

# THE NATURE OF LATTICE EXPANSION AND ITS RELATION TO HYDRATION IN MONTMORILLONITE AND VERMICULITE

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## ABSTRACT

Expansion of the interlayer space of montmorillonite and vermiculite, brought about by hydration, takes place in steps equivalent to monomolecular layers of water. The extent of expansion, however, for a given number of monomolecular layers depends on the manner of packing of the water molecules.

It is suggested that the manner of packing of the water molecules in montmorillonite changes during the course of hydration from a loose and discontinuous one, at low states of hydration, to a compact and continuous manner at high states of hydration. It was therefore concluded that it is not necessary to assume interleaving of lattice layers with different degrees of hydration to explain certain variations in interlayer distances.

One of the characteristic properties of the crystal lattices of vermiculite, montmorillonite, and related clay minerals is the ability to expand or contract along the  $c$  axis upon hydration or dehydration. The manner of expansion has been studied by means of  $x$ -ray measurements of materials at various degrees of hydration.

## STUDIES WITH MONTMORILLONITE

Hendricks and Jefferson (5) have concluded that expansion of the montmorillonite lattice by hydration takes place in monomolecular layers of water and suggested that certain observed ( $d001$ ) spacings which deviate from that caused by the absorption of a monomolecular layer of water may be accounted for by interleaving of lattices having different degrees of expansion—a condition quite possible at certain states of hydration. This view is also supported by Mering (9).

It is not always necessary, however, to assume interleaving to explain the observed variations in ( $d001$ ) spacing. These variations may be explained by the manner of packing of the water molecules in the interlayer space.

An evaluation of the interlayer expansion due to differences in packing of the water molecules yields the following results: If the centers of the oxygens of the water molecules are vertically above and below the centers of the oxygens of the lattice, the expansion of the layers would be the maximum that could be caused by the absorption of the water molecule, namely, 2.76 Å. (2), but if the water molecules form tetrahedra with the bases of the linked silica tetrahedra of the lattice—as indicated in Fig. 1 by  $a, b, c, d, e, f$ —the expansion of the layers will only be 1.78 Å.

The thickness of the expanded unit cells—equivalent to the ( $d001$ ) spacing—may be calculated by adding the thickness of a single mica sheet—i.e., of the four layers of oxygens which form the sheet—and the calculated expansion for one, two, or three monomolecular layers of water. The thickness of a single mica sheet for the present discussion will be taken to equal about  $10.16 \text{ \AA}$ .

The thickness, therefore, of a unit cell containing one monomolecular layer of water may be either (a)  $10.16 \text{ \AA} + 2.76 \text{ \AA} = 12.92 \text{ \AA}$  or (b)  $10.16 \text{ \AA} + 1.78 \text{ \AA} = 11.94 \text{ \AA}$ .

The interlayer spacing when two monomolecular layers of water are present will depend not only on the manner of superimposition of the

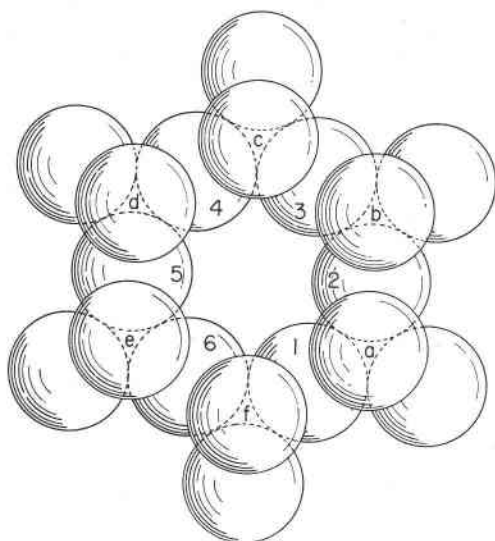


FIG. 1. Possible arrangement of water molecules in the interlayer space of montmorillonite and vermiculite.

water molecules on the oxygen sheets of the lattice but also on the manner of superimposition of one monomolecular layer of water on the other. Such consideration leads to at least three thicknesses: namely,

- (a) When the water molecules form tetrahedra at the water-oxygen interface and octahedra at the water-water interface; such an arrangement would give a thickness of

$$10.16 \text{ \AA} + 1.78 \text{ \AA} + 2.09 \text{ \AA} = 14.03 \text{ \AA}$$

- (b) When the water molecules form tetrahedra at the water-oxygen interface but are vertically above each other at the water-water interface; such an arrangement would lead to a thickness of

$$10.16 \text{ \AA} + 1.78 \text{ \AA} + 2.76 \text{ \AA} = 14.70 \text{ \AA}.$$

- (c) When the water molecules are vertically above and below the oxygens of the lattice at the water-oxygen interface and are also vertically above each other at the water-water interface; such an arrangement would give a thickness of

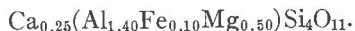
$$10.16 \text{ \AA} + 2.76 \text{ \AA} + 2.76 \text{ \AA} = 15.68 \text{ \AA}.$$

Similarly three thicknesses for the unit cell may be calculated when three monomolecular layers of water are present: namely, (a) 16.12, (b) 17.46, and (c) 18.44.

For a clearer understanding of the nature of the expansion of montmorillonite in water it is necessary to compare the relation between the expansion and the degree of hydration which may exist and those which were actually observed.

The degree of hydration in terms of per cent water per 100 grams of either ignited material or material which contains only crystal lattice  $\text{OH}^-$  ions, was calculated for a Ca saturated montmorillonite containing one or more monomolecular layers of water.

The chemical formula for a dehydrated half unit cell used in the calculation was obtained from the chemical composition and is as follows:



The calculations were carried out for the following moisture conditions:

- (1) Only crystal lattice water present ( $\text{OH}^-$  ions), namely, 1  $\text{H}_2\text{O}$  per half unit cell.
- (2) Enough water molecules to fill each hexagonal cavity in the oxygen rings of the linked silica tetrahedra not occupied by an exchangeable ion. The total number of water molecules for half unit cell for this condition is equal to 1.75. Since no water molecules in the form of a layer were assumed to be present, the lattice would remain contracted.
- (3) Enough water molecules for conditions (1) and (2), namely, 2.75.
- (4) One layer of water molecules:
  - (a) Water molecules organized into hexagonal rings in the same manner as the oxygens at the vertices of the silica tetrahedra (Fig. 1—*a, b, c, d, e, f*). The number of water molecules in such a layer per half unit cell would be 2.
  - (b) Water molecules arranged in hexagonal rings in the same manner as the oxygens of the bases of the linked silica tetrahedra (Fig. 1—1, 2, 3, 4, 5, 6). The number of water molecules in such a layer per half unit cell would be 3.

TABLE 1. CALCULATED PER CENT WATER CONTENTS AND ( $d001$ ) BASAL SPACINGS FOR A CA-SATURATED MONTMORILLONITE WITH 0, 1, 2, OR 3 MONOMOLECULAR LAYERS OF WATER

| Column No.   | 1       | 2    | 3     | 4     | (4+3) | 5     | (5+3) | 6     | (6+3) | 7     | (7+3) | 8     | (8+3) | 9     | (9+3) | 10    | (10+3) | 11    | (11+3) |
|--|---------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|--------|
| Number of monomolecular layers of water                                      | none    |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |        |       |        |
| Possible ( $d001$ ) basal spacings   | 10.16 Å |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |        |       |        |
| Number of H <sub>2</sub> O molecules per half unit cell (11.0 <sup>+</sup> ) | 1       | 1.75 | 2.75  | 2     | 4.75  | 3     | 5.75  | 4     | 6.75  | 4     | 6.75  | 6     | 8.75  | 8     | 10.75 | 9     | 11.75  | 12    | 14.75  |
| Per cent water content on ignited material                                   | 5.08    | 8.89 | 13.97 | 10.16 | 24.13 | 15.24 | 29.21 | 20.32 | 34.29 | 20.32 | 34.29 | 30.48 | 44.45 | 40.64 | 54.61 | 45.72 | 59.69  | 60.96 | 74.93  |
| Number of H <sub>2</sub> O molecules per half unit cell (12.0 <sup>+</sup> ) | 1       | 1.75 | 1.75  | 2     | 3.75  | 3     | 4.75  | 4     | 5.75  | 4     | 5.75  | 6     | 7.75  | 8     | 9.75  | 9     | 10.75  | 12    | 13.75  |
| Per cent water content on material containing OH <sup>-</sup> ions           | 4.84    | 8.47 | 8.47  | 9.68  | 18.15 | 14.52 | 22.99 | 19.36 | 27.83 | 19.36 | 27.83 | 29.04 | 37.51 | 38.72 | 47.19 | 43.56 | 52.03  | 58.08 | 66.55  |

- (c) Water molecules arranged in hexagonal rings as in (b) with an additional water molecule in the center of each ring making a total of 4 water molecules per half unit cell.
- (5) Two monomolecular layers of water:
- (a) With 2 molecules per layer or 4 per half unit cell.
- (b) With 3 molecules per layer or 6 per half unit cell.
- (c) With 4 molecules per layer or 8 per half unit cell.
- (6) Three monomolecular layers of water:
- (a) With 3 molecules per layer or 9 per half unit cell.
- (b) With 4 molecules per layer or a total of 12 water molecules per half unit cell.

The results of calculation on the basis of the foregoing assumptions are given in Table 1. These results indicate that (1) a considerable amount of water may be present even in a contracted lattice, and (2) the amount of water present for any one degree of expansion is not necessarily a constant quantity but depends on the manner of the organization of the water layer.

The results obtained by several investigators (3, 6, 7, 8, 10), on the relation between hydration and expansion of montmorillonite are summarized in Table 2.

A comparison between the data in Tables 1 and 2 reveals the following:

- (1) Expansion equivalent to one or two monomolecular layers of water

TABLE 2. A SUMMARY OF DATA CONCERNING THE RELATION BETWEEN HYDRATION AND EXPANSION IN Ca OR Ca AND Mg SATURATED MONTMORILLONITES

| Hofman and Bilke (7)               |                      | Maegdefrau and Hofmann (8)         |                      | Nagelschmidt (10)                  |                      | Bradley, Grim and Clark (3)        |                      | Hendricks, Nelson and Alexander (6)          |                      |
|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|--|----------------------|
| H <sub>2</sub> O on ignition bases | (d001) basal spacing | H <sub>2</sub> O on ignition bases | (d001) basal spacing | H <sub>2</sub> O on ignition bases | (d001) basal spacing | H <sub>2</sub> O on ignition bases | (d001) basal spacing | H <sub>2</sub> O on material with OH water % | (d001) basal spacing |
| %                                  | Å                    | %                                  | Å                    | %                                  | Å                    | %                                  | Å                    | %  | Å                    |
|                                    |                      |                                    |                      | 6.0                                | 10.5                 | 5.0                                | 9.6                  |  |                      |
|                                    |                      |                                    |                      | 8.5                                | 11.6                 |                                    |                      | 3.5  | 12.8                 |
| 10.0                               | 11.25                |                                    |                      | 10.9                               | 12.3                 |                                    |                      | 12.0   | 13.2                 |
| 13.9                               | 12.1                 | 13                                 | 11.88                | 14.8                               | 14.7                 |                                    |                      | 15.0   | 14.4                 |
| 19.5                               | 13.4                 | 20                                 | 13.48                | 19.1                               | 14.8                 | 20.0                               | 12.4                 | 19.0   | 14.6                 |
| 24.2                               | 14.6                 |                                    |                      | 25.0                               | 15.2                 |                                    |                      | 26.0   | 14.8                 |
| 29.5                               | 15.1                 | 29                                 | 15.15                | 30.6                               | 15.2                 |                                    |                      | 32.0   | 15.4                 |
| 36.3                               | 15.6                 | 37                                 | 15.70                | 35.5                               | —                    | 37.0                               | 15.4                 |  |                      |
| 41.8                               | 15.7                 |                                    |                      | 42.3                               | 15.4                 |                                    |                      |  |                      |
|                                    |                      |                                    |                      | 44.9                               | 15.4                 |                                    |                      | 46.0   | 15.7                 |
| 59.0                               | 17.8                 |                                    |                      | 56.2                               | 15.6                 | 50.0                               | 18.4                 |  |                      |
|                                    |                      | 65                                 | 18.90                | 75.4                               | 18.3                 |                                    |                      |  |                      |
|                                    |                      |                                    |                      | 104.0                              | 18.4                 |                                    |                      |  |                      |

- may take place at moisture contents far less than the amounts required to form continuous water layers arranged in hexagonal rings of even two water molecules (Fig. 1—*a, b, c, d, e, f*) per layer.
- (2) The expansion beyond the equivalent thickness of two monomolecular layers of water does not take place until two continuous monomolecular layers of water are formed consisting of either hexagonal rings with three molecules per layer (3, 6) or layers of closely packed water molecules, i.e., layers of hexagonal rings with water molecules in their centers.
  - (3) The third monomolecular layer also consists of closely packed water molecules.
  - (4) The range in values of the basal spacing, ( $d_{001}$ ), between about 11.8 to 13.0 Å, between 14.0 to 15.7 Å, or between 16.0 to 18.4 Å, may be explained on the manner of packing of the water molecules between the oxygen sheets of the lattice. At low moisture contents apparently the monomolecular layers are discontinuous and the water molecules tend to form tetrahedra with the bases of the linked silica tetrahedra. This type of packing results in the smallest observed expansions. However, as the water content increases the water molecules seem to form more closely packed layers consisting of hexagonal rings similar to the hexagonal rings of the linked silica tetrahedra (Fig. 1—1, 2, 3, 4, 5, 6) and are superimposed on the oxygen rings of the silica tetrahedra in such a manner as to result in the wider spacings.

#### STUDIES WITH VERMICULITE

Recent investigation (1) on the nature of vermiculite has shown that vermiculite is essentially a mica in which Mg, or Mg plus Ca, are the interlayer cations like K in ordinary mica, but having an expanded and hydrated lattice similar to that of montmorillonite. As in montmorillonite Mg and Ca ions exchange readily with other cations in solution. The exchange capacity of vermiculite is about 50 per cent higher than that of montmorillonite.

The contraction or expansion of the vermiculite lattice, whether brought about by base exchange, by heating, or by immersion in water (Table 3), also indicates that it takes place in steps each equivalent to a thickness of one molecular layer of water.

The interlayer spacing of air dried vermiculite lattice was shown to depend on the exchangeable ion. Thus the crystal lattices saturated with K, NH<sub>4</sub>, Rb, or Cs ions are essentially contracted lattices. The lattices saturated with Li, Na, or Ba ions are expanded to a thickness equivalent to a monomolecular layer of water; and those saturated with Mg or Ca

TABLE 3. THE RELATION BETWEEN HYDRATION AND EXPANSION IN VERMICULATE #2 (1)

| Saturating cation | Mg                                   |                                 | Ca                                   |                                 | Na                                   |                                 |
|-------------------|--------------------------------------|---------------------------------|--------------------------------------|---------------------------------|--------------------------------------|---------------------------------|
|                   | H <sub>2</sub> O on ignition bases % | ( <i>d</i> 002) basal spacing Å | H <sub>2</sub> O on ignition bases % | ( <i>d</i> 002) basal spacing Å | H <sub>2</sub> O on ignition bases % | ( <i>d</i> 002) basal spacing Å |
| Air dried         | 27.10                                | 14.33                           | 27.80                                | 15.07                           | 19.51                                | 12.56                           |
| Heated to 150° C. | 10.75                                | 11.77                           | 11.31                                | 11.77                           | 9.36                                 | 10.27                           |
| Heated to 250° C. | 7.38                                 | 10.34                           | 7.89                                 | 10.20                           | 6.77                                 | 10.13                           |
| Heated to 550° C. | 5.83                                 | 10.00                           | 6.20                                 | 10.00                           | 5.87                                 | 10.00                           |
| Heated to 750° C. | 0.00                                 | 9.50                            | 0.00                                 | 9.65                            | 0.00                                 | 9.60                            |
| Immersed in water | >100                                 | 14.47                           | >100                                 | 15.41                           | >100                                 | 14.76                           |

ions are expanded to a thickness equivalent to two monomolecular layers of water (1).

The amount of water found in natural vermiculites, i.e., Mg or Mg plus Ca saturated, is equal to about 4 molecules per half unit cell (1, 4). This amount of water, as was indicated previously, is only sufficient to form two monomolecular layers of water consisting of hexagonal rings similar to the hexagonal rings of oxygens at the vertices of linked silica tetrahedra (Fig. 1—*a, b, c, d, e, f*). The basal spacing (*d*002) found, namely 14.33, tends to confirm this type of organization of the water molecules. For, as was shown previously, such a basal spacing can be obtained only when the water molecules are at the vertex of each linked silica tetrahedron.

The interlayer spacing of vermiculite when immersed in water\* is reported in Table 3. It is seen that the interlayer spacing of the Mg saturated sample remained unchanged, that of the Ca saturated sample changed only slightly, but the interlayer spacing of the Na saturated sample changed very markedly with hydration. The change in the spacing of the Ca vermiculite possibly represents a reorganization of the water molecules from a configuration as indicated by *a, b, c, d, e, f*, of Fig. 1 to a configuration indicated by 1, 2, 3, 4, 5, 6, of Fig. 1. The change in the spacing of the Na vermiculite clearly represents an expansion equivalent to a monomolecular layer of water.

\* To obtain *x*-ray diagrams of material immersed in water, the sealed ends of capillary tubes packed with air dried material were broken off and immersed in water. After the samples became saturated with water by capillarity the two ends of the tube were sealed with De Khotinsky cement to prevent water loss during exposure to *x*-rays.

The manner of contraction of vermiculite upon dehydration (Table 3) clearly shows that the contraction is also in steps equivalent to monomolecular layers of water.\*\* These results also indicate that, as in montmorillonite, the lattice of the Ca or Mg vermiculite remains expanded to a thickness equivalent to a monomolecular layer at moisture contents which are far below the amount of water necessary to form a continuous water layer of even two water molecules per layer in half unit cell. The contraction which takes place between 550° to 700° has been discussed previously (1).

#### INTERLEAVING

One sample of vermiculite studied clearly demonstrates the effect of interleaving of expanded and contracted lattices. This sample consisted of biotite and vermiculite and was first described by Gruner (4) as a "hydrobiotite," from Libby, Montana. Base exchange studies (1) have shown that this sample consisted of 75% biotite and 25% vermiculite and that the vermiculite and biotite are interleaved in the proportion of three biotite sheets to one vermiculite sheet.

According to Hendricks and Jefferson (5) such an interleaved material when exposed to  $x$ -rays should show a basal spacing ( $d_{001}$ ) which is an average of the basal spacing of each material and that the  $x$ -ray line representing the resulting basal spacing should be broad. In the sample studied the average basal spacing should therefore be  $(3 \times 10.45 + 1 \times 15.07) \div 4 = 11.7 \text{ \AA}$  (10.45  $\text{\AA}$  is the biotite basal spacing of this sample and 15.07 is the vermiculite basal spacing) and the reflection should be represented by a broad line. The spacing actually obtained was 11.77  $\text{\AA}$  and the line representing this spacing was about 3 mm. broad. These results therefore substantiate Hendricks and Jefferson's conclusion.

However, interlayer spacing of powdered samples which consist of crystals with varying degrees of expansion are not necessarily average spacings. An average spacing apparently results only if the lattices are interleaved in a regular pattern as was shown to be the case in the "hydrobiotite" from Libby, Montana. If the crystal lattices with different

\*\* The author noted previously (1) that vermiculite rehydrates very rapidly after dehydration even when cooled in a desiccator containing  $\text{CaCl}_2$ . This rapid rehydration was given as the reason for obtaining both expanded and contracted lattices in samples which were heated moderately. It is for the same reason, perhaps, that Gruner (4) was unable to observe any contraction in vermiculites until heated to 700° C.

To overcome rehydration upon cooling and exposure to air while being prepared for  $x$ -ray analysis, the samples were packed in capillary glass tubing in the oven at the heating temperatures, namely 150° C. and 250° C. Samples, however, which were heated at 500° C. were transferred for packing to another oven at 250° C. To prevent rehydration during exposure to  $x$ -ray, the glass tubes were sealed with De Khotinsky cement as soon as filled.



degrees of expansion are separate entities and are merely mixed at random, a basal spacing for each lattice will be observed upon the  $x$ -ray diffraction pattern of the sample. An example of such a mixture was obtained in partially rehydrated vermiculite samples (1). It seems that in these samples the extremely small particles were completely rehydrated but the coarser ones remained dehydrated.

#### EXPANSION OTHER THAN IN MONOMOLECULAR LAYERS OF WATER

Expansion of a lattice other than in steps equivalent to a thickness of monomolecular layers of water was demonstrated by  $\text{NH}_4$ , Rb and Cs vermiculites (1). In these vermiculites the expansion of the lattice is believed to be brought about by the large dimensions of the exchangeable ions which presumably occupy the centers of the hexagonal oxygen rings of the linked silica tetrahedra of one mica sheet and water molecules which occupy similar cavities right across from the exchangeable ions in the opposite mica sheets. Since the diameters of these exchangeable ions are larger than the diameter of the cavities which they occupy, they protrude above the plane of the oxygen sheets of the lattice and this gives a correspondingly wider spacing. The amount of expansion was found to be proportional to the difference in dimension between the size of the ion and the size of the cavity which it occupies.

#### CONCLUSIONS AND SUMMARY

The expansion or contraction parallel to the (001) plane of the crystal lattice of montmorillonite and vermiculite brought about by hydration, dehydration, or by base exchange, seems to take place in steps equivalent to a thickness of monomolecular layers of water. It was suggested that an explanation for the variation of the interlayer space for a given number of monomolecular layers of water may be found in the manner of packing of the water molecules in the interlayer space.

In Ca and Mg montmorillonite and vermiculite expansion equivalent to one or two monomolecular layers takes place at very low states of hydration.

In montmorillonite expansion beyond the equivalent of two monomolecular layers of water apparently does not take place until each of the two layers consists of at least three water molecules per half unit cell and the layers cover the entire interlayer surface. In vermiculite expansion beyond the equivalent of two monomolecular layers of water was never observed to take place even when samples were immersed in water.

The water molecules in montmorillonite at relatively low states of hydration and in natural vermiculite tend to form tetrahedra with the bases of the linked silica tetrahedra of the lattice. This type of packing

gives rise to hexagonal rings of water molecules which are similar to the hexagonal rings of oxygens at the vertices of the linked silica tetrahedra of the individual mica sheets (Fig. 1—*a, b, c, d, e, f*).

At high states of hydration the water molecules in montmorillonite tend to form hexagonal rings of water molecules which are similar to the hexagonal rings of the oxygens at the bases of the linked silica tetrahedra (Fig. 1—1, 2, 3, 4, 5, 6), as suggested by Hendricks and Jefferson (5). At very high states of hydration even the centers of these hexagonal water rings, and the centers of the hexagonal oxygen rings of the linked silica tetrahedra not occupied by exchangeable ions seem to be filled with water molecules. Such monomolecular layers of water consist of closely packed water molecules and bring about the widest possible expansion of the lattice layers.

The interleaving of vermiculite and biotite clearly demonstrates the effect of interleaving of expanded and contracted lattice layers on the (*d*002) basal spacing as measured by *x*-ray diffraction patterns. The basal spacing obtained for such interleaved material supports Hendricks and Jefferson's conclusion (5) that in this case the interlayer spacing is an average with broad *x*-ray lines.

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