Clays and Clay Minerals, 1972, Vol. 20, pp. 109–123. Pergamon Press. Printed in Great Britain

RELATION BETWEEN SWELLING, WATER PROPERTIES AND *b*-DIMENSION IN MONTMORILLONITE–WATER SYSTEMS*

ISRAELA RAVINA† and PHILIP F. LOW
Department of Agronomy, Purdue University, Lafayette, Indiana 47907, U.S.A.

(*Received* 22 *February* 1971)

Abstract—The *b*-dimensions of the unit cells of six different Na-saturated montmorillonites were determined by X-ray diffraction at water contents ranging from 0 to 20 g per g of montmorillonite. In every case, the *b*-dimension increased progressively with water content from its initial value, which was characteristic of each dry montmorillonite, to a final value of ~9·0 Å, which was common to all montmorillonites. The latter value was reached when the water contents of the respective montmorillonites were equal to those at maximal swelling. When these water contents were plotted against the corresponding changes in *b*-dimension, a straight line that passed through the origin was obtained.

Different structure-sensitive properties of the water in montmorillonite–water systems (i.e. the partial specific volume, the amount remaining unfrozen at −5°C and the activation energy required for ions to move through it) were available, as functions of the species of exchangeable cation, from previous studies. Relevant *b*-dimensions were determined in the present study. It was found that all of these water properties were correlated with the *b*-dimension of the associated montmorillonite.

Our results indicate that epitaxy exists between the crystal lattices of montmorillonite and adsorbed water and that these lattices undergo mutual adjustment with each increment of water. The resulting loss of free energy causes water adsorption, i.e. swelling, to occur spontaneously. Swelling stops when no further adjustment takes place. This does not happen until the adsorbed water is several hundred angstroms thick and has achieved a preferred configuration.

INTRODUCTION

THERE is much evidence showing that the properties of water in clay–water systems are different than those of pure bulk water (Low, 1961; Low and White, 1970). The particle surfaces must be partly responsible for this difference because the exchangeable cations alone cannot account for it (e.g. Anderson and Low, 1958; Kolaian and Low, 1963; Davey and Low, 1971). Therefore, it has been assumed that a unique water structure is bonded to and propogated away from the surface oxygens of each particle, probably as suggested by Hendricks and Jefferson (1938), Macey (1942) or Bernal (1957). This assumption requires that there be a relation between the dimensions of the crystal lattice of the clay and its interaction with water. Such a relation has been indicated by recent work. Davidtz and Low (1970) found that the maximal swelling of any Na-saturated dioctahedral montmorillonite was linearly related to the *b*-dimension of its unit cell in the dry state. And Low, Ravina and White (1970) found that this cell dimension increased as the water content of the montmorillonite increased. Evidently, the interaction between montmorillonite and water is strong enough, not only to cause the entry of water between the planar crystal layers, but to modify the structure of these layers as well. These findings are significant as regards the mechanism and depth of clay–water interaction. They also add to our understanding of the important phenomenon of clay swelling. Therefore, we decided to verify and supplement them by additional research.

MATERIALS AND METHODS

The clays used in the present experiments were the Na-saturated montmorillonites prepared by Davidtz and Low (1970). They were suspended in water to make a 2% suspension and then dried on microscope slides covered with flexible plastic to form dry oriented films. Circular disks were cut from the films as needed.

After being weighed, each disk was wetted by lowering it into a drop of deionized water resting on a Mylar film stretched over the bottom of the "window" in a McCreery mount. Since the drop of water was delivered from a micropipette, its vol-

*Journal Paper No. 4348, Purdue University Agricultural Experiment Station.

†Present Address: Soil Science Laboratory, Israel Institute of Technology, Haifa, Israel.

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

ume (and, hence, its weight) was known precisely. To insure that the disk adhered to the Mylar film without wrinkling as it absorbed water, a special technique was used. This was to bring the edge of the disk into contact with the Mylar film near the periphery of the drop and then, using this point of contact as a pivot, slowly lower the rest of the disk into the drop. To prevent evaporation, the top of the "window" was covered with another Mylar film. Both films were sealed to the surfaces of the McCreery mount with rubber cement.

Following an equilibration period of 3–4 days, the swollen disk, still adhering to the Mylar film, was mounted vertically in a General Electric XRD-5 diffractometer so that the flat interface between the disk and Mylar film was flush with the knife edge and the knife edge was perpendicular to the X-rays when $2\theta = 0°$. Thus, when the diffraction peak was being determined, the disk bisected the angle between incident and reflected beams in accordance with the method of Rich (1957). A CuK_α source of X-rays was used and the slit system consisted of a 1° divergence slit, an MR soller slit and a 0·2° detector slit. The (060) reflection, from which the *b*-dimension of the unit cell was calculated, was obtained by scanning manually at least twice at 0·1° intervals between 60·5° and 63·5° (2θ). This procedure was repeated with disks having different water contents. The thickness of the disks varied over a limited range (0– < 2 mm) with water content. However, the characteristic diffraction peaks of powdered quartz (49·9 and 50·5 deg. 2θ), included as an internal standard in some of the disks, did not change with disk thickness. Neither did the (060) reflection of the montmorillonite when the water content was held constant. Therefore, disk thickness had no effect.

Additional disks were cut from the dried film of one Na–montmorillonite (Upton, Wyoming). After being weighed, each disk was lowered into a water drop of known volume in a conventional flat-layer specimen holder, allowed to swell completely, scraped level with the surface of the specimen holder and mounted in the diffractometer so that this surface rested against the knife edge (which was parallel to the X-rays at $2\theta = 0°$). Then the (001) reflection was determined, using a 0·4° divergence slit, by scanning at low angles at the rate of 0·2° (2θ) per min. This procedure was repeated with disks of different water content. Thus, the *c*-axis spacing was determined as a function of water content.

RESULTS AND DISCUSSION

Relation between swelling and b*-dimension*

Davidtz and Low (1970) showed that the free swelling (maximal swelling under no external constraint) of 15 Na-saturated dioctahedral montmorillonites decreased linearly with increasing *b*-dimension. Values of free swelling were obtained from their own experimental work and that of Foster (1955). Corresponding *b*-dimensions were calculated from the respective mineralogical compositions by means of an empirical formula (Radoslovich, 1962). Since measured *b*-dimensions are more reliable than calculated ones, we measured the *b*-dimensions of the air-dried* montmorillonites prepared by Davidtz and Low (1970). Then we plotted the values of free swelling that they measured against the values of *b*-dimension that we measured. The results are shown in Fig. 1. In this and subsequent figures each montmorillonite is identified by the name of its source.

Obviously, a straight line with a negative slope is obtained when free swelling is plotted against the measured *b*-dimension. Except for small differences in the slope and location of the line, this result is the same as that obtained when the calculated *b*-dimension was used (Davidtz and Low, 1970). Now, however, the data points fit the line better. Therefore, the linear relation between free swelling and *b*-dimension is confirmed.

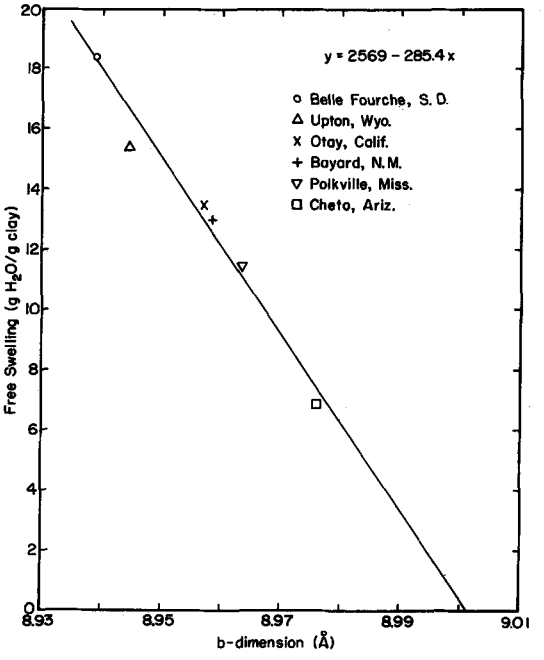


Fig. 1. Relation between free swelling and dry-state *b*-dimension for six Na-saturated dioctahedral montmorillonites.

*Since the relative humidity was about 10%, the water content of the air-dried montmorillonites was approximately 0·08 g/g clay.

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

The cation exchange capacities of the different montmorillonites were: Belle Fourche = 85, Upton = 100, Otay = 52, Bayard = 127, Polkville = 63 and Cheto = 96 meq per 100 g. It is interesting to note from Fig. 1 that, although the cation exchange capacity of the Bayard clay is almost 2·5 times that of the Otay clay, the data points for the two clays lie next to each other on the line passing through them. And the data points for the other montmorillonites of intermediate cation exchange capacities are located on either side. Consequently, it is safe to conclude that free swelling is not related to cation exchange capacity.

The best-fitting straight line in Fig. 1 intercepts the *b*-dimension axis at about 9·001 Å. The true value of the intercept could be slightly higher or lower. Thus, a Na–montmorillonite having a *b*-dimension of ~9·00 Å in the air-dried state should exhibit no swelling. We will refer to this *b*-dimension again later.

The linear relation between free swelling and *b*-dimension cannot be explained by the conventional theory of swelling, i.e. double-layer theory. This fact was discussed in detail by Davidtz and Low (1970). Instead of being related to the osmotic activity of the exchangeable cations, as required by that theory, free swelling is related to the dimensions of the montmorillonite lattice. Hence, a new theory of clay swelling is needed.

A few years ago Leonard and Weed (1967) observed that the *b*-dimension of a dioctahedral vermiculite dried at 25°C was slightly larger than that of the same vermiculite dried at 350°C. Apparently, the crystal lattice of the vermiculite expanded with the adsorption of one or two molecular layers of interlayer water. This observation, and the possibility that it might be due to epitaxy between the crystal lattices of the vermiculite and water, led us to examine the (060) X-ray diffraction peaks for our Na-montmorillonites at different water contents. Presented in Fig. 2 are the results for one of them (Upton, Wyoming). Similar results were obtained for the others.

Figure 2 shows that the location of the (060) diffraction peak shifted to smaller 2θ values with increasing water content. We regard this shift as being due to an increase in the *b*-dimension of the montmorillonite. Hence, our results agree with those of Leonard and Weed (1967). But they do not agree with the results of Nagasawa (1969) for kaolin or with the results of Eirish and Tret'yakova (1970) for montmorillonite. The latter authors reported a decrease in *b*-dimension with hydration. It is probable, however, that none of the results obtained previously can be compared to ours. They were obtained on clays that ranged from oven-dry to air-dry, whereas, our results were obtained on clays that ranged from air-dry to maximally swollen.

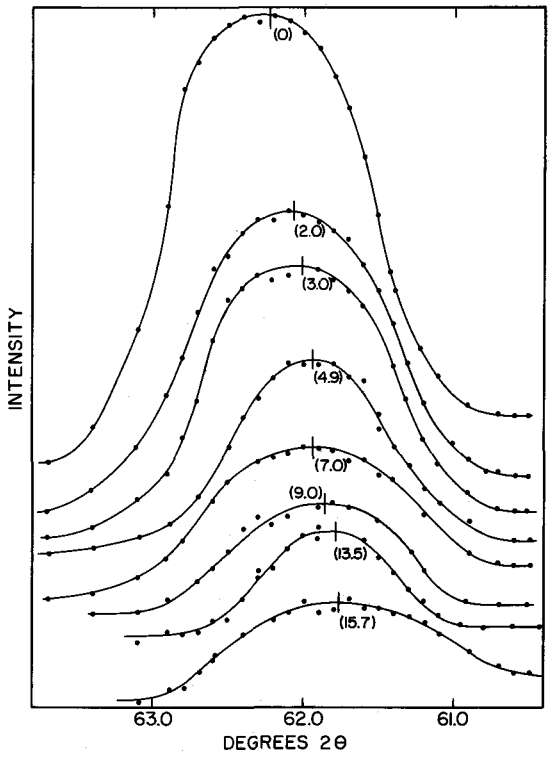


Fig. 2. The (060) X-ray diffraction peaks for Na–montmorillonite (Upton, Wyoming) at different water contents (figures in parenthesis in g/g clay).

Other possible factors* which might have caused the shift in the location of the diffraction peak are: (1) diffractometer geometry, (2) particle size, (3) X-ray absorption, or (4) crystal symmetry. A change in diffractometer geometry would accompany a change in disk thickness. But it is unlikely that this change was responsible. Neither the diffraction peak of montmorillonite at constant water content nor the diffraction peaks of the internal quartz standard shifted with disk thickness. Further, it is unlikely that a change in particle size was responsible. Particle size affects the intensity maxima when the crystallites are small (i.e. of the order of 100 Å) and then the maxima shift to higher values of 2θ with decreasing particle size (Brindley and Robinson, 1948). To account for the observed shift, the montmorillonite particles would have had to increase in size with increasing water content. There is no reason to expect that this would be the case. In fact, a decrease in particle size is more

*S. W. Bailey, private communication.

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

likely. X-ray absorption can also be excluded as the causative factor. Since the X-rays were transmitted through each disk, and since each disk was flat, of uniform thickness and homogeneous in composition, a change in water content would have affected the intensity of the diffraction peak but not its profile or position. However, the crystal symmetry may have changed with water content. When hexagonal symmetry obtains, $b = \sqrt{3}a$ and the diffraction peak in question is a combination of three superimposed reflections (Brindley, 1961). With departure from hexagonal symmetry, a partial resolution of the reflections takes place. Unfortunately, the diffraction peaks in Fig. 2, and the corresponding ones for the other montmorillonites, were not sufficiently well-defined at the higher water contents to ascertain whether or not such a resolution occurred. In any event, a change in crystal symmetry is consistent with a change in b-dimension and would not alter the explanation which we shall propose later.

In order to improve the sharpness of the (060) diffraction peak and to further test the effect of water content on its location, additional experiments were conducted, using improved diffraction equipment and techniques, on the Na–montmorillonite from Upton, Wyoming. The results of these experiments, which are currently being prepared for publication, substantiate those presented here. Diffraction peaks of much greater sharpness and intensity were obtained and they moved to lower values of 2θ with increasing water content. Further, they showed no evidence of being resolved into two or more component peaks.

Figure 3 presents curves of b-dimension versus water content for the different montmorillonites. From the figure it can be observed that: (1) the b-dimension of each montmorillonite changed continuously with water content until a final b-dimension was reached; (2) the final b-dimension was the same for all montmorillonites; (3) within experimental error, this b-dimension had the same value (~9·0 Å) as the intercept in Fig. 1; (4) the water content at which the final b-dimension was reached was different for each montmorillonite and approximated that at free swelling (see Fig. 1); (5) the curves moved upward as free swelling decreased; and (6) the curves exhibited a plateau in a specific range of water contents. These observations will be explained later.

There is an apparent inconsistency between the data in Fig. 1 and those in Fig. 3. One can ask how the amount of water in a fully swollen montmorillonite can be linearly related to the b-dimension it had before it started to swell when this dimension changes with swelling. The apparent inconsistency is resolved if free swelling, s_f, is proportional to

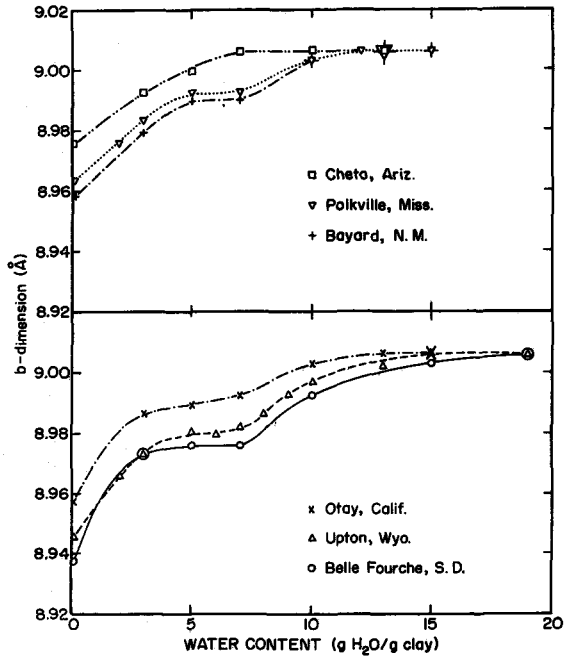


Fig. 3. Relation between b-dimension and water content for six Na-saturated dioctahedral montmorillonites (reproducibility of b-dimension = ±0·001 Å at low water content, ±0·003 at high water content).

the difference between the final b-dimension, b_f, and the initial b-dimension, b_i as follows:

$$S_f = k(b_f - b_i) \qquad (1)$$

where k is a proportionality constant. Then, since all of our montmorillonites had the same final b-dimension, free swelling would be proportional to the initial b-dimension regardless of the change in b-dimension with water content. Proof of equation (1) is provided by the data in Fig. 4. Observe from this figure that the best-fitting line goes through the origin. Clearly, free swelling is not only proportional to the initial b-dimension, it is also proportional to the change in b-dimension.

The data presented thus far indicate that dioctahedral Na–montmorillonites will swell until they reach a final common b-dimension. Then they will stop swelling. If they have this b-dimension to begin with, they will not swell at all. And their swelling is proportional to the change in b-dimension regardless of exchange capacity. The b-dimension appears, therefore, to be the significant factor.

The b-dimension of a dry montmorillonite is governed primarily by its mineralogical composition. This is evinced by the linear relation that exists between b-dimension and the amount of

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

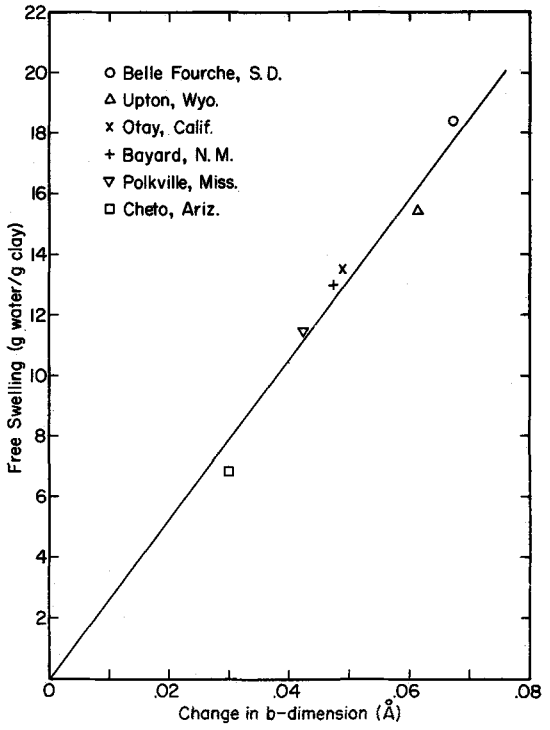


Fig. 4. Relation between free swelling and total change in *b*-dimension for six Na-saturated dioctahedral montmorillonites.

ionic substitution in octahedral and tetrahedral sites within the crystal (Radoslovich, 1962). But the mineralogical composition is supposed to remain constant during swelling. Therefore, the observed increase in *b*-dimension must derive from changes in bond angles and/or bond lengths. These changes affect the lattice energy. They cannot occur without the action of external forces. Let us consider what these forces may be.

Conceivably, forces emanating from exchangeable cations, adjacent crystal layers or water molecules could alter the *b*-dimension of the unit cell of a montmorillonite crystal. That the exchangeable cations exert a perturbing influence was shown by Leonard and Weed (1967). They found that the *b*-dimension of a dry vermiculite increased with the crystallographic radius of the exchangeable cation. As will be shown later, we also found that the exchangeable cation influences the *b*-dimension. Hence, it is reasonable to believe that, as the exchangeable cations dissociate from the crystal surface during swelling, electrical stresses produced by these cations are relieved and, as a result, the *b*-dimension increases. But cation dissociation cannot account for the constancy of the final *b*-dimension. It is improbable that the fractions of exchangeable cations dissociating from montmorillonites of greatly different exchange capacities would always reach values such that the remaining stresses would constrain the *b*-dimension of each of them to ~9·0 Å. And it cannot be assumed that the interionic forces within the crystal allow the *b*-dimension to extend to ~9·0 Å but no farther. These forces, being influenced by isomorphous substitution, would not be the same for each mineral. Therefore, forces emanating from exchangeable cations must not be the only ones involved.

Since the magnitude of the force exerted by one planar crystal layer on another depends on the interlayer distance, it is important to know how this distance varies with water content. Therefore, we determined the *c*-axis spacing of one of our Na–montmorillonites (Upton, Wyoming) at different water contents. The results are plotted in Fig. 5. Also plotted are the results of Foster, Savins and Waite (1955). The two sets of results are consistent and show the expected linear relation between *c*-axis spacing and water content. We assume that this relation is valid for all of our montmorillonites.

Interlayer forces cannot explain the increase in *b*-dimension with increasing water content, i.e.

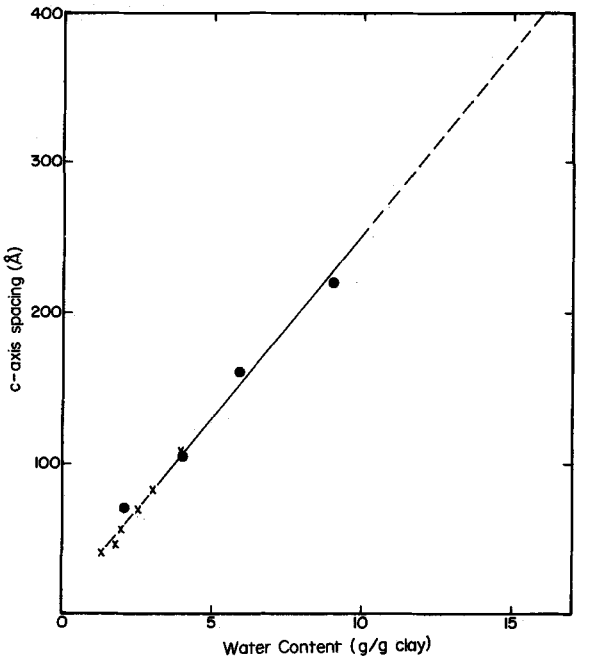


Fig. 5. Relation between *c*-axis spacing and water content for Na–montmorillonite (Upton, Wyoming). ●—data of present study; ×—data of Foster, Savins and Waite (1955).

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

interlayer distance. Electrostatic forces between the layers can be discounted because they depend on the charge density of the layer surfaces and, consequently, on the cation exchange capacity and fraction of exchangeable Na^+ that dissociates. The van der Waals' force can also be discounted. It varies inversely with either the third or fourth power of the interlayer distance, depending on whether it is normal or retarded (Tabor and Winterton, 1968). There is no obvious reason why, at maximal swelling, interlayer distances would always be such that the interplay of crystal-lattice and van der Waals' forces would produce a *b*-dimension of ~9·0 Å. Further, since the van der Waals' force varies monotonically with interlayer distance, and since interlayer distance is a linear function of water content, this force cannot account for the plateaus in the curves of Fig. 3.

From what has been said it is evident that neither forces emanating from exchangeable cations nor from adjacent crystal layers would be expected to impose a maximal *b*-dimension of ~9·0 Å upon the crystal lattice of montmorillonite. However, this *b*-dimension could be imposed by the water. If epitaxy exists between the crystal lattices of montmorillonite and water, it is conceivable that, in every montmorillonite-water system at maximal swelling, water assumes the same preferred configuration and constrains the montmorillonite to conform. Let us see, therefore, if epitaxy is possible.

Pseudomorphism between water and montmorillonite

Epitaxy is the oriented growth of one crystalline substance on a substrate of a different crystalline substance. It has been shown to extend to more than 1000 Å from the substrate surface (e.g. Pashley, 1965; Poh and Anderson, 1969; Bahl and Sharma, 1970) and even through intervening amorphous or polycrystalline films of appreciable thickness (Distler and Shenyavskaya, 1969; Distler and Obronov, 1969; Barna, Barna and Pocza, 1969; Henning, 1970; Distler and Obronov, 1971). A kind of epitaxy of special interest here is *surface pseudomorphism* which, in reference to thin deposits or overgrowths, is often called *pseudomorphism*. It is defined as the straining of an overgrowth structure to match a substrate structure (Chopra, 1969). The strained new structure may be called a *pseudomorph*. According to theory (van der Merwe, 1964; Jesser, 1969) the overgrowth structure is strained to match exactly the substrate structure up to a critical thickness which may exceed several hundred Å. This critical thickness depends on the misfit between the overgrowth and substrate structures, the strength of the bonds between them and their elastic properties. It is notable that, if the substrate itself is a thin crystal, the two structures may be strained toward each other (Kuntze, Chambers and Prutton, 1969). Thus, by such structural adjustments, there is a reduction in the interfacial energy which, in systems with a large surface to volume ratio, is an important component of the total energy. The existence of long-range pseudomorphism has been well established experimentally (e.g. Matthews, 1966; Matthews and Jesser, 1967; Chopra, 1969; Kuntze, Chambers and Prutton, 1969; Heavens, 1970).

For epitaxy or, more specifically, pseudomorphism to occur between water and montmorillonite, one requirement is that the misfit between their structures be small. Before considering whether or not this requirement is satisfied, let us consider what is meant by the term "structure" as it applies to water.

In a molecular crystal, the molecules oscillate about mean positions and the array of mean positions constitutes a structure having long-range order. The molecules also undergo rotational and translational displacements which are much less frequent than the oscillations. Since changes in structure take place by molecular displacements, the stability of the structure depends on the frequency of these displacements, which increases as the number and/or strength of the intermolecular bonds decreases. In ice at 0°C, there are $\sim 0{\cdot}5 \times 10^{13}$ oscillations (hindered translational mode) and $\sim 10^5$ displacements per sec. In liquid water at 0°C, the corresponding numbers are slightly greater than $0{\cdot}5 \times 10^{13}$ and $\sim 10^{11}$ per sec, respectively (Eisenberg and Kautzmann, 1969). It is this difference in the frequency of displacement that causes the change of phase.

At the critical temperature, water behaves as an unbonded structureless fluid and the frequency of displacement approaches that of oscillation. Assuming that the two frequencies are approximately equal in the absence of structure at any temperature, the difference between them can be used as a criterion of the amount of structure. By this criterion, as well as others, pure liquid water can be regarded as having some structure. Its structure is supposed to resemble that of ice I or have ice-I-like components in it (Davis and Litovitz, 1965; Kamb, 1968; Narten and Levy, 1969; Frank, 1970).

Now, let us compare the crystal structures of ice I and montmorillonite. The structure of the former, which is the stable crystalline state of water at below-freezing temperatures and atmospheric pressure, is diagrammed partly in Fig. 6(a). Note that the water molecules in this structure form puckered

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

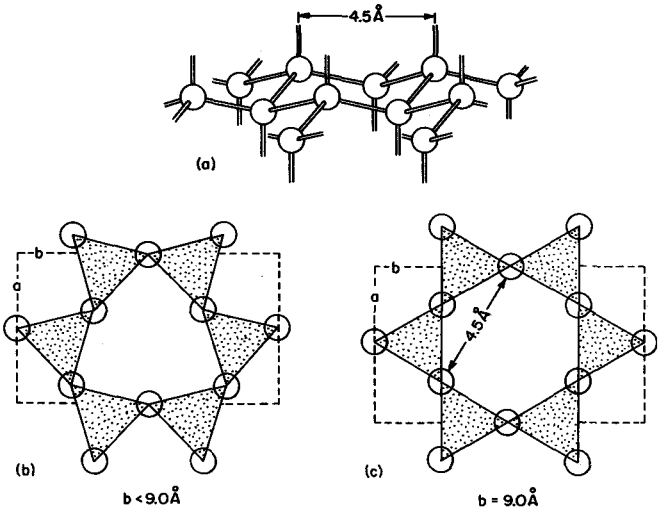


Fig. 6. (a) Diagram of the arrangement of water molecules (open circles) in ice I, (b) ditrigonal symmetry of the surface of a dry montmorillonite (○—oxygen atoms), (c) regular hexagonal symmetry of the surface of idealized montmorillonite (○—oxygen atoms).

hexagons containing three molecules in one plane and three others in a closely adjacent plane. The distance between water molecules in either plane is 4·5 Å.

An unconstrained sheet of silica tetrahedra has regular symmetry. Therefore the following equations apply to it.

$$b_{\text{tetra}} = 6r \sin \tau = 2t \qquad (2)$$

where b_{tetra} is the b-dimension of the unit cell, r is the Si–O bond length, τ is the O_{apex}–Si–O_{basal} angle and t is the distance between next-nearest oxygens in the basal plane. The value of r is given (Radoslovich and Norrish, 1962) by:

$$r = \left(1{\cdot}60 + \frac{0{\cdot}18}{4}x\right) \qquad (3)$$

where x is the number of Al atoms proxying for Si in four tetrahedral sites. This sheet is usually larger than the sheet of alumina octahedra in dioctrahedral montmorillonites. In order for the two sheets to interconnect, the misfit between them is eliminated by the alternate clockwise and counterclockwise rotation of the silica tetrahedra about their vertical axes. The angle of rotation, α, can be calculated by means of the following equation (Radoslovich and Norrish, 1962; Bailey, 1966):

$$\cos \alpha = b_{\text{obs}}/b_{\text{tetra}} \qquad (4)$$

where b_{obs} is the observed b-dimension of the unit cell of the montmorillonite. This equation is based on the assumption that the silica tetrahedra are approximately regular and that the tetrahedral sheet changes dimensions by simple tetrahedral rotation. Equations (2–4), and the assumption that τ was the regular tetrahedral angle (109° 28′), were used to obtain the values of α in Table 1. Evidently, all of the *dry* montmorillonites had ditrigonal symmetry similar to that depicted in Fig. 6(b).

The crystal structures of ice I (or structurally similar water) and montmorillonite would match exactly, i.e. the three coplanar water molecules in the puckered hexagon of the former would coincide with the next-nearest oxygens in the planar surface of the latter, if the structure of montmorillonite had regular hexagonal symmetry ($\alpha = 0$) and a b-dimension of 9·0 Å as illustrated in Fig. 6(c). This fact was first noted by Macey (1942). Now, the values of α and b-dimension listed in Table 1 differ only slightly from 0° and 9·0 Å, respectively. Also, calculations show that the corresponding distances between next-nearest surface oxygens differ from 4·5 Å by less than 10%. Therefore, the misfit between the two structures is small.

Observe from Table 1 that the values of α were smaller for the maximally swollen montmorillonites than for the dry ones. Also the former had b-dimensions that were closer to 9·0 Å. This means that swelling caused the crystal symmetry to become more nearly hexagonal. But the reported

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

Table 1. The effect of the number, x, of Al atoms in four tetrahedral sites on the angle of rotation, α, of the silica tetrahedra in dry and maximally swollen Na-montmorillonites

Origin of montmorillonite	x	b-Dimension Dry (Å)	b-Dimension Swollen (Å)	α Dry (deg)	α Swollen (deg)
Belle Fourche, S.D.	0·16	8·939	9·006	10·55	7·90
Upton, Wyom.	0·09	8·944	9·006	9·70	7·02
Otay, Calif.	0·02	8·957	9·006	8·50	6·02
Bayard, N.M.	0·00	8·959	9·006	8·18	5·73
Polkville, Miss.	0·07	8·964	9·006	8·77	6·78
Cheto, Ariz.	0·09	8·976	9·006	8·60	7·02

values of α depend on the assumptions underlying equation (4). It is possible that, besides rotating, the silica tetrahedra changed dimension as well. Certainly, the octahedra changed dimensions as swelling progressed; and there is no reason to believe that the tetrahedra would not do likewise. For the achievement of regular hexagonal symmetry at maximal swelling, as illustrated in Fig. 6(c), only minor adjustments would have been necessary. For example, equation (2) indicates that, in the maximally swollen montmorillonite from Upton, Wyoming, r would have had to be 1·591 Å if τ retained the value of 109°28′. Or τ would have had to be 110°45′ if r retained the value of 1·604 Å, given by equation (3). Since less energy would be required to change τ, this change is more probable. In any event, it is evident that the misfit between the lattices of ice I (or water) and montmorillonite is smaller when the latter is maximally swollen than when it is dry.

As noted earlier, the extent of pseudomorphism depends on the initial misfit between the overgrowth and substrate, the strength of the bonds between them, and their elastic properties. We have just shown that the misfit between the structures of water and montmorillonite is small. And others (Fripiat, Chaussidon and Touillaux, 1960; Farmer and Russell, 1967; Leonard, 1970; Farmer and Russell, 1971) have shown that water molecules form hydrogen bonds with oxygen atoms in the montmorillonite surface. Although some of these bonds appear to be weak, others may be strong (van der Marel, 1966; Low and White, 1970). Therefore, at least two factors favor pseudomorphism. The critical question is whether or not the interlayer water has sufficient long-range order and stability to be regarded as an elastic crystal, however weak. The data in Table 2 are pertinent to this question. The dielectric relaxion times reported there are the times required for the decay of macroscopic polarization when the applied field is removed and, as such, approximate the times required for molecular displacement. They were calculated by means of the following equations from Eisenberg and Kauzmann (1969)

$$\lambda^2/\tau_d = D = CkT/\eta \quad . \qquad (5)$$

where λ is the mean length of a diffusive jump in the direction of diffusion (=1·5 Å), τ_d is the dielectric relaxation time, D is the self-diffusion coefficient, C is a constant, k is the Boltzmann constant, T is the absolute temperature and η is the viscosity.

The values of τ_d show clearly that the interlayer water in clay minerals has a more stable structure than bulk water. However, there is a discrepancy between the values calculated from the data obtained by NMR (Wu, 1964; Graham, Walker and West, 1964) and the values calculated from the data obtained by neutron spectroscopy (Hunter, Stirling and White, 1971) or isotopic diffusion (Kemper, Maasland and Porter, 1964; Dutt and Low, 1962; Low, 1968). The former are closer to the values of ice than of bulk water, whereas, the latter are only slightly different from those of bulk water. Which are the more representative of the structural state of the water is not known.

There are additional data that relate to the order and stability of interlayer water. Miller and Low (1963) found that the water in Na-montmorillonite (water content = 0·8 g/g clay) had some elasticity because it did not flow until a finite pressure gradient was exceeded. Further, in the two layer hydrate of Mg-vermiculite, the residence times of the water molecules are long enough for them to be located by X-ray diffraction. In keeping with the concept of pseudomorphism, it was found (Shirozu and Bailey, 1966) that the water triads enclosing the Mg^{2+} are rotated towards the triads of surface oxygens so that normal hydrogen-bond lengths are maintained. The situation may be similar in the three-layer hydrate of Na-montmorillonite because the interlayer water molecules are organized with respect to the a and b-axes (Mering and

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

Table 2. Self-diffusion coefficient (D), viscosity (η) and dielectric relaxation time (τ_d) of interlayer water in clay minerals at 25°C

Clay mineral	Water content (g/g clay)	D ($cm^2/sec \times 10^5$)	η (poises)	τ_d (sec)	Ref.
Na–montmorillonite	0·4		330	$3·2 \times 10^{-7}$	Wu (1964)
	1·0		110	$1·0 \times 10^{-7}$	
Na–montmorillonite, etc.	>1·2		<600	$<5·9 \times 10^{-7}$	Graham *et al.* (1964)
Li–vermiculite	0·21	0·2		$1·1 \times 10^{-10}$	Hunter *et al.*
	2·77	2·4		$1·0 \times 10^{-11}$	(1971)
Na–montmorillonite	~0·25	0·72		$3·1 \times 10^{-11}$	Kemper *et al.*
	~3·6	1·68		$1·3 \times 10^{-11}$	(1964)
Na–montmorillonite	2·2		0·0182	$1·8 \times 10^{-11}$	Low (1968)
	3·8		0·0162	$1·6 \times 10^{-11}$	
Na–montmorillonite	2·3		0·0130*	$1·3 \times 10^{-11}$	Dutt and Low (1962)
Pure water		2·4	0·0089	$0·9 \times 10^{-11}$	Eisenberg and Kauzmann (1969)

*Calculated by equations presented by Low (1968).

Brindley, 1967). In addition, the data obtained by infrared spectroscopy indicate that the hydrogen bonds between some of these water molecules are elongated (Russell and Farmer, 1964; Jorgensen, 1968; Farmer and Russell, 1971). This would be expected if the water structure were strained to match a montmorillonite structure having the ditrigonal symmetry illustrated in Fig. 6(b).

Figure 3 indicates that the montmorillonite structure expands laterally with each increment of water. For pseudomorphism to occur, a concomitant adjustment must take place in the water structure. This adjustment need not be by lateral expansion alone. A higher-order structural change is also possible. That water molecules can form many different hydrogen-bonded structures is evident from the literature (e.g. Pauling, 1959; Kamb, 1968; Eisenberg and Kauzmann, 1969; Kamb, 1971).

Relation between water properties and b*-dimension.*

If pseudomorphism between water and montmorillonite does exist, there should be some relation between the structure-sensitive properties of the former and the b-dimension of the latter. That such a relation obtains is shown in Fig. 7. The b-dimensions reported in this figure were determined by X-ray analysis of the dry homoionic montmorillonites remaining from the study of Anderson and Low (1958); the activation energies for exchangeable ion movement are included because they are supposed to equal the energies required to displace water molecules in the respective water structures (Low, 1962). Hence, they are criteria of the integrity of these structures. The use of the dry-state b-dimensions is appropriate here because the three water properties were measured at relatively low water contents.

It appears that the different cations enhance the b-dimension in the relative order K > Li > Na. This order is not related directly to the radii of these ions. However, it is the order in which they are fixed or rendered less exchangeable in montmorillonite on drying (Tabikh, Barshad and Overstreet, 1960). Evidently, the effect of the exchangeable cations on the b-dimension depends on the degree to which drying causes them to become coordinated with or implicated in the crystal structure.

The available literature (e.g. Gurney, 1953; Robinson and Stokes, 1959; Kavanau, 1964) indicates that, in general, the alkali metal cations affect the properties of bulk water in the order Li > Na > K, or *vice versa*. This is not the order observed in Fig. 7. Therefore, these cations must affect the water indirectly when they are adsorbed on montmorillonite surfaces. Note that the three water properties in the different montmorillonite–water systems are directly related to each other but are inversely related to the b-dimension of the dry montmorillonite. Also, recall that free swelling was inversely related to this b-dimension. Therefore, it is reasonable to conclude that the exchangeable cations, like those proxying for Si and Al in tetrahedral and octahedral sites, affect the configuration of the montmorillonite lattice and it, in turn,

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

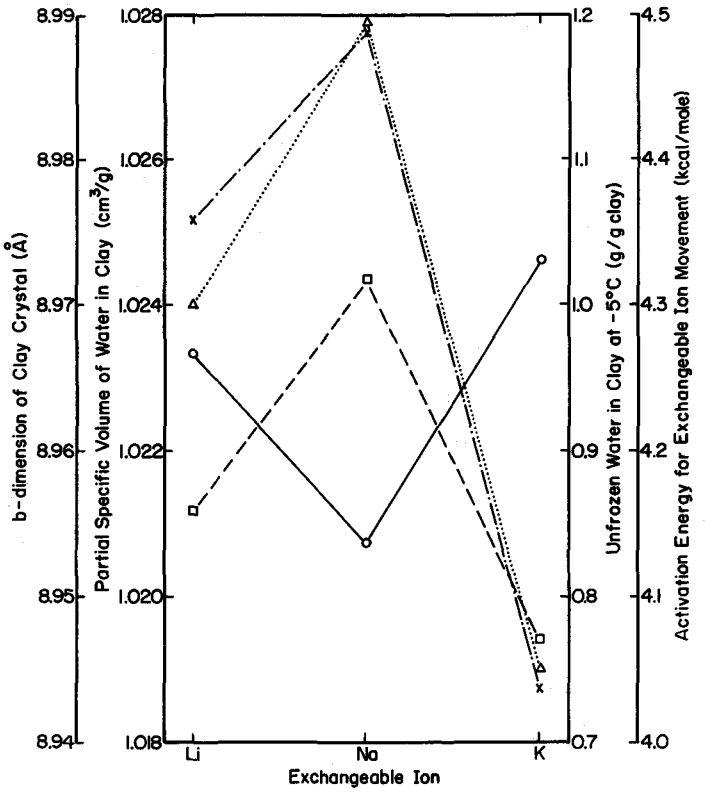


Fig. 7. The effect of the exchangeable cation on the *b*-dimension of Na-montmorillonite (Upton, Wyoming) in the dry state and on the partial specific volume of water, the amount of water remaining unfrozen at −5°C and the activation energy for ion transfer in aqueous systems of the same clay. ○—*b*-dimension of montmorillonite (present study); △—partial specific volume of water at a water content of 1·2 g/g clay (calculated from data of Anderson and Low, 1958); ⊡—unfrozen water at −5° (Kolian and Low, 1963); ×—activation energy for exchangeable ion movement at a water content of 1·5 g/g clay (Low, 1958).

affects the structure and properties of the expitaxial water. Of course, the cations may also exert a direct effect, e.g. by producing local defects in the water structure. But this effect appears to be of secondary importance.

Thermodynamic analysis

We have shown that the crystal structure of montmorillonite adjusts as interlayer water is adsorbed. Probably, the crystal structure of the water undergoes a simultaneous adjustment. Let us see how these adjustments relate to swelling. Figure 8 presents the relation between ΔF, the change in free energy, and n, the number of grams of water transferred from pure bulk water to 1 g of air-dried Na–montmorillonite (Upton, Wyoming). The data in this figure were calculated from relevant experimental data reported by Oster (1962); Low, Anderson and Hoekstra (1968); and Kay and Low (1970). According to thermodynamic theory,

$$[\partial(\Delta F)/\partial n] = (\bar{f} - \bar{f}^0) = -\bar{v}\pi \qquad (6)$$

where $\bar{f}$ and $\bar{v}$ are the partial specific free energy and partial specific volume, respectively, of water in the montmorillonite–water phase after the transfer, π is the swelling pressure of this phase when it is in contact with pure bulk water, and $\bar{f}^0$ is the partial specific free energy of pure bulk water. Note that $(f - f^0)$ equals, and π is proportional to, the slope of the curve in Fig. 8 at any value of n. It has been common to assume that the only factor

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

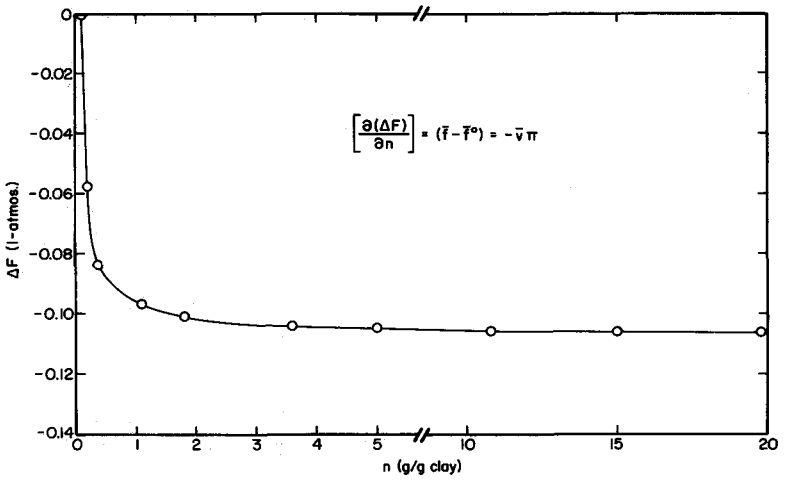


Fig. 8. The relation between ΔF, the change in free energy, and n, the number of grams of water transferred from pure bulk water to 1 g of air-dried Na-montmorillonite (Upton, Wyoming).

contributing to ΔF is the osmotic activity of the exchangeable cations. In other words, the free energy change accompanying the transfer of pure water to montmorillonite and that accompanying the transfer of pure water to a salt solution have been regarded as having the same cause. But now it is evident that, since the dimensions of the crystal lattice of the montmorillonite change on the addition of water, its lattice energy must also change. A similar conclusion is apropos to the water. Thus, both $\bar{f}-\bar{f}^0$ and π are at least partially dependent on changes in lattice dimensions.

Since $\pi = 0$ at free swelling, Fig. 1 can be regarded as a plot of water content vs. b-dimension when $\bar{f}-\bar{f}^0 = 0$. To obtain a similar plot when $\bar{f}-\bar{f}^0$ has another value, we can use the data on unfrozen water and b-dimension in Fig. 7. It can be shown (Low, Anderson and Hoekstra, 1968) that the $\bar{f}-\bar{f}^0$ of water in a montmorillonite–water system at a given *liquid* water content and any above-freezing ambient temperature, T_a, is related to the freezing point depression, θ, of the water at the same *liquid* water content by the equation

$$\bar{f}-\bar{f}^0 = -\frac{T_a l_0 \theta}{T_0^2} \qquad (7)$$

where l_0 is the heat of fusion at T_0, the freezing point of pure water. The necessary conditions for this equation are that $T_a \approx T_0$ and that θ be small. In the experiments on unfrozen water, θ was the same for all three homoionic systems because the unfrozen water was in equilibrium with ice at the same temperature, T_f, in each system ($\theta = T_0 - T_f$). From Fig. 7 we can determine the amounts of unfrozen or *liquid* water in the different systems when $\theta = 5°K$. These would equal the amounts of water the respective systems must contain at T_a if the water in them is to have the $\bar{f}-\bar{f}^0$ calculated by equation (7). When $T_a = 298°K$ and $\theta = 5°K$ the value of $\bar{f}-f^0$ is 1·59 cal/g. Consequently, we can make the plot shown in Fig. 9. For the purpose of comparison, this figure also includes a plot of water content versus b-dimension, for the same b-dimensions, when $\bar{f}-\bar{f}^0 = 0$. The latter plot was obtained by interpolation from Fig. 1.

Observe that both plots are linear even though the b-dimension was controlled in one case by the exchangeable cation and in the other by isomorphous substitution. Evidently, the water content of a montmorillonite–water system at any given value of $\bar{f}-\bar{f}^0$ (and, hence, any given value of π or θ) is a linear function of the b-dimension of the dry montmorillonite. Perhaps, as when $\bar{f}-\bar{f}^0 = 0$, it is also a linear function of the difference between the b-dimension at the given value of $\bar{f}-\bar{f}^0$ and the b-dimension in the dry state. This possibility will be investigated further.

Nature of montmorillonite–water interaction

In view of the evidence presented here, it is proposed that the initial misfit between the montmorillonite and water structures is sufficiently small, the hydrogen-bonding between them is sufficiently strong and their elastic moduli are of such magnitudes that pseudomorphism exists at all montmorillonite–water ratios. At first, when the interlayer water is thin, it is energetically favor-

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

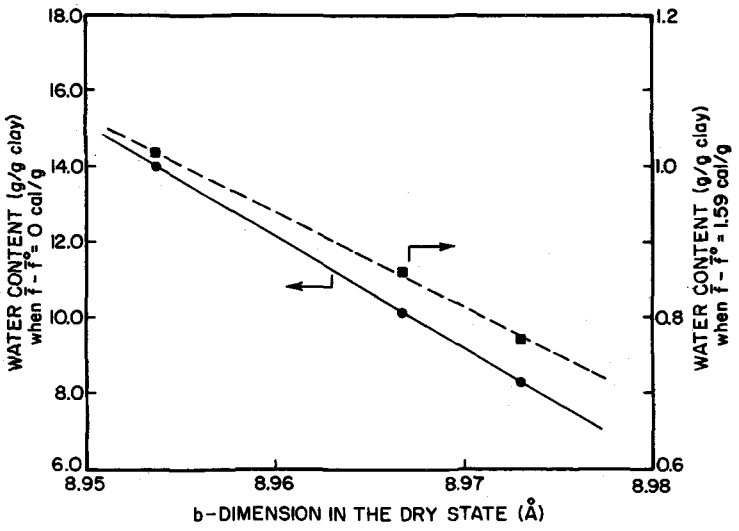


Fig. 9. Relation between the water content of Na–montmorillonite at each of two values of $\bar{f}-\bar{f}^0$, the relative partial specific free energy of the water, and the *b*-dimension of the Na–montmorillonite in the dry state.

able for its structure to conform to that of the montmorillonite. However as the interlayer water increases in thickness, the opposite becomes true. The water structure tends to assume a preferred configuration and the montmorillonite structure adjusts accordingly. This process does not occur at a constant rate because, in certain ranges of water content, the water and/or montmorillonite structure is more stable than in others. In the preferred configuration the water molecules have hexagonal symmetry like that in ice I*. As a result, the surface oxygens are pulled into a more expanded and nearly hexagonal arrangement and the *b*-dimension necessarily increases. Its final value is governed by the preferred configuration of the water and, hence, is the same for all Na–montmorillonites.

Alternatively, it is proposed that the crystal structure of the montmorillonite relaxes with a concomitant increase in *b*-dimension as stresses acting on it are relieved by the addition of water. For example, electrical stresses would be relieved by the enhanced dissociation of exchangeable cations. The crystal lattice of the epitaxial water changes comformably. Relaxation of the crystal lattice of the montmorillonite does not occur at a constant rate for the reasons noted earlier. However, it continues until the energy released thereby is less than the energy required to further alter the crystal structure of the water. This occurs when the latter has reached a preferred configuration. Thus, ultimately, the final *b*-dimension is governed, as before, by the water.

Regardless of which alternative is correct, the structure of the water is supposed to be interlocked with, and stabilized by, that of the montmorillonite. The structure of the latter, especially its surface symmetry, is indicated by its *b*-dimension. Therefore, the structure-sensitive properties of the water are related to the *b*-dimension of the montmorillonite.

Also, regardless of which alternative is valid, it is supposed that a net loss in free energy results from the changes in lattice energy and interstructure bond energy that accompany the mutual adjustment of both structures. Consequently, the montmorillonite absorbs water spontaneously and swells. Swelling stops when no further adjustment takes place, i.e. when the *b*-dimension reaches its final value. Thus swelling is related to the change in *b*-dimension.

The above concepts provide an explanation for the in-depth effect of montmorillonite on the properties of water in montmorillonite–water systems. In addition, they constitute a new theory of the swelling of montmorillonite. How they apply to other clay minerals remains to be seen.

*This arrangement cannot be identical to that of ice I because water will supercool in the presence of montmorillonite particles.

Acknowledgment—The authors wish to acknowledge, with appreciation, the many helpful discussions they had with Dr. Joe L. White on the obtaining and interpretation of the X-ray data.

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

REFERENCES

Anderson, D. M. and Low, P. F. (1958) The density of water adsorbed by lithium–sodium– and potassium–bentonite: *Soil Sci. Soc. Am. Proc.* **22**, 99–103.

Bahl, O. P. and Sharma, S. K. (1970) Structure of vapor deposited silver films: *Thin Solid Films* **1**, 263–272.

Bailey, S. W. (1966) The status of clay mineral structures: *Clays and Clay Minerals* **14**, 1–23.

Barna, A., Barna, P. B. and Pócza, J. F. (1969) Some remarks on the epitaxial growth of films on substrates coated with amorphous deposits: *Thin Solid Films* **4**, R32-R36.

Bernal, J. D. (1957) The function of the hydrogen bond in solids and liquids: In *Hydrogen Bonding* (Edited by Hadzi, D.), pp. 7–22, Pergamon Press, New York.

Brindley, G. W. (1961) Experimental methods: In *The X-ray Identification and Crystal Structures of Clay Minerals* (Edited by Brown, G.), pp. 1–50, Mineral. Soc. London.

Brindley, G. W. and Robinson, K. (1948) X-ray studies of halloysite and metahalloysite—I. The structure of metahalloysite, an example of a random layer lattice: *J. Mineral. Soc.* **28**, 393–406.

Chopra, K. L. (1969) Metastable thin-film epitaxial structures: *Phys. Status Solidi* **32**, 489–507.

Davey, B. G. and Low, P. F. (1971) Physico-chemical properties of sols and gels of Na–montmorillonite with and without adsorbed hydrous aluminum oxide: *Soil Sci. Soc. Am. Proc.* **35**, 230–236.

Davidtz, J. C. and Low, P. F. (1970) Relation between crystal-lattice configuration and swelling of montmorillonites: *Clays and Clay Minerals* **18**, 325–332.

Davis, C. M. and Litovitz, T. A. (1965) Two-state theory of the structure of water: *J. Chem. Phys.* **42**, 2563–2576.

Distler, G. I. and Obronov, V. G. (1969) Photoelectret mechanism of long range transmission of structural information: *Nature* **224**, 261–262.

Distler, G. I. and Obronov, V. G. (1971) Long range transmission and preservation of single crystal structural information by interfacial polycrystalline layers: *Nature Physical Sci.* **229**, 242–243.

Distler, G. I. and Shenyavskaya, L. A. (1969) Polarization structure of interfacial amorphous films: *Nature* **221**, 52–53.

Dutt, G. R. and Low, P. F. (1962) Relationship between the activation energies for deuterium oxide diffusion and exchangeable ion conductance in clay systems: *Soil Sci.* **93**, 195–203.

Eirish, M. V. and Tret'jakova, L. I. (1970) The role of sorptive layers in the formation and change of the crystal structure of montmorillonite: *Clay Minerals* **8**, 255–266.

Eisenberg, D. and Kauzmann, W. (1969) *The Structure and Properties of Water*. Oxford University Press, London.

Farmer, V. C. and Russell, J. D. (1967) I.R. absorption spectrometry in clay studies: *Clays and Clay Minerals* **15**, 121–142.

Farmer, V. C. and Russell, J. D. (1971) Interlayer complexes in layer silicates: the structure of water in lamellar ionic solutions: *Trans. Faraday Soc.* **67**, 2737–2749.

Foster, M. D. (1955) The relation between composition and swelling in clays: *Clays and Clay Minerals* **3**, 205–220.

Foster, W. R., Savins, J. G. and Waite, J. M. (1955) Lattice expansion and rheological behavior relationships in water–montmorillonite systems: *Clays and Clay Minerals* **3**, 296–316.

Frank, H. S. (1970) The structure of ordinary water: *Science* **169**, 635–641.

Fripiat, J. J., Chaussidon, J. and Touillaux, R. (1960) Study of dehydration of montmorillonite and vermiculite by i.r. spectroscopy: *J. Phys. Chem.* **64**, 1234–1241.

Graham, J., Walker, G. F. and West, G. W. (1964) Nuclear magnetic resonance study of interlayer water in hydrated layer silicates: *J. Chem. Phys.* **40**, 540–550.

Gurney, R. W. (1953) *Ionic Processes in Solution*. McGraw-Hill, New York.

Heavens, O. S. (1970) Thin film research today: *Nature* **228**, 1036–1039.

Hendricks, S. B. and Jefferson, M. E. (1938) Structures of kaolin and talc-pyrophyllite hydrates and their bearing on water sorption of the clays: *Am. Mineralogist.* **23**, 863–875.

Henning, C. A. O. (1970) Orientation of vacuum condensed overgrowths through amorphous layers: *Nature* **227**, 1129–1130.

Hunter, R. J., Stirling, G. C. and White, J. W. (1971) Water dynamics in clays by neutron spectroscopy: *Nature Physical Sci.* **230**, 192–194.

Jesser, W. A. (1969) Theory of pseudomorphism in thin films: *Mater. Sci. Engng* **4**, 279–286.

Jorgensen, P. (1968) I.R. study of water adsorbed on Wyoming bentonite: *Geologiska Føren. Stockholm Førh.* **90**, 213–220.

Kamb, B. (1968) Ice polymorphism and the structure of water: In *Structural Chemistry and Molecular Biology* (Edited by Rich, A. and Davidson, N.), Freeman, San Francisco.

Kamb, B. (1971) Hydrogen-bond stereochemistry and "anomalous water": *Science* **172**, 231–242.

Kavanau, J. (1964) *Water and Solute-Water Interactions*. Holden-Day, San Francisco.

Kay, B. D. and Low, P. F. (1970) Measurement of the total suction of soils by a thermistor psychrometer: *Soil Sci. Soc. Am. Proc.* **34**, 373–376.

Kemper, W. D., Maasland, D. E. L. and Porter, L. K. (1964) Mobility of water adjacent to mineral surfaces: *Soil Sci. Soc. Am. Proc.* **28**, 164–172.

Kolaian, J. H. and Low, P. F. (1963) Calorimetric determination of unfrozen water in montmorillonite pastes: *Soil Sci.* **95**, 376–384.

Kuntze, R., Chambers, A. and Prutton, M. (1969) Pseudomorphism in the (100) Ni–Cu system: *Thin Solid Films* **4**, 47–60.

Leonard, R. A. (1970) I.R. analysis of partially deuterated water adsorbed on clay: *Soil Sci. Soc. Am. Proc.* **34**, 339–343.

Leonard, R. A. and Weed, S. B. (1967) Influence of exchange ions on the *b*-dimensions of dioctahedral vermiculite: *Clays and Clay Minerals* **15**, 149–161.

Low, P. F. (1958) The apparent mobilities of exchangeable alkali metal cations in bentonite–water systems: *Soil Sci. Soc. Am. Proc.* **22**, 395–398.

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

Low, P. F. (1961) Physical chemistry of clay-water interaction: *Advances in Agronomy* **13**, 269–327.
Low, P. F. (1962) Influence of adsorbed water on exchangeable ion movement: *Clays and Clay Minerals* **9**, 219–228.
Low, P. F. (1968) Observations on activity and diffusion coefficients in Na–montmorillonite: *Israel J. Chem.* **6**, 325–336.
Low, P. F., Anderson, D. M. and Hoekstra, P. (1968) Some thermodynamic relationships for soils at or below the freezing point 1. Freezing point depression and heat capacity: *Water Resources Res.* **4**, 379–394.
Low, P. F., Ravina, I. and White, J. L. (1970) Changes in *b*-dimension of Na–montmorillonite with interlayer swelling: *Nature* **226**, 445–446.
Low, P. F. and White, J. L. (1970) Hydrogen bonding and polywater in clay–water systems: *Clays and Clay Minerals* **18**, 63–66.
Macey, H. H. (1942) Clay–water relationships and the internal mechanism of drying: *Trans. Br. Ceramic Soc.* **41**, 73–121.
Matthews, J. W. (1966) Accomodations of misfit across the interface between single-crystal films of various face-centered cubic metals: *Phil. Mag.* **13**, 1207–1221.
Matthews, J. W. and Jesser, W. A. (1967) Experimental evidence for pseudomorphic growth of platinum on gold: *Acta Met.* **15**, 595–600.
Mering, J. and Brindley, G. W. (1967) X-ray diffraction band profiles of montmorillonite – influence of hydration and of the exchangeable cations: *Clays and Clay Minerals* **15**, 51–60.
Miller, R. J. and Low, P. F. (1963) Threshold gradient for water flow in clay systems: *Soil Sci. Soc. Am. Proc.* **27**, 605–609.
Nagasawa, K. (1969) Kaolin minerals in Cenozoic sediments of central Japan: *Proc. Internatl. Clay Conf. Tokyo Japan* **1**, 15–30.
Narten, A. H. and Levy, H. A. (1969) Observed diffraction pattern and proposed models of liquid water: *Science* **165**, 447–454.
Oster, J. D. (1962) *Activation energy for ion movement in thin water films on montmorillonite*: M. Sc. Thesis, Purdue University.
Pashley, D. W. (1965) The nucleation, growth, structure and epitaxy of thin surface films: *Adv. Physics* **14**, 327–416.
Pauling L. (1959) The structure of water: In *Hydrogen Bonding* (Edited by Hadzi D.), Pergamon Press, Oxford.
Poh, K. J. and Anderson, J. C. (1969) The structure and growth of epitaxial PbSe films: *Thin Solid Films* **3**, 139–156.
Radoslovich, E. W. (1962) The cell dimensions and symmetry of layer-lattice silicates – II. Regression relations: *Am. Mineralogist* **47**, 617–636.
Radoslovich, E. W. and Norrish, K. (1962) The cell dimensions and symmetry of layer-lattice silicates – I. Some structural considerations: *Am. Mineralogist* **47**, 599–616.
Rich, C. I. (1957) Determination of (060) reflections of clay minerals by means of counter type X-ray diffraction instruments: *Am. Mineralogist* **42**, 569–570.
Robinson, R. A. and Stokes, R. H. (1959) *Electrolyte Solutions*: Butterworths, London.
Russell, J. D. and Farmer, V. C. (1964) I.R. spectroscopic study of the dehydration of montmorillonite and saponite: *Clay Minerals Bull.* **5**, 443–464.
Shirozu, H. and Bailey, S. W. (1966) Crystal structure of a two-layer Mg–vermiculite: *Am. Mineralogist* **51**, 1124–1143.
Tabikh, A. A., Barshad, I. and Overstreet, R. (1960) Cation exchange hysteresis in clay minerals: *Soil Sci.* **90**, 219–226.
Tabor, D. and Winterton, R. H. S. (1968) Surface forces: Direct measurement of normal and retarded van der Waals forces: *Nature* **219**, 1120–1121.
van der Marel, H. W. (1966) Cation exchange, specific surface and adsorbed water molecules: *Z. Pflanz. Düngung, Bodenkunde* **114**, 161–175.
van der Merwe, J. H. (1964) Interfacial misfit and bonding between oriented films and their substrates: In *Single Crystal Films* (Edited by Francombe M. H. and Sato H.), pp. 139–163, Macmillan, New York.
Wu, T. H. (1964) A nuclear magnetic resonance study of water in clay: *J. Geophysical Res.* **69**, 1083–1091.

Résumé – La dimension *b* de la maille de six montmorillonites Na différentes a été mesurée par diffraction X, à des teneurs en eau allant de 0 à 20 g d'eau par g d'argile. Dans chaque cas, la dimension *b* augmente progressivement avec la teneur en eau, d'une valeur initiale caractéristique pour chacune des montmorillonites à l'état sec, jusqu'à une valeur finale de ~ 9, 0 Å commune à tous les échantillons. Cette dernière valeur est atteinte lorsque la teneur en eau est égale, pour chaque montmorillonite, à celle qui assure le gonflement maximum. Lorsque les teneurs en eau sont portées en fonction des variations correspondantes de la dimension *b*, on obtient une ligne droite qui passe par l'origine.

On dispose, grâce à des travaux antérieurs, de différentes données concernant l'eau dans les systèmes eau–montmorillonite sensibles à la structure de l'eau (par exemple, volume spécifique partiel, quantité d'eau ne gelant pas à -5°C et énergie d'activation requise pour que les ions puissent s'y déplacer). Dans ce travail, on a déterminé les dimensions *b* correspondantes. On a trouvé que toutes ces propriétés de l'eau sont en corrélation avec la dimension *b* de la montmorillonite associée.

Nos résultats indiquent qu'il existe une épitaxie entre les réseaux cristallins de la montmorillonite et l'eau adsorbée et que ces réseaux subissent un ajustement mutuel à chaque variation incrémentaire de la teneur en eau. La perte d'énergie libre qui en résulte fait que l'adsorption de l'eau, c'est-à-dire le gonflement, est un phénomène spontané. Le gonflement s'arrête lorsqu'il n'y a plus aucun ajustement. Cette situation n'est pas atteinte tant que l'épaisseur de l'eau adsorbée est inférieure à plusieurs centaines d'angstroems et qu'une configuration préférentielle n'est pas réalisée.

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press

Kurzreferat – Die *b*-Dimensionen der Einheitszellen von sechs verschiedenen Na-gesättigten Montmorilloniten wurde durch Röntgenbeugung bei Wassergehalten von 0 bis 20 g pro g Montmorillonit bestimmt. In jedem Falle nahm die *b*-Dimension mit zunehmendem Wassergehalt von einem für jeden trockenen Montmorillonit charakteristischen anfänglichen wassergehalt bis zu einem Endwert von ~ 9,0 Å zu, der allen Montmorilloniten gemeinsam war. Der letztgenannte Wert wurde erreicht wenn die Wassergehalte der betreffenden Montmorillonite gleich denen bei maximaler Schwellung waren. Wurden diese Wassergehalte gegen die entsprechenden Änderungen in der *b*-Dimension aufgetragen, so wurde eine Gerade erhalten, die durch den Ursprung verlief.

Aus früheren Arbeiten waren verschiedene gefügebedingte Eigemschaften des Wassers in Montmorillonit–Wasser Systemen (d.h. das spezifische Teilvolumen, der bei −5°C ungefroren bleibende Anteil sowie die für den Durchgang erforderliche Aktivierungsenergie der Ionen), als Funktionen der Sorten austauschbarer Kationen, bekannt die belangvollen *b*-Dimensionen wurden in der gegenwärtigen Arbeit bestimmt. Es wurde festgestellt, dass alle diese Eigenschaften des Wassers in einer Beziehung zu der *b*-Dimension des betreffenden Montmorillonits standen.

Andere Ergebnisse dueten darauf hin, dass zwischen den Kristallgittern von Montmorillonit und adsorbiertem Wasser Epitaxix besteht, und dass mit jeder Zunahme des Wassergehaltes eine gegenseitige Angleichung dieser Gitter stattfindet. Der sich daraus ergebende Verlust an freier Energie gibt Anlass zu spontaner Wasseradsorption d.h. Quellung. Die Quellung endet wenn keine weitere Angleichung mehr stattfindet. Das erfolgt erst wenn das adsorbierte Wasser einige Hundert Angström stark geworden ist und eine bevorzugte Anordnung erreicht hat.

Резюме — *b*-размеры элементарных ячеек шести различных насыщенных Na монтмориллонитов определялись дифракцией рентгеновских лучей при содержании воды от 0 до 20 гр на 1 гр монтмориллонита. В каждом случае *b*-размер прогрессивно увеличивался по сравнению с начальной величиной с увеличением содержания воды, что было характерно для каждого сухого монтмориллонита, до конечной величины ~ 9.0 Å общей для всех монтмориллонитов. Последняя величина достигалась, когда содержание воды в соответствующих монтмориллонитах равнялось максимальному набуханию. При составлении кривой содержания воды и соответствующих изменений *b*-размеров, получалась прямая линия, проходящая через начальную величину.

От предыдущих исследований были получены, как функции катионообменных видов, различные структурно-чувствительные свойства воды в системах монтмориллонит/вода, (напр. парциальный удельный объем, незамерзающее при −5°C количество и требуемая энергия активации для продвижения ионов). Настоящее исследование определило соответствующие *b*-размеры. Оказалось, что все эти свойства воды согласуются с *b*-размером соответствующего монтмориллонита.

Наши результаты показывают, что между кристаллическими решетками монтмориллонита и адсорбированной водой существует эпитаксия и что эти решетки взаиморегулируются с каждым увеличением количества воды. Получающаяся в результате потеря энергии причиняет появляющуюся самопроизвольно адсорбцию воды, т.е. набухание. Набухание останавливается, когда регулировка уже не происходит. Это не случается до тех пор, пока адсорбированная вода не будет в несколько сот ангстрем толщиной и не будет достигнута требуемая конфигурация.

https://doi.org/10.1346/CCMN.1972.0200302 Published online by Cambridge University Press