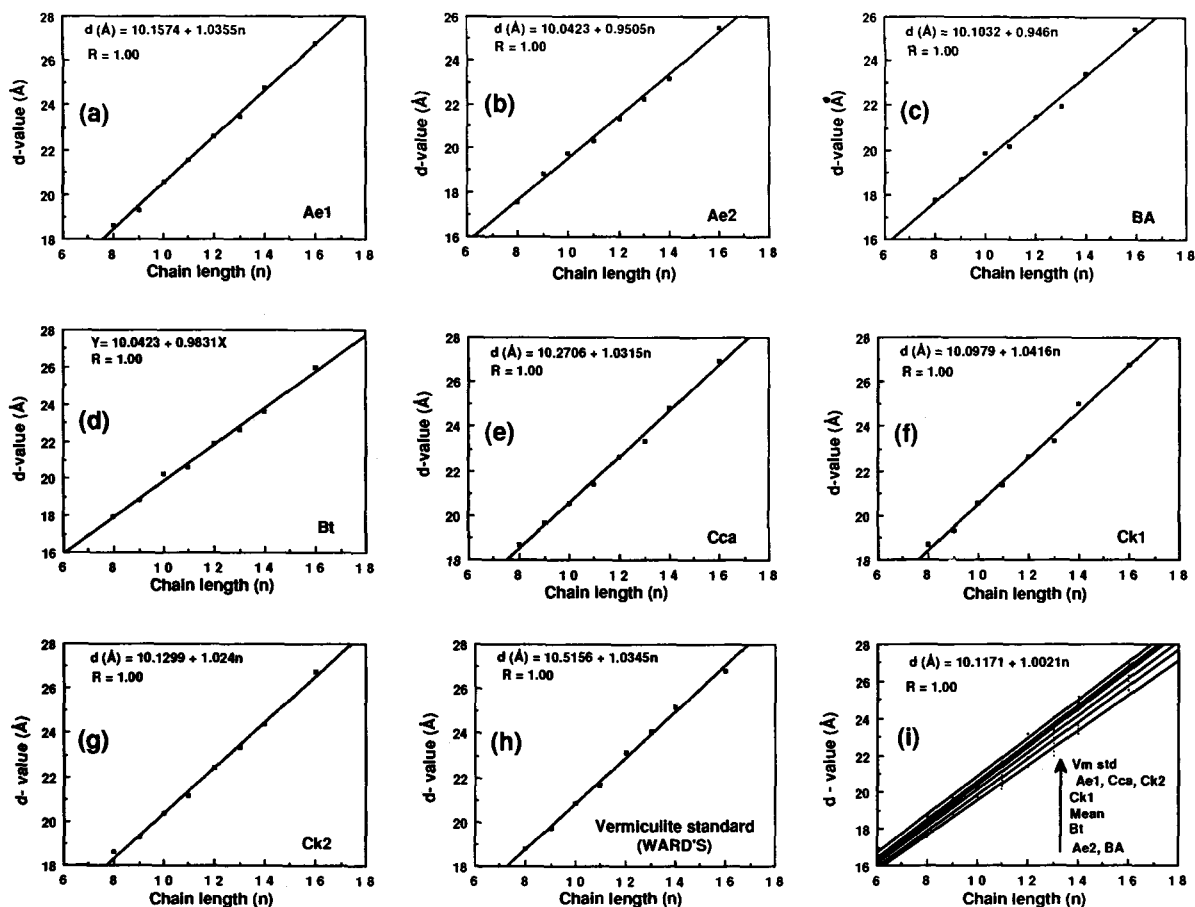
Figure 1. Relationship between the basal spacings of n-alkylammonium-vermiculite and chain lengths for: (a–g) plots for the sand-size (100–250 μm) vermiculite (weathered biotite) samples isolated from the different horizons of the Gray Luvisol; (h) vermiculite standard obtained from Ward's Natural Science Establishment, Rochester, New York; and (i) a combination of all the above.

Cation-exchange capacity (CEC) was determined by Ca-saturation and replacement by Mg (Rich, 1961) after 0.5-hr exchange, 24-hr exchange, and after removal of free oxides (a single 5-min dithionite-citrate-bicarbonate (DCB) extraction; Mehra and Jackson, 1960) followed by 24-hr exchange. In all procedures, the samples were shaken continuously on a rotary shaker.

RESULTS AND DISCUSSION

The chemical compositions of the sand-size weathered biotite isolated from various horizons are presented in Table 1. The weathered biotite, recovered in essentially pure form (i.e., devoid of contaminating minerals) by the magnetic separation was shown to consist dominantly of vermiculite as evidenced by sharp XRD peaks at 14.6, 7.2, 4.81, and 3.56 Å for both Mg-saturated and the Mg-glycerol-solvated samples, with a collapse to 10 Å following K-saturation and 300°C heat treatment (Ghabru *et al.*, 1987a). The data in

Table 1 indicate low K_2O and high water contents of the weathered biotite particles. The structural iron is mostly oxidized, and some evidence exists for the loss of structural Fe from the surface horizons compared with the Ccaj and Ck horizons (Table 2). The low octahedral cation occupancy (2.4–2.6 per half unit cell) is due to the loss of Fe from the structure and suggests a transformation from a tri- to a dioctahedral structure. The charge deficit calculated from the chemical composition of sand-size particles (Table 2) is 0.70 to 0.76 per half unit cell compared with 0.94 for the biotite standard. These latter data confirm the vermiculitic nature of the mineral in terms of being a high-charge 2:1 layer silicate.

Cation exchange by alkylammonium ions

The d-values observed after alkylammonium exchange of the sand-size samples plotted against the chain lengths (n_c) for all horizons are given in Figure 1. All the plots indicate a typical linear relationship
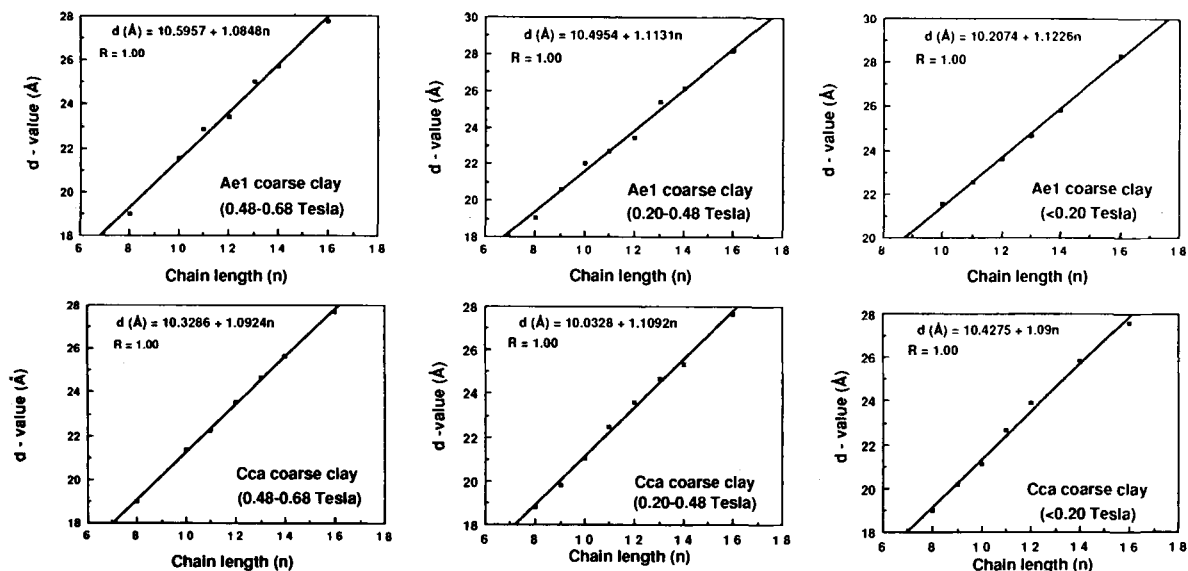
Figure 2. Relationship between basal spacings of n-alkylammonium-vermiculite and chain lengths for various magnetic-flux-density fractions of 2–0.2-μm size clay from the Gray Luvisol.

between the two variables, with a simple correlation value of r = 1.00. The linearity of the relationship indicates the presence of a paraffin-type arrangement of the alkylammonium cations in the vermiculite interlayers and the existence of a homogeneous charge distribution. These characteristics also indicate high layer-charge density, somewhat comparable to that of the Llano vermiculite (Lagaly, 1982). Similar linear relationships were also observed for the vermiculite present in various magnetic-flux-density fractions of coarse clay (2–0.2 μm) separated from the Ae1, Bt, and Ccaj horizons of this profile (Figure 2). The d-values obtained by the XRD analyses were supported by the HRTEM observations (Figure 3) for all the samples exchanged with different chain lengths of alkylammonium cations.

The values of tilt angles for the sand-size samples in the profile, calculated from the mean increase in basal spacing with increasing chain length, varied between 49.3° and 56.9° (Table 3). If these tilt angles are plotted on the standard curve published by Lagaly and Weiss (1969), the values of layer charge obtained are much lower (0.59–0.67) than those calculated from the chemical composition; moreover, the curve is not applicable to tilt angles <54° (Table 3).

Layer-charge calculation

For high-charge 2:1 phyllosilicates, if the area required for the flat-lying alkylammonium cations is more than twice the area available for each monovalent cation, the transition from a bilayer to a pseudotrimolecular layer occurs. Inasmuch as the latter arrangement is energetically unstable, alkylammonium cations form

paraffin-type structures (Lagaly and Weiss, 1969). In the paraffin-type structures, the angle at which the cations stand (tilt angle) is controlled by the layer charge density and increases to a maximum of 90° for a layer charge of two per unit cell. The tilt angle (α) is calculated from the mean linear increase in basal spacing (Δd) which is caused by an increase from one to the next higher alkylammonium chain: ($\alpha = \sin^{-1} \cdot \dfrac{\Delta d}{1.26}$).

An empirical relationship between tilt angle and layer charge density for paraffin-type structures was suggested by Lagaly and Weiss (1969) to calculate the layer charge for high-charge vermiculites. According to Lagaly (1982), high-charge vermiculites are characterized by basal spacings linearly increasing with the chain length and have paraffin-type interlayers if the layer charge is at least 0.75 per half unit cell. For one high-charge vermiculite, the Llano vermiculite, several values of layer charge (per half unit cell) have been reported: 0.67 (Lagaly and Weiss, 1969), ≥0.80 (Lagaly, 1982), 0.80 (van Olphen, 1965), and 0.72–0.95 (Norrish, 1973). The tilt angles observed by Lagaly (1982) for these samples (50° and 51°), however, cannot be plotted on their standard curve (Figure 5 of Lagaly and Weiss, 1969), as these values are below the lower range of the curve (tilt angle = 54°; layer charge = 0.5 per half unit cell).

The above-mentioned discrepancy and the charge deficit calculated from the chemical composition of sand-size particles clearly show that the empirical relationship between the layer charge and the tilt angles of the alkylammonium cations in the high-charge vermiculite interlayers, as proposed by Lagaly and Weiss
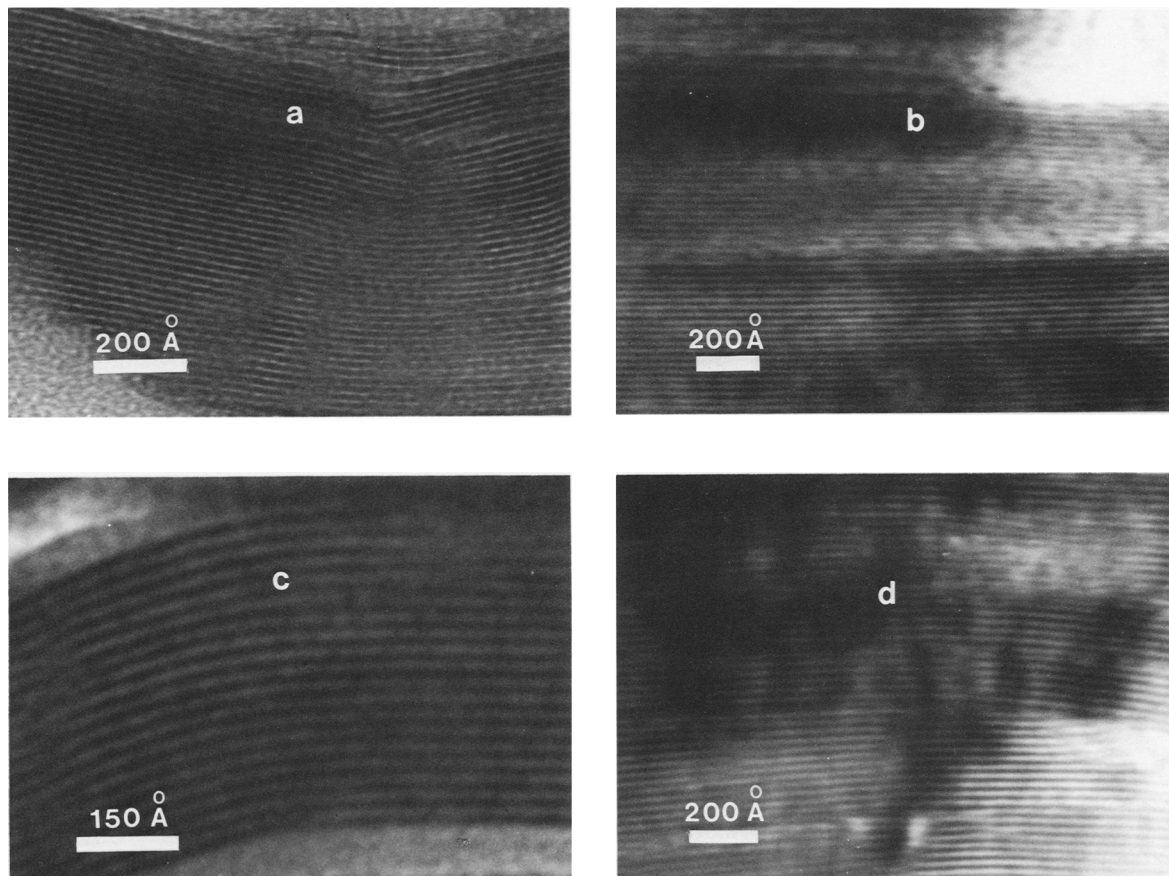
Figure 3.   High-resolution transmission electron micrographs of the alkylammonium-saturated sand-size (100–250 μm) vermiculite (weathered biotite) grains from different horizons of the Gray Luvisol, showing uniformly expanded layers: (a) octylammonium-exchanged vermiculite (weathered biotite) particles from the Ae2 horizon showing a d-value of 17.6 Å; (b) undecylammonium-exchanged vermiculite (weathered biotite) particle from the Ccaj horizon showing a d-value of 21.5 Å; (c) tetradecylammonium-exchanged vermiculite (weathered biotite) particles from the Bt horizon showing a d-value of 23.6 Å; and (d) hexadecylammonium-exchanged vermiculite (weathered biotite) particles from the Ae2 horizon showing a d-value of 25.5 Å.

(1969), cannot be used for tilt angles <54°. Furthermore, Lagaly and Weiss (1969) reported that the charge estimation error increases to 14% at angles <70°.

Theoretical consideration

Oriented alkylammonium ions projected onto a plane parallel to *bc* (100 projection) within the interlayer space of a homogeneous, high-charge 2:1 clay mineral are depicted in Figure 4. Theoretically, only two alkylammonium cations can be accommodated at a tilt angle of 90° in one unit cell ($b = 9.25$ Å), in which the layer charge is 1 per half unit cell (Figure 4a). If the molecules are tilted due to a lower charge density of the clay, i.e., the negative charges are laterally farther apart (Figure 4b), fewer molecules can be accommodated within the same space. At a given tilt angle, α, the width of the interlayer occupied by the molecules increases to $b + y$ and the d-value decreases by Δd

(i.e., $d_1 - d_2$). The increased distance between negative charges can be measured theoretically in terms of the *b* parameter, thickness of the alkylammonium molecule, $\sim b/2$, and the tilt angle. The tilt angle, α, can be calculated using the length (Å) of alkylammonium molecules of a given n_c and the vertical distance between the two silicate layers, d(Å), which can be measured by XRD analysis. Assuming that numerically the charge density decreases as a function of α proportionally to the increase in distance between charges, the layer charge at angle α can be estimated by the relationship: charge per half unit cell = $\sin \alpha = b/(b + y)$ (Figure 4a). For example, if the tilt angle is 45°, the corresponding layer charge is approximately 0.71 per half unit cell. Using the angles reported by Lagaly (1982) for Llano vermiculite (50° and 51°) results in a layer charge of 0.77 per half unit cell, which is much higher than values obtained from the Lagaly and Weiss (1969) curve and

Table 3. Tilt angles and layer charge values of sand-size (100–250 μm) vermiculite (weathered biotite) isolated from the Gray Luvisol.

Horizon	Tilt angle (α) (degrees)	Charge per half unit cell	
		A[1]	B[2]
Ae1	56.4	0.76	0.65
Ae2	49.3	0.71	—
BA	49.4	0.71	—
Bt	51.6	0.72	—
Ccaj	56.9	0.76	0.67
Ck1	56.5	0.76	0.65
Ck2	55.4	0.75	0.59
Vermiculite standard	59.1	0.78	0.75

[1] A = charge obtained from proposed curve of present study (Figure 5, curve 'a').
[2] B = charge obtained from Figure 5 of Lagaly and Weiss (1969) (Figure 5, curve 'b').
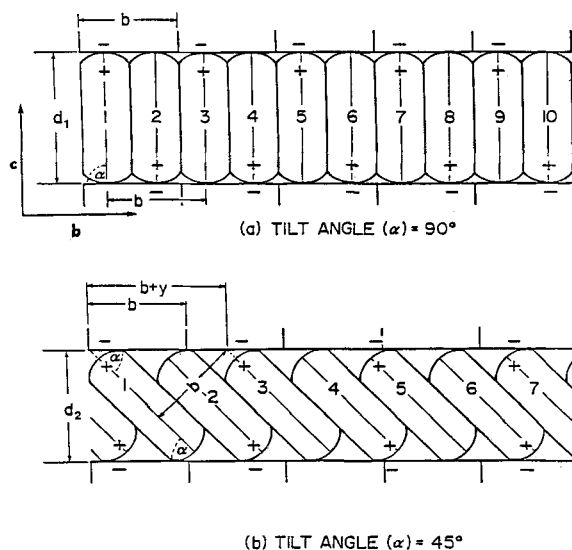

Figure 4. Schematic presentation of idealized paraffin-type arrangement of alkylammonium cations in the interlayer space of a high-charge, 2:1 phyllosilicate at different angles, (a) $\alpha = 90°$; (b) $\alpha = 45°$, representing different charge densities.

more representative of the values and the criteria reported in the literature for high-charge vermiculites. Because the exact shape and arrangement of the alkylammonium molecules between the layers are not known, this estimation method is conjectural.

Experimental evidence

Points for the layer charge values calculated from the chemical composition (Table 2) of the sand-size weathered biotite plotted against the angle obtained from the alkylammonium exchange are shown in Figure 5. A linear regression of the line through these points (not shown) results in a slope of 138.72 (y = −47.82 + 138.72x) and a regression coefficient r = .86. If the point representing the theoretical maximum of 1.00 for a tilt angle of 90° is included, the regression line (y = −47.82 + 137.82x) has almost the same slope, but the regression coefficient increases to unity (Figure 5, line 'a'). More experimental data are necessary, however, to confirm the linearity of the relationship. The layer charge values for sand-size vermiculite samples obtained from the new curve (Figure 5, line 'a') using the tilt angles given in Table 3 vary between 0.72 and 0.77 per half unit cell in the various horizons, but are at variance with values obtained using the Lagaly-Weiss curve. The structural charge deficit agrees well with the amount of interlayer cations calculated from the total chemical analyses, with the exception of minor differences in some horizons. These data provide credence to the 'conjectural' approach used above. The values also indicate that the vermiculite present in this Gray Luvisol has a high layer charge. Little difference in layer charge between different horizons was noted.

The data in Table 4 show the tilt angles for the vermiculite present in various magnetic flux density fractions of coarse (2–0.2 μm) clay from the Ae1 and Ccaj horizons. The layer charge values for these tilt angles obtained from the relationship published by Lagaly

and Weiss (1969) (Figure 5, curve 'b') are much higher and have a larger variation (0.83–0.90) than those obtained from the proposed relationship (0.80–0.84) in Figure 5 (line 'a'). The slightly higher layer-charge values of the clay-size particles compared with those of the sand-size particles (Table 3) reflects the effect of complete oxidation and greater loss of structural Fe due to weathering from the clay-size particles (Ghabru et al., 1987b) than that observed for the sand-size particles.

Weathered vs. unweathered biotite

The alkylammonium method, in its simpler forms, is workable and useful for determining layer charge of expandable clays from soils (Ross and Kodama, 1987; Senkayi et al., 1985); however, some workers (Mackintosh et al., 1971; Laird et al., 1987; Ross and Kodama, 1987) also have expressed concern over the efficiency of alkylammonium chlorides to exchange K and to expand micas and soil illites. As mentioned above, the sand-size (100–250 μm) weathered biotite samples isolated from the Ae horizon had some 10- and 12-Å components coexisting with vermiculite (Ghabru et al., 1987a). XRD analysis after alkylammonium exchange using the chain lengths $n_c = 8-14$, and 16 showed that these two components expanded as fully as vermiculite.

HRTEM observations on several samples confirmed these expanded d-values (Figure 3). All the samples examined under HRTEM showed expanded layers. No evidence of unexpanded (10 Å) layers or interstratifications was found. A standard biotite (Bancroft, On-
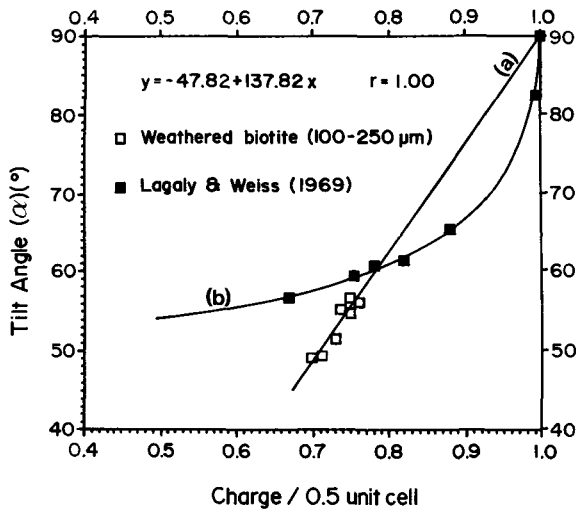
Figure 5. Dependence of tilt angle (α, in degrees) of alkyl-ammonium cations on layer charge density of high-charge 2:1 layer phyllosilicates: Curve 'a' (regression line) represents data points shown for the sand-size (100–250 μm) weathered biotite plus the theoretical maximum of 1 for a tilt angle of 90°; curve 'b' is redrawn from Lagaly and Weiss (1969) for comparison.

Table 5. Cation-exchange capacity (CEC) of sand-size (100–250 μm) vermiculite (weathered biotite) isolated from the Gray Luvisol.

Horizon/sample	CEC[1] (meq/100 g)		
	A	B	C
Ae1	23.20	38.67	106.54
Ae2	24.95	33.18	104.79
BA	37.18	64.87	152.69
Bt	49.15	94.81	155.44
Ccaj	60.38	154.69	168.91
Ck1	71.11	163.42	173.90
Ck2	54.89	158.93	167.17
Biotite[2]	1.25	1.88	2.50

[1] A = 0.5-hr exchange, B = 24-hr exchange, C = 24-hr exchange after dithionite-citrate-bicarbonate treatment.
[2] Biotite standard (100–250 μm), Bancroft, Ontario.

tario) sample cut to similar particle size (100–250 μm) and treated with different alkylammonium chain lengths ($n_c = 8$–14, 16) in the same manner as the other samples showed no sign of exchange or expansion. Grinding pure biotite samples to clay size likely damages the crystal structure and could, therefore, result in some K-exchange from the damaged edges. Further, Ghabru *et al.* (1987a) reported that the 10- and 12-Å components in the Ae horizon samples are a result of repotassification of vermiculites in the Luvisol studied. Thus, the concerns of Mackintosh *et al.* (1971) and Laird *et al.* (1987) may be related to samples that were either damaged by grinding or were repotassified (pedogenic mica). Repotassified vermiculite (or pedogenic

Table 4. Tilt angles and layer charge density of vermiculite in 2–0.2-μm clay fractions of the Gray Luvisol.

Magnetic fraction (Tesla)	Ae1 horizon			Ccaj horizon		
	Tilt angle (α) (degrees)	Charge per half unit cell		Tilt angle (α) (degrees)	Charge per half unit cell	
		A1	B2		A1	B2
Total clay	66.6	0.84	0.90	63.9	0.81	0.86
<0.20 T	64.8	0.83	0.87	63.7	0.81	0.86
0.20–0.48 T	66.9	0.84	0.90	62.0	0.80	0.83
0.48–0.68 T	64.3	0.82	0.87	62.8	0.80	0.84
0.68–1.38 T	65.8	0.83	0.89	63.3	0.81	0.85

[1] A = Charge obtained from proposed curve of present study (Figure 5, curve 'a').
[2] B = Charge obtained from Figure 5 of Lagaly and Weiss (1969) (Figure 5, curve 'b').

mica) and soil illites usually are richer in K_2O, more hydrated and, if trioctahedral, contain oxidized iron. These factors may be responsible for their susceptibility to exchange K and reexpansion on alkylammonium intercalation carried out at 65°C for 24 hr. Alkylammonium cations, in other words, may be useful in differentiating between original unweathered mica and repotassified vermiculite components (pedogenic mica) or soil illite, showing a 10-Å spacing with Mg-saturation in routine XRD analysis.

Layer charge vs. cation-exchange characteristics

The CEC determinations on the weathered biotite samples (100–250 μm) from different horizons of the profile (Table 5) present some interesting features. The CEC values obtained after a 30-min exchange were much lower than those expected from the layer charge for these samples. The values for solum horizons (23–49 meq/100 g) were lower than those of samples from the C horizons (60–71 meq/100 g). After the 24-hr exchange, however, the CECs showed a sharp increase, particularly for samples from the C horizons which increased to 155–163 meq/100 g. This increase suggests that the larger particles (100–250 μm) require longer equilibration to complete the exchange reaction. The CECs determined after removal of the free oxides from the samples, followed by the 24-hr exchange, were even greater. This increase was less for samples from the C horizon (9–15 meq/100 g) than for those from the solum horizons (67–88 meq/100 g). Scanning electron microscopic studies (Ghabru *et al.*, 1987a) have shown that the weathered biotite particles from the solum horizons are heavily coated, particularly around the edges, whereas the particles from the C horizons are relatively free of coatings. Thus, the free oxide coatings appeared to have prevented the exchange cations from entering the interlayers. The effect of the removal of free oxides was, therefore, more pronounced for the samples from the solum horizons. The lower CEC of samples from the Ae1 and Ae2 horizons (105–107 meq/

100 g) is probably due to their higher K_2O content. Interlayers containing K apparently did not respond to this exchange reaction, but were expanded by the alkylammonium cations, because the alkylammonium exchanges (unlike CEC procedures) were carried out at a higher temperature (65°C). These observations suggest that in addition to particle size, free oxide coatings, nature of exchange solution, contact period, and temperature can significantly affect the results of cation-exchange behavior. Further, the high CECs also support the high layer charge obtained from chemical composition as well as from the reaction with alkylammonium using the proposed relationship suggested in Figure 5 (line 'a').

SUMMARY AND CONCLUSIONS

The layer charge based on structural calculations (0.70–0.76 per half unit cell) and the high CECs (105–174 meq/100 g) for the vermiculite component of the weathering products of the sand-size biotite isolated from the Gray Luvisol suggest a high-charge mineral. Evidence exists for oxidation and loss of structural iron, and smaller octahedral cation occupancies (2.4–2.6) indicate a tendency of trioctahedral biotite to transform to a dioctahedral vermiculite.

A serious problem exists in using the empirical relationship between tilt angle (α) and layer charge, as suggested by Lagaly and Weiss (1969), for calculating the layer charge of high-charge vermiculites at lower tilt angles (<54°); also, at higher angles (>62°), a large change in the tilt angle results in a smaller change in the layer charge. The results of this study, utilizing layer charge data obtained from the chemical composition of the sand-size particles show a possible linear relationship.

The layer charge determined by alkylammonium exchange of the sand-size (100–250 μm) vermiculite (0.70–0.76) is fairly constant within the profile. The vermiculite in the coarse clay fractions from different horizons has a higher layer-charge density (0.80–0.84) than the sand-size particles.

Although a short equilibration time may be sufficient for the clay-size particles, a longer equilibration period (24 hr) was required for the determination of CEC of the sand-size particles. The presence of free oxide coatings gave lower CECs.

Alkylammonium exchange fully expanded the 10- and 12-Å components (potassified vermiculite) present in the Ae horizon samples. HRTEM confirmed these observations and gave no evidence of unexpanded (10 Å) layers or interstratifications in the weathered biotite. The biotite standard sample was totally unaffected by the alkylammonium ions. This behavior suggests a distinction between an original unweathered mica (10 Å) and a potassified vermiculite (10 Å) or the mixed-layer mineral (12 Å) created by potassification of vermiculite. Further studies on this aspect may prove helpful in confirming the use of this technique as a means of differentiating the original unweathered mica from the repotassified vermiculite components (pedogenic mica) or soil illite, all of which show a 10-Å value with Mg-saturation in routine XRD analysis.

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