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STACKING ORDER IN A 14.30-Å Mg-VERMICULITE

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Abstract—The stacking order of a 14.30-Å Mg-vermiculite from Santa-Olalla, Spain, has been determined from Weissenberg photographs. The results prove that the Mg-vermiculite structure is not a 2-layer polytype structure, but a semi-ordered one. Because the structure is semi-ordered, its resolution needed a dual approach: (1) a direct approach using an electron density projection along the y axis in conjunction with a one-dimensional electron-density projection onto the z axis; and (2) an indirect approach in which the observed intensities along the (0,*k*) and (1,*k*) reciprocal rods were compared to the calculated intensities given by model defect structures. The semi-ordered structure of the Mg-vermiculite results from $\pm b/3$ shifts in the stacking of the silicate layers. The shifts are randomly either along $+b$ or $-b$.

Key Words—Crystal structure, Ordering, Polytype, Stacking, Vermiculite.

INTRODUCTION

It is well known that vermiculites may have various layer stacking sequences depending on the nature of the interlayer cation and the relative humidity (RH). The several different layer stacking types were studied by de la Calle (1977), de la Calle *et al.* (1975a, 1975b, 1978a, 1978b, 1985), and Suquet and Pézerat (1987). A close relationship between the order in the layer stacking and the configuration of the interlayer space clearly exists. The layer stacking sequences which induce 3-dimensionally ordered structures exist only if the configuration of the interlayer space is such that the ditrigonal cavities of the adjacent layers face one another (de la Calle *et al.*, 1977, 1978b; Slade *et al.*, 1985). On the other hand, semi-ordered structures exist if adjacent layers shift such that ditrigonal cavities no longer face each other (de la Calle *et al.*, 1980).

Structural studies of vermiculites and the determination of factors that influence the layer stacking sequences have been investigated to understand the effects caused by water and various organic materials (de la Calle, 1977; de la Calle *et al.*, 1980; Slade and Stone, 1984). The behavior of soil materials has also been simulated in the laboratories in order to determine the mechanisms involved in these transformations. The behavior of soil vermiculites of different geographic origin can be compared if a reference state is defined (Ben Rhaïem *et al.*, 1986). This reference state corresponds to the condition in which the sample occurs in the soil, i.e., with Mg as the interlayer cation and hydrated with two-water layers (d(001) = 14.3 Å).

The aim of the present investigation was to determine the structure of this reference state for vermiculites by means of X-ray diffraction techniques. The study has confirmed the viability of the methods previously used by de la Calle *et al.* (1984) to examine the one-layer Na-vermiculite structure. These methods relied upon the classical techniques of Fourier projections and also a method in which the observed intensities along each (0,*k*) and (1,*k*) reciprocal space rods were compared to the values of calculated intensities given by model defect structure (Plançon, 1981; de la Calle *et al.*, 1984).[4]

MATERIALS AND METHODS

Materials

The vermiculite used in this study came from Santa Olalla, Spain. The geology of the Santa Olalla region was studied by González García and García Ramos (1960), Velasco (1977), Casquet and Velasco (1978), Puga and Fontbote (1979), and Velasco *et al.* (1981). These authors reported that the vermiculite was formed by the weathering of phlogopite. The phlogopite crystals range from a few millimeters across to plates 30 cm in size; their edges are always transformed to vermiculite.

The structural formula of the vermiculite is:

[4] For semi-ordered stacks, the reciprocal space cannot be described by a set of *hkl* reciprocal spots (*h, k, l* integers), but by reciprocal rods (*h,k*) with a continuous variation of the intensity along the rod depending on the nature of the layers and the way they are stacked (Méring, 1949; Plançon, 1981).

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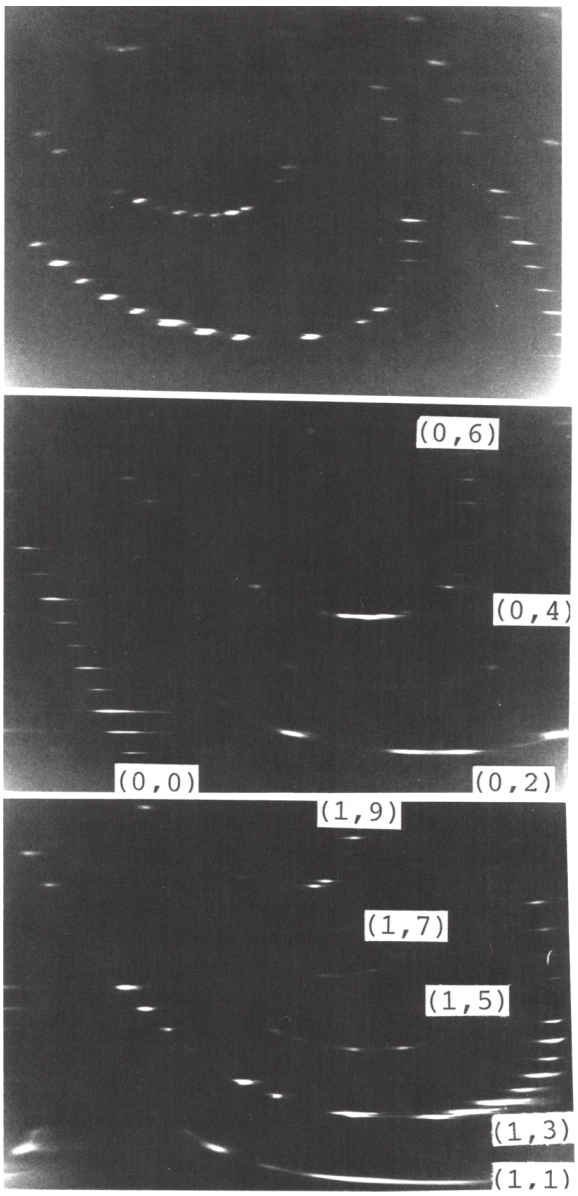


Figure 1. Weissenberg photographs of Santa Olalla Mg-vermiculite. (upper) *h0l* diffraction spots, (middle) (0,*k*) rods, (lower) (1,*k*) rods (CuKα radiation).

$(Si_{2.718}Al_{1.282})(Mg_{2.593}Al_{0.059}Fe^{3+}{}_{0.236}Fe^{2+}{}_{0.029}Ti_{0.083})O_{10}(OH)_2(Mg_{0.388}Ca_{0.024})$ for a half layer (de la Calle, 1977).

X-ray diffraction data were obtained on a section, 1 × 2 × 0.1 mm in size, cut from a larger cleavage flake and carefully pressed flat to minimize distortion arising from the cutting operation. All data refer to the flake in its natural state without further hydration or cation exchange. Unit-cell parameters a = 5.346 ± 0.002 Å, b = 0.259 ± 0.002 Å, c = 14.42 ± 0.01 Å and β = 96°57′ ± 2′ (least-squares refinement from 15 data) were determined by X-ray powder diffraction techniques (Guinier de Wolff camera, and monochromatized CoKα radiation; Si as standard).

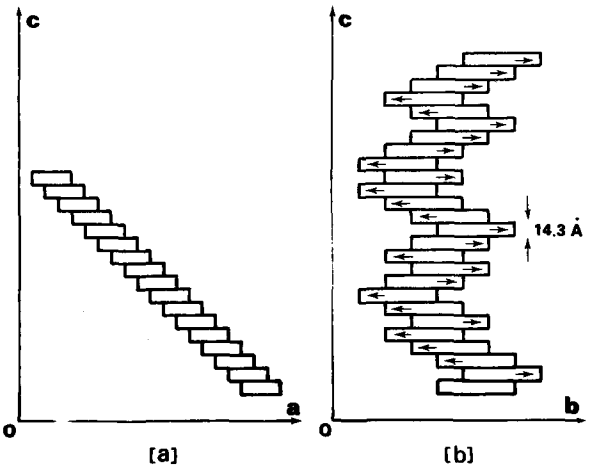


Figure 2. Scheme of a semi-ordered stacking. (a) [010] view, (b) [100] view.

X-ray diffraction

Intensity data were recorded on the Weissenberg goniometer using monochromatic CuKα radiation. For each set of two film packs, exposures of 15 to 100 hr were made. Integration was not used during intensity recording, because the continuous variation of the intensity along some rods did not allow it. The intensities were estimated visually by comparison with a standard multiple scale and corrected for the Lorentz and polarization factors. Because the aim of the present work was to determine the stacking faults in a Mg-vermiculite and not to refine the structure, the absorption corrections were neglected. In fact, absorption effects are not very important (Shirozu and Bailey, 1966) compared with other effects in disordered structures.

STRUCTURAL DETERMINATION

Qualitative analysis of experimental patterns

An examination of Weissenberg films (Figure 1) containing the intensity distribution along the (*h*,0), (0,*k*), and (1,*k*) reciprocal rods shows that they fall into two groups: (1) those (*h*,0), (0,6), (1,3) and (1,9) rods containing sharp (*h*0*l*, 06*l*, 13*l*, 19*l*) diffraction spots; and (2) those (0,2), (1,1), (1,5) and (1,7) rods containing more or less diffuse bands. From these results, the x0z projection appears to be ordered but layers are displaced by *b*/3 parallel to the y axis (Méring, 1949; Brindley and Robinson, 1946, 1947; de la Calle *et al.*, 1984) (Figure 2).

Layer stacking sequence deduced from the h0l *diffraction spots*

*Electron-density distribution normal to (00*l*).* The one-dimensional Fourier projection of the structure of the

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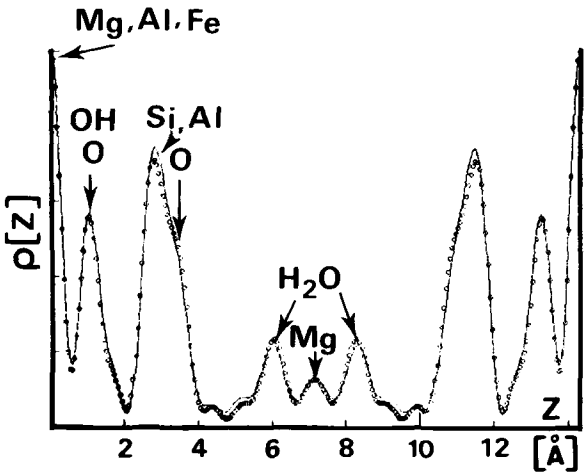


Figure 3. One-dimensional Fourier synthesis from 001 diffraction intensities of the Mg-vermiculite. —— theoretical and -o-o-o-o- experimental values.

Santa Olalla vermiculite onto 00*l* was carried out using the first 17 00*l* reflections (Figure 3). The basal spacing of the sample was taken as 14.30 Å. Phases for the 00*l* sharp diffraction spots were computed from the known configuration of the silicate part of the structure and assigned to the structure amplitudes. This approach assumed that the contribution to the total scattering from the interlayer material was comparatively small. The positional parameters for the atoms of the silicate structure were taken from the study of the two-water layer Ca-vermiculite (de la Calle *et al.*, 1977) and modified for the unit cell of the present material. The experimental and the final theoretical one-dimensional projections (R = 5%) are also compared in Figure 3.

Table 1. Atomic parameters for Mg-vermiculite.

Atom	x/a	z/c	B (Å²)	m
Octahedral cations				
1	0.0	0.0	1	2.96
Tetrahedral cations				
1	0.394	0.190	1.5	4
Hydroxyl group				
1	0.355	0.066	1	2
Oxygen				
O1	0.353	0.080	1	4
O2	0.138	0.231	2	4
O3	0.444	0.224	2	2
Interlayer cations				
Mg	0.500	0.500	2.5	0.39
Ca	0.500	0.500	2.5	0.02
Water				
H_2O	0.142	0.42	3	2.46

B = temperature factor; m = multiplicity.

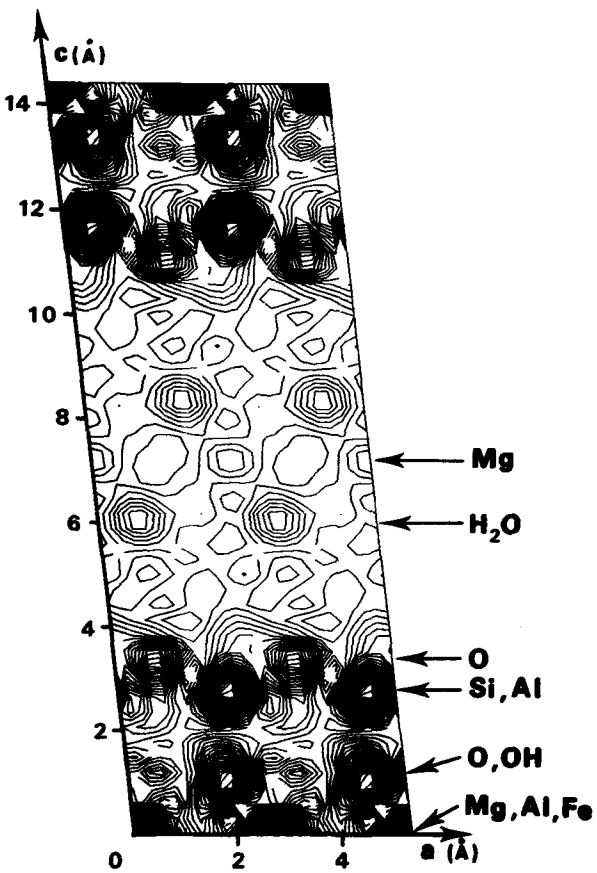


Figure 4. Electron density distribution on (010) for Mg-vermiculite.

Table 1 lists the final atomic parameters. The electron-density curve shows that: (1) Mg^{2+} is located midway between the silicate layers; (2) water molecules (6–7 H_2O/Mg^{2+}) are arranged on either side of the central cations in sheets 2.71 Å from the sheets of surface oxygens in the adjacent silicate layers. The RH range in which the 14.30-Å phase exists is so large (between 5 and 100% RH) that the amount of water found (at ~40% RH) cannot easily be compared with the values previously reported in the literature. A one-dimensional synthesis obtained by neutron diffraction on the Santa Olallo Co-vermiculite (Adams and Riekel, 1980) indicates that the *z* values for the protons are in agreement with those of the present X-ray diffraction study.

Projection along the b-*axis.* The electron-density distribution on the x0z plane was calculated from 66 *h*0*l* sharp diffraction spots (Figure 4). The phases for the *h*0*l* spots were determined in the same way as for the one-dimensional projection. Space group *P*2 was used for the calculation of structure factors. The structure factors $F_{calc}(h0l)$ were calculated from the atomic coordinates listed in Table 1. The analysis of this projection allowed the z-coordinates to be refined and the

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Table 2. Comparison of observed and calculated structure factors for Mg-vermiculite.[1]

hkl	F_c	F_{obs}
001	157.8	157.8
002	8.2	7.9
003	−33.8	−38.9
004	101.5	107.0
005	138.0	140.8
006	−23.1	−26.5
007	−66.9	−58.8
008	−32.2	−31.5
009	49.0	44.6
0010	80.6	71.1
0011	54.4	58.2
0012	56.4	65.6
0013	22.9	24.4
0014	27.7	38.2
0015	37.7	36.7
0016	45.6	56.2
0017	29.5	32.5
200	69.3	82.9
201	98.1	115.7
202	135.9	120.8
203	65.7	78.8
204	86.0	99.4
205	53.5	56.7
206	122.6	115.2
207	90.2	91.7
208	15.8	21.7
209	−28.8	−36.2
2010	−23.3	−29.3
2011	41.6	48.8
2012	51.2	54.1
$20\bar{1}$	−7.3	−3.9
$20\bar{2}$	−90.0	−95.3
$20\bar{3}$	−8.5	−14.4
$20\bar{4}$	46.5	69.4
$20\bar{5}$	92.9	78.2
$20\bar{6}$	29.8	30.4
$20\bar{7}$	−29.6	−29.6
$20\bar{8}$	76.7	71.0
$20\bar{9}$	120.1	107.2
$20\bar{1}\bar{0}$	126.7	129.4
$20\bar{1}\bar{1}$	25.1	37.5
$20\bar{1}\bar{2}$	−11.5	−14.5
$20\bar{1}\bar{3}$	15.2	24.4
$20\bar{1}\bar{4}$	47.7	83.9
$20\bar{1}\bar{5}$	39.0	79.5
$20\bar{1}\bar{6}$	−35.6	−20.0
400	−55.3	−55.6
401	30.6	39.6
402	63.8	69.3
403	38.5	40.7
404	−11.2	−11.9
405	−6.6	0
406	64.8	66.9
407	74.3	66.9
408	66.8	53.9
$40\bar{1}$	−33.7	−42.1
$40\bar{2}$	67.2	55.1
$40\bar{3}$	109.6	134.2
$40\bar{4}$	82.9	81.6
$40\bar{5}$	3.7	0
$40\bar{6}$	32.8	29.1
$40\bar{7}$	61.9	50.8
$40\bar{8}$	86.5	77.3
$40\bar{9}$	39.5	38.6
$40\bar{1}\bar{0}$	−6.8	−17.1
$40\bar{1}\bar{1}$	−9.9	−16.7

[1] Projection along *b*-axis.

x-coordinates to be determined for the components of the interlayer space. The contoured electron density map located the water molecules at x = 0.142, z = 0.42 and the interlayer cations at x = 0.5, z = 0.5. Table 2 compares observed and calculated structure factors. The final reliability factor was R = 14%.

Layer stacking structure deduced from the intensity distribution of the (0,k) and (1,k) reciprocal rods

As noted above, the Weissenberg films showed that the intensity distribution along the (0,*k*) and (1,*k*) reciprocal rods for which $k \neq 3n$ were more or less diffuse. Therefore, a direct image of the structure could not be obtained from the intensity distribution of the (0,*k*) and (1,*k*) reciprocal rods. A quantitative description however was obtained by comparing the experimental intensity distribution with a theoretical intensity distribution calculated from an average model of the layer stacking (de la Calle *et al.*, 1984).

Previous workers (Hendricks and Teller, 1942; Méring, 1949; Kakinoki and Komura, 1952; Maire and Méring, 1970; Plançon, 1981) calculated the diffuse intensity distribution due to stacking of M layers. These studies permit all systems formed by irregular stacking of two-dimensional structural elements to be examined. In the present study the expression developed by Plançon (1981) (Appendix) was assumed to be most valid if the arrangement of layers followed the law whereby only adjacent layers interact. The calculated intensity essentially depends on two factors (Appendix): (1) the nature and number of the two-dimensional structural elements that are stacked; and (2) the relative positions of these elements within the stacking.

For vermiculites, the basic elements constituting any stacking arrangement are 2:1 silicate layers and interlayer molecules and cations. In the present report, these two elements are called the "A layers" and the "B layers", respectively. Here, the expression "layer" means that the structural unit consists of a silicate layer and the interlayer molecules and cations. A and B denote different locations of the water coordination poly-

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Table 3. Tendencies of the silicate layers to have ordered or disordered stacking ($w_+ = w_- = 0.5$, $P_{++} = \alpha$).

	P_{++}	P_{+-}	P_{-+}	P_{--}
Ordered stacking → 2-layer polytype	0	1	1	0
Tendency 2-layer polytype	0.25	0.75	0.75	0.25
Disordered stacking → random	0.50	0.50	0.50	0.50
Tendency segregation	0.75	0.25	0.25	0.75
Ordered stacking → segregation	1	0	0	1
↓ α				

hedron in relation to the silicate surface. An "A layer" enables a shift of $+b/3$ between adjacent layers to permit hydrogen bonds to be established between the water-coordination polyhedron and surface oxygens. In a "B layer", a $-b/3$ shift enables hydrogen bonds to form.

Four probabilities P_{++}, P_{+-}, P_{-+}, and P_{--} are then defined: i.e., P_{+-} represents the probability that a $+b/3$ shift is followed by a $-b/3$ shift *or,* in other words, an "A layer" is followed by a "B layer". These four probabilities allow statistical characterization of the stacking model. The symbols w_+ and w_- are also defined as the relative proportions of the $+b/3$ and $-b/3$ shifts, i.e., the proportions of the "A" and "B" layers present.

Assuming that w_+ and $w_- = 0.5$, the probability, α, of having a $+b/3$ translation followed by another $+b/3$ translation is $P_{++} = P_{--} = \alpha$ (see Appendix). Similarly, $P_{+-} = P_{-+} = 1 - \alpha$. A schematic presentation of the different tendencies of the silicate layers to have ordered or disordered layer stacking is reported in Table 3.

Interlayer space. The structure of the interlayer space was previously studied by Mathieson and Walker (1954), Mathieson (1958), Bradley and Serratosa (1960),

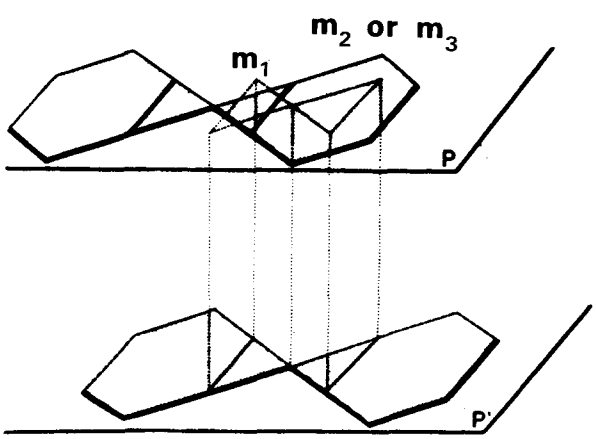


Figure 5. Relative position of two adjacent silicate layers in Mg-vermiculite. m_1, m_2, and m_3, sites for hydrated interlayer cations.

Table 4. Atomic parameters for "A" and "B" layers.

	x'/a	y'/b	z'/c	B (Å²)	m
Silicate layer					
Octahedral cations					
1	−0.076	0.333	0.229	1	0.987
2	−0.076	0.667	0.229	1	0.987
3	−0.076	0.000	0.229	1	0.987
Tetrahedral cations					
1	0.256	0.333	0.418	1.5	1.00
2	0.256	0.667	0.418	1.5	1.00
3	0.592	0.667	0.041	1.5	1.00
4	0.592	0.333	0.041	1.5	1.00
Hydroxyl group					
1	0.257	0.000	0.295	1	1
2	0.591	0.000	0.164	1	1
Oxygen					
1	0.862	0.269	0.000	2	1
2	0.862	0.731	0.000	2	1
3	0.554	0.500	0.007	2	1
4	0.597	0.333	0.150	1	1
5	0.597	0.667	0.150	1	1
6	0.251	0.333	0.309	1	1
7	0.251	0.667	0.309	1	1
8	0.294	0.500	0.452	2	1
9	−0.014	0.269	0.458	2	1
10	−0.014	0.731	0.458	2	1
Interlayer space					
Mg over the m_1 site		(1)	(2)		
Mg	0.260	0.667	0.333	0.725	2.5	0.39
Ca	0.260	0.667	0.333	0.725	2.5	0.02
H_2O					
1	−0.072	0.667	0.333	0.646	3	0.41
2	0.428	0.54	0.190	0.646	3	0.41
3	0.428	0.82	0.470	0.646	3	0.41
4	0.586	0.667	0.333	0.805	3	0.41
5	0.086	0.547	0.190	0.805	3	0.41
6	0.086	0.82	0.470	0.805	3	0.41
Mg over the m_2 or m_3 sites					
Mg	0.260	0.333	0.000	0.725	2.5	0.39
Ca	0.260	0.333	0.000	0.725	2.5	0.02
H_2O					
1	−0.072	0.333	0.000	0.646	3	0.41
2	0.428	0.190	−0.130	0.646	3	0.41
3	0.428	0.470	0.150	0.646	3	0.41
4	0.586	0.333	0.000	0.805	3	0.41
5	0.086	0.190	−0.130	0.805	3	0.41
6	0.086	0.470	0.150	0.805	3	0.41

(1) y'/b for "A" layer; (2) y'/b for "B" layer.

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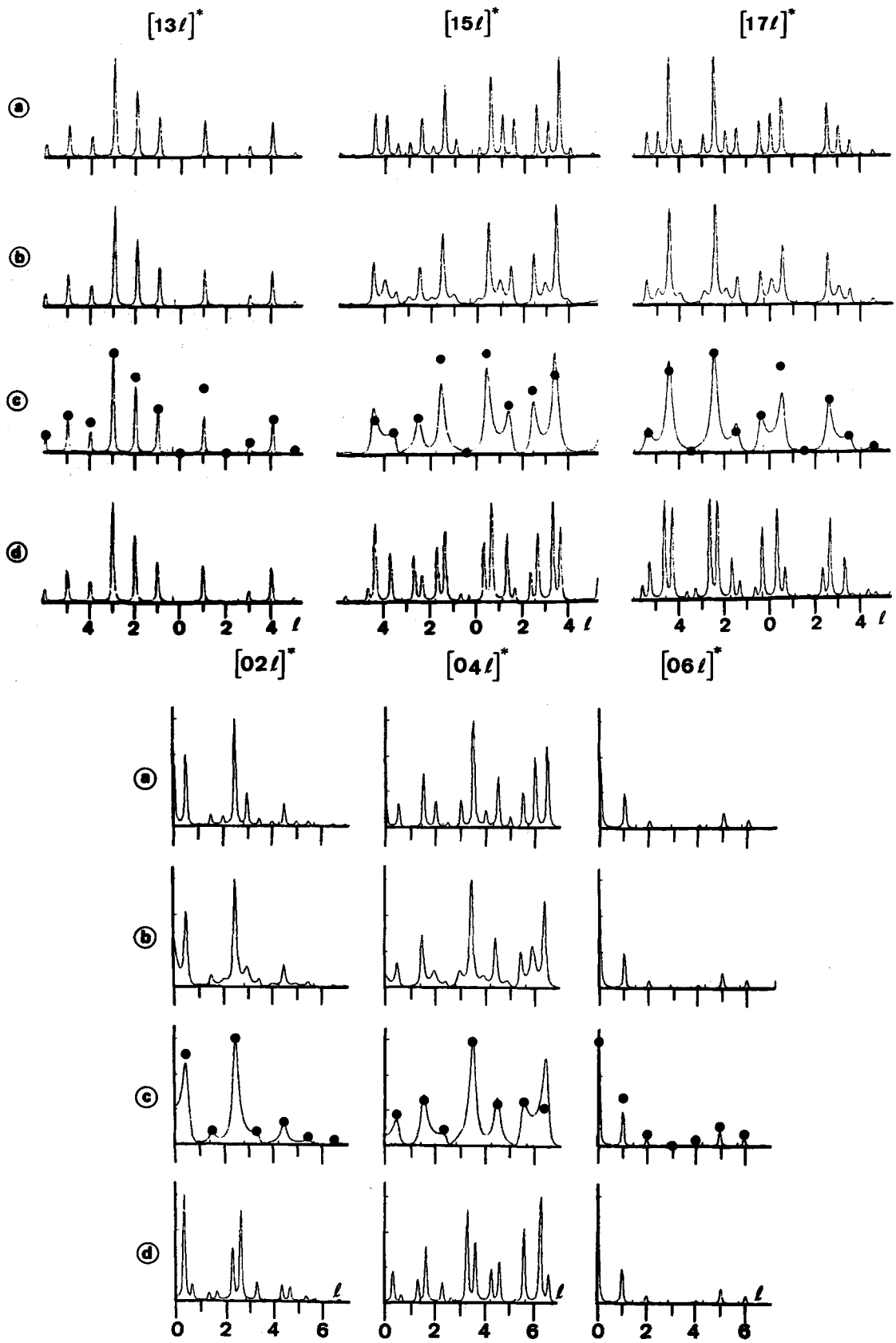


Figure 6. Calculated intensity along the (0,k) and (1,k) rods for (a) a two-layer polytype, (b) tendency to disorder, (c) a random stacking, (d) segregation. (Interlayer Mg cation in m_1 sites.) ● Experimental values.

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Table 5. Comparison of the observed and calculated intensities for Mg-vermiculite. (0,*k*) and (1,*k*) reciprocal rods.

hkl	I_{obs}	I_{cal}	*hkl*	I_{obs}[1]	I_{cal}[1]	*hkl*	I_{obs}[1]	I_{cal}[1]	*hkl*	I_{obs}[1]	I_{cal}[1]	*hkl*	I_{obs}[1]	I_{cal}[1]	*hkl*	I_{obs}	I_{cal}
130	0	0	150	100	86	170	92	61	020	85	75	040	31	26	060	100	100
131	69	32	151	50	43	171	0	0	021	15	11	041	45	48	061	45	33
132	0	0	152	60	50	172	54	50	022	100	100	042	15	11	062	10	7
133	10	11	153	70	100	173	15	18	023	15	11	043	100	100	063	0	0
134	35	36	154			174	7	7	024	18	18	044	43	48	064	6	4
135	2	4							025	10	7	045	46	44	065	23	15
13$\bar{1}$	46	43	15$\bar{1}$	0	0	17$\bar{1}$	38	39	026	6	4	046	35	85	066	9	7
13$\bar{2}$	77	68	15$\bar{2}$	91	75	17$\bar{2}$	21	29									
13$\bar{3}$	100	100	15$\bar{3}$	35	39	17$\bar{3}$	100	100									
13$\bar{4}$	30	21	15$\bar{4}$	21	21	17$\bar{4}$	0	0									
13$\bar{5}$	38	32		33	46	17$\bar{5}$	85	93									
13$\bar{6}$	15	11					20	25									

[1] Intensity of maxima on the observed and calculated profiles.

Shirozu and Bailey (1966), and Alcover and Gatineau (1980). As de la Calle *et al.* (1975a, 1975b, 1977, 1980) and Suquet and Pézerat (1987) established, a relationship exists in 2:1 phyllosilicates between the order or semi-order of the layer stacking and the reactivity of the minerals internal surface.

For a given interlayer cation and RH, the interlayer space has a specific structure. The silicate layers relate to this structure so as to minimize the energy of the layer-interlayer assemblage. In each of the following structures to be considered for Mg-vermiculite, a silicate layer is displaced by either $+b/3$ or $-b/3$ relative to the adjacent one. In reference to the models of Mathieson and Walker (1954) and Shirozu and Bailey (1966), the present models for the layer stacking provide equivalent oxygen environments about the interlayer space.

The hydrated cations $Mg(H_2O)_6^{2+}$ may occupy two types of interlayer sites: (1) between the bases of opposite tetrahedra (m_1 sites of Mathieson and Walker (1954)); here, the hydrated cation is surrounded by six oxygens; or (2) between a ditrigonal cavity and a tetrahedral base; here, an asymmetric environment exists with six oxygens on one side and three on the other (m_2 and m_3 sites of Mathieson and Walker (1954)) (Figure 5).

In the following, two models are considered: (1) a model in which the stacking by "A" and "B" layers places Mg^{2+} in the m_1 site; and (2) a model in which the stacking by "A" and "B" layers distributes Mg^{2+} over the m_2 or m_3 sites. The atomic parameters for the various "A" and "B" layers of the two models are listed in Table 4. They were determined by considering the planar cell (*a*,*b*) of the silicate layer and by placing the surface oxygens at the level z = 0.

Determination of the layer stacking sequence. First, the layer stacking sequence was determined by locating Mg^{2+} on the m_1 site. The I(*l*) profiles calculated for the various cases ($\alpha = 0$, $\alpha = 0.25$, $\alpha = 0.5$, and $\alpha = 1$) are reported in Figure 6. The calculated profiles were compared with the visually estimated experimental intensities (Table 5). For the ordered model ($\alpha = 0$, i.e., two-layer polytype) and for the disordered model ($\alpha = 0.5$), the calculated intensities along rods where $k \neq 3n$ were totally different. By a comparison of these calculated data with the experimental results, the ordered model can be rejected.

The tendency to an ordered stacking ($\alpha = 0.25$, i.e., the tendency to the two-layer polytype) may be ex-

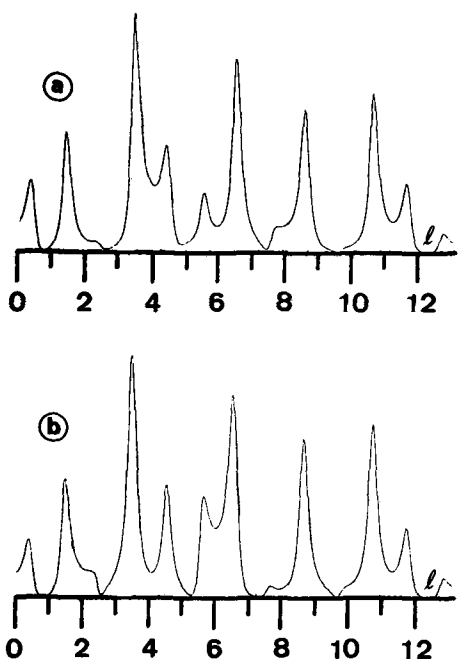


Figure 7. Calculated intensity along the (0,4) rod for the following two models: (a) interlayer Mg cation in m_2 or m_3 sites, (b) interlayer Mg cation in m_1 sites.

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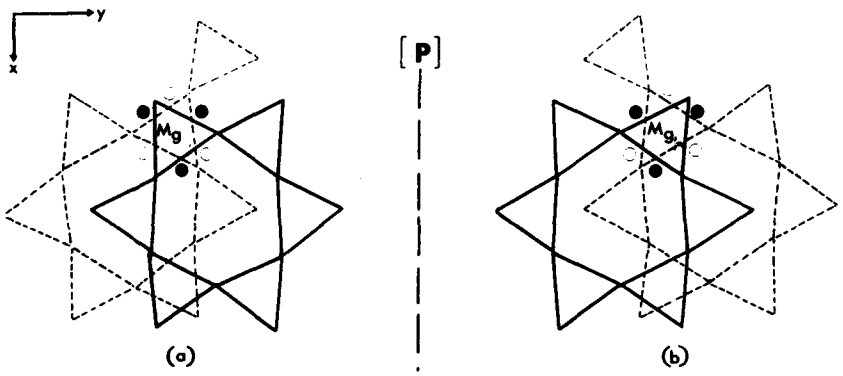


Figure 8. Relative positions of two adjacent oxygen surfaces. (a) $+b/3$ interlayer shift, (b) $-b/3$ interlayer shift. ●, ○ Water molecules.

cluded because of the large difference between the calculated and observed intensities, in particular for the (1,5) reciprocal rod. A model having segregated $+b/3$ and $-b/3$ shifts can also be excluded by comparing the calculated intensity distribution along the $(1,k)$ rods with the experimental results. The calculated intensity distribution based upon random model best fits the experimental data, both with respect to the positions and intensities of the maxima. Table 4 lists maxima on the observed profiles.

The same calculations were carried out for a model in which the hydrated cations were located over the m_2 or m_3 sites. The curves are very close to those obtained in Figure 6. The modulation of the experimental intensity (0,4) along the rod, particularly between $l = 2$ and $l = 8$ (Figure 7), shows, however, that the hydrated cation is probably located in the m_1 site. The m_1 position reported by Shirozu and Bailey (1966) for the hydrated cation is confirmed here. With the exchangeable cation located in the m_1 site, the six water molecules lie in two sheets at a distance of 2.7 Å from the surface oxygens, compatible with hydrogen bonds. On the basis of an infrared study of partially deuterated Mg-vermiculite Fornes *et al.* (1980) reported some short hydrogen bonds. The water molecules form a skeleton in the interlayer space similar to an anionic framework.

SUMMARY AND CONCLUSION

In the semi-ordered structure of Mg-vermiculite (d(001) = 14.3 Å) there is a 50% probability of a stacking fault parallel to the y axis. Each layer is displaced by $+b/3$ or $-b/3$ relative to the preceding layer and independent of its second neighboring layer. In the terminology established by Brown and Bailey for the chlorites (1962), the silicate layer-interlayer assemblage of Mg-vermiculite is I*a*. Because the silicate layers are randomly shifted by $\pm b/3$ along the y axis, the whole structure of Mg-vermiculite may be described by a random succession of I*a*-4 and I*a*-6 assemblages.

The structure of the interlayer space fundamentally determines the layer stacking sequence. Therefore, we considered the structure of the hydrated cation in relation to the crystal chemical nature of the oxygen surfaces and their relative positions ($+b/3$ or $-b/3$). Figure 8 represents the relative positions of the surface oxygens of two adjacent silicate layers surrounding $Mg(H_2O)_6^{2+}$. Translations of $+b/3$ or $-b/3$ are shown. This figure demonstrates that the two polyhedra and their oxygen surroundings are symmetrical relative to a fictitious plane P. Because the Si-Al substitutions are randomly distributed (Herrero *et al.*, 1985a, 1985b; Bailey, 1986), the two assemblages correspond to fairly similar bonding energies between the silicate layers and the interlayer sheet. Therefore, the shift of one layer relative to another by $+b/3$ and $-b/3$ is equally probable.

The present study demonstrates that classic methods and indirect methods for studying semi-random structures can be very usefully applied in characterizing stacking faults.

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APPENDIX

Calculation of the diffracted intensity I(l) on the h,k *rods*

The methods developed by various authors allow the continuous intensity I(l) on various reciprocal lattice rods to be calculated by postulating different kinds of translation between the layers. The intensity diffracted at the 2θ angle along an hk rod can be calculated from the matrix expression developed by Plançon (1981):

$$I_{hk}(s) = \text{Trace}\left\{\text{Re}\left[[F_{hk}][w]\left\{[I] + 2\sum_{n=1}^{n}(M - n)/M[Q]^n\right\}\right]\right\}$$

where:

Re = real part of . . . ,

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M = the number of layers by stacking,
$[F_{hk}]$ = matrix of the structure factors,
[I] = unit matrix,
[w] = matrix that represents the proportion of the different translation between the layers, and
[Q] = matrix that represents the interference phenomena between adjacent layers and that depends only on the relative positions of the layers in the stacking.

For Mg-vermiculite (with two translations $\vec{T}_+$ and $\vec{T}_-$ and two different elements called "A layers" and "B layers"), the matrix Q is given by:

$$[Q] = \begin{vmatrix} P_{++}\exp(-2\pi i\vec{s}\vec{T}_+), & P_{+-}\exp(-2\pi i\vec{s}\vec{T}_+) \\ P_{-+}\exp(-2\pi i\vec{s}\vec{T}_-), & P_{--}\exp(-2\pi i\vec{s}\vec{T}_-) \end{vmatrix},$$

where $\vec{s}$ is the scattering vector.

If w_+ and w_- are the relative abundances of the $\vec{T}_+$ and $\vec{T}_-$ translations, the relationship between proportion and probabilities can be written:

$$w_+ + w_- = 1;\ P_{++} + P_{+-} = 1;\ P_{-+} + P_{--} = 1;$$
$$w_+P_{+-} = w_-P_{-+}.$$

Because four equations and six parameters exist, two of the parameters must be independent. If α is the probability of having a $\vec{T}_+$ translation followed by another $\vec{T}_+$, and if w_+ is chosen as the second independent parameter, the six parameters are then given by the expressions

$$w_- = 1 - w_+,$$

$$P_{+-} = 1 - \alpha,$$

$$P_{-+} = \frac{w_+}{(1 - w_-)}(1 - \alpha), \text{ and}$$

$$P_{--} = 1 - P_{-+}.$$

Thus, the calculated intensity essentially depends on two factors: (1) the nature [F] and the number [w] of the two-dimensional elements that are stacked, and (2) the relative position of these elements within this stacking [Q].

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