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INTERSTRATIFICATION IN MALAWI VERMICULITE: EFFECT OF BI-IONIC K-Mg SOLUTIONS

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Abstract—The conversion of Malawi vermiculite into K-vermiculite by treatment with bi-ionic K-Mg solutions of 1 N total ion concentration (KCl and $MgCl_2$ mixed solutions of ionic strength equal to 0.5) was studied by following the 00*l* X-ray powder diffraction (XRD) reflections. Flakes of Mg-saturated samples were treated at 160°C during 24 hr with bi-ionic solutions, with the K concentration varying from zero to pure 1 N KCl solution. The K-Mg interlayer exchange began at a critical value $x_K = .0196$ (K/Mg = 1/100) of the molar fraction of K in the solution. Above the critical concentration and extending to pure 1 N KCl, the XRD diagrams were characteristic of a 10-Å/14-Å interstratification that had a marked tendency towards regularity. Experiments with KCl and $MgCl_2$ mixed solutions of ionic strength equal to 0.75 and 1.0 showed that the exchange began at the same critical value x_K as the experiments with ionic strength equal to 0.5, if the K added was equivalent. X-ray fluorescence analysis further showed that the amount of K adsorbed was proportional to the molar fraction x_K and to the proportion of K-saturated layers (10 Å) in the interstratification. To explain the mechanism of this quasi-regular interstratification, a crystallochemical rather than a thermodynamic mechanism is proposed.

Key Words—Interstratification, Ion exchange, Magnesium, Potassium, Vermiculite, X-ray powder diffraction.

INTRODUCTION

Numerous examples of randomly interstratified phyllosilicates in mineral deposits and in soil clays have been reported. The occurrence of regularly interstratified phyllosilicates or interstratified phyllosilicates having a high tendency towards regularity, however, is less common (Bailey, 1982). The presence of biotite in deep horizons of certain soils, of biotite/vermiculite interstratifications in the intermediate horizons, and of vermiculite in the upper horizons of soils suggests that biotite transforms to vermiculite by means of an interstratified structure (Walker, 1950; Jackson *et al.*, 1952; Stephen, 1952; Brindley *et al.*, 1983; Newman and Brown, 1987) with extended weathering. Boettcher (1966), Rhoades and Coleman (1967), Sawhney (1969), and Sawhney and Reynolds (1985) demonstrated that the reverse transformation of vermiculite to mica also takes place through an intermediate interstratified state.

The aim of the present work was to study the transformation of Mg-vermiculite to K-vermiculite by treating it at 160°C for 24 hr with bi-ionic solutions of K and Mg having compositions ranging from pure 1 N $MgCl_2$ to pure 1 N KCl solutions.

The phrase "homogeneous phase" is used herein to indicate a phase in which, along the direction perpendicular to the plane of the layers, the structure is ordered, i.e., the phase consists of a regular alteration of 2:1 silicate layers and the same interlayer material for all the interlayer spaces. The transformation from one homogeneous phase to another occurs through structures, herein termed inhomogeneous (or intermediate). For phyllosilicates, in particular vermiculite, these states are termed interstratified. Their structure in a direction perpendicular to the plane of the layers is thus more or less disordered in the sense of the irregular alteration of 2:1 silicate layers having different interlayer material from one interlayer to another (Pons *et al.*, 1989).

MATERIALS AND METHODS

Materials

The vermiculite used in this study was from Nyasaland (Malawi). The geology of the basement complex of Southern Nyasaland was studied by Morel (1955). The structural formula of the vermiculite is:

$$(Si_{5.68}Al_{2.08}Fe^{3+}_{0.24})(Mg_{5.07}Mn_{0.01}Fe^{3+}_{0.83}Ti_{0.11})O_{20}(OH)_4Ca_{0.61}K_{0.005}$$

(Norrish, 1973). Total chemical analysis was carried

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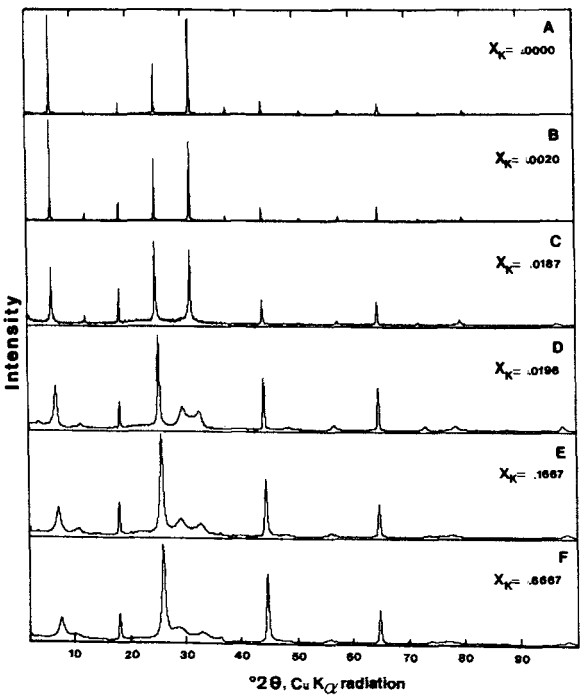


Figure 1. X-ray powder diffraction diagrams of (A) homogeneous 14.34- and (B) 14.40-Å phases (region A); (C) transition phase (region B); (D), (E), and (F) interstratified states (region C).

out by Norrish on Ca-saturated samples to avoid ambiguity in assigning interlayer cations.

Cation-exchange treatments

To produce a homoionic Mg starting vermiculite, natural flakes of about 1.5 × 2.5 × 0.1 mm were treated with a 1 N $MgCl_2$ solution for 24 hr at 160°C, washed with distilled water, and dried at room temperature.

Bi-ionic K-Mg-vermiculite was obtained by treating flakes with mixed aqueous solutions of K and Mg with K/Mg equivalent ratios ranging from 10^{-4} to 10 (KCl and $MgCl_2$ mixed solutions of ionic strength equal to 0.5). The quantity x_K is defined as the molar fraction of potassium in solution. Experiments were carried out in a Teflon pressure vessel of 20-ml capacity at 160°C. The internal pressure was the vapor pressure of water at the temperature of the experiment. The temperature of 160°C was selected to obtain a faster transformation (room temperature and 75°C were also tested). One flake of homoionic Mg-vermiculite and about 10 ml of K-Mg solution were placed in the Teflon vessel and brought to temperature. After 24 hr, the treated flakes were washed with distilled water and dried at room temperature. The stability of all phases in contact with air was verified by a second X-ray powder diffraction (XRD) examination three months after the sample had first been examined. Experiments with KCl and $MgCl_2$ mixed solutions of ionic strength 0.75 and 1.0 were also carried out.

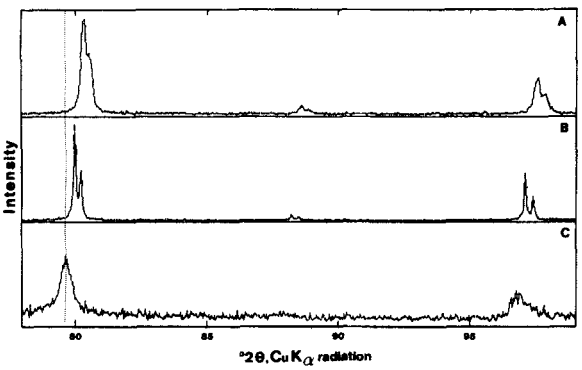


Figure 2. Large-angle region of X-ray powder diffraction patterns corresponding to samples (A), (B), and (C) of Figure 1, showing evidence of structural alteration. Note presence or absence of the $K\alpha_1$-$K\alpha_2$ doublet and the modification of the basal spacings.

Methods

X-ray powder diffraction studies. XRD studies were carried out with a Siemens D-500 apparatus equipped with a Cu anticathode at 40 kV and 20 mA. The horizontal goniometer allowed patterns to be obtained between 2° and 100°2θ; the anti-diffusion slits had an opening of 1°, and the analysis slit had an opening of 150 μm. A graphite monochromator placed behind the sample allowed CuKβ radiation to be totally eliminated. The slit system was selected to ensure that the sample was totally bathed in the X-ray beam at all angles of 2θ. Under these conditions, the angular geometric correction as given by Brindley and Gillery (1956) could be used. The experimental intensities (I_{exp}) were corrected using the Lorentz correction, the polarization correction, and corrections for the geometric factor and absorption. The corrected intensity (I_{corr}) was obtained by applying the appropriate formula (Brindley and Gillery, 1956; Guinier, 1964; Pons *et al.*, 1989):

$$I_{corr} = \frac{2 \sin 2\theta}{(1 + \cos^2 2\theta) \sin\theta (1 - \exp(-2\mu x/\sin\theta))} I_{exp},$$

where x is the thickness of the crystal studied.

The corrected experimental intensities were analyzed using an Olivetti microcomputer M24, type PC, equipped with a high-resolution EGC graphical output (600 × 400), and using the DRX program elaborated by Vila *et al.* (1988). This program allowed data to be obtained from the program chart (DACO-MP) of the diffractometer and subsequent modifications to be carried out (e.g., smoothing, measure of area, determination of reflection angle, graphical representation).

The homogeneous phases (Mg-treated vermiculite)

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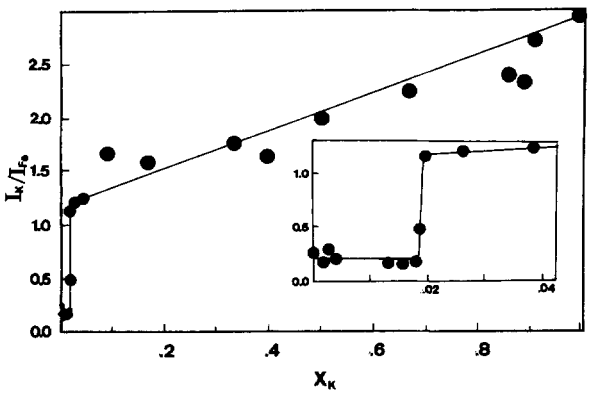


Figure 3. I_K/I_{Fe} ratio determined by X-ray fluorescence for lines corresponding to K and Fe as a function of the molar fraction, x_K.

were examined by one-dimensional Fourier transform of 00*l* reflections. Interstratification analyses were carried out by the INTER-program of Vila and Ruiz-Amil (1988).

X-ray fluorescence analysis. The quantity of K adsorbed by the crystals as a function of the K/Mg equivalent ratio in the bi-ionic solution was determined by X-ray fluorescence analysis, using a Philips PW1404 spectrometer equipped with a Sc tube and a LiF analyzer. The lines used were the K lines of Fe and K. Fe in the sample was used as an internal reference; the intensity of the radiation corresponding to different crystals was normalized by using the intensity of the Fe peaks corresponding to the same crystals.

RESULTS

Diagnostic patterns

XRD patterns for the natural vermiculite and for several bi-ionic K-Mg vermiculite products are shown in Figure 1. The diagrams can be classified into three groups corresponding to the three regions of variation for the molar fraction x_K.

Region A:0 ≤ x_K ≤ .0179 (0 ≤ K/Mg ≤ 1/110). The diagrams of all samples treated with bi-ionic solutions having a molar fraction $x_K \leq .0179$ are identical with those obtained for the homogeneous phase (d(001) = 14.4 Å) corresponding to a sample treated in the same conditions with a pure 1 N $MgCl_2$ solution. This similarity of XRD patterns suggests that for K molar fractions < .0179, the K did not penetrate into the interlayer space. For these samples, the reflections were rational, and the $K\alpha_1$-$K\alpha_2$ doublet was well-defined for the high-index reflections (Figure 2B), indicating a high degree of ordering for this phase in the direction perpendicular to the plane of the layers.

Figure 2A shows the pattern of natural, untreated vermiculite. Although the reflections are rational as

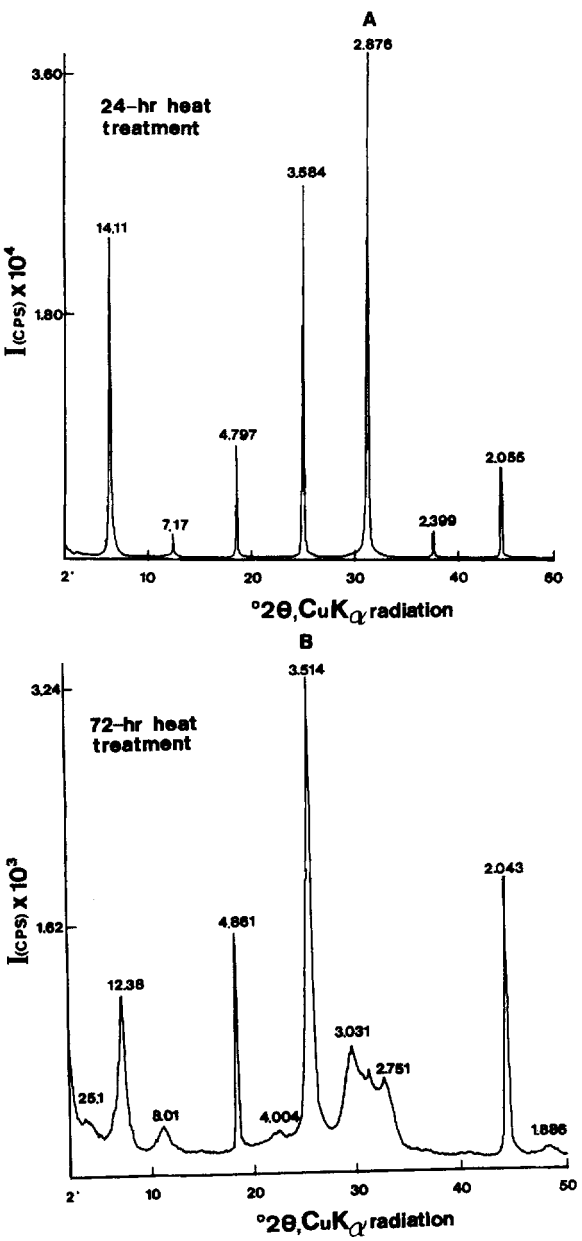


Figure 4. X-ray powder diffraction diagrams of Mg-vermiculite treated with a K-Mg bi-ionic solution of molar fraction x_K = .0187 at 160°C for (A) 24 hr (B) 72 hr. Intensity is given in absolute scale (c.p.s. = counts per second).

above, the $K\alpha_1$-$K\alpha_2$ doublet is not as well resolved as for the samples treated with solutions containing molar fraction of K < .0179 (K/Mg < 1/110), suggesting some structural disorder perpendicular to the plane of the layers. The basal spacings of this sample and samples treated with solutions of molar fraction of K < .0179 were different: d(001) = 14.34 Å for the natural air-dry vermiculite, and d(001) = 14.4 Å for the treated

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Table 1. Coefficient of variation (CV) and I_K/I_{Fe} ratio determined by X-ray fluorescence and statistical parameters relating to interstratification, as a function of the molar fraction x_K.[1]

	K/Mg	x_K	I_K/I_{Fe}					
A	$MgCl_2$	.0000	0.27					
	1/1000	.0020	0.18					
	1/250	.0079	0.15					
	1/125	.0157	0.15					
	1/110	.0179	0.17					
B	1/105	.0187	0.49	CV	WA	PAA	PAB	PBA	PBB
C	1/100	.0196	1.16	2.88	.40	.05	.95	.63	.37
	1/50	.0385	1.24	1.62	.42	.05	.95	.68	.32
	1/10	.1667	1.60	0.74	.43	.10	.90	.68	.32
	1/3	.3976	1.62	2.45	.48	.15	.85	.78	.22
	1	.6667	2.25	3.20	.52	.20	.80	.86	.14
	5	.9091	2.75	20.90	.58	.36	.64	.88	.12
	KCl	1.0000	2.96	—	.65	.50	.50	.92	.08

[1] WA = proportion of A layer; P_{AB} = probability of a B layer succeeding an A layer; W_B, P_{AA}, P_{BB} and P_{BA} are similarly defined.

samples, using bi-ionic solutions in which $x_K \leq .0179$ (K/Mg $\leq$ 1/110).

Region B: .0179 $\leq x_K \leq$ .0196 (1/110 $\leq$ K/Mg $\leq$ 1/100). Figures 1C and 2C suggest that a structural change took place compared with the initial sample if the vermiculite was treated with a solution having a molar fraction $x_K = .0187$ (K/Mg = 1/105). This change is marked by: (1) The disappearance of the $K\alpha_1$-$K\alpha_2$ doublet; (2) the fact that the basal spacings are no longer rational; and (3) a change in the relative intensities in the strongest of the 00*l* spacings.

The diagrams indicate a tendency towards disorder, corresponding to an interstratification due to the appearance of a few 10-Å distances following the initiation of K adsorption between the layers.

Region C: .0196 $\leq x_K \leq$ 1 (1/100 $\leq$ K/Mg $\leq$ 1). In region C, the diagrams show the presence of a ~24-Å reflection and the higher orders corresponding to this spacing, which suggests interstratification between K-saturated layers and layers containing the $Mg(H_2O)_n$ complex in interlayer positions.

To estimate the regularity of the interstratification, the coefficient of variation, CV, as defined by Bailey (1982), was calculated for the samples (Table 1). "Regular" is herein defined as an interstratification of two layer types A and B having sufficient regularity of alteration of spacings to give a well-defined series of at least ten 00*l* summation spacings $d_{AB} = d_A + d_B$, for which the sub-orders are integral and the even-odd sub-orders have similar diffraction breadths. The CV of the d(00*l*) values should also be <0.75 to demonstrate adequate regularity. Except for the sample treated with a solution of molar fraction of K = .1667 (CV = 0.74), the samples examined here had CVs that were too large to allow interstratified structures to be defined as regular interstratifications. These samples were designated as interstratified K-Mg-vermiculites having a marked tendency towards regularity.

Potassium analysis by X-ray fluorescence

To define the interlayer K content of the different structure corresponding to the three regions shown by the XRD, a relative measure of the K content was made, taking as an internal reference the Fe content of the crystals, which was assumed to be constant from one crystal to another. The difference in the ratio between the intensities of the lines corresponding to K and Fe allowed the variation of the K content to be followed as a function of the molar fraction, x_K, of K in the bi-ionic K-Mg solution. These determinations were made on the same crystals as those used for the XRD.

Figure 3 shows the variation of the I_K/I_{Fe} ratio (Table 1) as a function of the molar fraction, x_K, of K in solution. A correlation exists between the absence of K in the interlayer space and the presence of homogeneous phases, as well as between the presence of K and the existence of an interstratified phase. In particular: (1) The K did not appear to penetrate between the layers x_K values < .0179 (K/Mg = 1/110), thereby explaining the fact that the patterns in this region were identical to that of the natural vermiculite treated with 1 N $MgCl_2$ solution. (2) K was adsorbed at a x_K value of .0187 (K/Mg = 1/105), confirming that the difference in the XRD patterns was due to the penetration of K in the interlayer space and that some interstratification had taken place. (3) For x_K = .0196 (K/Mg = 1/100), appreciable K adsorbed (beginning of region C), with the formation of an interstratified structure having marked tendency towards regularity, indicating a structural transition due to the presence of K between the layers. From this value of the molar fraction to

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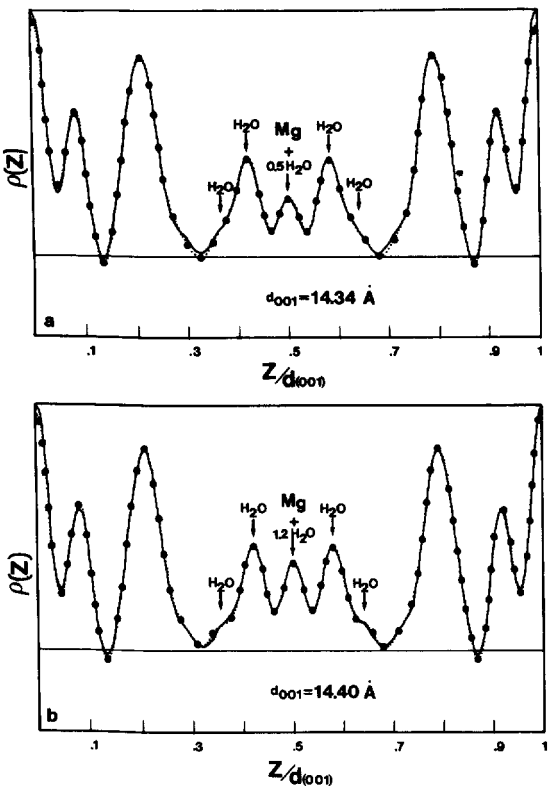


Figure 5. One-dimensional Fourier synthesis from 00*l* diffraction intensities of the 14.34-Å natural vermiculite and the 14.40-Å Mg-vermiculite. ——— theoretical, and ····· experimental values.

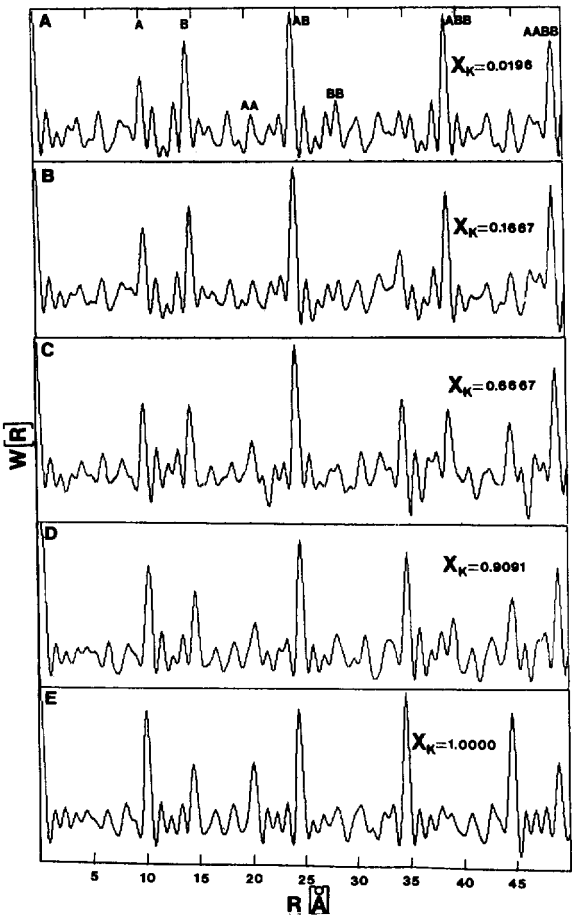


Figure 6. Distribution functions W(R) of the interlayer distances calculated from the observed 00*l* diffraction intensities. W(R) = probability that one silicate layer will be found at a distance R(Å) from another silicate layer.

larger values, the amount of interlayer K increased steadily.

Exchange kinetics: qualitative study

To study the stability of the different structural phases, a qualitative study was made of the cation-exchange kinetics and of the evolution of the structure with time. For this purpose the crystal was left in the same solution at 160°C for 72 hr instead of 24 hr. After 72 hr, for all x_K values noted above (except x_K = .0187), the XRD patterns were identical to those obtained after 24 hr of reaction. Thus, in these conditions, the maximum quantity of Mg exchanged for K was reached after 24 hr for all samples treated with bi-ionic solutions of $x_K > .0196$.

For x_K = .0187 (K/Mg = 1/105), in the region of transition, the crystal structure changed and after 72 hr an interstratified structure formed that was identical to that formed in the x_K = .0196 (K/Mg = 1/100) experiment (Figure 4). Probably, the homogeneous structure (d(001) = 14.4 Å) transformed to the interstratified structure at $.0179 < x_K < .0187$.

Quantitative analysis of the XRD patterns

The XRD patterns indicated two types of assemblages: homogeneous phases and interstratified structures. The homogeneous phases showed rational 00*l* reflections and a $K\alpha_1$-$K\alpha_2$ doublet that suggests ordering in the direction perpendicular to the plane of the layers. Here, a method of analysis giving the electron density projection resulting from unidimensional Fourier transform was utilized. The patterns of the assemblages of interstratified structures were characterized by non-rational 00*l* reflections. The analysis were carried out by a method suitable for interstratified structures (Méring, 1949; MacEwan *et al.*, 1961; MacEwan and Ruiz-Amil, 1975; Reynolds, 1980; Pons, 1980; Pons *et al.*, 1989). The computer program of Vila and Ruiz-Amil (1988) was also utilized.

Homogeneous phases (x_K < .0179). The transformation of intensities to structure factors was carried out

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Table 2. Observed and calculated structure factors for 14.34-Å and 14.4-Å homogeneous Mg-vermiculite phases.[1]

00*l*	14.34		14.40	
	F_{obs}	F_{cal}	F_{obs}	F_{cal}
1	123.0	125.8	104.8	106.8
2	15.0	18.9	28.2	36.1
3	−42.5	−34.5	−52.2	−48.2
4	102.6	102.6	111.5	110.1
5	169.5	168.0	159.3	162.1
6	−47.2	−41.2	−34.8	−31.6
7	−68.6	−61.9	−71.2	−65.6
8	−37.2	−29.3	−33.7	−30.9
9	41.7	49.5	47.7	47.1
10	87.5	98.8	96.3	99.3
11	42.3	41.6	42.9	41.4
12	60.7	57.4	67.0	60.9
13	18.9	20.4	14.9	16.7
14	40.8	42.3	45.1	45.6
R	.071		.048	

[1] R = reliability factor.

by applying Lorentz corrections, polarization corrections, and corrections for geometric factor and adsorption, as outlined above. First, phases for the 00*l* reflections were obtained from the known 2:1 silicate layer using the coordinates and the thermal vibration factors given by de la Calle *et al.*, (1988) and assigned to the structure amplitudes. The definitive signs were finally obtained by introducing the contribution of the interlayer spaces. The atomic diffraction factors were from the International Tables of Crystallography. The atoms of the layers were assumed to be completely ionized (Radoslovich, 1960).

Tables 2 and 3 list observed and calculated structure factors and values of various parameters obtained for the natural sample (d(001) = 14.34 Å) and the natural sample treated with 1 N $MgCl_2$ solution (d(001) = 14.40 Å). The values corresponding to the proportion of water molecules and Mg were adjusted to obtain the best reliability factor R ($R = \Sigma||F_c| - |F_0||/\Sigma|F_0|$). Comparisons of the calculated and experimental electron-density profile corresponding to two of the samples studied are shown in Figure 5.

From these data, these two samples differed by the amount and the position of water molecules in their interlayer space. The increase in water content in the treated sample (1.1 H_2O/half unit cell) was accompanied by a structural rearrangement.

Study of interstratified states. Here, the interstratification was considered to consist of two components, A and B. To calculate a binary interstratification the six coefficients defined in the literature (MacEwan *et al.*, 1961; MacEwan and Ruiz-Amil, 1975; Reynolds, 1980), W_A (proportion of the A layers), W_B (proportion of the B layers), P_{AA} (probability of A succeeding A), P_{AB} (probability of B succeeding A), P_{BB}, and P_{BA} must

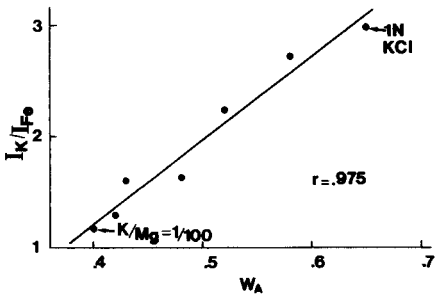


Figure 7. The I_K/I_{Fe} ratio determined by X-ray fluorescence for line intensities corresponding to K and Fe as a function of the amount of K layers (type A).

be known, but because these coefficients are not independent, it is sufficient to give definite values to two of them, for example, W_A and P_{AA}.

To determine these six coefficients, the distribution function of the interlayer distances (MacEwan *et al.*, 1961), must be calculated. The function W(R) is defined as the probability of finding another layer at a distance R (measured perpendicularly) from any given layer.

The functions W(R) and the W_A and P_{AA} parameters were determined by the INTER program (Vila and Ruiz-Amil, 1988), in which the effective structure factor F is defined as:

$$F^2 = W_A \cdot F_B^2 + W_B \cdot F_B^2,$$

where F_A and F_B are the structure of factors of the A and B layers.

Figure 6 shows the distribution function of the W(R) distances obtained from the experimental diagrams.

Table 3. Atomic parameters for 14.34- and 14.40-Å homogeneous vermiculite phases.[1]

Phases	14.34		14.40		B
	m	Z	m	Z	
Layer cations					
Mg	2.535	0.000	2.535	0.000	0.7
Fe^{3+}	0.415	0.000	0.415	0.000	0.7
Ti	0.055	0.000	0.055	0.000	0.7
OH	2.000	0.920	2.000	0.920	0.8
O1	4.000	1.140	4.000	1.140	0.8
Si	2.840	2.750	2.840	2.750	1.0
Al	1.040	2.750	1.040	2.750	1.0
Fe^{3+}	0.120	2.750	0.120	2.750	1.0
O2	2.000	3.220	2.000	3.220	1.0
O3	4.000	3.320	4.000	3.320	1.0
Interlayer material					
Mg	0.310	7.170	0.310	7.200	2.0
H_2O	0.200	5.150	0.400	5.150	3.5
H_2O	4.400	5.950	4.600	6.010	3.5
H_2O	0.500	7.170	1.200	7.170	3.5

[1] B = temperature factor, m = multiplicity, Z = z coordinates in Å.

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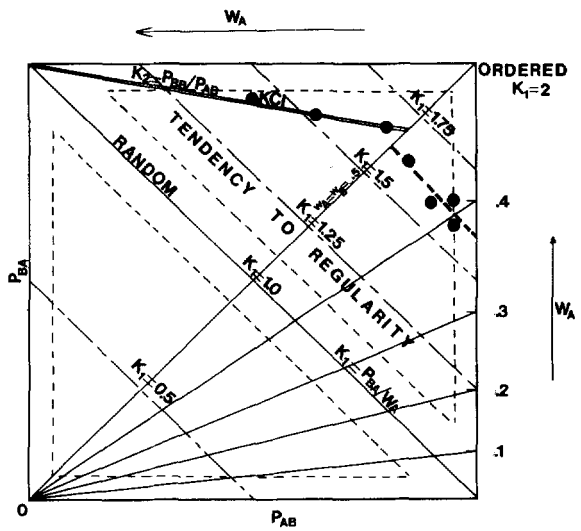


Figure 8. Evolution of interstratified structure of experimentally treated Mg-vermiculite. P_{AB} = probability that a A layer succeeds a B layer; W_A = proportion of A layer; P_{BA} and W_B are similarly defined. A = potassium phase; B = magnesium phase.

For each sample (Figures 6A–6E), two maxima of the function W(R) were obtained corresponding to the distances between layers of 10.1 Å (layer A) and of 14.4 Å (layer B). These distances are characteristic for the K-vermiculite and for the Mg-vermiculite observed before the transition, and were utilized to determine the effective structure factors for the A and B layers. To calculate the structure factors, the following assumptions were made: (1) For layer A, the K is situated in the middle of the interlamellar space and penetrates the ditrigonal cavities of the surface that to face each other. (2) For layer B, the interlamellar space is identical to that before the transition. The six coefficients W_A, P_{AA}, P_{AB}, P_{BB}, etc., which were determined from the INTER program (Vila and Ruiz-Amil, 1988), are listed in Table 1.

The I_K/I_{Fe} ratio determined by XRF as a function of the proportion W_A of layers type A are given in Figure 7. As can be seen, the correlation between the amount of K present in the sample and the proportion of layers type A is good (correlation coefficient = .975).

To follow the development of the interstratification, the P_{BA} probabilities are shown as a function of P_{AB} in Figure 8, which is analogous to that proposed by Sato (1965). The experimental points can be divided into two groups: (1) $W_A < .5$. In this group, the points lie on a straight line $P_{BA} = K_1 - P_{AB}$. This line corresponds to the relationship $P_{BA}/W_A = P_{AB}/W_B = K_1$, where K_1 is a constant. Thus, starting from the interstratified compound obtained at the transition and with the probability $P_{AB} = .95$, the probability of obtaining a pair BA by the creation of A-type layers can be obtained by reducing P_{AB}. This implies that the interstratification cannot develop towards one which is more regular than that obtaining at the beginning of the transition. The different tendencies towards interstratified structures are shown in Figure 8 as a function of the experimental value of the ratio K_1. The $K_1 = 1.75$ value obtained and the values of CVs (Table 1) show that the experimental points with $W_A < .5$ were in the region with interstratification tending towards regularity. (2) $W_A > .5$. In this group, the law of variation is different, and the points are aligned on a straight line defined by $P_{BA} = 1 - K_2 \cdot P_{AB}$. This straight line corresponds to the ratio $P_{BB}/P_{AB} = K_2$, where K_2 is a constant equal to 0.175. As the tendency is towards the creation of layers A, the formation of an A layer brings about a diminution of the probability of AB pairs and BB pairs in the sample. Thus, the exchange of Mg can occur equally well in a pair AB (thus creating an AA pair) as in a pair BB (thus creating a BA pair). If such a law were followed, it is theoretically possible to exchange all the potassium. In the present work, the reaction stopped for $W_A = .65$. Probably, exchange kinetics or the internal structure that characterizes the layers of this sample were involved.

DISCUSSION

Reorganization of natural vermiculite

The structure of the natural Malawi vermiculite changed to a more homogeneous state when it was treated at 160°C for 24 hr in a 1 N $MgCl_2$ solution or in a bi-ionic K/Mg solution having a molar fraction less than that of the discontinuity of adsorption of potassium. Taking its origin into account, the Malawi vermiculite must have been subjected to an intensive leaching (Morel, 1955). The Fe^{2+} present in the initial mica was oxidized to Fe^{3+}, and part of the Fe^{3+} may have moved into the interlamellar space to produce inhomogeneous, unorganized layers. The $MgCl_2$ treatment should have ordered the structure by homogenizing the cation content in the interlamellar space. The substitution of cations such as Fe^{3+}, Ca^{2+} and Al^{3+}, which were less easily hydrated than Mg^{2+}, should have led to an increased water content, explaining the larger quantity of interlayer water in treated vermiculite. To confirm this hypothesis the supernatant solution was analyzed by atomic absorption after the exchange. The absence of cations, such as Fe^{3+}, and Ca^{2+} in the solution negated this hypothesis, and the process probably consisted of a reorganization of the layers by adsorption of supplementary water molecules. To test this, the Malawi vermiculite was left in distilled water for 24 hr at 160°C. The XRD pattern of the product was identical with that of a sample treated by the $MgCl_2$ solution. The presence of more water compared with that present in the natural sample suggests a reorganization that was due simply to a larger number of hy-

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drogen bonds between the interlamellar space and the silicate layers.

Discontinuity of potassium adsorption

Interlamellar K adsorption by Mg-vermiculite took place if the molar fraction of K in the bi-ionic solution was equal to .0196 (K/Mg = 1/100). From this solution the sample was interstratified with a strong tendency towards regularity (WA = .4, P_{AB} = .95). Such regularity suggests that the exchange of K^+ for Mg^{2+} did not begin until sufficient K was present in the solution to displace an amount of Mg^{2+} corresponding to 40% of the exchange capacity. Thus, from this molar fraction and 0.5 N ionic strength, the sample changed from purely magnesian behavior to bi-ionic behavior, the structure corresponding to an interstratification that had a strong tendency towards regularity. Thus, the transformation of the homogeneous phase to the interstratified state can be defined as one of the first order. On the other hand, experiments with bi-ionic solutions of ionic strength equal to 0.75 and 1.0 N were made. The results showed that the exchange occurred similarly to the experiments in which the ionic strength was equal to 0.5 if the K added was equivalent, suggesting that the penetration of K in the interlayer space was a function of the activity of K ion in the bi-ionic solution.

Mechanism of formation of interstratified structures

Several hypotheses exist about the mechanisms of formation of regularity in mica-vermiculite layer sequences. The collapse of the alternate layers in the vermiculites by K requires that the collapse of one layer must affect the adjacent layer, thereby preventing replacement of the hydrated cation by K in this layer. To explain the formation of hydrobiotite, Basset (1959) suggested that if K in one layer of biotite is replaced by hydrated Ca or Mg, the bonding of that layer decreases, whereas the bonding in the adjacent layer increases. Therefore, the next layer of K ions to be replaced by the hydrated ions is not the adjacent layer, but the next layer beyond the adjacent layer. Basset did not, however, explain why K in the layer adjacent to that occupied by the hydrated ion is more strongly held than before. Sawhney (1967) postulated that for an interstratified Ca-K-vermiculite, the replacement of Ca and water by K in one layer reduces the effective negative charge on the adjacent layer. Consequently, the bonding energy between the K ion and the silicate layer of reduced charge must become smaller than the hydration energy of the Ca cation. Hence, the K cannot replace the Ca in this layer but in the next layer, forming an interstratified state.

To explain the interaction between adjacent interlayer regions, Norrish (1973) proposed the following mechanism. In the octahedral sheet, each metal ion is in contact with four oxygens and two hydroxyls. The OH groups face the "holes" in which interlayer K ions are located, and, according to Radoslovich (1963) and Giese (1971), the near proximity of the K alters the OH bond so that it makes a smaller angle with the layer plane. If this bond angle increases with the loss of interlayer K, a decrease in the angle of the OH bond of the other hydroxyl that is attached to the same octahedral cation probably exists, but it must face the adjacent interlayer region. The bonding of interlayer K is dependent on hydroxyl orientation; if the OH bond angle is reduced, the remaining K ions will be bound more strongly. The above mechanism results in interlayer regions in which K is held very strongly adjacent to interlayer regions in which K is replaced, i.e., the two regions alternate. This configuration can be found for dioctahedral and trioctahedral minerals, particularly as OH orientation is changed by the oxidation of iron. Farmer *et al.* (1971) and Weed and Leonard (1968) commented on the fact that high-iron micas tend to form regularly interstratified structures, if the iron is oxidized.

A study of other vermiculite samples is under way to determine why the exchange process begins in regions in which the K is in an environment that is favorable to the enclosure of the layer to a 10-Å space.

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