

# THE MECHANISM OF DEHYDRATION OF Mg-VERMICULITE

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## ABSTRACT

The hydrated Mg-vermiculite lattice contains double sheets of water molecules interleaved with silicate layers. In the fully hydrated condition, each water sheet is arranged in a regular hexagonal pattern and the interlayer cations are located midway between water sheets in octahedral coordination.

Release of water molecules from interlayer positions leads at first to a gradual contraction of the basal spacing from 14.81 Å, during which the water network becomes increasingly distorted. The contraction ceases temporarily at 14.36 Å while further water is withdrawn. When the probability that a cation has a complete octahedral "shell" of water molecules at a given instant falls below a certain value, an abrupt contraction to 13.82 Å takes place during which the cations are displaced to sites near the silicate layer surfaces.

Release of further water causes a contraction to a lattice (11.59 Å) in which single sheets of water molecules are interleaved with the silicate layers. The 11.59 Å phase is stable until only a small proportion of the interlayer water remains, when an approximately regular interstratification of 11.59 Å and 9.02 Å (dehydrated) layers develops. The final traces of interlayer water are retained in the interior of the crystal with great tenacity owing to the sealing of the crystal near the edges.

## INTRODUCTION

The intracrystalline swelling of layer silicates has interested investigators for many years. In particular, attention has been paid to the members of the montmorillonite group. Hendricks, Nelson, and Alexander (1940) and others have shown that the entry of water molecules into, or their removal from, interlayer positions takes place in discrete steps of about 3 Å separation. As many as four sheets of water molecules may enter the lattice in this stepwise fashion depending on the nature of the saturating cation. Norrish and Quirk (1954) and Norrish (1954) have recently drawn attention to a further type of intracrystalline swelling in montmorillonoids at higher water contents. In this type, which is osmotic in nature and macroscopic, the swelling proceeds in a linear manner with respect to the water content up to very large separations. The transition to macroscopic swelling occurs with small monovalent cations which have hydration energies sufficient to overcome the potential barrier due to the electrostatic attractive forces acting between silicate layers. The hydration energies of the larger monovalent ions are insufficient to effect the transition so that their swelling is limited to a maximum of two molecular thicknesses of water. With polyvalent ions, the higher hydration energies are offset by other factors and, here also, swelling is limited to two or three molecular steps.

Comparatively little attention has been given to the swelling process in vermiculites, in spite of the obvious advantages of working with crystals that are large enough for single-crystal x-ray study. In view of the similarities of the crystal structures and dehydration curves of the two groups, there seems little doubt that their hydration processes must be essentially similar, although not

identical because of the relatively greater surface density of charge of the vermiculites. In general the swelling properties of the vermiculites tend to be less marked so that, whereas up to three sheets of interlayer water may be introduced in Mg-saturated montmorillonoids, the maximum number in Mg-vermiculite appears to be two. Nevertheless, "osmotic" swelling has been observed in some Li-saturated vermiculites although no detailed study has so far been attempted.

Although basal spacings of vermiculites saturated with a variety of cations have been published by Barshad (1948) and Walker and Milne (1950), most x-ray studies of vermiculites to date have been made on Mg-vermiculites. Structural work on the hydration phases of these minerals has now proceeded to a stage at which a first attempt may be made to sketch the mechanism of the dehydration process, from the phase in which two complete sheets of water molecules are interleaved with each pair of silicate layers to the phase from which interlayer water has been excluded. The process turns out to be unexpectedly complex and six separate phases have been identified. Detailed structure analyses of only two of the phases have been undertaken and one of these is still incomplete, but the structural modifications involved in all the phase changes can be inferred to some extent from the data available and by reference to the phases analyzed.

### STRUCTURAL ASPECTS OF THE PHASES

The vermiculite used in this study is a specimen from West Chester, Pennsylvania,<sup>1</sup> with a cation-exchange capacity of 158 meq per 100 g, all the exchange positions being occupied by Mg<sup>2+</sup>. The structural formula is:



In discussing the 14.36 Å phase, the structure analysis of the Kenya vermiculite (Mathieson and Walker, 1954) has been used as a guide, and the West Chester vermiculite is assumed to be structurally equivalent to the Kenya specimen although differing in chemical composition. The justification for this assumption lies in the very similar nature of the x-ray spectra of both specimens. X-ray data for the other phases mentioned have been obtained from the West Chester vermiculite, and water contents, where quoted, also refer to this specimen.

Apart from the 14.36 Å and 11.59 Å phases, x-ray measurements have been limited to a determination of basal spacing<sup>2</sup> and  $\beta$  angle; in addition, the intensity distribution of certain sets of reflections has been invoked in order to decide between alternative structures. In each case, the data enable the mutual arrangement of the silicate layers to be determined. The four possible methods of stacking the silicate layers are illustrated in Figure 1. If the  $\beta$  angle is 90°, the arrangement is as shown in A. If the  $\beta$  angle is not 90°, its value varies between 97° and 101° depending on the basal spacing [ $\beta = (\tan^{-1}a/3)/d_{(001)}$ ],

<sup>1</sup> Obtained through the courtesy of Mr. R. O. Chalmers of the Australian Museum, Sydney (no. D10001).

<sup>2</sup> The basal spacings quoted are accurate to  $\pm 0.02$  Å, except for the 20.6 Å mixed-layer phase.

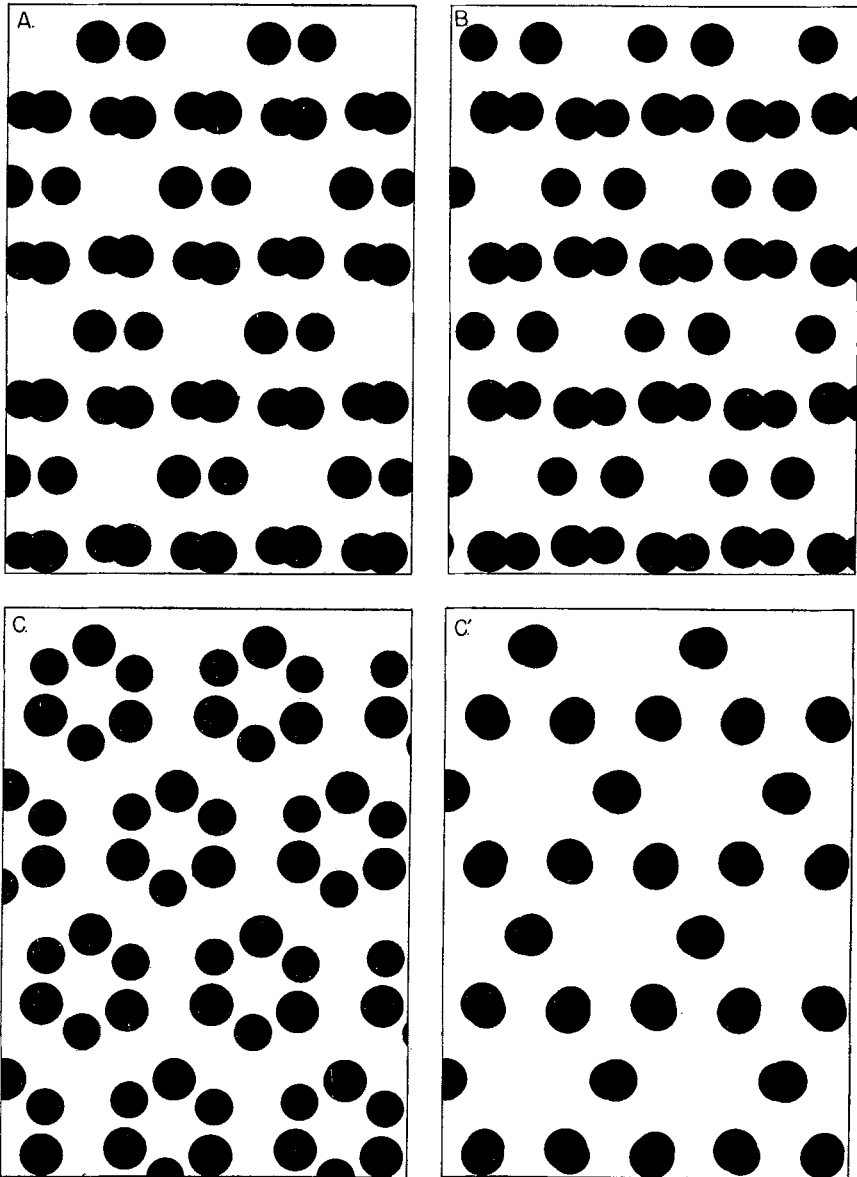


FIGURE 1. — The four methods of stacking the silicate layers (only the oxygens of opposing silicate layer surfaces are shown; large and small circles refer to oxygens in different surfaces).

and the silicate layers are displaced by  $+a/3$  or  $-a/3$  with respect to each other. If arrangements C and C' are considered to be displaced  $+a/3$ , B is displaced in the opposite direction, viz.,  $-a/3$ , and B can be distinguished from C and C' by reference to the intensity distribution of the  $h0l$  and  $h3l$  spectra. The distinction of C and C' may be effected in some cases by means of the diffuse  $k \neq 3n$  spectra.

#### 14.36 A Phase

In the structure analysis of the Kenya vermiculite (Mathieson and Walker, 1954), consideration of the sharp  $h0l$  and  $h3l$  spectra indicated four possible methods of stacking the silicate layers. Reference to the relatively diffuse  $k \neq 3n$  spectra excluded two of the possibilities and indicated that the two remaining methods of stacking occur with equal probability. In the photographs of the 14.36 A phase of the West Chester vermiculite, the sharp spectra are very nearly identical with those of the Kenya vermiculite. The  $k \neq 3n$  spectra, however, tend to be even more diffuse than, although coincident with, those of the Kenya specimen. This observation points to a less regular alternation of the two stacking arrangements in the West Chester vermiculite. It is evident, however, that the crystal structures of the two minerals are effectively equivalent.

The structure analysis of the Kenya vermiculite (14.36 A phase) located the interlayer water molecules and exchangeable cations in definite sites in the crystal lattice.<sup>1</sup> In the specimen examined, rather more than two-thirds of the interlayer water molecule sites were occupied, and approximately the same degree of hydration, under normal atmospheric conditions, has been observed in other vermiculites, including the West Chester specimen referred to herein. The interlayer water network was shown to consist of two sheets, each arranged in a distorted hexagonal pattern, the cation sites being determined by the requirement for octahedral coordination of water molecules around the cations. In order to account for the asymmetric electron density distribution of the water molecule peak, a small displacement of the water molecules from regular hexagonal sites was postulated, although its magnitude could not be defined accurately from the data. The water-cation network and its relationship to the surface oxygens of the adjacent silicate layer surfaces is shown in Figure 2.

A distortion of the oxygen network in the silicate layer surface was noted by Mathieson and Walker (1954) in the 14.36 A phase of the Kenya vermiculite, and ascribed to an attractive force acting between the surface oxygens and the octahedrally coordinated cations at the centers of the silicate layers. This distortion is probably present in all phases of both the Kenya and West Chester vermiculites, since precisely the same distortion is observed in the electron density map of the 11.59 A phase of the latter specimen (Mathieson and Walker, unpublished).

<sup>1</sup> Since their paper was published, Mathieson and Walker have detected two arithmetical errors in their calculations, which necessitate the alteration of bond lengths in the interlayer region as follows: H<sub>2</sub>O—H<sub>2</sub>O within a sheet in the vicinity of a cation site, 2.97 Å; H<sub>2</sub>O—H<sub>2</sub>O between sheets, 2.78 Å; Mg—H<sub>2</sub>O, 1.99 Å; H<sub>2</sub>O—O, 2.90 Å. The general structural scheme remains unaffected by these adjustments.

## 14.81 A Phase

A crystal of Mg-vermiculite (14.36 A phase) placed in water shows a gradual increase in the basal spacing to 14.81 Å. This increase is continuous and, at room temperatures, takes several days to complete, so that intermediate stages can be readily observed. The rationality of the higher orders of the basal reflection is preserved as the spacing increases, indicating that the swelling normal to the cleavage plane is regular throughout the crystal.

Water-content determinations indicate that all or almost all the interlayer water molecule sites are occupied in the 14.81 Å phase. From the  $\beta$  angle and the diffuse nature of the  $k \neq 3n$  spectra, it is probable that the silicate layer relationships correspond to C in Figure 1, although the possibility that C' also occurs cannot be excluded on structural grounds. However, since the 14.81 Å phase is derived from the 14.36 Å phase by a gradual and continuous swelling, it is reasonable to infer that the silicate layer relationships of the former are the

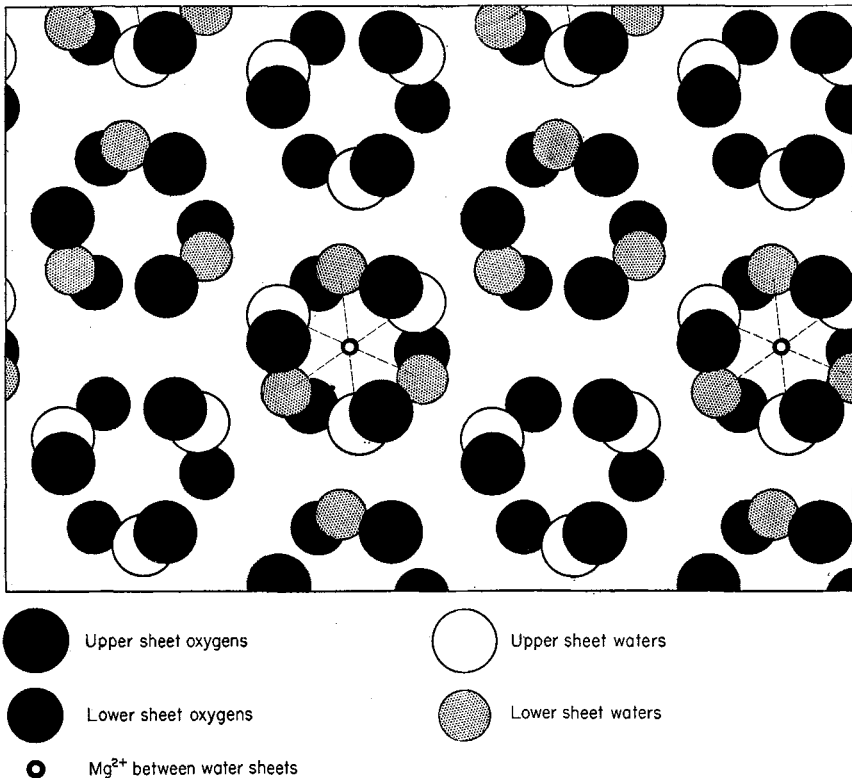


FIGURE 2. — The relationship of opposing silicate layer surfaces and the interlayer water-cation network in the 14.36 Å phase.

same as those found in the 14.36 Å phase, viz., C. In the 14.36 Å phase, the distortion in a single sheet of water molecules leads to H<sub>2</sub>O—H<sub>2</sub>O approach distances of either 2.97 Å or 3.40 Å within the sheet, and enables each water molecule to approach more closely an oxygen in the adjacent silicate layer surface.

As water molecules enter the lattice and the spacing increases, it would appear that the 3.40 Å approach distance can no longer be maintained because of dipole interaction, so that the interlayer water molecules tend to rotate and progressively weaken their linkages with the surface oxygens. As a consequence, the H<sub>2</sub>O—O distance increases from 2.90 Å in the 14.36 Å phase to about 3.1 Å in the 14.81 Å phase and, at the same time, the water sheets progressively lose their distortion and adopt a regular hexagonal pattern in which each water molecule site is located directly over an octahedral site of the adjacent silicate layer (Fig. 3).

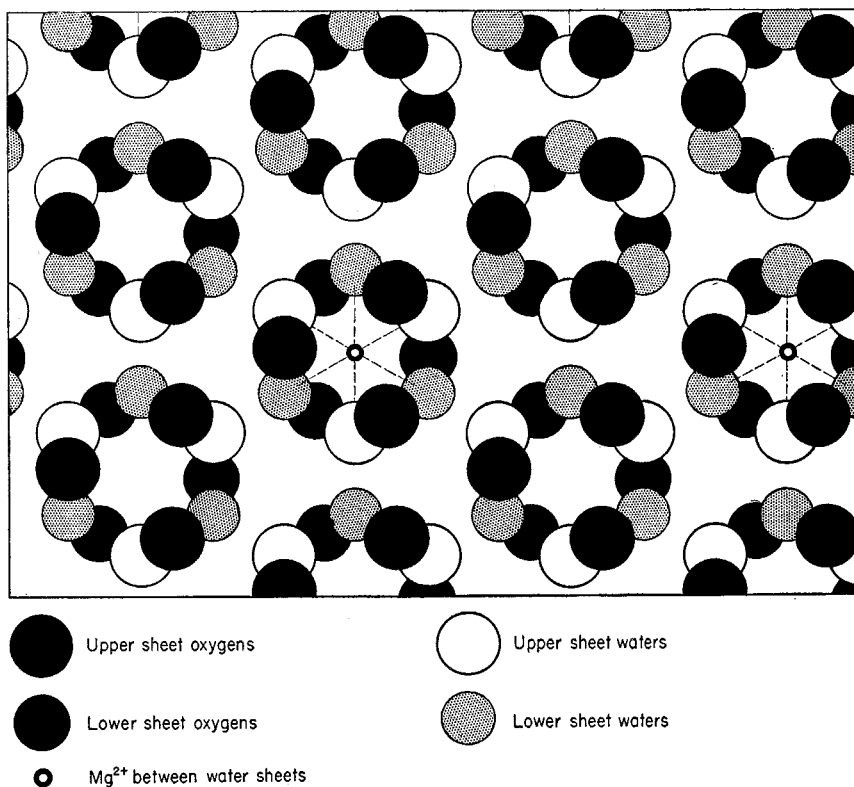


FIGURE 3.— The relationship of opposing silicate layer surfaces and the interlayer water-cation network in the 14.81 Å phase.

*13.82 Å Phase*

Removal of water molecules from the 14.36 Å phase of the West Chester vermiculite leads to an abrupt contraction of the lattice to a phase having a basal spacing of 13.82 Å. The structure of this phase has not been examined exhaustively, but the interlayer cations almost certainly occupy the same sites as in the subsequent 11.59 Å phase. Since the complete solution to the latter phase has not been obtained, the structures proposed here for the 13.82 Å and 11.59 Å phases must be regarded as provisional.

In the 13.82 Å phase, there is still a double thickness of water molecules between successive silicate layers, but the interlayer cations have migrated to new sites near the silicate layer surfaces, and appear to lie over the centers of triads of oxygens (i.e., directly over tetrahedral Si—Al sites). As with the 11.59 Å phase (see below), it is probable that the cations in a given interlayer region are associated with only one of the silicate layer surfaces, so that the resulting structure is asymmetric. The observed  $\beta$  angle of  $90^\circ$  requires the displacement of the silicate layers with respect to one another by  $a/3$  (i.e., to arrangement A, Fig. 1). According to the scheme proposed for the 13.82 Å phase (Fig. 4), the two sheets of water molecules are related to each other in the same manner as in the 14.36 Å phase, although fewer water molecule sites are occupied than in the latter. The upper sheet of water molecules, moreover, is related to the adjacent surface oxygens as in the 14.36 Å phase. The relation between the lower sheet of water molecules and the adjacent oxygen surface, however, has altered corresponding to a mutual displacement by  $a/3$ .

Although the mobility of the water molecules is probably high in this phase, there is still a tendency for them to group around the cations. The water network may therefore be considered, in accordance with the idealized view shown in Figure 4, as consisting of groups of water molecules in the vicinity of the cations with a triad of water molecules arranged around and in contact with a cation so as to form an imperfect octahedron with the underlying triad of oxygens.

*11.59 Å Phase*

The removal of a small amount of water from the 13.82 Å phase causes a further abrupt contraction of the lattice to 11.59 Å. The latter phase corresponds to a structure in which complete single sheets of water molecules are interleaved with the silicate layers. A two-dimensional synthesis projected along the *b*-axis of this phase has been made (Mathieson and Walker, unpublished), but certain anomalies have been encountered in the detailed interpretation of the data and these have not been finally resolved. Complete details of this structure analysis will be published elsewhere.

In the present discussion, attention will be confined to the probable location of the interlayer water molecules and cations with respect to the silicate layer surfaces. As in the 13.82 Å phase, the  $\beta$  angle of this phase is  $90^\circ$  so that the silicate layer relationships are as in arrangement A, Figure 1. According to present indications, the structure of this phase is asymmetric with the cations located near one of the silicate layer surfaces directly over triads of oxygens.<sup>1</sup>

<sup>1</sup> The evidence for the location of the cations in these sites, however, is not unequivocal; the cation sites may in fact be associated in some way with the hexagon "holes" formed by the oxygens of the silicate layer surfaces.

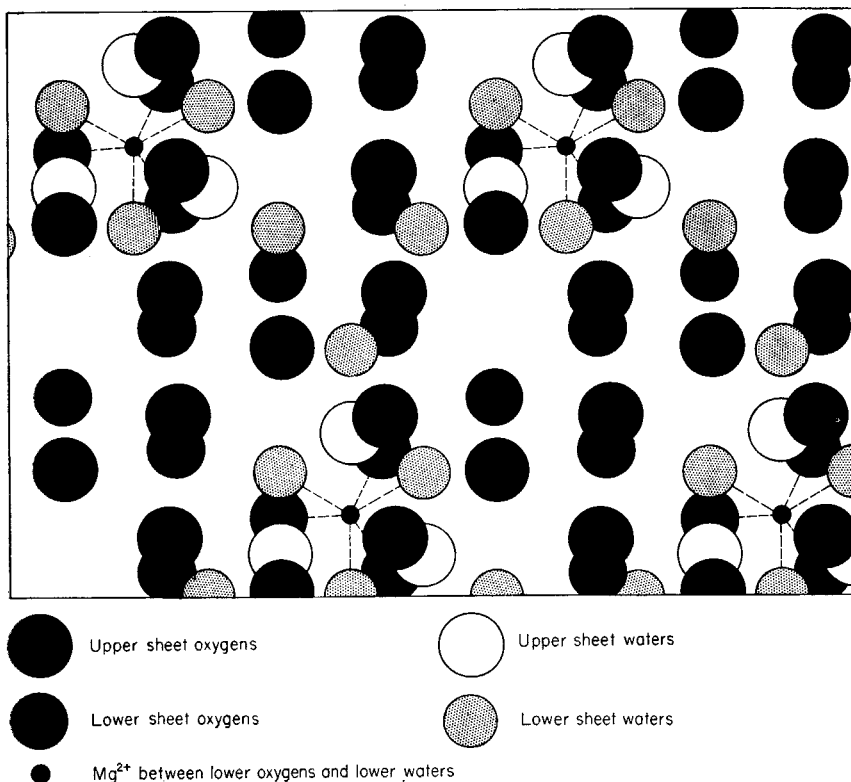


FIGURE 4. — The relationship of opposing silicate layer surfaces and the interlayer water-cation network in the 13.82 Å phase.

The arrangement of the water molecules allows each cation to occupy an imperfect octahedral environment consisting of three water molecules and three oxygens (Fig. 5). In this scheme, the oxygens of the opposing silicate layer surfaces are not equivalent with respect to the interlayer water molecule sites. The structure differs from that of the 13.82 Å phase in that the upper sheet of water molecules has been eliminated and the distance between the silicate layers correspondingly reduced.

#### 20.6 A Mixed-layer Phase

Removal of water molecules from the 11.59 Å phase leads eventually to a contraction of the lattice to 9.02 Å representing a phase in which there is no interlayer water. This contraction, however, can be considered as occurring in two stages, the first of these being the development of an approximately regular interstratification of 11.59 Å and 9.02 Å layers.



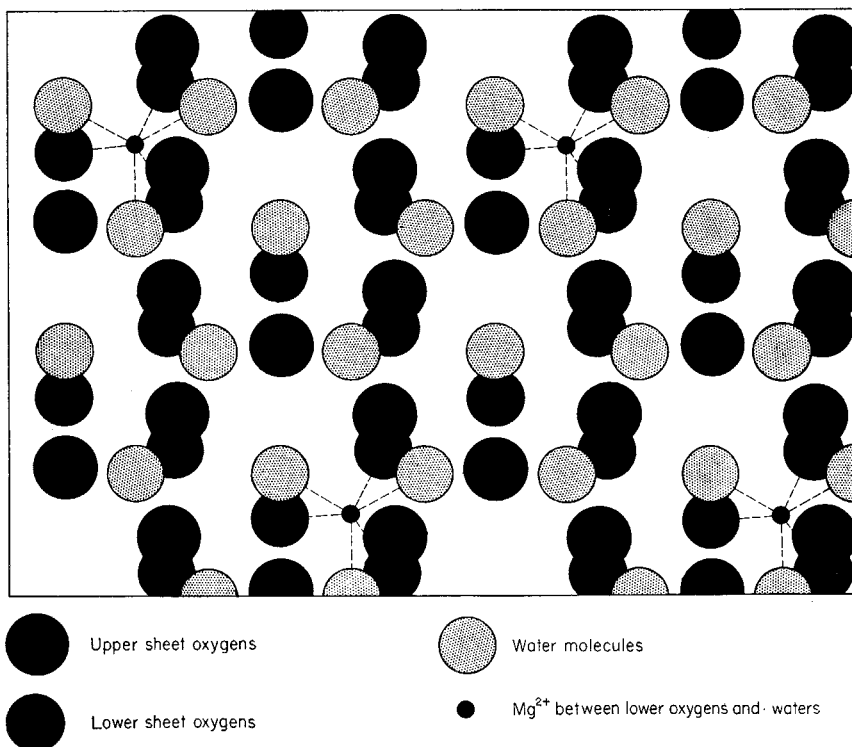


FIGURE 5.— The relationship of opposing silicate layer surfaces and the interlayer water-cation network in the 11.59 Å phase.

Measurements on the basal reflections of the 20.6 Å mixed-layer phase are listed in columns 2 and 3 of Table 1. The large number of higher orders of the basal reflection observed indicates a high degree of regularity in the lattice, and comparison with columns 4 and 5 of the table reveals good agreement between the observed data and values calculated for a lattice consisting of equal numbers of regularly alternating 11.6 Å and 9 Å layers of assumed equal scattering power. On the other hand, relatively poor agreement is obtained with calculations based on a random stratification of equal numbers of 11.6 Å and 9 Å layers. A curve of the intensity distribution to be expected from a lattice of this type, derived by the method of Hendricks and Teller (1942), is shown in Figure 6.

Examination of flakes of the West Chester vermiculite heated at various temperatures for 15 hours<sup>1</sup> shows that the development of the 20.6 Å phase takes

<sup>1</sup> The specimens were heated in glass capillaries and sealed at the required temperature. Unless rehydration is prevented, the 11.6 Å layers revert spontaneously to 14.4 Å giving a regular mixed-layer lattice based on a 23.4 Å repeat distance. With suitable controls, lattices can also be obtained with spacings of 22.8 Å and 23.8 Å corresponding to regular alternations of 9 Å layers with 13.8 Å and 14.8 Å layers respectively.

TABLE I.—COMPARISON OF OBSERVED BASAL REFLECTIONS FOR 20.6 Å PHASE WITH CALCULATED VALUES BASED ON A REGULAR INTERSTRATIFICATION OF 11.6 Å AND 9 Å LAYERS OF EQUAL SCATTERING POWER ( $I_{calc.} = F^2/100. L_p$ ).

Order	Observed		Calculated	
	dÅ	$I_{obs.}$	dÅ	$I_{calc.}$
1	20.5	med. str. diff.	20.6	186
2	10.22	v. str.	10.30	331
3	—	—	6.87	9
4	4.95	w.	5.15	19
5	4.12	w.	4.12	20
6	3.312	med. str. diff.	3.433	50
7	2.951	v. str.	2.943	148
8	—	—	2.575	0
9	2.294	med.	2.289	8
10	—	—	2.060	2
11	1.852	med.	1.873	15
12	—	—	1.717	0
13	1.561	w.	1.585	9
14	1.476	med.	1.471	16
15	—	—	1.373	5
16	1.289	med.	1.288	10
17	—	—	1.212	0
18	1.142	w.	1.144	5
19	—	—	1.084	0
20	1.0192	w.	1.0300	5
21	—	—	0.9810	2
22	0.9289	w. diff.	0.9364	7
23	0.8968	w. diff.	0.8957	10

place over a range of temperatures (Fig. 7), in which respect it differs from the other phases. Thus, at 120° C, the first signs of 9 Å layers appear on the x-ray photographs and, at 150° C, about 25 to 30 percent of the 11.6 Å layers have been replaced by 9 Å layers. Even at this stage, signs of regularity in the distribution of the layers is apparent. At about 180° C, the numbers of 11.6 Å and 9 Å layers are approximately equal.

### 9.02 Å Phase

The breakdown of the 20.6 Å phase commences at about 250° C, the large majority of 11.6 Å layers being reduced rapidly to 9 Å so that, at 290° C, the proportion of 9 Å layers is about 90 to 95 percent. At this stage, however, the process slows down and it is not until the 600° to 700° C temperature range that a completely regular 9.02 Å lattice develops (Fig. 7). In the 9.02 Å phase, the interlayer cations are nonexchangeable and the lattice no longer rehydrates spontaneously although forced rehydration, for example by autoclaving, may effect a substantial degree of regeneration.

The contraction from 11.59 Å to 9.02 Å is accompanied by the displacement by  $a/3$  of the silicate layers with respect to each other, and the observed  $\beta$  angle of 101° is consistent with a reversion to the stacking sequence shown by the 14.81 Å and 14.36 Å phases. Inspection of the intensity distribution of the 20l

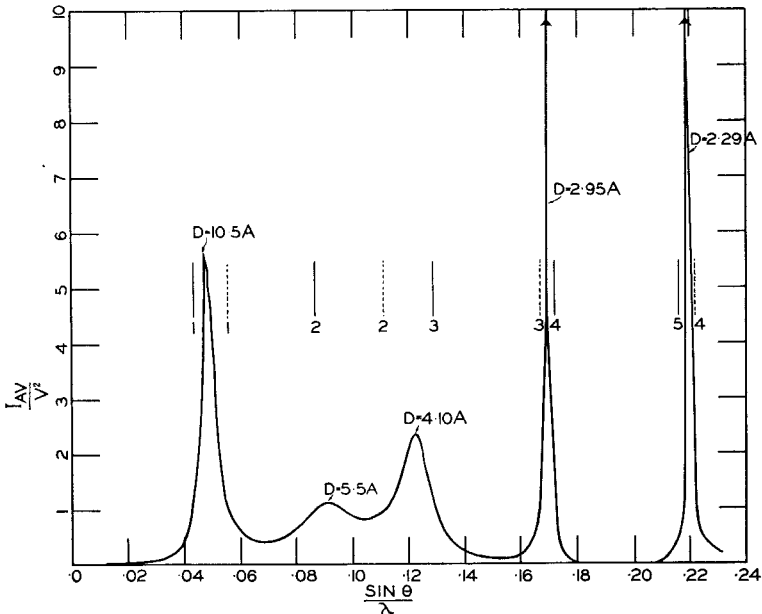


FIGURE 6. — Scattering from a random mixture of 11.6 Å and 9 Å layers of equal scattering power.

spectra (Table 2), however, shows that arrangement C or C' cannot occur and that the silicate layer relationships must be as in B (Fig. 1). Since triads of oxygens in opposing silicate layer surfaces are not octahedrally related in structure B, interlayer cations can no longer occupy an octahedral environment. If the cations were located over triads of oxygens on one surface, impossibly short Mg—O distances would be required in order to obtain a 9.02 Å basal spacing. The possibility of the displacement of certain surface oxygens in a direction normal to the plane of the layers so as to provide more reasonable Mg—O distances offers no solution, calculations based on this assumption being inconsistent with the observed 00 $l$  intensity distribution. The cations, therefore, appear to be located in hexagon "holes" in the silicate layer surfaces although their exact positions have not been determined. Calculations suggest that they are unlikely to be situated midway between silicate layers.

#### THE PROPOSED MECHANISM OF DEHYDRATION

The structure analysis of the 14.36 Å phase of the Kenya vermiculite showed that there are 24 water molecule sites per unit cell. On this basis, the West Chester vermiculite has approximately 16 water molecule sites per interlayer cation since there are 1.52 exchangeable Mg ions in its unit cell.<sup>1</sup> All the sites

<sup>1</sup> The differential thermal analysis curve of this specimen is discussed by Walker and Cole (1956).

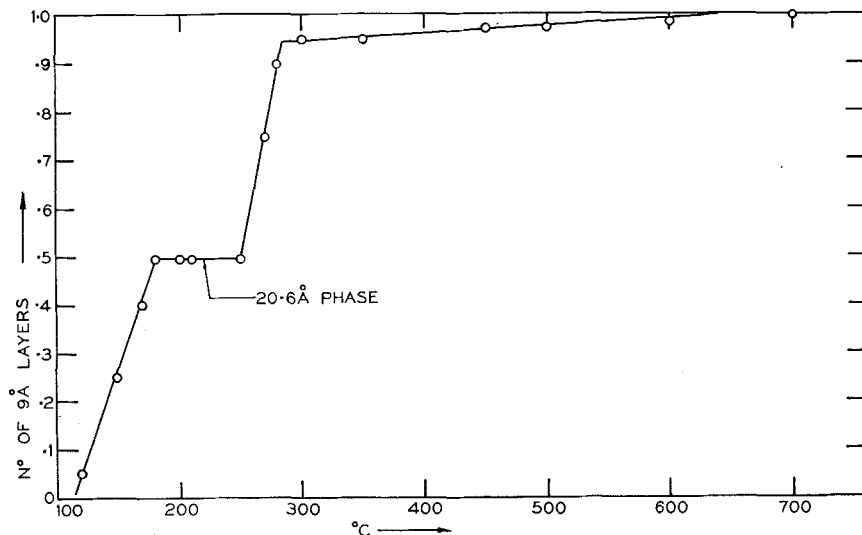


FIGURE 7.—Relative proportion (approximate) of 9 Å layers and 11.6 Å layers as a function of temperature. Samples held at temperature 15 hours; heating rate 5° C per minute.

are occupied in the 14.81 Å phase, so that two complete sheets of water molecules are interleaved with each pair of silicate layers. This phase, which is more highly hydrated than that normally observed at room temperatures and pressures, is stable only when the crystal is immersed in water or held at very high relative pressures.

TABLE 2.—OBSERVED INTENSITIES FOR 20*l* REFLECTIONS OF 9.02A PHASE COMPARED WITH CALCULATED STRUCTURE AMPLITUDES FOR SILICATE LAYER RELATIONSHIPS *B* AND *C* (OR *C'*) RESPECTIVELY ( $I_{\text{calc.}} = F^2/100.L.p.e^{-B \sin^2 \theta/\lambda}$ ).

20 <i>l</i>	2 sin $\theta$	$I_{\text{est.}}$	$I_{\text{calc.}} (B)$	$I_{\text{calc.}} (C, C')$
205	1.10	strong.....	20.0	0.0
204	0.96	medium.....	7.5	27.5
203	0.85	.....	0.0	24.3
202	0.71	strong.....	23.0	17.7
201	0.63	.....	0.9	92.7
200	0.56	strong.....	14.6	45.0
201	0.55	strong.....	18.8	5.5
202	0.61	very strong.....	88.9	0.6
203	0.68	medium strong.....	30.4	21.5
204	0.80	medium.....	12.3	1.1
205	0.92	strong.....	29.5	1.0
206	1.05	weak.....	1.1	17.5

Release of water molecules from the 14.81 Å phase at first leads to a gradual contraction of the basal spacing. The introduction of vacant sites allows each water molecule to approach more closely an oxygen in the adjacent silicate layer surface. In the process, the water molecules are displaced increasingly from their regular hexagonal sites and a distortion of the network develops. When the number of water molecules per cation is reduced to about 12, an equilibrium position is attained. At this stage, the basal spacing is 14.36 Å and it remains at this value temporarily while further water molecules are withdrawn from interlayer sites.

Although there will be a tendency for the water molecules to occupy sites in the vicinity of cations more frequently, it is certain that migration of water molecules and cations is constantly taking place. The probability that a cation is surrounded by a complete octahedral shell of water molecules at a given instant is, therefore, reduced as the number of water molecules decreases and their mobility increases. This factor becomes critical while there are still 9 water molecules per cation, and an abrupt phase-change takes place. In the transition to the 13.82 Å phase, the cations apparently move to sites immediately above triads of oxygens in one of the silicate layer surfaces where they acquire a permanent "half-shell" of 3 oxygens. A displacement by  $a/3$  of the adjacent water sheet provides 3 water molecules to complete an approximately octahedral environment for each cation. The octahedron formed in this way is less regular than that previously available for the cation, so that the new sites are selected only when the number of water molecules is reduced below the critical value. The displacement of the water sheet with respect to the adjacent silicate layer is accompanied by an equal displacement of the second water sheet and the opposing silicate layer.

Almost immediately following the formation of the 13.82 Å phase, the lattice undergoes another contraction to 11.59 Å. It is probable that the 11.59 Å phase develops as soon as the number of water molecules is reduced to a point where a single complete sheet, consisting of 8 water molecules per cation, can form. In the contraction to 11.59 Å, the silicate layer relationships are preserved as in the 13.82 Å phase, and the transition can be viewed as a displacement of the water molecules from the second water sheet into vacant sites in the sheet adjacent to the cations. Withdrawal of water molecules from the 11.59 Å phase proceeds without accompanying structural changes until the number of molecules per cation is reduced from 8 to about 3, presumably those 3 which form the "half-shell" around the cation. Hitherto, the removal of water from the lattice has taken place in an entirely uniform manner throughout the crystal with each interlayer region losing an equal number of water molecules as the dehydration proceeds. During the removal of the last 3 water molecules from the 11.59 Å phase, however, this uniformity is partly lost and a mixed-layer structure develops. The high degree of regularity of the resultant 20.6 Å phase calls to mind other regularly alternating layer silicate structures such as rectorite (Bradley, 1950) and alleverdite (Caillère, Mathieu-Sicaud, and Hénin, 1950; Brindley, 1956), and analogous systems occur with non-silicate layer structures such as graphite or bismuth oxide (Wadsley, 1955). The existence of such systems presents an interesting thermodynamic problem.

The great tenacity with which the last traces of interlayer water are retained in the lattice (Fig. 6) may be due to the trapping of water molecules in the in-

terior of the crystal. The progressive extraction of those interlayer water molecules nearest to crystal edges and the resultant convergence of the silicate layers in these regions will tend increasingly to inhibit the removal of further water molecules from the interior. The bending of the silicate layers involved and their lateral displacement with respect to one another seem to be quite feasible (Walker, 1956). There is some evidence that the trapping of water molecules by a mechanism of this kind and their subsequent explosive release may be the main causative factor in the heat-exfoliation of the vermiculites.

The displacement of the silicate layers, during the contraction from 11.59 Å to 9.02 Å, to arrangement B rather than C (Fig. 1) is unexpected at first sight since, in the latter arrangement, interlayer cations situated between triads of oxygens in the opposing silicate layer surfaces would have an octahedral environment such as appears to be favored by the cations in the more hydrated phases. It is evident that some overriding factor prevents the attainment of an octahedral environment for these cations in the 9.02 Å phase. The possibility that the interlayer cations, having had their shells of oxygens and water molecules disrupted by the elimination of the water, tend to bury themselves in the silicate layers cannot be excluded. What evidence is available suggests that they no longer remain midway between layers. The silicate layer relationships in the 9.02 Å phase may therefore depend less on the influence of the cations than on the interaction of oxygens from the opposing surfaces. So far as the surface oxygens are concerned, arrangements A and B (Fig. 1) would be the same were it not for the distortion of the surface oxygen network, previously described. It appears that arrangement B has a lower potential energy than A in the 9.02 Å lattice because of this distortion.

It is evident from the foregoing that the mechanism of the dehydration process is still not completely understood. Indeed, further work may necessitate revision of some of the interpretations placed on the data at present available. The publication of an interim statement, however, may be justified on the grounds that the seeming complexity of the process suggests that final solutions may not be obtained easily or quickly.

The question as to whether all Mg-vermiculites dehydrate in a manner essentially similar to that of the West Chester specimen is relevant. Examination of Mg-batavite<sup>1</sup> and of the Kenya Mg-vermiculite indicates that the same phases occur in these specimens as in the West Chester vermiculite. The temperatures of formation of the more hydrated phases in these specimens, moreover, are similar to those of the West Chester vermiculite, but the development of 9 Å layers does not take place so readily as in the latter. This is probably due to the composition of the silicate layers and to variations in the surface density of charge rather than to essential structural differences, but the data are too limited at present to allow of an unequivocal answer.

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<sup>1</sup> Obtained through the kindness of Professor U. Hofmann (see Weiss and Hofmann, 1951).

countered during the dehydration process, and to Mr. N. Buckley for help with the experimental work and in the preparation of the diagrams.

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