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CATION EXCHANGE SELECTIVITY IN MICA AND VERMICULITE

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Abstract

Layer charge density differences between potassium saturated, dried micas and vermiculite resulted in a cation exchange selectivity (CES) for potassium in biotite and muscovite (1.7 and 4.0, expressed as equivalent ratios, $KX/Ca_{1/2}X$) which were 4 and 10 times, respectively, the CES in vermiculite (0.4). Interlayer wedge sites created by the potassium saturation and drying treatment (which made the cation exchange capacity nearly the same for the three materials, 8 to 10 meq/100 g) increased the CES both of the micas and of vermiculite by a factor of two, relative to that in the undried vermiculite, biotite, and muscovite (0.2, 0.9, and 1.7, respectively). In addition to effects on CES of charge of the layers making up the crystal wedges and external (001) cleavage faces, the obliqueness of the hydroxyls in dioctahedral layers contributed considerably to the range in CES for the potassium relative to calcium on the external sites of vermiculite, biotite, and muscovite (0.0, 1.3, and 3.7, respectively).

Introduction

The selective exchange of lyotropic series cations by layer silicate minerals is controlled by the mineral structural configurations and layer charge densities in addition to the well-known effects of the cation properties such as valence, size, and degree of hydration. Structural properties of layer silicate minerals which give rise to differences in cation exchange selectivity (CES) appear to arise from the presence of interlayer wedges and the charge density of the layers making up the wedges (Dolcater *et al.*, 1968). Such wedges occur (Jackson, 1963; 1968) at the boundary between opened (weathered) and unopened (unweathered) portions of micaceous vermiculite formed by weathering.

This paper shows that the charge density of layers on the (001) cleavages, in addition to the presence of interlayer wedges and the charge density of layers making up the wedges present in micaceous vermiculite, biotite, and muscovite, affects the selective adsorption of potassium relative to calcium.

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EXPERIMENTAL

Vermiculite (size fraction $<5\mu$m, biotitic, from Transvaal, South Africa), biotite, and muscovite (both of size fraction 2–0.2μm, from Ward's Natural Science Establishment, Rochester, N.Y.) were separated by sedimentation following treatment of a water suspension of large flakes in a Waring blender. Each fine material was divided into two portions, one of which was sodium saturated and left undried, while the other was potassium saturated and dried at 110°C. Samples of both portions were then washed with a solution 0.005 N with respect to both KCl and $CaCl_2$. The CES was determined as the equivalent ratio of exchangeable potassium to calcium ($KX/Ca_{1/2}X$, in which X represents one charge of the cation exchanger anion). The potassium and calcium selectivity values were determined and calculated according to the procedure given by Dolcater *et al.* (1968).

RESULTS

The potassium saturated and dried vermiculite, biotite, and muscovite gave K/Ca equivalent ratios (Fig. 1) of 0.4, 1.7, and 4.0, respectively, which were double those for the sodium saturated and undried materials (0.2, 0.9, and 1.7, respectively). These ratios were

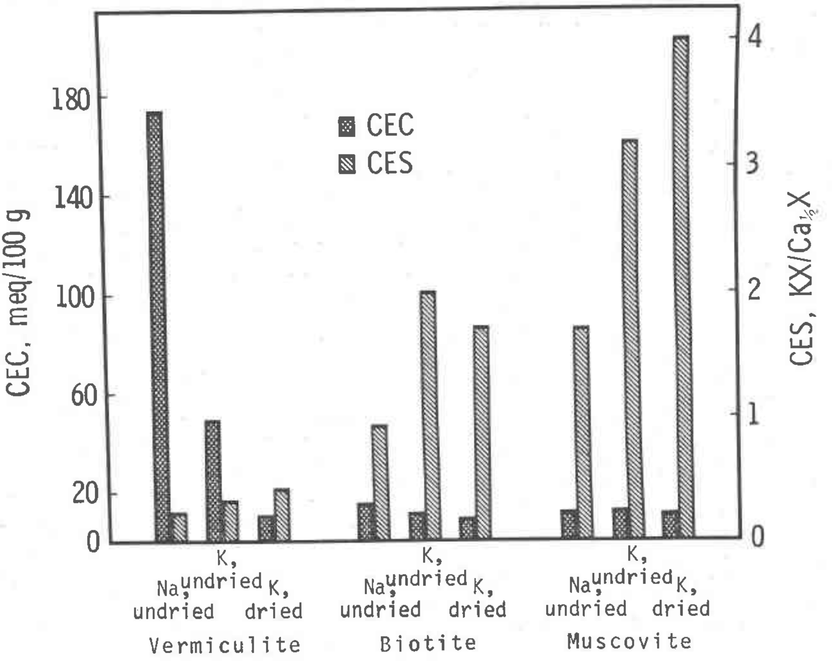

FIG. 1. CEC and K/Ca CES for sodium saturated (undried), potassium saturated (undried), and potassium saturated then dried vermiculite, biotite, and muscovite.

inversely related to the cation exchange capacity (CEC) of each material (Fig. 1). This relationship suggests that the interplanar sites of vermiculite are more selective for calcium relative to potassium than the exchange sites of the micas. The doubling of the selectivity values as a result of potassium fixation was attributed (Dolcater *et al.*, 1968) to an increase in the proportion of interlayer wedge sites to interplanar sites. After potassium saturation and drying, which reduced the CEC of the three materials to essentially the same value (8 to 10 meq/100 g, Table 1), muscovite and biotite had CES values 10 and 4 times as great, respectively, as that of vermiculite. These higher selectivity values for the micas compared to vermiculite point to the importance of the layer charge density of not only the layers making up the wedges, but also that of layers exposed on external cleavage faces, in the selective adsorption of small, unhydrated cations such as potassium. The three–fold difference in CES between the dioctahedral and trioctahedral micas, which have nearly equal charge densities, is attributable to the orientation of the hydroxyls (Serratosa and Bradley, 1958) below the ditrigonal holes in the silica sheets.

Discussion

The relative contribution of the external planar surface charge density effects and the interlayer wedge effects were evaluated by consideration of the following cases:

Case 1. The value of a–b (Table 1) was assumed to be an estimate of the quantity of interlayer wedge sites, which were occupied by potassium.

Case 2. A value of 3.6 meq/100 g (van Olphen, 1966) was taken as an estimate of the quantity of external planar surface sites.

Case 3. A value of 5.0 meq/100 g (Alexiades and Jackson, 1965) was taken as an estimate of the quantity of external planar surface sites.

Exchangeable potassium was assigned first to the wedge sites whereas exchangeable calcium was assigned first to the external planar sites. The excess of either ion was secondarily assigned to the alternative site. Many other possible assumptions besides cases 1, 2, and 3 were considered, but had to be rejected on the basis of the experimental data in Figure 1 and in Table 1.

Calculations made for each of these three cases show the distribution of exchangeable potassium and calcium on the external planar surfaces and in the interlayer wedges (Table 2). In the first case, calcium in the equilibration solution apparently caused a small amount of opening of wedges in the potassium saturated materials, thereby exposing additional cation exchange sites (a–b in Table 1). If these sites are largely filled with potassium, and considerable evidence suggests they are selective for potassium (Jackson, 1963; Bolt *et al.*, 1963; Rich and Black, 1964; Scott and Bates, 1967; Dolcater *et al.*, 1968), the selectivity value of the wedge sites would approach infinity. The selectivity values for the surface sites of biotite and muscovite are then 3 and 9 times as great, respectively, as the overall value for vermiculite (Table 2). Thus, the surfaces of the micas show a high degree of selectivity for potassium, which can be explained satisfactorily only as a result of their higher external surface charge densities than that of vermiculite (Fig. 2).

The K selectivity difference between biotite and muscovite is explained primarily by the oblique orientation of the hydroxyl groups in muscovite (Serratosa and Bradley, 1958), giving a greater attraction for K by muscovite. In addition, decrease in layer charge through such ionic reactions as iron valence change or substitution of other cations and/or hydrogen (Jackson, 1963; 1968) produces the local areas shown with no net negative charge (Fig. 2).[1] The remaining areas of high charge are relatively selective for potassium and such areas have a frequency: muscovite > biotite > vermiculite.

In case 2, the interpretations are similar, except that the selectivity of the surface sites of the micas is somewhat lower because more than 50 percent of the CEC is attributable to wedge sites for each of the three materials (Table 2). Such a high percentage of wedge sites would be unlikely (especially in micas); however, the exchange sites on the (001) cleavage of biotite and muscovite still show a high selectivity for potassium (Table 2) relative to those of vermiculite, an effect attributed to the higher charge density of the mica layers. The indicated potassium selectivity of the sites on the (001) cleavages

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[1] The charge density of biotite (Fig. 2) has been taken as being lower than that of muscovite because of the lower K/EC (column b, Table 1). The layer charge densities (m^{-2}) and K/EC give specific surface areas of 25 and 22 m^2/g for these 2–0.2 μm fractions of muscovite and biotite, respectively. Taking any higher charge density for biotite would further lower the calculated specific surface of biotite, an unreasonable premise. Lowering the biotite layer charge by a 10 percent deficiency in K$^+$ (through compensating trivalent octahedral ions) and 5 percent by surface weathering reactions is assumed to be a plausible basis for the 3.0 meq/10^{3}m^2 layer charge represented in Figure 2. The specific surface for vermiculite (2.4 meq/10^{3}m^2 and 6.9 meq/10^{2}g) is 29 m^2/g, suggesting cleavage into much thinner particles in <5 μm fraction employed.

TABLE 1. CATION EXCHANGE CAPACITY OF VERMICULITE, BIOTITE, AND MUSCOVITE AND SITES EXPOSED BY Ca PRESENT IN THE MIXED K + Ca EQUILIBRATION SOLUTION

Material	Cation exchange capacity CEC ($KX+Ca_{\frac{1}{2}}X$) K, dry (a)	 K/EC[a] (K/NH_4OAc) weighed (b)	Portion of CEC on sites exposed by Ca (a-b)
	meq/100 g		
Vermiculite	9.5	6.9	2.6
Biotite	7.7	6.5	1.2
Muscovite	9.7	9.1	0.6

[a] Washed with 0.5 *N* KOAc and 0.01 *N* KCl to clean; weighed and dried in 0.01 *N* KCl; K displaced in 0.5 *N* NH_4OAc. K/EC (as distinct from KEC measured without drying) indicates that the K-saturated sample was dried at 110°C.

TABLE 2. EXCHANGEABLE K AND Ca ON INTERLAYER WEDGE AND EXTERNAL PLANAR SURFACE SITES OF VERMICULITE, BIOTITE, AND MUSCOVITE IN THE MIXED K + Ca EQUILIBRATION SOLUTION

Exchange site location	Vermiculite KX	 $Ca_{\frac{1}{2}}X$	 $KX/Ca_{\frac{1}{2}}X$	Biotite KX	 $Ca_{\frac{1}{2}}X$	 $KX/Ca_{\frac{1}{2}}X$	Muscovite KX	 $Ca_{\frac{1}{2}}X$	 $KX/Ca_{\frac{1}{2}}X$
	(meq/100 g)			(meq/100 g)			(meq/100 g)		
Overall	2.8	6.7	0.41	4.9	2.8	1.7	7.8	1.9	4.0
Case 1. Distribution of KX and $Ca_{\frac{1}{2}}X$ assuming that a-b (Table 1) is an estimate of the quantity of wedge sites:									
Wedge	2.6	0	--	1.2	0	--	0.64	0	--
Surface	0.18	6.7	0.027	3.7	2.8	1.3	7.1	1.9	3.7
Case 2. Distribution of KX and $Ca_{\frac{1}{2}}X$ assuming that 3.6 meq/100 g is an estimate of the quantity of external planar surface sites:									
Wedge	2.8	3.1	0.89	4.1	0	--	6.1	0	--
Surface	0	3.6	0	0.79	2.8	0.28	1.7	1.9	0.86
Case 3. Distribution of KX and $Ca_{\frac{1}{2}}X$ assuming that 5.0 meq/100 g is an estimate of the quantity of external surface sites:									
Wedge	2.8	1.7	1.6	2.7	0	--	4.7	0	--
Surface	0	5.0	0	2.2	2.8	0.78	3.1	1.9	1.6

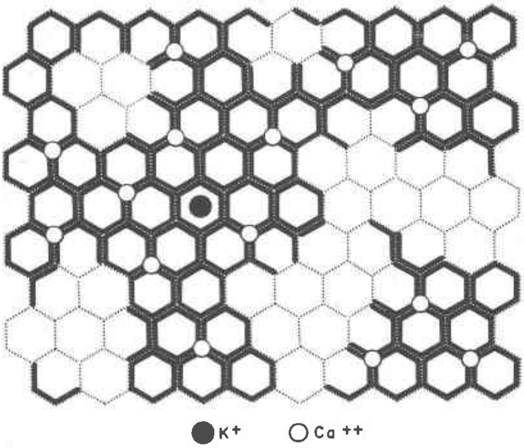
VERMICULITE

MOLAR RATIO

$KX / CaX_2 = 0.067$

EQUIVALENT RATIO = CES

$KX / Ca_{1/2}X = 0.033$



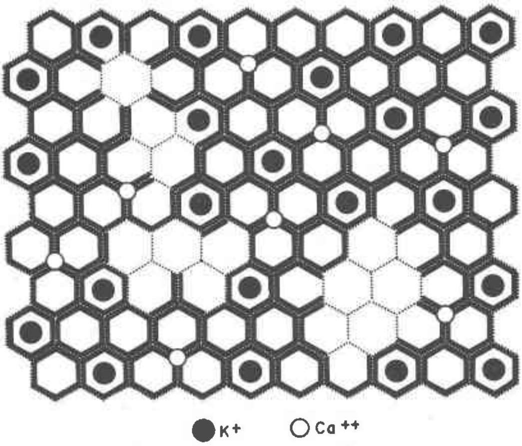
BIOTITE

MOLAR RATIO

$KX / CaX_2 = 2.8$

EQUIVALENT RATIO = CES

$KX / Ca_{1/2}X = 1.4$



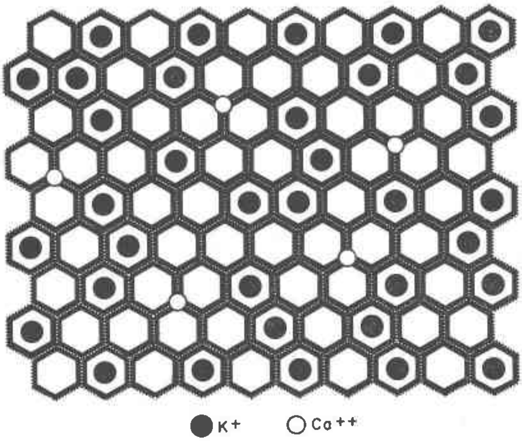
MUSCOVITE

MOLAR RATIO

$KX / CaX_2 = 7.0$

EQUIVALENT RATIO = CES

$KX / Ca_{1/2}X = 3.5$



of micas is higher still in case 3 than it was in case 2, because the percentage of the CEC attributable to the wedge sites is smaller (Table 2). If the values of 96 percent external surface sites and 4 percent wedge sites (Bolt *et al.*, 1963) are used, the selectivity of the sites on the (001) cleavages of the micas becomes even higher.

CONCLUSIONS

The conclusion from this research is that, in addition to cation selectivity of the wedge sites, sites on (001) cleavages of micas have an appreciably greater selectivity than those of vermiculite for potassium as compared to calcium. The best explanation for this high selectivity of mica relative to that of vermiculite appears to be the difference between the layer charge density of mica and vermiculite. The higher potassium selectivity of the muscovite exchange sites relative to those of biotite can be explained by the smaller ditrigonal holes in the tetrahedral layer of muscovite (Radoslovich and Norrish, 1962) and the oblique orientation of the hydroxyl groups in the bottom of the holes of muscovite (Serratosa and Bradley, 1958; Bassett, 1960), both of which result in a stronger polar bonding (Shainberg and Kemper, 1966) of potassium to muscovite than to biotite. The stronger adsorption of cesium than sodium on the surface cleavages of muscovite macroflakes was also explained (Mokma *et al.*, 1970) by this reasoning. Any tendency for the development (on weathering) of oblique orientation of the hydroxyls, favoring K selectivity (Barshad and Kishk, 1970), in this biotite and this biotitic vermiculite is apparently more than offset by the extensive lowering of the charge in the layers.

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FIG. 2. Distribution of Ca^{2+} and K^{+} ions on planar cleavage surfaces on which each shaded side of a structural hexagon (oxygen at each apex) carries a net CEC charge of —1/12. Layer structural ion reactions are assumed to have eliminated the surface charge in indicated (not shaded) areas of vermiculite (2.4 meq/10^{3}m^2; 170 meq/100 g) and biotite (3.0 meq/10^{3}m^2; 210 meq/100 g) as compared to the full theoretical charge of muscovite (3.5 meq/10^{3}m^2; 250 meq/100 g). The K equivalent to the wedge sites (a–b in Table 1) has been subtracted from *KX* before the varying selectivity ratios of the cleavage surfaces were derived (approximately case 1).

When either vermiculite or mica is considered individually, the interlayer wedge sites have a greater selective adsorption for potassium relative to calcium than do the external planar surface sites. When comparing these two materials, however, the greater selectivity of the micas is attributable to the higher charge density of the layers on the (001) cleavage surfaces of the micas. Consequently, the contribution of the layer charge density of minerals to the selective adsorption of cations should be given consideration, especially in studies concerning the selective adsorption of cations in fertilizers, radioactive debris and wastes, and various other pollutants.

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