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POTASSIUM AND CESIUM ION SELECTIVITY IN RELATION TO CLAY MINERAL STRUCTURE

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Abstract—Selectivity of a number of vermiculites, montmorillonites and micas for K and Cs ions was determined by sorption of these ions from equilibrium solutions of diverse concentrations. The selectivity coefficients were related to the layer charge density and the area of the frayed edges in layer silicates.

Montmorillonites had the smallest selectivity for the two ions, while biotite and illite had the greatest selectivity. Selectivity of biotite and illite was limited to small concentrations of K, however. At greater concentrations the selectivity of vermiculite for K exceeded the selectivity of the micas.

The greater selectivity of vermiculites than montmorillonites for K and Cs ions was attributed to the greater layer charge density in vermiculites. The greater selectivity of micas than montmorillonites and vermiculites was attributed to the frayed edges of micas in addition to their larger layer charge density. As the frayed edges in illite were increased in area by removal of the interlayer K, the selectivity of illite for K also increased; thus confirming the selectivity of frayed edges for the K ions.

INTRODUCTION

SELECTIVE sorption of K and Cs ions by clays in relation to other cations in solution has been observed by several investigators (Krishnamoorthy and Overstreet, 1950; Wiklander, 1950; and Marshall and Garcia, 1959). The relationships between the cation selectivity and the structure of different minerals are not well understood, however.

Cationic selectivity of an exchanger is generally determined by measuring the uptake of cations from an equilibrium solution. The selectivity is then expressed as the ratio of the cations sorbed by the exchanger to their ratio in solution. Recent interest in the disposal of radioactive effluents containing small amounts of ^{137}Cs has prompted investigations of selective uptake of Cs by different clay minerals and soils. Illite and vermiculite have been found to sorb Cs more selectively than montmorillonite and kaolinite, and the selectivity increased with decreasing Cs concentration (Jacobs and Tamura, 1960; Wahlberg and Fishman, 1962 and Sawhney, 1965). More than one type of exchange site is involved in Cs sorption (Jacobs, 1963; Coleman and LeRoux, 1965; and Sawhney, 1966). In contrast to Cs, most determinations of K selectivity have been limited to large concentrations only. Thus, the selectivity of different clay minerals for K and Cs ions has not been determined over a wide range of saturation with these ions.

A slightly different approach to the determination of K selectivity by clay minerals and soil clays has been used in recent years (Schwertmann, 1962; Rich and Black, 1964 and Dolcater *et al.*, 1968). The exchanger is saturated with K and a competing cation by exhaustive leaching of the exchanger with a solution of the two cations. Relative replacement of the two by a third cation then gives an estimate of the cations sorbed and hence their selectivity by the exchanger. As pointed out by Dolcater *et al.* (1968), the exchange selectivity determined in this manner would be different from the selectivity determined from relative uptake of the cations from an equilibrium solution. Apparently, this method would yield greater estimates of K selectivity because: first, exhaustive leaching of the exchanger with a solution containing two cations, one of which is sorbed preferentially, would favor saturation of the exchanger with that ion. Thus, if an exchanger sorbed K in preference to Ca then relatively more K is likely to be sorbed by leaching the exchanger repeatedly with a solution equimolar in K and Ca than by the uptake from a solution of the same composition. Second, prolonged leaching of the exchanger with a K-free solution to replace the sorbed cations may remove some fixed interlayer K from weathered micas and K-saturated vermiculite. In addition, selectivity determinations by this procedure have been restricted to only one concentration of the K ion.

To understand the relation between clay mineral structure and the selectivity for K and Cs ions, the effect of di- and tri-octahedral nature, layer charge, and interlayer configuration of the mineral on the sorption of these ions was investigated. Potassium

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and Cs ions were sorbed from equilibrium solutions over a wide range of concentrations by a number of di- and tri-octahedral montmorillonites, vermiculites and micas of different charge. To investigate the effect of interlayer configuration the frayed edges of illite were further increased in area by extracting interlayer K from illite, and then the sorption of K by the altered illite was compared with the original illite.

MATERIALS AND METHODS

Montmorillonites (Wyoming and Arizona), interstratified montmorillonite-illite sold as beidellite (Pakistan), hectorite (California), Vermiculites (Montana and Transvaal), Fithian illite (Illinois) and biotite (Canada) were obtained from Ward's Natural Science Establishment, Rochester, New York. Nontronite was obtained through the courtesy of S. B. Hendricks, U.S. Department of Agriculture, Beltsville, Brazil bentonite through R. Fortes of Paraiba and Llano vermiculite through C. J. Mankin of the University of Oklahoma. Two soil clays which contained Al interlayers were also included.

Interlayer K was extracted from illite with sodium tetraphenylboron (Scott and Reed, 1962). Illite that was partially depleted of interlayer K will be hereinafter referred to as illite-D.

Stock suspensions of clays were obtained by commutating the minerals in a Waring blender in the presence of about 1N NaCl solution that was renewed several times. Excess salt was then removed and the clays were separated by sedimentation. The clays were then saturated with Ca by five centrifuge washings with 1N $CaCl_2$ solution, freed of chloride ion and suspended in distilled water. Soil clays were separated using the procedure outlined by Jackson (1956) and saturated with Ca as above. Cation exchange capacity was determined by the method of Sawhney *et al.* (1959).

Six aliquots from Ca-saturated suspensions of each clay containing 0·1 g colloid were centrifuged. Colloids were then suspended in KCl or CsCl solutions varying in concentrations from 0·01 N to 1·0 N, and allowed to equilibrate for 72 to 96 hr. The suspensions were then centrifuged, and Ca in the supernatant solution was determined by titrating with EDTA. Hydroxy naphthol blue was used as the indicator. In some cases, the supernatant solution was corrected for the small amount of Ca occluded in the colloid. In others, the occluded Ca was replaced by a 5-ml washing with water and included in the supernatant solution for Ca determination. Both determinations gave essentially the same estimates for Ca.

The selectivity coefficient, *ks*, for K or Cs ions was calculated as follows:

$$ks = \frac{n_{K(ad)}}{n_{Ca(ad)}} \cdot \frac{m^{\frac{1}{2}}_{Ca}}{m_K}.$$

Where n is the number of milliequivalents of the cation, K or Ca adsorbed (ad) by the exchanger, and m is the molarity of the cation in solution. Thus, *ks* has the dimensions $(1/\text{m mol})^{1/2}$.

RESULTS AND DISCUSSION

Cation exchange capacity (CEC) and the nature of the predominant mineral present in the clays are shown in Table 1. The clays represent dioctahedral as well as trioctahedral members of the montmorillonite, vermiculite and mica group of minerals. The cation exchange capacity varies from 28 m-equiv./100 g for illite to 146 m-equiv./100 g for Llano vermiculite. Thus, clay minerals of diverse layer charge are included in this investigation.

Table 1. Nature of predominant mineral and cation exchange capacity (CEC) of clays

Sample	Di-or tri-octahedral	CEC (m-equiv./100 g)
Arizona bentonite	Di	132
Beidellite*	Di	55
Brazil bentonite	Di	80
Wyoming bentonite	Di	86
Hectorite	Tri	130
Nontronite	Tri	112
Libby vermiculite	Tri	137
Llano vermiculite	Tri	146
Transvaal vermiculite	Tri	127
Biotite	Tri	34
Illite	Di	28
K-depleted illite†	Di	60
Gloucester A_1–A_2†	Di	61
Gloucester B_{21}†	Di	55

*X-ray diffraction analysis showed that the specimen consists of regularly interstratified montmorillonite-illite layers.

†Mixtures of vermiculite and illite.

Selectivity of montmorillonites for K *and* Cs *ions*

Calculation of the selectivity coefficient from the K or Cs and Ca ions adsorbed and their concentration in solution is illustrated in Table 2. Selectivity coefficients of montmorillonites for K and Cs ions remain constant over the entire range of saturation with the ions. The selectivity coefficient estimates of a dioctahedral montmorillonite, Brazil bentonite, are similar in magnitude to the estimates of a trioctahedral montmorillonite, nontronite. The

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Table 2. Calculations of selectivity coefficients of Brazil bentonite and nontronite for K and of Wyoming bentonite for Cs

K or Cs sorbed, CEC%	$\frac{^{n}K \text{ or } Cs(ad)}{^{n}Ca(ad)}$	$\frac{^{m1/2}Ca}{^{m}K \text{ or } Cs}$	k_s
	Brazil bentonite		
23	0·272	0·1741	0·047
33	0·484	0·0945	0·046
46	0·848	0·0526	0·045
64	1·778	0·0298	0·053
74	2·887	0·0187	0·054
84	4·790	0·0096	0·046
	Nontronite		
18	0·224	0·2051	0·046
28	0·384	0·1046	0·041
41	0·686	0·0607	0·042
59	1·441	0·0340	0·049
70	2·357	0·0215	0·051
83	4·947	0·0113	0·056
	Wyoming bentonite		
32	0·479	0·8660	0·415
47	0·905	0·3746	0·340
80	3·978	0·1203	0·479
86	6·349	0·0544	0·345

K selectivity coefficients of the other montmorillonites listed in Table 1 also remained constant over the entire range of K and Ca saturation. The mean selectivity coefficients for the montmorillonites were: Arizona bentonite, $0{\cdot}073 \pm 0{\cdot}011$; interstratified montmorillonite-illite $= 0{\cdot}052 \pm 0{\cdot}005$; Wyoming bentonite $= 0{\cdot}047 \pm 0{\cdot}004$; and hectorite $= 0{\cdot}027 \pm 0{\cdot}002$. Similar estimates of Wyoming bentonite selectivity for K ions were obtained by Rich and Black (1964).

Although both di- and tri-octahedral montmorillonites appear to have similar selectivity for K, the dioctahedral Arizona bentonite has greater selectivity than the trioctahedral montmorillonites, nontronite and hectorite, of comparable CEC.

Whereas the mean selectivity coefficient of Wyoming bentonite for K was 0·047, the coefficient for Cs was 0·395. The greater selectivity for Cs than K is attributed to the smaller hydration energy of the Cs ion.

Selectivity of vermiculites for K *and* Cs *ions*

As in montmorillonites, the selectivity coefficients of vermiculites from Libby, Llano and Transvaal for K ions (Table 3) vary only slightly over the entire range of K- and Ca- saturation. Vermiculite from Libby exhibits the greatest while the vermiculite from Llano exhibits the smallest selectivity. A comparison of tables 2 and 3 shows

Table 3. Selectivity coefficients of vermiculites for K and Cs

K sorbed, CEC%	$k_s, \frac{K^+}{Ca^{2+}}$	Cs sorbed, CEC%	$k_s, \frac{Cs^+}{Ca^{2+}}$
	Libby vermiculite		
34·5	0·075	35·7	1·600
73·0	0·184	47·9	1·114
77·2	0·151	54·7	0·765
80·7	0·160	58·4	0·560
85·0	0·168	62·6	0·088
	Transvaal vermiculite		
31·3	0·056	43·4	2·120
53·9	0·090	54·6	1·140
67·5	0·081	60·4	0·771
74·9	0·080	63·9	0·591
88·1	0·091	83·2	0·272
	Llano vermiculite		
32·0		19·5	4·410
53·3	0·065	37·1	2·035
73·0	0·073	49·8	1·330
89·0	0·104	61·9	0·710
92·5	0·079	93·1	0·564

that vermiculites show slightly greater selectivity for K than montmorillonites. Rich and Black (1964) and Dolcater *et al.* (1968), using a different method, also observed that vermiculite was more selective for K than montmorillonite.

The selectivity coefficients of vermiculites for Cs are several fold greater than for K (Table 3). In addition, the selectivity coefficients of vermiculites for Cs increased with decreasing Cs-saturation, while for the K ion the coefficients were fairly constant.

As in vermiculites, the selectivity coefficients of Wyoming bentonite for Cs were also much greater than the selectivity coefficients for K (Table 2). However, the selectivity of the bentonite did not increase with a decrease in Cs-saturation but remained essentially constant throughout the Cs-saturation range.

Since dioctahedral vermiculite is not available as a reference mineral, selectivity of a sample of K-depleted illite, whose characteristics are similar to a dioctahedral vermiculite, will be discussed later.

Selectivity of micas and soil clays for K *ions*

The selectivity coefficients for K of biotite mica and the soil clays are similar in magnitude, while the selectivity coefficients of illite are slightly smaller (Table 4). Predominant minerals in these soil clays are Al-interlayered vermiculite and illite. Similar selectivities of micas and soil clays, there-

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Table 4. Selectivity coefficients of micas and soil clays for K

Micas		Soil Clays	
K sorbed, CEC%	$k_s, \frac{K^+}{Ca^{2+}}$	K sorbed, CEC%	$k_s, \frac{K^+}{Ca^{2+}}$
Biotite		Gloucester A_1–A_2	
16·6	0·394	18·7	0·268
27·4	0·212	25·5	0·120
39·3	0·175	35·7	0·102
54·8	0·173	49·3	0·097
69·0	0·157	62·9	0·090
78·6	0·128	74·8	0·080
Illite		Gloucester B_{21}	
17·7	0·251	23·1	0·350
24·2	0·117	33·6	0·188
30·6	0·075	42·0	0·128
38·7	0·056	54·6	0·115
53·2	0·056	67·2	0·100
67·7	0·057	71·4	0·060
Illite-D			
27·5	0·438		
38·9	0·268		
48·6	0·257		
68·1	0·195		
86·7	0·194		

fore, suggest that the selectivity of Al-interlayered vermiculite for K is comparable to micas.

The selectivity for K of micas and soil clays are greater than the selectivity of montmorillonites over the entire range of K-saturation. However, the selectivity of micas and soil clays is greater than vermiculites only at low K-saturation. As K-saturation increases, the selectivity coefficient of biotite approaches the coefficient of vermiculite from Libby. When K-saturation equals 50 per cent or more, the selectivity coefficients of vermiculites for K become greater than the coefficients of illite for K. Thus, the greater selectivity of micas than vermiculites is limited to low K-saturation.

Illite from which a portion of the interlayer K was removed (illite-D) showed greater selectivity for K than illite or biotite. The greater selectivity of illite-D will be discussed further in relation to mineral structure.

In contrast to montmorillonites and vermiculites where K selectivity remained essentially invariant, the selectivity coefficients of micas increased with decreasing K-saturation (Fig. 1). The selectivity coefficients of biotite, illite and illite-D increased 3 to 4 fold when K-saturation decreased from 80 to 20 per cent of CEC. Similarly, in a study of the release of K from illite, Bolt *et al.*, (1963) observed an 8 fold increase in the exchange constant with decrease in exchangeable K. Thus, per cent satura-

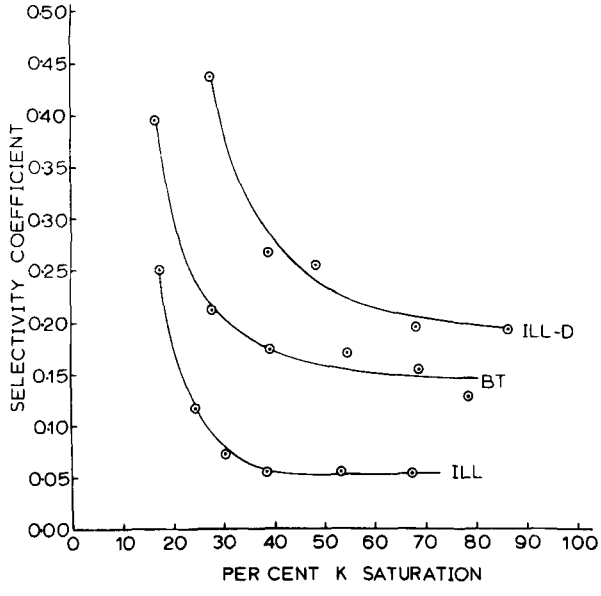


Fig. 1. Selectivity coefficients of micas in relation to per cent K saturation. Ill = illite, Bt = Biotite, and Ill-D = illite depleted of interlayer K.

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tion with a cation should be considered in discussions of the relative selectivities of different minerals for a cation.

Ionic selectivity and mineral structure

Differences in the selectivity of montmorillonite, vermiculite and micas for K [or Cs] can be related to: (1) density of layer charge (charge per unit area) and (2) area of frayed edges. Differences in the selectivity of vermiculite and montmorillonite are related to the differences in layer charge density, while the differences between micas and vermiculite on the one hand, and montmorillonite, on the other, are related to the area of frayed edges in addition to the differences in layer charge density.

The greater the layer charge density of the mineral, the easier is the interlayer collapse (Sawhney, 1969) and hence, the greater is the selectivity for the cations that induce interlayer collapse. Thus, vermiculites with greater layer charge density than montmorillonites exhibit greater selectivity for K and Cs ions.

Micas show the greatest selectivity for K [or Cs] ions for two reasons: first, the charge density of micas is greater than that of montmorillonites and vermiculites. Second, the interlayers in micas are frayed at the edges (Jackson, 1963 and Rich and Black, 1964). The frayed interlayer edges collapse readily on K or Cs sorption and hence sorb these ions more selectively than the expanded interlayers of vermiculites and montmorillonites. However, the selectivity of micas is limited to small K concentrations, because an appreciable portion of the exchange sites on micas are on the planar surfaces and broken bond edges that are not selective for K sorption. At greater concentrations, the selectivity of micas is reduced due to sorption on these non-selective sites.

The greater selectivity of illite-D than illite (Table 4) further supports the contention that the frayed interlayer edges control the selectivity of K by weathered micas. The removal of interlayer K from the collapsed central portion of illite particles increased the area of the frayed edges, changing the 10 Å basal spacing of illite to a broad diffraction maximum corresponding to a spacing between 10 Å and 14 Å. Consequently, the larger frayed edges caused the mineral to have greater selectivity for K.

Similarly, the large selectivity of biotite and soil clays is attributed to the frayed edges. In biotite, the frayed edges were likely produced by the removal of interlayer K during the separation of clay particles. The relatively large CEC, 34 m-equiv./100 g (Table 1) indicates the formation of frayed edges. In soil clays, the natural weathering should form the frayed edges in micaceous particles.

This investigation, thus, shows that the layer charge density and the area of the frayed edges in layer silicates control the selectivity for K and Cs ions. Vermiculites with greater layer charge density show greater selectivity for K and Cs ions than montmorillonites with smaller charge density. Micas show the greatest selectivity for the two ions not only because the charge density in micas is greater than vermiculite and montmorillonite, but also because micas have frayed edges. The selectivity of micas was limited to small concentrations of K. However, as the area of the frayed edges of micas was increased, the selectivity for K also increased.

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Résumé—La sélectivité d'un certain nombre de vermiculites, de montmorillonites, et de micas pour les ions K et Cs a été déterminée par la sorption de ces ions à partir de solutions d'équilibres de diverses concentrations. Les coefficients de sélectivité se rapportaient à la densité de charge de la couche et à la surface des bords éraillés dans les silicates de couche. Les montmorillonites ont eu la plus petite sélectivité pour les deux ions, tandis que le biotite et l'illite ont eu la plus grande sélectivité. La sélectivité des biotites et illite a été limitée à des petites concentrations de K. A des concentrations plus grandes, la sélectivité du vermiculite pour K a dépassé la sélectivité des micas. La plus grande sélectivité des vermiculites que des montmorillonites pour les ions K et Cs a été attribuée à une densité de charge plus élevée de la couche dans les vermiculites. La plus grande sélectivité des micas que des montmorillonites et des vermiculites a été attribuée aux bords éraillés des micas, en plus de leur densité de charge plus élevée. Du fait que les bordures éraillées dans l'illite se sont accrues dans la surface, par suite de la suppression de la couche intermédiaire K, la sélectivité de l'illite pour K a également augmentée; ceci confirmant la sélectivité des bordures éraillées pour les ions de K.

Kurzreferat—Die Selektivität einer Reihe von Vermiculiten, Montmorilloniten und Glimmer für K und Cs Ionen wurde durch Adsorption dieser Ionen aus Gleichgewichtslösungen verschiedener Konzentrationen bestimmt. Die Selektivitätskoeffizienten wurden in Beziehung gebracht zur Schichtenladungsdichte und zum Gebiet des abgefaserten Kanten in Schichtsilikaten. Montmorillonite haben die geringste Selektivität für die beiden Ionen, während Biotit und Illit die grösste Selektivität haben. Allerdings war die Selektivität von Biotit und Illit auf geringe Konzentrationen von K beschränkt. Bei höheren Konzentrationen übertraf die Selektivität von Vermiculit für K die Selektivität der Glimmer. Die grössere Selektivität der Vermiculite für K und Ca gegenüber den Montmorilloniten wurde der grösseren Schichtenladungsdichte in Vermiculiten zugeschrieben. Die grössere Selektivität der Glimmer gegenüber derjenigen der Montmorillonite und Vermiculite wurden den abgefaserten Kanten der Glimmer, zusätzlich zu deren grösseren Schichtenladungsdichte zugeschrieben. Bei zunehmenden Abfaserungsflächentim Illit durch Entfernung des Zwischenschichten K, nimmt auch

Резюме—Избирательность ряда вермикулитов, монтмориллонитов и слюд в отношении поглощения ионов K и Cs была определена по сорбции этих ионов из равновесных растворов различных концентраций. Установлена связь коэфициентов селективности с плотностью заряда слоев и площадью оборванных связей.

Монтмориллониты имеют наименьшую, а биотит и иллит—наибольшую селективность для обоих ионов. Селективность биотита и иллита ограничивается, однако, малыми концентрациями ионов калия. При больших концентрациях селективность вермикулита для K превосходит селективность слюд.

Более высокая селективность вермикулитов по сравнению с монтмориллонитами для K и Cs свябана с более высокой плотностью заряда слоев. Более высокая чем у монтмориллонитов и вермикулитов селективность слюд связана с оборванными связями на краяхъастмц, действующими дополнительно к их большей плотности зарядов слоев. Когда доля оборванных связей на краяхъастмц иллита была увеличена, после удаления межслоевых катионов K, селективность иллита в отношении K также увеличилась; этим была подтверждена селективность оборванных связей в отношении ионов K.

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