

EFFECTS OF POTASSIUM REMOVAL ON THE *b*-DIMENSION OF PHLOGOPITE*

R. A. LEONARD† and S. B. WEED‡

Department of Soil Science, North Carolina Agricultural Experiment Station,
North Carolina State University, Raleigh, N.C. 27607

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Abstract—Potassium was removed from 5 to 20- μ size fractions of two phlogopites by treatment with sodium tetraphenylboron and replaced with various exchange ions. The *b*-dimension of the mica increased with K⁺ removal, which suggests that the K⁺ ion in phlogopite acts to constrain *b*. This being the case, the K—O bond in phlogopite must be lengthened and weakened relative to the K—O bond in dioctahedral micas.

INTRODUCTION

RECENT studies have shown that the structural layers in phyllosilicates have considerable flexibility in response to changing forces within the crystal (Brown, 1965; Leonard and Weed, 1967). The dimensions of the tetrahedral layer in the plane of the layer are diminished by rotation of the silicon-oxygen tetrahedra. The dimensions of the octahedral layer are changed with somewhat more difficulty. In micas, the oxygen triads are thought to “lock” onto the interlayer cation. Burns and White (1963 a,b) found that the *b*-dimension contracted when the K⁺ ions were removed from muscovite by treatment in molten LiNO₃. More recently, Leonard and Weed (1967) have shown that the *b*-dimensions of dioctahedral vermiculites prepared from muscovite micas are affected by the interlayer ion present. The magnitude and direction of *b*-axis changes should reveal how interatomic forces are balanced with respect to the K—O bond. Results for vermiculites prepared by K⁺ removal from trioctahedral micas are reported herein.

MATERIALS AND METHODS

Chemical composition of the two phlogopite micas used for this study is described in Table 1. The naturally occurring mica, P1, was obtained from Ward's Natural Science Establishment and was analyzed for major constituent elements (Shapiro and Brannock, 1956). Mica P2 is a

synthetic fluorphlogopite obtained from the Mycalex Corporation, Caldwell, New Jersey. The composition given in Table 1 for P2 was calculated from the theoretical formula supplied by the Mycalex Corporation. The micas were wet-ground in a ball mill and 5–20 μ size classes were fractionated by sedimentation. Thin, well-crystallized plates of mica were individually selected for grinding. X-ray diffraction powder patterns of the 5–20 μ fractions showed no evidence of impurities or interstratification.

Interlayer K⁺ was removed and replaced with other cations using sodium tetraphenylboron and salt solution treatments as previously described (Leonard and Weed, 1967).

Cation exchange capacities (CEC) were determined by an X-ray emission procedure using Sr²⁺ as the exchange cation (Weed and Leonard, 1963). Residual Na⁺ and K⁺ were determined by flame photometric procedures after dissolution with HF (Shapiro and Brannock, 1956).

Basal spacings, *d*(001), were examined using oriented aggregate preparations dried on 2.5 × 7.6 cm glass microscope slides. Each slide contained about 2 mg of mica per cm². Solvation with ethylene glycol was accomplished by a vapor technique (Kunze, 1955). To obtain reproducible basal spacings for dehydrated specimens, it was necessary to obtain the diffraction patterns at an elevated temperature. A heated sample stage designed for this purpose maintained each sample at 350°C during irradiation.

The *b*-axis dimensions reported here were computed from measured (060) reflections in the 1.54 Å region of the diffraction pattern. A specially designed sample mount was used to enhance the (060) reflection and to prevent rehydration of dried samples during irradiation (Leonard and Weed, 1967). Diffraction patterns were obtained

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†Research Soil Scientist USDA, Watkinsville, Georgia 30677 (formerly Instructor, Department of Soil Science, North Carolina State University, Raleigh, North Carolina).

‡Professor of Soils, North Carolina State University Raleigh, North Carolina

Table 1. Composition of parent micas

Constituents	Per cent composition	
	P1	P2*
SiO ₂	36.68	41.69
Al ₂ O ₃	22.99	11.79
Fe ₂ O ₃	2.23	
FeO	4.09	
MgO	19.37	28.00
CaO	0.12	
Na ₂ O	0.47	
Li ₂ O	0.03	
K ₂ O	9.04	10.90
MnO	0.07	
TiO ₂	1.28	
H ₂ O [†]	3.66	
F		13.19
Subtotal	100.03	105.57
Less O = F [‡]		5.57
Total	100.03	100.00

*Theoretical.

†Loss on ignition.

‡A correction required since when F⁻ is present all cations are not associated with the O⁻ anion as expressed above.

using a General Electric* XRD-5 diffractometer equipped with a Ni-filtered CuK α radiation source, a 3° divergence slit, a medium resolution Soller slit, and a 0.1° detector slit. Scans were made at the rate of 0.2° 2 θ /min. Diffracted intensities were recorded on paper moving at 60 in./hr. A linear recording mode with an 8-sec time constant was used for all scans. Quartz was used as a standard to correct for slight day-to-day variations in diffractometer alignment.

RESULTS AND DISCUSSION

Some of the properties of the K⁺-depleted micas used in this study are given in Table 2. These materials are considered to be vermiculites. The letter designation of the corresponding parent mica is retained, and the prefix "V" is added to indicate a degraded mica. The data indicate that these materials do have properties typical of vermiculites, e.g., CEC and basal spacings. Charge on expanded layers was computed by assigning all the residual K⁺ and part of the residual Na⁺ to nonexpanded layers (Mehra and Jackson, 1959). Sodium in nonexpanded layers was assumed to be present in the same ratio to K⁺ as in the original mica.

*Trade names and company names are included for the benefit of the reader and do not imply endorsement of preferential treatment of the product listed by the U.S. Department of Agriculture.

Table 2. Charge characteristics and basal spacings of K⁺-depleted micas

	Degraded mica	
	VP1	VP2
Layer charge, me/100 g		
Parent mica	208	237
Expanded layers	169	220
Residual K ⁺ content, me/100 g	8	19
CEC, me/100 g	156	195
Basal spacings, <i>d</i> (001) Å		
Mg ²⁺ -saturated, air-dried	14.4	13.8
Mg ²⁺ -saturated, ethylene glycol	14.0	13.7

The Na⁺ remaining, which resulted from incomplete replacement by Sr²⁺, and the exchangeable Sr²⁺ were then assigned to expanded layers, the fraction of which was computed from K⁺ content. The residual Na⁺ assigned to expanding layers was less than 5 per cent of the total CEC.

Some charge reduction apparently occurred during K⁺ depletion. (Table 2). Oxidation of octahedral ferrous iron to ferric iron may account for some of the reduction of charge on VP1. However, no iron was present in VP2 and some other mechanism such as proton incorporation must account for this apparent reduction in charge (Raman and Jackson, 1966).

Each Mg²⁺-saturated vermiculite gave basal spacings close to 14 Å as expected. The values for VP2 were slightly under 14 Å, possibly because of the high charge on this material. The ready collapse of the basal spacings to near 10 Å indicates that interlayer contaminants such as polymeric hydrous aluminum oxide were not present (Table 3). At 350°C both Mg-vermiculites, i.e. VP1 and VP2, collapsed to 10 Å and gave rational higher orders. According to Walker (1956), anhydrous vermiculite layers should have a spacing of 9 Å. He found regular interstratification of 9 and 11 Å in the last stages of dehydration giving rise to 10 Å reflections. In his study the interstratified stage was not stable at 350°C. It is not clear in this study why the vermiculites did not collapse to 9 Å. Some residual water may have been trapped in the interlayers and limited contraction. If this is the case, this water probably affected the *b*-dimensions reported. However, final conclusions of this study would not be affected.

Measured *d*(060) reflections were used to compute the *b*-dimensions (Table 4). It is evident from Figs. 1 and 2 that the 1.54 Å region of the powder pattern of vermiculite is quite complex. Caution must be used in indexing the lines. In each case, the most intense peaks were indexed (060) and are indicated by short vertical lines drawn at the

Table 3. Basal reflections of vermiculites VP1 and VP2 in relation to ion saturation and extent of hydration

Exchange ion	$d(001)$ (Å)	$d(002)$ (Å)	$d(003)$ (Å)
VP1			
Air-dried, 25°C, 35% R. H.			
Li ⁺	12.20	6.07	4.04
Mg ²⁺	14.35	7.16	4.77
Ca ²⁺	11.94	5.96	3.97
Sr ²⁺	12.27	6.10	4.07
Dehydrated at 350°C			
Li ⁺	10.10	5.12	3.40
Mg ²⁺	10.10	5.02	3.34
Ca ²⁺	10.10	absent	3.11*
Sr ²⁺	10.10	4.98	3.20*
VP2			
Air-dried, 25°C, 35% R. H.			
Li ⁺	12.10	6.09	4.04
Mg ²⁺	13.80	absent	4.59
Ca ²⁺	12.44	5.98*	3.37*
Sr ²⁺	12.27	6.12	4.09
Dehydrated at 350°C			
Li ⁺	10.10	5.12	3.40
Mg ²⁺	10.10	5.02	3.34
Ca ²⁺	10.16	5.01	3.13*
Sr ²⁺	10.10	4.98	3.20*

*Irrational spacing.

peaks' maxima. The adjacent peaks were thought to be (330), (332), or (334) reflections from the expanded vermiculite phase. The diffraction maxima which were indexed (060) remained in the same region for both dehydrated and hydrated samples. Peaks thought to be other (hkl) reflections disappeared when the samples were dehydrated, since the positions of these reflections

are a function of the *c*-dimension as well as the *b*-dimension. With dehydration, intense reflections appeared in the (061) region for Mg²⁺ and Li⁺-vermiculite. Whether these peaks are (061) reflections or other (hkl) reflections, their intensities appear related to the electron density of the interlayer region, since this peak did not occur in the pattern of Cs⁺-vermiculite.

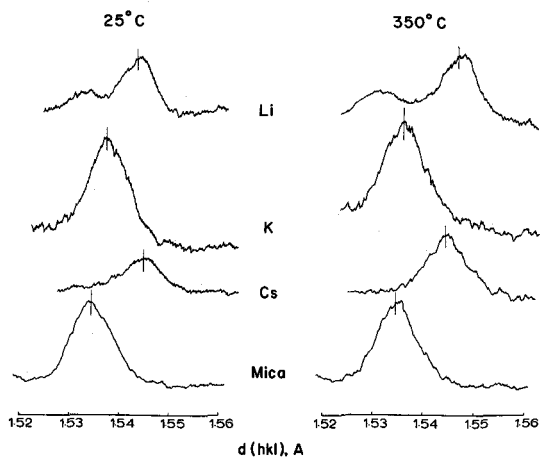


Fig. 1. X-ray diffraction traces of the 1.54 Å region of the non-oriented powder patterns of vermiculite VP1 saturated with various monovalent cations.

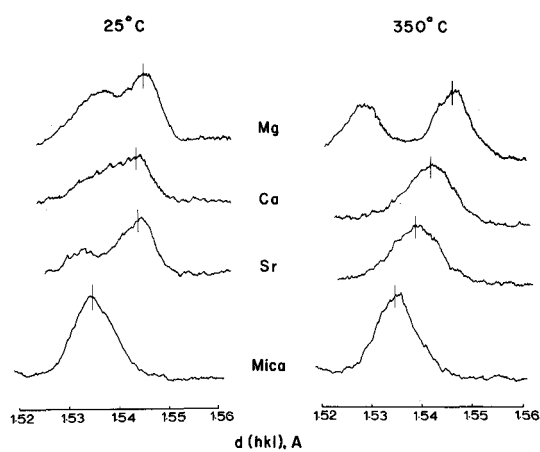


Fig. 2. X-ray diffraction traces of the 1.54 Å region of the non-oriented powder patterns of vermiculite VP1 saturated with various divalent cations.

Table 4. Computed *b*-dimensions of vermiculite VP1 and VP2 in relation to ion saturation and hydration

Treatment	Exchange ion	Computed <i>b</i> (Å)	Δb^* (Å)
VP1			
Air-dried	K ⁺ (mica)	9.200	
	K ⁺ (vermiculite)	9.223	+0.023
	Li ⁺	9.250	+0.050
	Cs ⁺	9.260	+0.060
	Mg ²⁺	9.258	+0.058
	Ca ²⁺	9.250	+0.050
	Sr ²⁺	9.253	+0.053
Dehydrated, 350°C	K ⁺ (mica)	9.200	+0.015
	K ⁺ (vermiculite)	9.215	+0.015
	Li ⁺	9.275	+0.075
	Cs ⁺	9.262	+0.062
	Mg ²⁺	9.270	+0.070
	Ca ²⁺	9.241	+0.041
	Sr ²⁺	9.222	+0.022
VP2			
Air-dried	K ⁺ (mica)	9.184	
	K ⁺ (vermiculite)	9.205	+0.021
	Li ⁺	9.196	+0.012
	Cs	9.215	+0.031
	Mg ²⁺	9.225	+0.041
	Ca ²⁺	9.206	+0.022
	Sr ²⁺	9.209	+0.025
Dehydrated, 350°C	K ⁺ (mica)	9.184	
	K ⁺ (vermiculite)	9.208	+0.024
	Li ⁺	9.221	+0.037
	Cs ⁺	9.212	+0.028
	Mg ²⁺	9.226	+0.042
	Ca ²⁺	9.187	+0.003
	Sr ²⁺	9.179	-0.005

* $\Delta b = b$ vermiculite - b mica.

Values of the *b*-dimensions of vermiculite formed from micas P1 and P2 show that as K⁺ was removed and replaced by other ions, the *b*-dimension generally increased (Table 4). The amount of increase depended on the replacing ion. Only for Sr²⁺-saturated, dehydrated VP2 did the spacing contract slightly. Saturation of the samples with Li⁺ or Mg²⁺ plus heat to induce dehydration caused the greatest increases in *b*. Note that K⁺-saturated vermiculite had a greater *b*-dimension than the original mica. This may be related to the reduced charge on the structure or to some interlayer water present. The vermiculite was first Mg²⁺-saturated and all of this Mg²⁺ may not have been replaced by K⁺ in the resaturation.

Conceivably the intense reflections thought to be (061) for dehydrated Mg²⁺ and Li⁺-vermiculite

are (060) reflections from a vermiculite component which becomes smaller than the original *b*-dimension. Dioctahedral vermiculites are known to contract in *b* with dehydration (Leonard and Weed, 1967). No i.r. data on the pleochroic behavior of OH groups in P1 are available to assess the prevalence of octahedral vacancies or dioctahedral-like components. The computed structural formula of P1 indicates that slightly more than 2.9 of the possible 3 octahedral positions are occupied by cations. The basal spacings of Mg²⁺ and Li⁺-dioctahedral vermiculite dehydrated at 350°C were found to be near 9.9 Å and had irrational higher orders (Leonard and Weed, 1967). The dioctahedral vermiculites also rehydrated with difficulty. Heating Mg²⁺ and Li⁺ saturated VP1 and VP2 to 350°C produced basal reflections near

10-1 Å which had integral higher orders (Table 3). Vermiculites VP1 and VP2 rehydrated very readily. Therefore, dioctahedral-like components are evidently absent in the phlogopites of this study and it is highly unlikely that any component is present that becomes smaller in *b* than the original mica.

The data of this study are supportive evidence for Radoslovich's interpretation of the *b*-dimension of vermiculite (Radoslovich, 1963). He 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, increasing *b*. In the present study, the *b*-dimensions increased with K^+ replacement both under hydrated and dehydrated conditions. Small ions, such as Mg^{2+} and Li^+ , may allow large increases in *b* with dehydration because they cannot contact sufficient oxygens around the ditrigonal cavity to constrain *b*. The Cs^+ ion, however, being a much larger ion, can force the oxygen triads open, resulting in an increase in *b*.

With the above observations in mind, it may be concluded that the K^+ ion acts to constrain the *b*-dimension of trioctahedral micas. This indicates that the K^+ ion is of a critical size for it to function as it does. (Drits, 1969) also concluded that the presence of K^+ in trioctahedral micas results in a decrease in *b*. Earlier, it was shown that the *b*-dimension of dioctahedral micas tended to contract with K^+ removal (Leonard and Weed, 1967).

The role that K^+ plays in constraining *b* in trioctahedral micas indicates that the K—O bond in trioctahedral micas is lengthened and weakened relative to the K—O bond in dioctahedral micas. These observations in addition to considerations of differences in O—H group orientations may help explain some of the differences that have been

observed in the ease of K^+ removal from micas (Leonard and Weed, 1970).

REFERENCES

- Brown, G. (1965) Significance of recent structure determinations of layer silicates for clay studies: *Clay minerals* 6, 73–82.
- Burns, A. F. and White, J. L. (1963a). Removal of potassium alters the *b*-dimension of muscovite: *Science* 139, 39–40.
- Burns, A. F. and White, J. L. (1963b). the effect of potassium removal on the *b*-dimension of muscovite and dioctahedral soil micas: *Proc. Intern. Clay Conf.*, Stockholm, pp. 9–17.
- Drits, V. A. (1969) Some general remarks on the structure of trioctahedral micas: *Proc. Intern. Clay Conf.*, Tokyo, Vol. 1, 51–69.
- Kunze, G. W. (1955) Anomalies in the ethylene glycol solvation technique used in X-ray diffraction: *Clays and Clay Minerals* 3, 88–93.
- Leonard, R. A. and Weed, S. B. (1967) Influence of exchange ions on the *b*-dimensions of dioctahedral vermiculite: *Clays and Clay Minerals* 15, 149–161.
- Leonard, R. A. and Weed, S. B. (1970) Mica weathering rates as related to mica type and composition: *Clays and Clay Minerals* 18, 187–195.
- Mehra, O. P. and Jackson, M. (1959) Constancy of the sum of mica unit cell potassium surface and interlayer sorption surface in vermiculite-illite clays: *Soil Sci. Soc. Am. Proc.* 23, 101–105.
- Radoslovich, E. W. (1963) The cell dimensions of layer silicates. IV. Interatomic forces: *Am. Mineralogist* 48, 76–99.
- Raman, K. V. and Jackson, M. L. (1966) Layer charge relations in minerals of micaceous soils and sediments: *Clays and Clay Minerals* 14, 53–68.
- Shapiro, L. and Brannock, W. W. (1956) Rapid analysis of silicate rocks: *U.S. Geol. Surv. Bul.* 1036c, 19–56.
- Walker, G. F. (1956) The mechanism of dehydration of Mg-vermiculite. *Clays and Clay Minerals* 4, 101–115.
- Weed, S. B. and Leonard, R. A. (1963) Determination of Sr by X-ray emission in cation-exchange capacity determinations of clays: *Soil Sci. Soc. Am. Proc.* 27, 474–475.

Résumé—Le potassium a été extrait de fractions de 2 phlogopites mesurant entre 5 et 20 μ , par un traitement au tétraphényl-bore de sodium et remplacé par différents ions échangés. La dimension *b* du mica a augmenté avec l'extraction de K^+ , ce qui suggère que l'ion de K^+ dans le phlogopite limite la dimension *b*. Dans ce cas la liaison K—O dans le phlogopite doit être allongée et rendue plus faible par rapport à la liaison K—O dans les micas dioctahédriques.

Kurzreferat—Aus den Fraktionen in einem Grössenbereich von 5 bis 20 μ zweier Phlogopite wurde durch Behandlung mit Natriumtetraphenylbor das Kalium entfernt und durch verschiedene Austauschionen ersetzt. Die *b*-Dimension des Glimmers erhöhte sich bei der Entfernung des K^+ , was darauf hindeutet, dass das K^+ Ion im Phlogopit eine *b* einschränkende Wirkung ausübt. Wenn das der Fall ist, so muss die K—O Bindung in Phlogopit im Vergleich mit der K—O Bindung in dioctahedralen Glimmern verlängert und geschwächt sein.

Резюме—Обработкой натриевым тетрафенилбором фракций от 5 до 20 мк двух образцов флогопита было осуществлено вымывание из них калия с заменой его на различные обмен-

ные ионы. С удалением K^+ параметр b слюды увеличивается; это свидетельствует о том, что ионы K^+ во флогопите сжимают структуру в направлении оси b . На этом основании делается вывод о том, что связь $K-O$ во флогопите должна быть длиннее и слабее, чем в диоктаэдрических слюдах.