INFLUENCE OF EXCHANGE IONS ON THE
b-DIMENSIONS OF DIOCTAHEDRAL VERMICULITE*

by

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ABSTRACT

THE 1–5 μ size fractions of different ground muscovites were treated for a 30-day period for K$^+$ removal with a pH 7.5 solution containing sodium tetraphenylboron. The initial K$^+$ contents ranged from 211 to 219 me/100 g. After the extraction period, the final K contents ranged from 21 to 37 me/100 g. The apparent structural charge on the expanded material decreased to values ranging from 156 to 184 me/100 g, which are within the charge range for natural vermiculites. The b-dimensions of these laboratory-produced vermiculites were found to vary with the exchange ion and with the hydration state of the ion. For hydrated samples, saturation with Cs$^+$, Li$^+$, and Mg^{2+} ions increased the observed b-dimension in comparison to that of the corresponding parent mica, whereas saturation with Sr^{2+} and La^{3+} ions had little effect on b. After dehydration at 350°C, only Cs$^+$-saturated samples had a b-dimension greater than that of the parent mica. The observed b-dimension for the dehydrated samples was found to be a direct function of the crystal radius of the interlayer ion. Apparently, as the ion dehydrates, the surface oxygen triads rotate until some of the oxygens "lock" onto the ion, limiting the minimum b-dimension. Before dehydration, however, the water of hydration in the interlayer region is evidently held with sufficient energy to limit rotations of the oxygen triads that give rise to a decrease in b. When Li$^+$ and Mg^{2+} ions occupy the interlayer region, their water network apparently even produces a slight increase in the observed b-dimension.

INTRODUCTION

IN RECENT years, crystal structures of layer silicates have been determined with much more precision than before. As a result, ideas about these structures have also been revised. The layers in these silicates now appear to have considerable flexibility in response to forces within the crystal (Brown, 1965). According to the model of Radoslovich and Norrish (1962) the dimensions of the tetrahedral layer in the plane of the layer can be readily diminished by rotation of the silicon–oxygen tetrahedra. The octahedral layer can be extended or contracted with somewhat more difficulty. In micas particularly the oxygen triads which form the bases of the tetrahedra are thought to

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"lock" onto the interlayer cation. The extent of tetrahedral rotation can be calculated from a knowledge of the structural formula and the observed b–dimension of the mineral (Radoslovich, 1961). These calculations are based on the assumption that the observed b–dimension is determined mainly by the dimension of the octahedral layer since this layer is relatively less flexible than the tetrahedral layer. Since the surface oxygen triads in micas are thought to "lock" onto the interlayer cations the size and abundance of the cations should also influence the magnitude of the observed b–dimension (Radoslovich, 1962).

One mechanism of vermiculite formation is thought to involve the stripping of K^+ layers from mica and replacement by hydrating ions such as Ca^{2+} or Mg^{2+} (Jackson, 1963). In acid soils K^+ in dioctahedral mica may be replaced by H_3O^+ and Al^{3+}. With hydrolysis, the hydrated Al^{3+} may then polymerize in the interlayer region giving rise to the common form of dioctahedral vermiculite (Brown, 1953; Rich, 1960). One result of mica weathering is a change in interatomic forces within the interlayer region. According to recent structure proposals, changes in b-dimensions of the silicate unit may be expected to occur in response to these changing forces. Radoslovich (1963) noted that b-dimensions of vermiculites are usually greater than those of phlogopite. It was reasoned that as interlayer K^+ is replaced by ions which are displaced from the mineral surface by water of hydration, the surface oxygens of the silica sheet acquire an increased surface charge density and therefore repel each other. This repulsion should decrease the oxygen triad rotation and increase the observed b to the value normally observed for vermiculite. Burns and White (1963a, b) found that the observed b-dimension of muscovite was decreased as interlayer K^+ was removed by treatment with molten $LiNO_3$. Their conclusion was that removal of K^+ allowed increased tetrahedral rotations with a concomitant decrease in the observed b. In view of these observations, it was considered desirable to carry out a detailed study of b-dimension changes of mica as interlayer K^+ is replaced by other ions. It was thought that magnitudes and directions of b-axis changes as micas weather to vermiculites would indicate the degree of layer flexibility and type of interatomic forces involved. Studies with dioctahedral minerals are reported here. Results of similar studies using trioctahedral micas will be reported in a later paper.

MATERIALS AND METHODS

Eight muscovite micas were collected from mining excavations in western North Carolina. Each mica was chemically analyzed for major constituent elements (Shapiro and Brannock, 1956). Sample designations and chemical analyses are given in Table 1.

The micas were wet-ground in a ball mill and 1–5 micron size classes were fractionated by sedimentation. Interlayer K^+ was removed from these fractions using a solution 0.2 M in sodium tetraphenylboron (NaTPB), 1 M in

TABLE 1.—COMPOSITION OF DIOCTAHEDRAL MICAS

Constituents	Per cent composition							
	M1	M2	M3	M4	M5	M6	M7	M8
SiO_2	44.76	44.75	45.15	45.16	44.83	45.15	44.97	45.77
Al_2O_3	36.38	37.44	37.07	32.49	36.56	32.97	35.12	35.52
Fe_2O_3	0.70	0.44	0.78	4.46	1.46	4.95	0.90	0.91
FeO	0.39	0.68	0.41	1.74	0.78	1.36	0.88	0.75
MgO	0.59	0.49	0.17	0.44	0.56	0.44	0.59	0.26
CaO	0.15	0.17	0.09	0.03	0.16	0.03	0.09	0.06
Na_2O	1.14	0.45	0.38	0.48	0.68	0.36	0.68	0.55
Li_2O	0.03	0.03	0.03	0.21	0.09	0.11	0.02	0.03
K_2O	10.14	9.91	10.07	10.19	10.09	10.27	10.19	10.21
MnO	0.06	0.02	0.04	0.09	0.06	0.12	0.02	0.03
TiO_2	0.23	0.64	0.10	0.16	0.20	0.18	0.77	0.90
H_2O^{+*}	4.36	4.74	4.53	4.61	4.48	4.70	4.46	4.39
F	0.01	0.05	0.06	0.08	0.04	0.06	0.05	0.03
Subtotal	98.94	99.81	98.88	100.14	99.99	100.70	98.74	99.41
less O = F	<0.01	0.02	0.03	0.04	0.02	0.03	0.02	0.01
Total	98.94	99.79	98.85	100.10	99.97	100.67	98.72	99.40

* Loss on ignition.

NaCl, and 0.01 M in disodium ethylene diaminetetraacetate (EDTA) (Reed and Scott, 1962). The pH of this solution was adjusted to 7.5 with NaOH. The mica–NaTPB suspensions were mixed continuously for 30 days employing a rotating shaker device. At the end of the extraction period most of the precipitated K^+ was removed from suspension by foam flotation. The degraded micas were recovered from suspension by centrifugation and freed from the remaining precipitate by repeated washes with 50% aqueous solutions of acetone. The acetone solutions were 1 N in the appropriate chloride salt depending on the ion saturation desired. Samples of each degraded mica were saturated with Li^+, Mg^{2+}, and Sr^{2+} ions by this process. Excess salt was removed by repeated washes with centrifugation using methanol and finally acetone as the solvent. The K^+-depleted micas were then allowed to dry from acetone at room temperature. Small sub-samples of each degraded mica previously Mg^{2+}-saturated were later saturated with K^+, Cs^+, and La^{3+} using the appropriate chloride salt.

Cation exchange capacities (CEC) were determined by the X-ray emission procedure of Weed and Leonard (1963). Residual Na^+ and K^+ were determined by flame photometric procedures after sample dissolution with HF (Shapiro and Brannock, 1956).

Basal spacings, $d(001)$, were examined using oriented aggregate preparations dried on 1×3 in. glass microscope slides. Each slide contained about 2 mg of mica per cm^2. Solvation with ethylene glycol was accomplished by the vapor technique (Kunze, 1955). To obtain reproducible basal spacings for

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dehydrated specimens, it was necessary to obtain the diffraction patterns while keeping the specimen at an elevated temperature. A heated sample stage designed for this purpose maintained each sample at 350°C during irradiation.

Diffraction patterns in the 1.50Å region were obtained using special end-loaded powder mounts to partially overcome preferred basal orientation. The mount consisted of an aluminum block with a groove cut on one face to contain the sample material. The entire block was enclosed in a thin aluminum foil envelope (0.004 in. thick) which served to hold the sample material in place and to retard rehydration of dry samples. The sample mount with its foil envelope was held between two Lucite blocks during loading. Material was packed from the end using a strip of paper cut from an index card. Fully packed, the holder contained about 75 mg of sample. Where dehydration was desired, the holder with its sample material was heated to 350°C for a 90-min period immediately before irradiation. The open end of the foil envelope was crimped and folded after heating to further retard rehydration. Diffraction patterns were obtained using a General Electric XRD-5 diffractometer equipped with a Ni-filtered Cu radiation source, a 3° beam divergence slit, a medium resolution Soller slit and a 0.1° detector slit. Scans were made at the rate of 0.2° 2θ per minute with diffracted intensities recorded on paper moving at 60 in. per hour. A linear recording mode of 200 cps full scale with an 8-sec time constant was used. Angular positions of each diffraction line obtained were corrected for slight day-to-day variations in diffractometer alignment using quartz powder as a standard.

RESULTS AND DISCUSSION

The K-depleted micas used in this study were considered to be "dioctahedral vermiculites" (Brown, 1953) though no interlayer Al was present. In making reference to the vermiculites in this presentation the letter designation of the corresponding parent micas is retained and the prefix "V" is added to indicate degraded mica. An examination of the data in Table 2 shows that even though these materials were synthesized in the laboratory by K^+-depletion of muscovites they do have properties normally associated with vermiculites, e.g. CEC and basal spacings. Charge on expanded layers was computed by first assigning all the residual K^+ and part of the residual Na^+ to non-expanded layers (Mehra and Jackson, 1959). Sodium in non-expanded layers was assumed to be present at the same ratio to K^+ as in the original mica. The remaining Na^+ and exchangeable Sr^{2+} was then assigned to expanded layers, the fraction of which was computed from the residual K^+ content. Computed values of layer charge are well within values usually reported for vermiculite (Alexiades and Jackson, 1965). Since computed layer charge is much lower than the original mica charge, a reduction in charge evidently took place during K^+-depletion. None of the micas contained sufficient Fe^{2+} to account for observed charge reduction, assuming oxidation

TABLE 2.—CHARGE CHARACTERISTICS AND BASAL SPACINGS OF K^+-DEPLETED MICAS

Degraded mica	Layer charge meq per 100 g		Residual K^+ content meq per 100 g	CEC meq per 100 g	Basal spacings, $d(002)$, Å	
	Parent mica	Expanded layers			Mg^{2+}-saturated, air-dried	Mg^{2+}-saturated, ethylene glycol
VM1	262	165	25	139	14.1	14.0
VM2	232	161	25	130	14.0	13.8
VM3	232	182	37	142	14.0	13.7
VM4	233	174	21	148	14.0	13.9
VM5	243	156	22	132	14.0	13.8
VM6	233	179	21	153	14.0	14.0
VM7	245	183	37	142	14.0	13.8
VM8	237	184	39	143	14.0	13.8

of octahedral Fe^{2+} to Fe^{3+} could effectively lower the charge. Therefore, some other mechanism must be operating. A mechanism of proton incorporation as proposed by Raman and Jackson (1966) seems to be the most plausible.

Each Mg^{2+}-saturated vermiculite, both when air-dried and when solvated with ethylene glycol, exhibited a basal spacing near 14Å, as expected. A very slight shoulder near 10Å was noted, however, in most diffraction patterns, supporting the assumption that the residual K^+ was mainly in unexpanded layers. Basal spacings were somewhat less than normally observed for trioctahedral vermiculites under similar conditions (Walker, 1958; Weed and Leonard, 1964).

Cook and Rich (1963) observed that dioctahedral vermiculites formed by boiling mica in salt solutions contained Al interlayers similar to those found occurring in natural dioctahedral vermiculites. Interlayer contaminants are apparently not present in materials of this study as evidenced by the ease with which the layers were collapsed with dehydration at $350°C$ (Table 3).

The data shown in Table 3 represent relationships observed between basal reflections, ion saturation and degree of hydration. Diffraction lines were indexed assuming the 2M structure to be inherited from the parent mica. Although all samples contracted readily to around 10Å when heated to $350°C$, some samples, notably those saturated with Mg^{2+} or Li^+ did not contract to spacings as short as expected for complete dehydration (Walker, 1956). The irrationality of higher-order basal reflections for samples saturated with Sr^{2+}, Li^+, and La^{3+} also suggests that dehydration was incomplete. The rational reflections obtained for the Mg^{2+}-vermiculite are thought to be due to the existence of the $Mg^{2+} \cdot H_2O$ (monohydrate) ion at $350°C$ (Russell and Farmer, 1964). A prolonged heating at $450°C$ caused irreversible collapse of the Mg^{2+}-vermiculite. At this stage basal spacings around 9.4–9.5Å were obtained. Apparently with lattice contraction, some water may be trapped and held to rather high temperatures. As will be discussed later, this residual water is thought to affect observed b-dimensions.

The primary objective of this study was to observe changes in the b-dimensions of mica occurring with K^+ depletion. As is customary, b-dimensions were computed from $d(060)$ reflections. Angular positions were taken at the center of the diffraction peaks at half-intensity. Caution was used in indexing diffraction lines in the powder patterns in the region of the 060 reflection i.e. 1.50Å. As Brindley (1961) pointed out, reflections such as 331 or 332 which may be equally strong as the 060 may coincide or nearly coincide with the 060 reflection. For 2M_1 muscovite used in this study the powder line of interest is actually a superposition of 060 and $33\bar{1}$ reflections which are practically of the same intensity (Yoder and Eugster, 1955). However, since the mica structure may be considered pseudo-hexagonal, the 060 and $33\bar{1}$ may be regarded as one entity, normally designated 060, $33\bar{1}$.

Saturation of the K^+-depleted micas with different monovalent ions had a pronounced effect on the 1.50Å region of the diffraction patterns examined in this study (Fig. 1). This was especially true after dehydration at $350°C$.

Compared to the parent mica, Li-saturation produced only a slight increase in the *d*-spacing of the diffraction maximum before dehydration, but a marked decrease was noted after dehydration. Even for the hydrated Li^+-sample, a small low-spacing shoulder which corresponds closely to the spacing of the dehydrated material is evident in the diffraction pattern. Apparently, dehydration of some layers must have taken place at room temperature although this partial dehydration was not evident from basal spacings. Saturation with Cs^+, a much larger ion, produced a marked increase in the
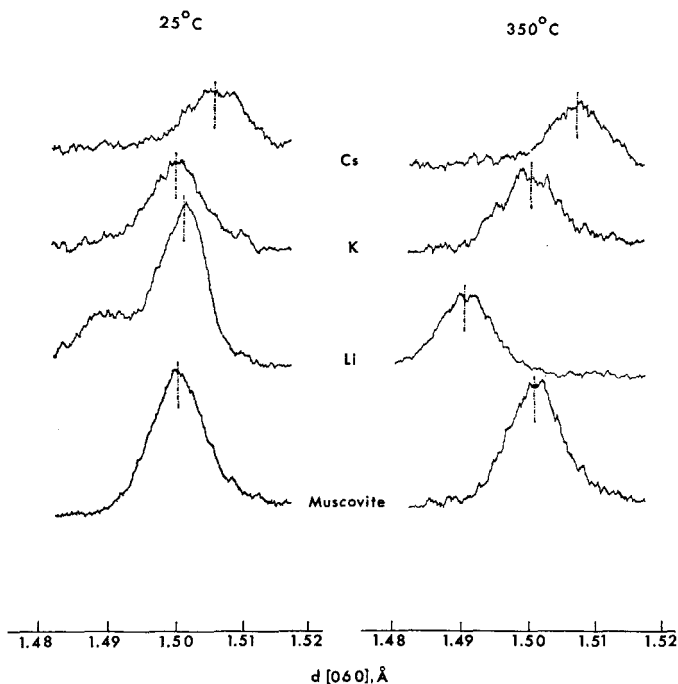

FIG. 1. X-ray diffraction traces of the 060 region of the powder pattern of dioctahedral vermiculite VM1. Saturation with monovalent cations.

d-spacing both before and after heating; however, the increase found after heating was slightly greater than before. When the K^+ ion was re-introduced after prior Mg^{2+}-saturation, the original *d*-spacing was restored even though the total number of interlayer ions was less than in the parent mica due to charge reduction. Saturation with Mg^{2+}, Sr^{2+}, and La^{3+} ions also produced variable *d*-spacings (Fig. 2). Before dehydration, Mg^{2+}-saturation increased the *d*-spacing, whereas Sr^{2+}-saturation decreased the spacing. Lanthanum-saturation had little effect although a definite peak broadening is apparent. After dehydration, all ion saturations shown in Fig. 2 produced a decrease in the *d*-spacing with Sr^{2+}-saturation showing the greatest decrease.

The contraction of the *d*-spacing with heat was found to be somewhat reversible with rehydration (Fig. 3), though the initial spacings were not fully recovered. However, an examination of basal spacings also indicated that rehydration was incomplete.

Observed *d*(060) spacings are not directly related to observed basal spacings (Table 3), as might be expected if observed changes in the 1.50 Å region were due solely to changes in *c*-dimensions through the effects of a superimposed *hkl* reflection. Observed changes in *d*-spacings, therefore, must reflect changes in *b*-dimensions.
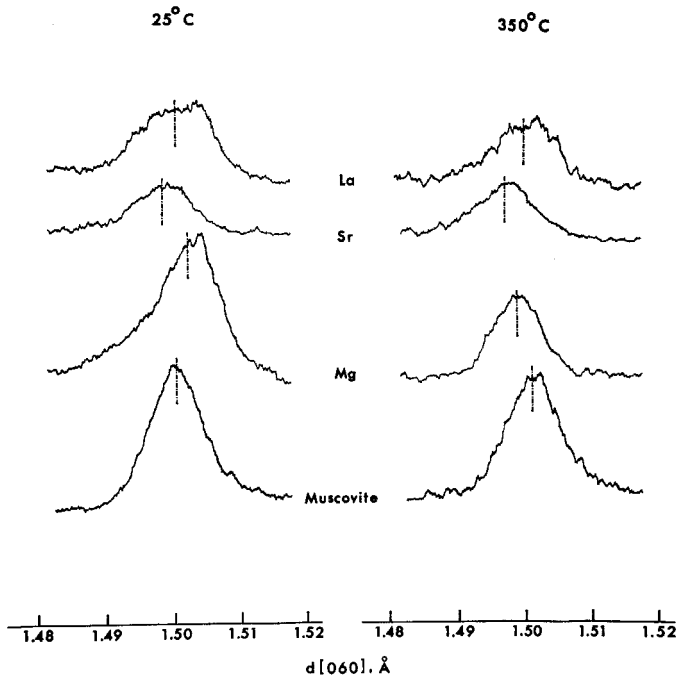

FIG. 2. X-ray diffraction traces of the 060 region of the powder pattern of dioctahedral vermiculite VM1. Saturation with Mg^{2+}, Sr^{2+} and La^{3+} ions.

Observed *b*-dimensions found in this study are given in Tables 4 and 5. Only data for vermiculite VM1 are shown since other vermiculites gave similar results. The *b*-dimensions of hydrated samples saturated with Mg^{2+} and Li^+ were not much different from the parent micas. For all eight Mg^{2+} and Li^+-saturated vermiculites *b* was larger for the hydrated than for the dehydrated samples, the difference being greater for Mg^{2+}-saturation (Table 5). The observed increases are not much greater than experimental error but are considered real. The experimental error in obtaining *b*-dimensions is thought to be of the order of ± 0.001 Å. This is evident from the variation in

b of the untreated mica before and after heating (Table 5). Because of the low Fe^{2+} content of these micas their *b*-dimensions should not be significantly altered by heat; however, differences of 0.002 Å were observed.

Considering the entire study reported here, the maximum increase in *b* observed was around 0.04 Å, which was noted for dehydrated Cs^+-vermiculite. The maximum decrease in *b*, near 0.06 Å, was found for dehydrated Li^+-vermiculite. These two ions were the largest and smallest monovalent ions studied. In general, a relationship between the size of the dehydrated exchange ion and the observed *b*-dimension was found to exist (Fig. 4). Evidently, as
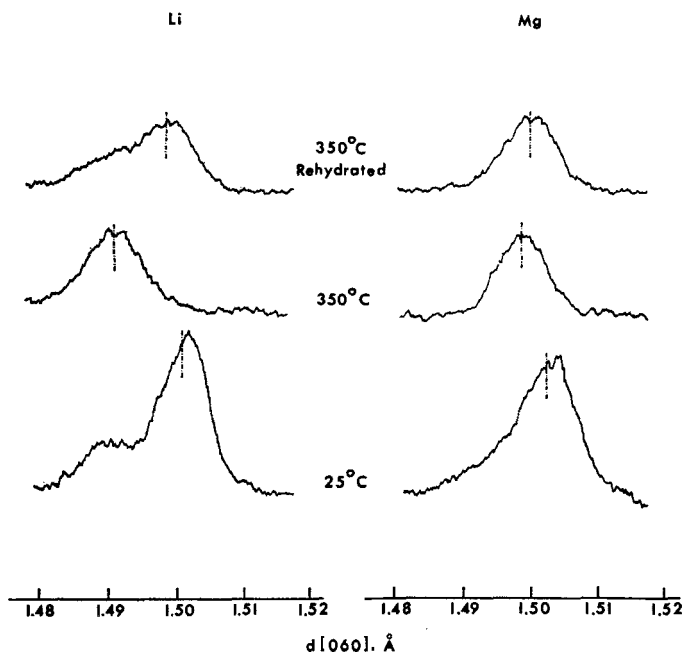

FIG. 3. X-ray diffraction traces of the 060 region of the powder pattern of dioctahedral vermiculite VM1. The effects of rehydration.

the radius decreased, rotations of the surface oxygen triads increased with a resultant shortening of *b*-dimensions. Apparently, rotations in the tetrahedral layer may occur freely as the size of the ion is changed. Contraction of the *b*-dimension of dehydrated Mg^{2+}-vermiculite did not occur to the extent expected based on its ionic size and the general relationship obtained for most of the other ions. However, as noted previously, complete ionic dehydration was not obtained at the 350°C dehydration temperature employed. Since the water molecule is similar in size to the K^+ ion, residual water in collapsed layers would probably limit the contraction of *b*. The fact that K^+-saturated vermiculite had the same *b*-dimension as the parent mica, even

Table 3.—Basal Reflections of Vermiculite VM1 in Relation
to Ion-saturation and Extent of Hydration

Exchange ion	$d(002)$, Å	$d(004)$, Å	$d(006)$, Å
Air-dried, 25°C, 35% R.H.			
Li^+	12.1	6.00	absent
Mg^{2+}	14.1	7.02	4.69
Sr^{2+}	12.3	6.12	absent
La^{3+}	12.5	5.98*	absent
Dehydrated, 350°C			
Li^+	9.9	4.72*	3.09*
Mg^{2+}	10.2	5.06	3.36
Sr^{2+}	9.8	4.84*	3.23*
La^{3+}	9.9	absent	3.16*

* Irrational spacing.

Table 4.—Observed b-Dimensions of Dioctahedral Vermiculite VM1 as
a Function of Ion Saturation and Dehydration

Treatment	Exchange ion	Observed b (Å)	Δb (Å)*
Air-dried, 25°C	K^+ (mica)	8.994	—
	K^+ (vermiculite)	8.996	$+0.002$
	Li^+	8.996	$+0.002$
	Cs^+	9.029	$+0.035$
	Mg^{2+}	9.006	$+0.012$
	Sr^{2+}	8.982	-0.012
	La^{3+}	8.994	0
Dehydrated, 350°C	K^+ (mica)	8.996	$+0.002$
	K^+ (vermiculite)	8.995	$+0.001$
	Li^+	8.937	-0.057
	Cs^+	9.036	$+0.042$
	Mg^{2+}	8.984	-0.010
	Sr^{2+}	8.975	-0.019
	La^{3+}	8.990	-0.004
Rehydrated after	Li^+	8.982	-0.012
dehydration at 350°C	Mg^{2+}	8.992	-0.002
100% R.H.	Sr^{2+}	8.975	-0.019
	La^{3+}	8.995	$+0.001$

* $\Delta b = (b_{\text{vermiculite}}) - (b_{\text{mica}})$.

TABLE 5.—OBSERVED b-DIMENSIONS OF Li$^+$- AND Mg^{2+}-SATURATED
DIOCTAHEDRAL VERMICULITES

Dioctahedral vermiculite	Exchange ion	Air–dried at 25°C		Dried at 350°C	
		Observed b, (Å)	Δb^*, (Å)	Observed b, (Å)	Δb^*, (Å)
VM2	K$^+$ (mica)	9.003	—	9.003	0
	Li$^+$	9.003	0	8.950	−0.053
	Mg$^+$	9.010	+0.007	9.993	−0.010
VM3	K$^+$ (mica)	8.988	—	8.990	+0.002
	Li$^+$	8.992	+0.004	8.938	−0.049
	Mg^{2+}	8.998	+0.010	8.978	−0.010
VM4	K$^+$ (mica)	9.026	—	9.026	0
	Li$^+$	9.029	+0.003	8.973	−0.053
	Mg^{2+}	9.035	+0.009	9.017	−0.009
VM5	K$^+$ (mica)	9.013	----	9.013	0
	Li$^+$	9.019	+0.006	8.953	−0.060
	Mg^{2+}	9.022	+0.009	9.003	−0.010
VM6	K$^+$ (mica)	9.035	—	9.034	−0.001
	Li$^+$	9.036	+0.001	8.984	−0.051
	Mg^{2+}	9.046	+0.011	9.032	−0.002
VM7	K$^+$ (mica)	9.012	—	9.010	−0.002
	Li$^+$	9.008	−0.004	8.960	−0.052
	Mg^{2+}	9.019	+0·007	8.999	−0.013
VM8	K$^+$ (mica)	9.008	—	9.008	0
	Li$^+$	9.017	+0.009	8.872	−0.036
	Mg^{2+}	9.022	+0.014	9.002	−0.006

* $\Delta b = (b_{\text{vermiculite}}) - (b_{\text{mica}})$.

though the number of interlayer ions present was less, suggests that H_2O may occupy some of the original K^+ sites. The minimum b-dimension obtained for dehydrated vermiculite (Li$^+$-saturated) was not as small as that usually reported for paragonite, the Na$^+$-mica (Radoslovich and Norrish, 1962). Seemingly, Li$^+$-saturation should produce a b-dimension at least as short as that of paragonite, but here again small amounts of residual water may prevent maximum rotation of all tetrahedra.

Considering unconstrained dimensions of the tetrahedral and octahedral layers of muscovite, there should be a tendency for b-dimensions to decrease once K^+ is removed (Burns and White, 1963a, b). Observations reported here suggest that this tendency exists. However, when ions which have high polarizing power and large hydration energies replace K^+ this tendency may be overcome. This is illustrated by the fact that both Li$^+$ and Mg^{2+} ions, when hydrated, produced a slight increase in b rather than allowing a decrease. The Sr^{2+} ion, which has a lower polarizing power, did not increase b and for some vermiculites a slight decrease was noted even while hydrated. It is thought
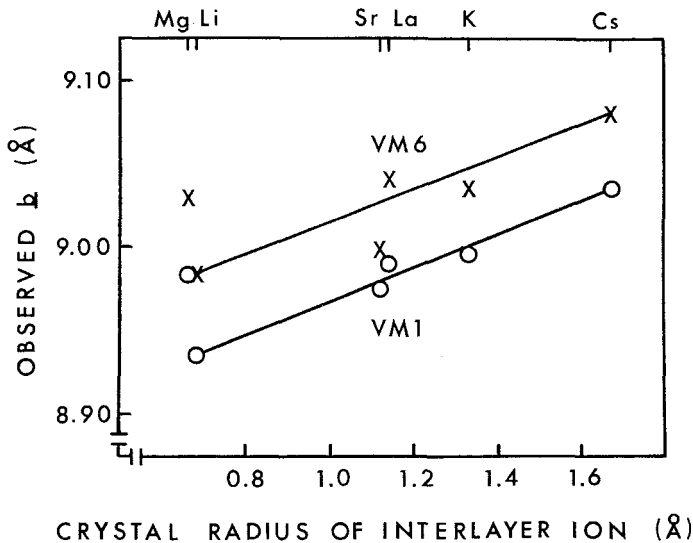
FIG. 4. Relation between observed b-dimension of dioctahedral vermiculite and radius of the interlayer ion. Samples dehydrated at 350°C.

that those ions that have high polarizing power either produce a water network that has sufficient rigidity to limit tetrahedral rotations which decrease b or that these ions are sufficiently shielded from the oxygen surface by their hydration water such that increased surface charge density on the oxygen network (Radoslovich, 1963) produces repulsive forces which limit tetrahedral rotations. If increased repulsive forces leading to b-axis expansion are present in the oxygen layer of vermiculites, as proposed by Radoslovich, these repulsive forces are apparently very nearly balanced in dioctahedral vermiculite by opposite forces imposed by the shorter octahedral layer since very little increase in b was found.

Observations reported in this study are thought to illustrate an important property of layer silicates, i.e. the ability of the surface oxygen network to change in configuration with changing surface environments. This being the case, layer silicates should not be considered inert substrates for adsorption. On the atomic level, seemingly minor displacements in oxygen configuration at the surface may contribute significantly to bonding mechanisms and bonding energy.

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