STACKING ORDER IN A K/Mg INTERSTRATIFIED VERMICULITE FROM MALAWI

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Abstract—The stacking order of a bi-ionic K/Mg vermiculite from Malawi (Nyasaland), has been determined from Weissenberg data. The sample corresponds to a K/Mg interstratified vermiculite containing 50% K layers ($d_K = 1.01$ nm) and 50% Mg layers with two layers of water ($d_{Mg} = 1.44$ nm). The observed intensities along (0, 0), (h, 0), (0, k) and (1, k) reciprocal rods were compared to the calculated intensities given by model defect structures. It was found that: 1) The (h, 0), (0, k) and (1, k) rods reveal the interstratification phenomenon which was previously observed on the (0, 0) rod; 2) The exchange of Mg by K does not occur randomly in a single interlayer, but occurs in interlayer domains sufficiently extensive to allow the reorganisation of the layer stacking and development of the ordered K-vermiculite structure from the semi-ordered structure characteristic of magnesium vermiculites; 3) For this sample, the interlayer water of the Mg phase occurs in two coexisting configurations; one configuration has water molecules forming octahedral coordination around the Mg^{2+}, the other has water which is not linked to the Mg^{2+} cation forming two planes.

Key Words—Crystal structure, Interstratification, Ion exchange, Ordering, Stacking, Vermiculite.

INTRODUCTION

For phyllosilicates, an interstratified state will generally be intermediate between two states, each of which is called "homogeneous." The term "homogeneous" refers to the periodicity in the direction perpendicular to the planes of the layers (defined here as Z). This periodicity is characterised by a unique translation from layer to layer along the Z direction.

By X-ray diffraction analysis along Z, Boettcher (1966), Rhoades and Coleman (1967), Sawhney and Reynolds (1985) and Martin de Vidales *et al.* (1990) showed that an intermediate interstratified state is involved during the transformation from Mg vermiculite to K vermiculite.

The structure of the homogeneous states of vermiculites has been studied by de la Calle *et al.* (1975a, 1975b, 1978, 1985, 1988) and de la Calle and Suquet (1988). With shifts along $\vec{a}$ and/or $\vec{b}$ (axis of the two dimensional unit-cell), vermiculites show different types of superposition of layers as a result of many factors including the type of interlayer cation and the relative humidity. These authors showed that there is a relationship between the stacking mode of different layers and the nature of the interlayer material. For example, Mg vermiculite shows a semi-ordered stacking mode of the layers and anhydrous K vermiculite shows an ordered stacking mode.

By X-ray diffraction analysis of the whole reciprocal space, the aim of this study is to determine the stacking

mode of a K/Mg interstratified vermiculite and the relationship between this stacking and the stacking modes of Mg and K vermiculite homogeneous states (e.g., to determine a structure which is a mixture of a semi-ordered and ordered structures). The X-ray diffraction analysis of Weissenberg data was done by an indirect approach which consisted of comparing the observed intensity with theoretical intensity calculated from structural models.

MATERIALS AND METHODS

Materials

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

$$(Si_{5.68}Al_{2.08}Fe_{0.24})(Mg_{5.07}Mn_{0.01}Fe_{0.83}Ti_{0.11})O_{20}(OH)_2$$
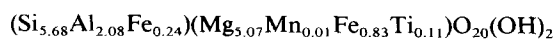
(Norrish, 1973). The chemical analysis was performed by Norrish on Ca-saturated samples to avoid ambiguity in assigning interlayer cations.

Cation-exchange treatments

Bi-ionic K/Mg vermiculite was obtained by treating cleaved sheets with mixed aqueous solutions of KCl and $MgCl_2$ with K/Mg equivalent ratio equal to 1/5. Experiments were made in a 20 ml teflon pressure vessel at 160°C to accelerate the transformation. The internal pressure was the water vapor pressure at the temperature of the experiment. One cleaved sheet of
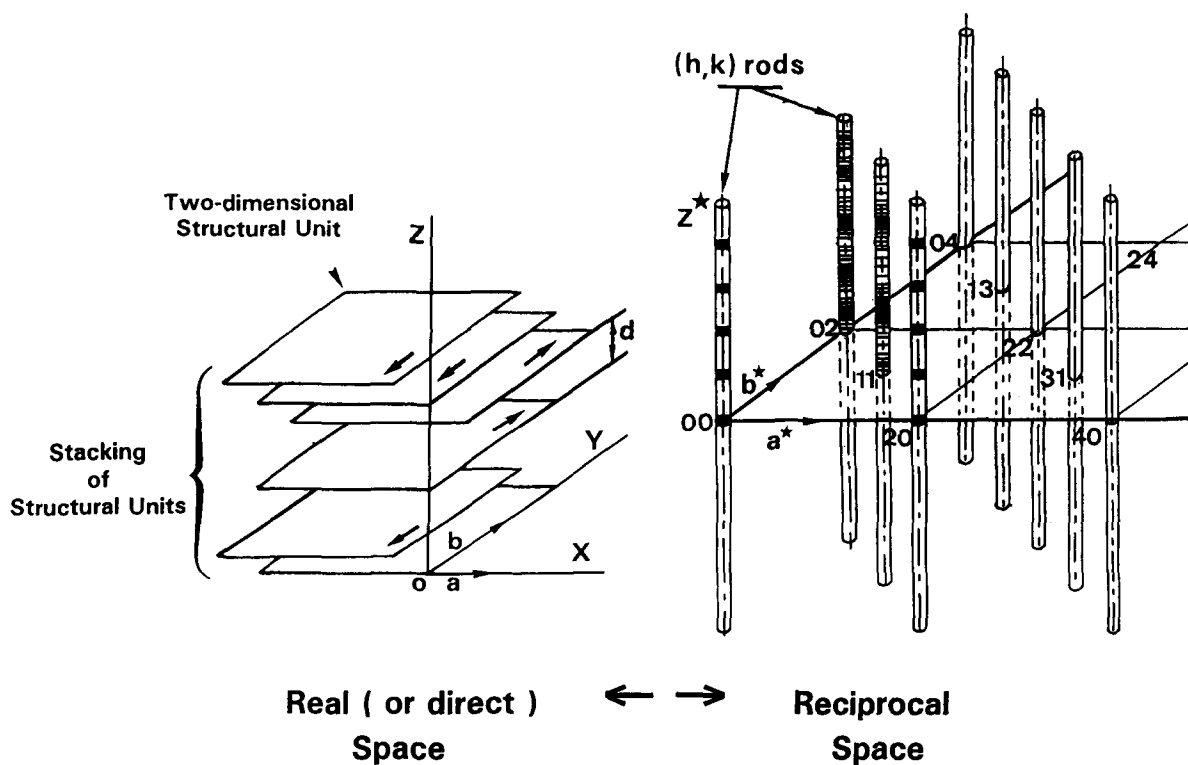
580

Figure 1. Schematic representation of the reciprocal space corresponding to a semi-ordered stacking mode with $\pm b/3$ translation faults along Y direction. Note the presence of modulated reciprocal rods (h, k) with k # 3n.

Mg vermiculite (1 mm, 5 mm, 0.1 mm) and 10 ml of K-Mg solution were placed in the teflon vessel, reacted for 24 h, and the sheet was washed with distilled water and dried at room temperature. The stability of the phase, in contact with air, was verified by X-ray diffraction (XRD) studies 90 days after the sample was treated.

Calculation of the diffracted intensity

General. For interstratified and semi-ordered structures, it is difficult to use the direct methods which involve a Fourier transform of the intensity (de la Calle *et al.*, 1988). The only possible method is to compare the observed intensity with the theoretical intensity calculated from a structural model.

The vermiculites are generally composed of macroscopic single crystal-like sheets similar in appearance to micas. Although it is not possible to consider vermiculites as single crystals, the structure of the reciprocal space is similar to the reciprocal space of a single crystal but with some intensity maxima that cannot be interpreted by the single crystal application of the Bragg's law.

In fact, for disordered layered structures, reciprocal space cannot be described by a set of hkl reciprocal spots (h, k, l integers) but by modulated reciprocal rods (h, k) with a continuous variation of the intensity along

the rods that depends on the nature of the two-dimensional structural units and the way they are stacked (Mering, 1949; Guinier, 1964). The rods are cylinders of infinite length and small basal area centered on the hk nodes of the reciprocal lattice of the two-dimensional structural units and perpendicular to the plane of this lattice (Figure 1).

Many authors (Hendricks and Teller, 1942; Méring, 1949; Kakinoki and Komura, 1952; Maire and Méring, 1970; Plançon, 1981; de la Calle *et al.*, 1985; de la Calle *et al.*, 1988) had calculated the diffuse intensity distribution due to stacking of M structural units by:

$$I_{hk} = \text{Spur} \left(\text{Re}([F_{hk}][W][[I] + 2\Sigma ((M - n)/M)[Q]^n)) \right)$$

where:

Re = real part of . . .
M = number of structural units by stacking
[Fhk] = matrix of structure factors
[I] = unit matrix
[W] = matrix that represents the proportion of the different translations between the structural units
[Q] = matrix that represents the interference phenomena between adjacent structural units that depend only on the relative positions of the structural units in the stacking.

This expression permits the treatment of all systems formed by irregular stacking.

Interlayer space in Mg and K vermiculites. For vermiculites, the structural units constituting any stacking arrangement are 2:1 silicate layers and interlayer molecules and cations. In this work, we define three structural units called "Mg(+)-layer," "Mg(−)-layer" and "K-layer," Mg(+), Mg(−) and K denote the different locations of cations and water molecules in relation to the silicate surface. Then, the *structural unit* consists of a silicate layer and the interlayer molecules and cations. The "Mg(+)-layer" and "Mg(−)-layer" define two translations,

$$\overrightarrow{T_{Mg+}} = -\overrightarrow{a}/3 + \overrightarrow{b}/3 + d_{Mg} \cdot \overrightarrow{k_z} \text{ and}$$

$$\overrightarrow{T_{Mg-}} = -\overrightarrow{a}/3 - \overrightarrow{b}/3 + d_{Mg} \cdot \overrightarrow{k_z}$$

($\overrightarrow{k_z}$: unit vector along the Z direction), between adjacent structural units to permit hydrogen bonds between the water-coordination polyhedron and surface oxygens. The "K layer" defines one translation $\overrightarrow{T_K} = -\overrightarrow{a}/3 + d_K \cdot \overrightarrow{k_z}$ between adjacent structural units (de la Calle and Suquet, 1988).

Form of the different matrices. For an interstratification with three layers, the matrices [Fhk], [W] and [Q] take the forms:

$$[Fhk] = \begin{vmatrix} F^*_{Mg+}F_{Mg+} & F^*_{Mg+}F_{Mg-} & F^*_{Mg+}F_K \\ F^*_{Mg-}F_{Mg+} & F^*_{Mg-}F_{Mg-} & F^*_{Mg-}F_K \\ F^*_K F_{Mg+} & F^*_K F_{Mg-} & F^*_K F_K \end{vmatrix}$$

where F_{Mg+}, F_{Mg-} and F_K are the structure factors of the "Mg(+)-layer", "Mg(−)-layer" and "K-layer" respectively.

$$[W] = \begin{vmatrix} W_{Mg+} & 0 & 0 \\ 0 & W_{Mg-} & 0 \\ 0 & 0 & W_K \end{vmatrix}$$

where W_{Mg+}, W_{Mg-} and W_K are respectively defined as the proportions of the $\overrightarrow{T_{Mg+}}$, $\overrightarrow{T_{Mg-}}$ and $\overrightarrow{T_K}$ translations.

$$[Q] = \begin{vmatrix} P_{Mg+/Mg+}\exp(iA) & P_{Mg+/Mg-}\exp(iA) & P_{Mg+/K}\exp(iA) \\ P_{Mg-/Mg+}\exp(iB) & P_{Mg-/Mg-}\exp(iB) & P_{Mg-/K}\exp(iB) \\ P_{K/Mg+}\exp(iC) & P_{K/Mg-}\exp(iC) & P_{K/K}\exp(iC) \end{vmatrix}$$

where:

1) A, B and C represent respectively the scalar products $2\pi\overrightarrow{T_{Mg+}} \cdot \overrightarrow{s}$, $2\pi\overrightarrow{T_{Mg-}} \cdot \overrightarrow{s}$ and $2\pi\overrightarrow{T_K} \cdot \overrightarrow{s}$ ($\overrightarrow{s}$ = diffraction vector defined by $|s| = 2 \sin(\Theta)/\lambda$; λ = wave length).

2) $P_{Mg+/Mg-}$, $P_{Mg-/Mg-}$, etc., are the probabilities of passing from one structural unit to its nearest neigh-

bour. For example, $P_{Mg+/Mg-}$ represents the probability that a +b/3 shift is followed by a −b/3 shift or, in other words, that the "Mg(+)-layer" is followed by a "Mg(−)-layer." These nine probabilities allow the statistical characterization of the stacking model. Let g be the number of types of layers and let the ith structural unit be (Mg(+), Mg(−) or K) and the jth first neighbour be (Mg(+), Mg(−) or K), thus;

$$\sum_{i=1}^{g} Wi = 1 \qquad \sum_{j=1}^{g} Pij = 1 \qquad Wi = \sum_{j=1}^{g} WjPij$$

Thus 12 parameters Wi and Pij are related by 2g relations (the relation $\Sigma Wi = 1$ is redundant with the last one) and the calculation requires g(g-1) parameters. For a structure with 3 structural units, the system has 6 independent parameters.

Determination of the parameters defining the interstratification for the particular case of Mg/K vermiculite. For Mg/K vermiculite, the Mg-vermiculite phase has the following characteristics:

1) The "Mg(+) and Mg(−)-layer" have the same thickness d_{Mg} and the same composition of the interlayer space (de la Calle and Suquet, 1988). Thus, the structure factors for the calculation of the intensity along the (0, 0) rod are identical for the "Mg(+)-layer" and the "Mg(−)-layer."

2) The *proportions* of the "Mg(+)-layer" and "Mg(−)-layer" are equal and the structural units are randomly shifted by ±b/3 along the Y direction (de la Calle et al., 1988).

As a result of these characteristics, the six coefficients may be determined in two stages using; 1) the intensity along the (0, 0) rod; and 2) the intensity along the (0, k), (1, k) and (h, 0) rods.

Analysis along the (0, 0) rod. The physical interpretation of the equality of the structure factors of the "Mg(+)-layer" and the "Mg(−)-layer" is that no distinction can be made between a "Mg(+)-layer" and a "Mg(−)-layer." The system is reduced to two translations d_{Mg} and d_K along Z which correspond to the "Mg-layer" and the "K-layer." If the origin of the translations is chosen at the level of the basal oxygens of the silicate layer, the matrices take the following forms:

$$[F_{oo}] = \begin{vmatrix} F^*_{Mg}F_{Mg} & F^*_{Mg}F_K \\ F^*_K F_{Mg} & F^*_K F_K \end{vmatrix} \quad [W] \begin{vmatrix} W_{Mg} & 0 \\ 0 & W_k \end{vmatrix}$$

$$[Q_{oo}] = \begin{vmatrix} P_{Mg/Mg}\exp(-2\pi i d_{Mg}.s) & P_{Mg/K}\exp(-2\pi i d_{Mg}.s) \\ P_{Mg/K}\exp(-2\pi i d_K.s) & P_{K/K}\exp(-2\pi i d_K.s) \end{vmatrix}$$

There are 6 parameters of which 2 are independent, for example W_{Mg} and $P_{Mg/K}$. Comparison between the experimental and the calculated patterns allows the determination of the two independent parameters and the deduction of the other four.

Analysis along the (1, k), (0, k) and (h, 0) rods. For these rods, there are three structure factors and the associated translations. The matrices have the general form cited above.

This system has six independent parameters. These parameters are determined from the proportion W_{Mg} and from the probability $P_{Mg/K}$ derived from the analysis of the (0, 0) rod. Assuming that the "Mg(+)-layer" and the "Mg(−)-layer" are randomly shifted by $\pm b/3$ along Y and that the proportions of the "Mg(+) and Mg(−)-layers" are identical, we write:

$$W_{Mg+} = W_{Mg-} = W_{Mg}/2$$
$$P_{Mg+/Mg+} = P_{Mg+/Mg-} = P_{Mg-/Mg+} = P_{Mg-/Mg-}.$$

From the (0, 0) rod analysis, we deduce:

$$W_K = 1 - W_{Mg}$$
$$P_{K/K} = 1 - P_{K/Mg}$$

and thus,

$$P_{Mg+/K} = P_{Mg-/K} = \frac{W_K \cdot P_{Mg/Mg}}{W_{Mg}}$$
$$P_{Mg+/Mg+} = P_{Mg+/Mg-} = P_{Mg-/Mg+}$$
$$= P_{Mg-/Mg-} = (P_{Mg/Mg})/2$$
$$P_{K/Mg+} = P_{K/Mg-} = (1 - P_{KK})/2.$$

For a K/Mg vermiculite interstratification, all the statistical parameters may be fully determined by analysis of the (0, 0) rod.

The comparison between the experimental intensity and the theoretical intensities for the (h, k) rods leads, however, to the following possibilities:

1) To verify *a posteriori*, the hypothesis of a Mg phase having two randomly distributed translations $\pm b/3$. This hypothesis may be confirmed when the number and the position of the maxima corresponding to the experimental intensity are identical to the number and the position of those corresponding to the calculated intensity.

2) To verify that the K phase of the interstratified compound corresponds to the ordered K phase which has only a single translation $\vec{T}_K = -\vec{a}/3 + d_K \cdot \vec{k}_z$ with the interlayer K cations placed in the site analogous to K in micas (e.g., in the ditrigonal cavities of the surface of adjacent silicate layers situated face-to-face with each other).

3) To determine the position of the molecules and the cations of the interlayer material relative to the Mg phase. To do this, the theoretical intensity is calculated using a first set of (x, y, z) coordinates for all atoms and molecules comprising the 2:1 silicate layer and its interlayer material using previously published work (de la Calle *et al.*, 1988). Intensity maxima are then compared for both position and intensity for the calculated and the experimental spectra. If important differences are obtained, the configuration of the interlayer ma-
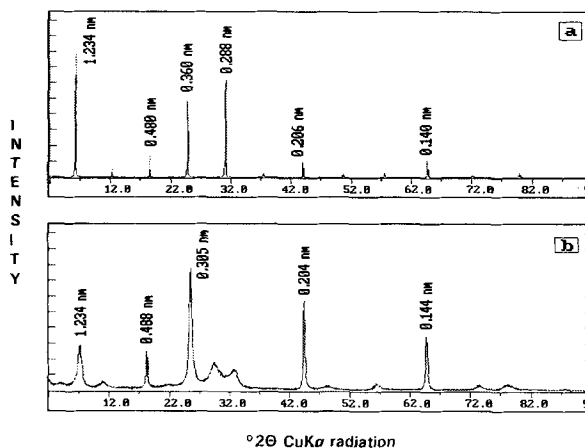

Figure 2. X-ray diffraction patterns along the (0,0) rod: a) Malawi vermiculite before treatment with the bi-ionic K/Mg solutions; b) Malawi vermiculite after treatment with the K/Mg solution = 1/5 at 160°C for 24 hr.

terial is varied by successive approximations to achieve the best agreement between experimental and theoretical diffraction spectra.

EXPERIMENTAL RESULTS AND DISCUSSION

Analysis of the (0, 0) rod

Qualitative analysis. Intensity data along the (0, 0) rod were recorded with a Siemens D-500 diffractometer with a Cu X-Ray tube (40 kV and 20 mA). The data were obtained between 2° and 100° 2θ. The divergent and receiving slits had respective openings of 1° and 150 μm. A graphite monochromator allowed CuKβ to be totally eliminated. The slit system was selected to ensure that the sample was completely within the X-ray beam at all angles of 2θ. Under these conditions, an angular geometric correction (Brindley and Gillery, 1956) was used. The experimental intensity was corrected for Lorentz, polarization, geometric and absorption factors (Martin de Vidales *et al.*, 1990).

Figure 2 shows the X-ray patterns corresponding to the Malawi vermiculite sample before and after treatment with the bi-ionic solution K/Mg = 1/5. Note the presence in Figure 2b of diffuse diffraction maxima in which the maxima are not at rational positions. This result indicates an interstratification of the "Mg-layer" (d_{Mg} = 1.44 nm) and the "K-layer" (d_K = 1.01 nm) (Martin de Vidales *et al.*, 1990).

Quantitative analysis. The "Mg-layer" and "K-layer" structure factors were calculated using the coordinates along the Z direction, the multiplicity, and the isotropic temperature factors of all cations and molecules given by Martin de Vidales *et al.* (1990) (Table 1).

Figure 3 shows the theoretical curves corresponding to a random interstratification (Figure 3a) and a regular interstratification (Figure 3c). Figure 3b shows the best agreement obtained between the experimental and the-

Table 1. Atomic parameters along the Z direction for Malawi vermiculite homogeneous states.

	Mg layer		K layer		
	m	z	m	z	B
Layer cations					
Mg	2.535	0.000			0.7
Fe3+	0.145	0.000			0.7
Ti	0.055	0.000			0.7
OH	2.000	0.920			0.8
O1	4.000	1.140	Idem		0.8
Si	2.840	2.750	Mg layer		1.0
Al	1.040	2.750			1.0
Fe3+	0.120	2.750			1.0
O2	2.000	3.220			1.0
O3	4.000	3.320			1.0
Interlayer material					
Cation	0.310	7.170	0.620	5.050	2.0
$(H_2O)_2$	4.600	6.010	—	—	3.5
$(H_2O)_1$	1.200	7.170	—	—	3.5
dool (Å)	14.41		10.10		

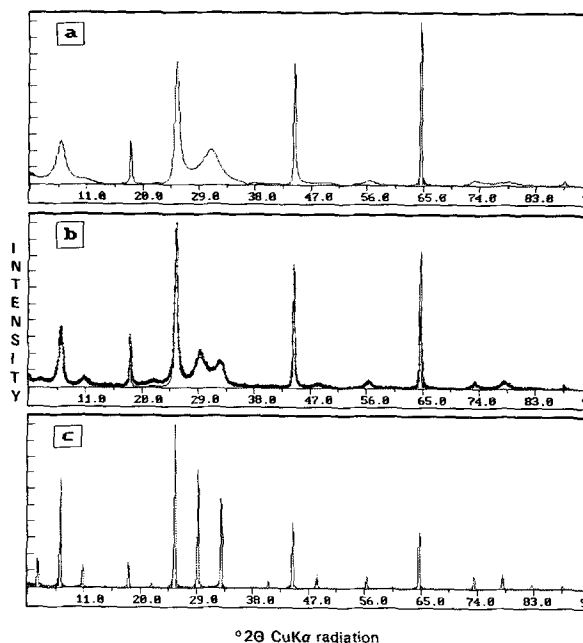m = multiplicity. B = Isotropic temperature factor.

°2θ CuKα radiation

Figure 3. Comparison between the experimental and calculated curves for the (0, 0) rod: a) random interstratification ($W_{Mg} = 0.5$; $P_{Mg/Mg} = 0.5$); b) the agreement obtained between the experimental and calculated patterns ($W_{Mg} = 0.5$; $P_{Mg/Mg} = 0.7$); c) regular interstratification ($W_{Mg} = 0.5$; $P_{Mg/Mg} = 1.0$).

oretical curves. The results indicate that the sample has equal numbers of "Mg-layers" and "K-layers" ($W_{Mg} = W_K = 0.5$) with a tendency to regular interstratification ($P_{Mg/K} = 0.7$).

Analysis of the (0, k), (1, k) and (h, 0) rods

Qualitative analysis. Intensity data were recorded with a Weissenberg goniometer using monochromatic CuKα radiation from a rotating anode (Rigaku P = 12 kW). To determine continuous variation of intensity along the rods, an integration method of recording could not be used. Intensities were estimated visually by comparison with a standard multiple scale and corrected for the Lorentz and polarization factors. The absorption corrections were neglected (de la Calle *et al.*, 1988) because the interest here was to determine the nature of the stacking mode and not to refine the structure. Shirozu and Bailey (1966) noted also that absorption effects are not very important in comparison with other effects in disordered structures.

Weissenberg patterns (Figure 4) show that, before treatment (Figure 4a) with the bi-ionic solution K/Mg = 1/5 (Mg vermiculite), the (h, 0), (0, k) and (1, k) reciprocal rods may be divided into two groups; the group of (h, 0), (0, 6), (1, 3) and (1, 9) rods with sharp diffraction spots and the group of (0, 2), (1, 1), (1, 5) and (1, 7) rods where the intensities are diffuse. Thus, the Mg vermiculite has an ordered structure in the (aOz) projection and a disordered structure in the (bOz) projection similar to other Mg vermiculites (de la Calle and Suquet, 1988; de la Calle *et al.*, 1988). The layer stacking is characterised by translation faults ±b/3 which are random by shifts along the Y direction (Méring, 1949; Brindley and Robinson, 1946, 1947; de la Calle *et al.*, 1975a, 1975b, 1988).

After treatment by the bi-ionic solution K/Mg = 1/5 (Figure 4b) Weissenberg patterns show that the intensities along all the reciprocal rods are diffuse with maxima and that the number of maxima is greater than for the original sample. These patterns show the effect of interstratification between "Mg-layers" and "K-layers." In this case, the two (aOz) and (bOz) projections are characteristic of a disordered stacking.

Quantitative analysis. We have assumed that the "Mg(+)-layer" and the "Mg(−)-layer" structural units occur with the same frequency and with a random distribution of the translations between structural units. Consequently, the stacking mode relative to the "Mg(+) and Mg(−)-layers" is conserved in the interstratified sample produced by exchange of Mg by K.

Most parameters of the [W] and [Q] matrix were determined from the values of the proportions W_{Mg} and $W_{Mg/K}$ which were obtained by quantitative analysis of the (0, 0) rod. The values obtained were:

$$W_{Mg+} = W_{Mg-} = 0.25; \quad W_K = 0.5; \quad P_{KK} = 0.3$$
$$P_{Mg+/Mg+} = P_{Mg+/Mg-} = P_{Mg-/Mg+} = P_{Mg-/Mg-} = 0.15$$
$$P_{Mg+/K} = P_{Mg-/K} = 0.7$$
$$P_{K/Mg+} = P_{K/Mg-} = 0.35$$

To calculate theoretical intensities, it is essential to identify and locate the molecules and cations in the "Mg-layer's interlayer space." The chemical constituents and the z coordinates are given by a one dimen-
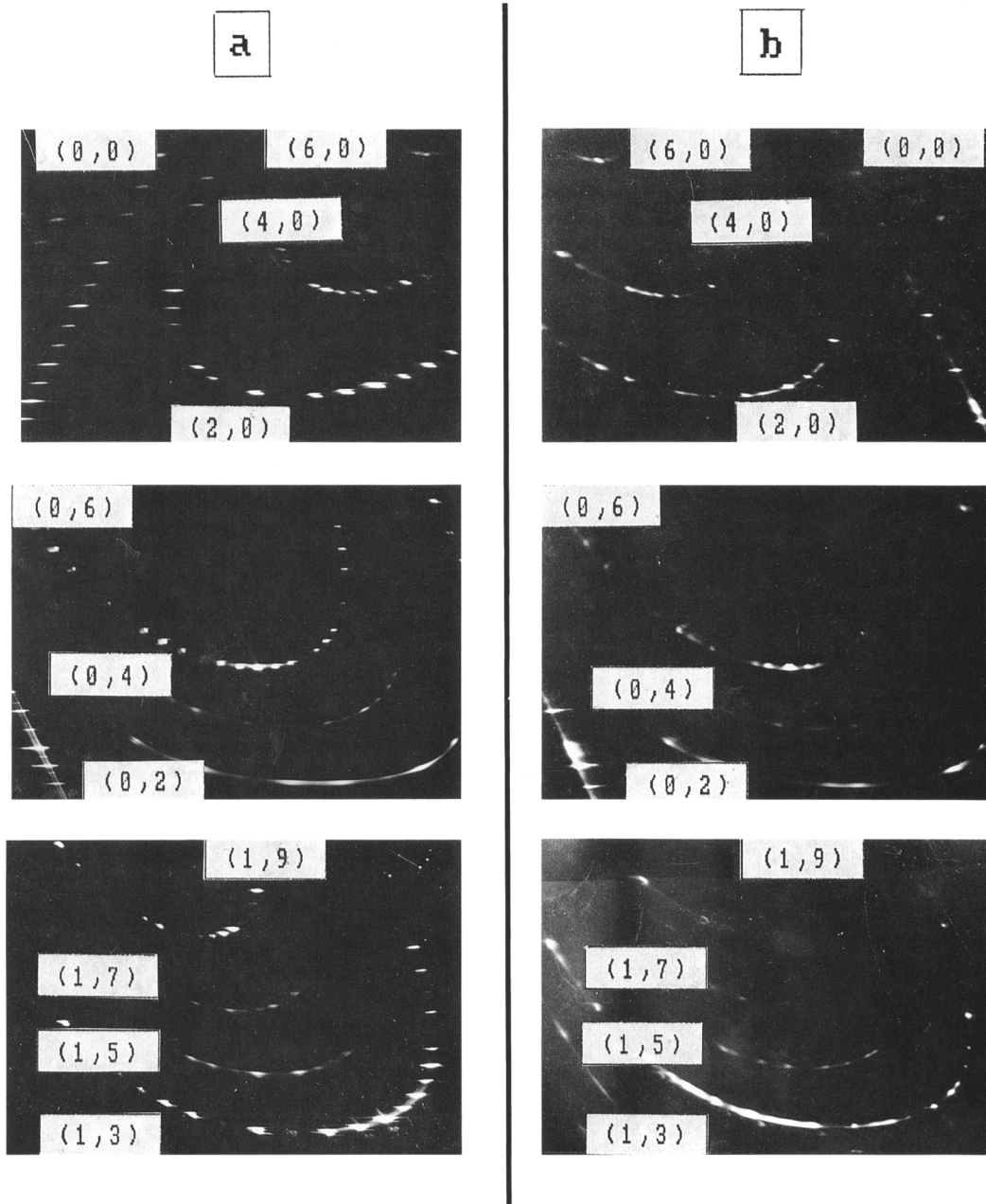
Figure 4. Weissenberg photographs corresponding to the (h, 0) (upper), (0, k) (middle) and (1, k) (lower) rods: a) Mg vermiculite sample before exchange; b) the same sample after treatment with the bi-ionic K/Mg solution = 1/5 at 160°C for 24 hr.

sional Fourier projection of the structure of the pure Mg phase along the Z direction (Martin de Vidales *et al.*, 1990). The results given in Table 1 show two types of interlayer water:

1. Water of type $(H_2O)_1$ (1.2 molecules per half unit cell) situated in the middle of the interlayer space and having the same Z coordinate as the Mg cation.

2. Water of type $(H_2O)_2$ (4.6 molecules per half unit

cell) situated in two planes on either side of the center of the interlayer space.

In Mg vermiculites with a high charge and with two layers of water (e.g., Llano and Santa Olalla), the structure of the interlayer space has been studied by Mathieson and Walker (1954), Mathieson (1958), Bradley and Serratosa (1960) and de la Calle *et al.* (1988). For vermiculite from Santa Olalla with a charge of 0.82

Table 2. Atomic parameters for "Mg(+) and Mg(−) layers."

a.) Te-Oc-Te silicate layer

	x/a	y/b	z (Å)	m[1]	B[2]
O1	−0.062	0.269	0.000	1.000	1.0
O2	−0.062	−0.269	0.000	1.000	1.0
O3	−0.370	0.500	0.100	1.000	1.0
Si	−0.331	0.333	0.580	0.710	1.0
Si	−0.331	−0.333	0.580	0.710	1.0
Al(T)	−0.331	0.333	0.580	0.260	1.0
Al(T)	−0.331	−0.333	0.580	0.260	1.0
Fe3+(T)	−0.331	0.333	0.580	0.030	1.0
Fe3+(T)	−0.331	−0.333	0.580	0.030	1.0
O4	−0.326	0.333	2.160	1.000	1.0
O5	−0.326	−0.333	2.160	1.000	1.0
OH	−0.333	0.000	2.360	1.000	1.0
Mg	0.000	0.000	3.300	0.845	1.0
Mg	0.000	0.333	3.300	0.845	1.0
Mg	0.000	−0.333	3.300	0.845	1.0
Fe3+(O)	0.000	0.000	3.300	0.138	1.0
Fe3+(O)	0.000	0.333	3.300	0.138	1.0
Fe3+(O)	0.000	−0.333	3.300	0.138	1.0
Ti	0.000	0.000	3.300	0.018	1.0
Ti	0.000	0.333	3.300	0.018	1.0
Ti	0.000	−0.333	3.300	0.018	1.0
OH	0.333	0.000	4.240	1.000	1.0
O6	0.326	0.333	4.440	1.000	1.0
O7	0.326	−0.333	4.440	1.000	1.0
Fe3+(T)	0.331	0.333	6.020	0.030	1.0
Fe3+(T)	0.331	−0.333	6.020	0.030	1.0
Al(T)	0.331	0.333	6.020	0.260	1.0
Al(T)	0.331	−0.333	6.020	0.260	1.0
Si	0.331	0.333	6.020	0.710	1.0
Si	0.331	−0.333	6.020	0.710	1.0
O8	0.370	0.500	6.500	1.000	1.0
O9	0.062	0.269	6.600	1.000	1.0
O10	0.062	−0.269	6.600	1.000	1.0

b.) Interlayer material for "Mg(+)-layer."

Nature	x/a	y/b	z (Å)	m[1,3]
Interlayer water				
H_2O	0.0040	0.0000	9.270	0.57
H_2O	0.0040	0.3333	9.270	0.57
H_2O	0.0040	0.6667	9.270	0.57
H_2O	0.5000	0.5000	10.400	0.60
H_2O	0.0000	0.3333	10.400	0.60
H_2O	−0.0040	0.0000	11.540	0.77
H_2O	−0.0040	0.3333	11.540	0.77
H_2O	−0.0040	0.6666	11.540	0.77
H_2O	0.1680	0.1667	9.270	0.20
H_2O	0.1680	0.5000	9.270	0.20
H_2O	0.1680	0.8333	9.270	0.20
Interlayer cation				
Mg	0.3333	0.6667	10.400	0.31

Table 2. Continued

c.) Interlayer material for "Mg(−)-layer."

Nature	x/a	y/b	z (Å)	m[1,3]
Interlayer water				
H_2O	0.0040	0.0000	9.270	0.77
H_2O	0.0040	0.3333	9.270	0.77
H_2O	0.0040	0.6667	9.270	0.77
H_2O	0.5000	0.5000	10.400	0.60
H_2O	0.0000	0.6667	10.400	0.60
H_2O	−0.0040	0.0000	11.540	0.57
H_2O	−0.0040	−0.3333	11.540	0.57
H_2O	−0.0040	−0.6667	11.540	0.57
H_2O	0.5040	0.1667	11.540	0.20
H_2O	0.5040	0.5000	11.540	0.20
H_2O	0.5040	0.8333	11.540	0.20
Interlayer cation				
Mg	0.3333	0.3333	10.400	0.31

[1] m = multiplicity.
[2] B = Isotropic temperature factor.
[3] Isotropic temperature factor B = 3 for Mg and H_2O.

cell, indicates that there is little water which is not directly linked to a compensating Mg cation.

For this sample from Malawi with a charge of 0.62 per half unit cell, it is noted that the quantity of interlayer water is larger than that found in other vermiculites. Of the 4.6 $(H_2O)_2$ molecules, 2.8 molecules ("excess" water) are not directly linked to the Mg cation.

To establish the likely location of the "excess" water, two models were considered. The first model assumes that the "excess" water would have the same structure as the $(H_2O)_2$ water directly linked to Mg cations. Calculated intensities show important differences for the (1, 3) and the (2, 0) rods for this model. In addition, an unlikely symmetry around the $(H_2O)_1$ water occurs with six oxygens on one side and three on the other. This arrangement produces short $(H_2O)_2$ and $(H_2O)_1$ distances. Thus, this model may be rejected.

The second model supposes that the $(H_2O)_2$ water molecules have two types of positions, with 1.8 water

per half unit cell, de la Calle *et al.* (1988) showed that the Mg cations and the interlayer water molecules form $Mg(H_2O)_6^{2+}$ polyhedra occupying the m_1 sites, based on the nomenclature of Mathieson and Walker (1954). This site is between the two (SiO_4) tetrahedra of the adjacent silicate layers (Figure 5). The water molecules of this polyhedron are located in two planes on either side of the center of the interlayer space. The total content of interlayer water, 2.46 molecules per half unit
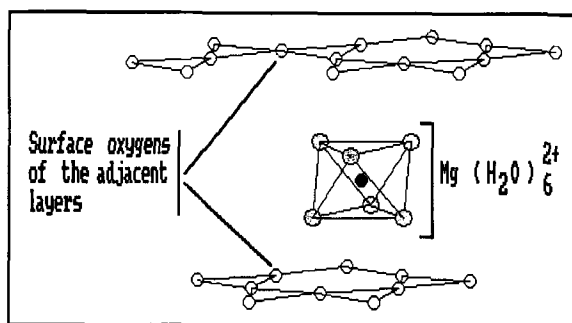

Figure 5. Schematic representation of the interlayer space in a Santa Olalla vermiculite (charge = 0.82, de la Calle *et al.*, 1988) with a low interlayer water content.
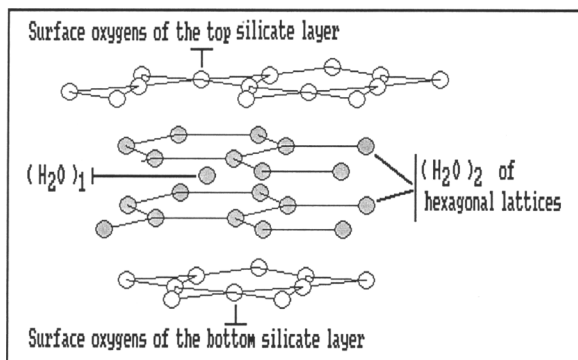
Figure 6. Schematic representation of the configuration of the interlayer "excess" water that is not linked to the Mg cation.

molecules linked to the Mg cation and forming an $Mg(H_2O)_6^{2+}$ polyhedron and with 2.8 molecules forming a structure in two hexagonal lattices situated above and below the center of the interlayer space (Figure 6). This structure type corresponds to that proposed by Barshad (1949), Mamy (1968), de la Calle (1977) and Pons et al., (1980). The $(H_2O)_1$ water molecules are positioned in the projection along Z at the center of the hexagons formed by the $(H_2O)_2$ water molecules (Table 2b and 2c). In this configuration, the distances $(H_2O)_2$-$(H_2O)_1$, are acceptable. The $(H_2O)_2$ molecules

not linked to Mg are bounded by interactions with the surface oxygens of adjacent silicates layers.

Figure 7 presents the theoretical curves for the rods studied based on this model, as well as the experimental intensities. The agreement is satisfactory for all the data.

DISCUSSION

Characterization of the stacking mode

The indirect method has allowed characterization of the interstratified structure in the direction perpendicular to the ab plane and in this plane. The analysis of the data shows a correlation between the nature of the interlayer material and the stacking mode of the Mg and K layers. The stacking mode of the intermediate state has the characteristics both of the homogeneous state before Mg cation is exchanged by K cation and the homogeneous state after exchange of all of the Mg cation by K cation (Figure 8).

Thus, the exchange of Mg by K does not occur in a random manner in a given interlayer space. The exchange involves the removal of all water in the interlayer and occurs in domains which are sufficiently extended laterally to permit the reorganization of the layers in this plane and the transition from the semi-ordered structure of Mg vermiculites to ordered K vermiculites.

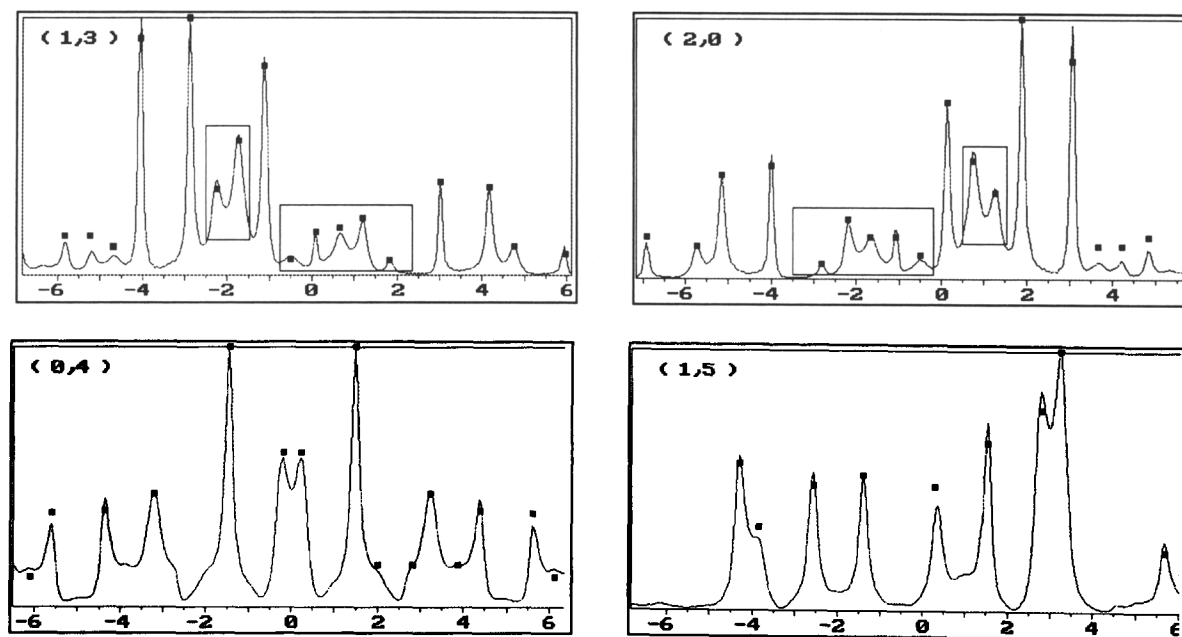In addition, the agreement obtained between exper-

Figure 7. Comparison between experimental and theoretical intensities for the (1, 3), (2, 0), (0, 4) and (1, 5) rods corresponding to the model in which the water is structured in two configurations according to whether it is linked or not to the Mg cation (dots = experimental data).
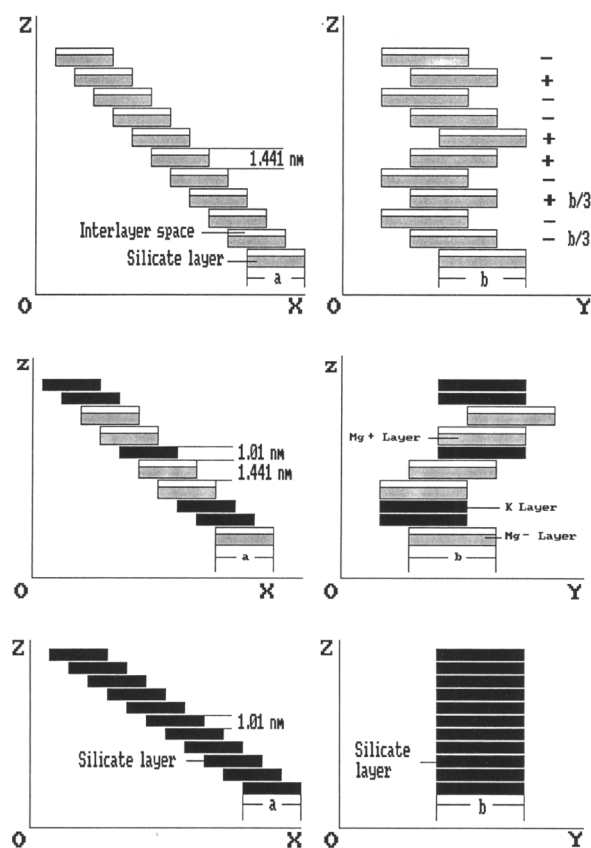
Figure 8. Schematic representation of the stacking modes: Semi-ordered stacking (upper) = two layers of water Mg vermiculites; intermediate stacking (middle) = mixture of semi-ordered and ordered stacking modes; ordered stacking (lower) = anhydrous K vermiculites.

imental and calculated diffraction data shows that the interactions are nearest neighbour interactions and that the stacking mode of a silicate layer with respect to the adjacent silicate layer is related to the nature of the interlayer material.

Structure of the interlayer material

The interlayer material corresponding to the "K-layer" after exchange of the Mg is identical to that observed in micas. For the "Mg(+) or Mg(−)-layer" the data show that, for this sample, the interlayer water has a very characteristic structure. It is structured differently according to whether or not it is linked to the Mg cation.

The $Mg(H_2O)_6^{2+}$ polyhedra are located between two tetrahedra of adjacent silicate layers (m_1 sites). This position permits the local charge balance between the Mg^{2+} cations and the tetrahedral charges. With such configuration, the surface area covered per polyhedron amounts to 25 Å. For three unit cells, Malawi vermiculite converts to one unit cell without a $Mg(H_2O)_6^{2+}$ polyhedron, thus, we have about 100 Å available sur-

face. Statistically, this available surface can be occupied by the "excess water" located above the surface oxygens of the silicate layers.

Although the quantity of "excess" water may be greater than the quantity associated with Mg, it is the $Mg(H_2O)_6^{2+}$ polyhedra which impose a stacking mode similar to Mg-vermiculites having a low content of interlayer water (de la Calle *et al.*, (1988).

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