

RELATION BETWEEN CRYSTAL-LATTICE CONFIGURATION AND SWELLING OF MONTMORILLONITES*

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Abstract—Prompted by Foster's observation that free swelling is related to octahedral substitution, the authors determined the free swelling of six Na-montmorillonites with different amounts of octahedral and tetrahedral substitution. They found that the montmorillonites exhibited marked differences in free swelling. These differences were not related to differences in cation exchange capacity. Nor were they related to differences in ζ potential, which is a criterion of cation dissociation. Further, calculations indicated that they could not be accounted for by differences in double-layer repulsion or van der Waals attraction. Therefore, to see if dimensional changes produced by isomorphous substitution were responsible, free swelling was plotted against the b -dimension of the clay structure, which was calculated from its mineralogical composition. The result was a straight line with a negative slope. A similar result was obtained with Foster's data. In addition, free swelling was plotted against the degree of tetrahedral rotation in the clay structure, which was also calculated from its mineralogical composition. The result was a family of nearly parallel straight lines that were distinguished from each other by the amount of tetrahedral Al^{3+} in the clays identified with them. These results led to the proposal that the clay surface acts as a template for the structure of the adjacent water and that, as the configuration of the surface changes, the water structure changes accordingly. This causes a change in the free energy of the water and, hence, in the swelling of the clay.

INTRODUCTION

SEVERAL years ago, Foster (1953, 1955) studied the relation between ionic substitution and swelling in Na-montmorillonites. She found that: (1) swelling was unrelated to the cation exchange capacity but decreased curvilinearly with increasing octahedral substitution‡; (2) the substitution of Fe^{3+} for Al^{3+} in octahedral positions had the same effect on swelling as the substitution of Mg^{2+} for Al^{3+} ; (3) the substitution of Al^{3+} for Si^{4+} in tetrahedral positions had little effect on swelling, and (4) the oxidation of Fe^{2+} to Fe^{3+} in octahedral positions increased the swelling markedly. Foster's interpretation, in keeping with the current concept that osmotically active cations are responsible for swelling, was that octahedral substitution decreases the degree of cation dissociation from montmorillonite. However, she admitted

that her interpretation was speculative. Later, Leonard and Low (1964) questioned this interpretation and proposed that the decrease in swelling with increasing octahedral substitution could have been due partly to a reduction in clay-water interaction. Their proposal was based on the concept of Low and Deming (1953) and Hemwall and Low (1956) that clay-water interaction lowers the partial molar free energy of the water and, thereby, increases the swelling. To test their proposal, they intended to relate the properties of water in suspensions of different Na-montmorillonites to the degree of octahedral substitution. Although they did show that clay-water interaction occurred in all suspensions, their work was inconclusive. The reason was that, in their experiments, octahedral substitution was not the only independent variable. Their clays also differed in particle size and, because of inadequate treatment, in degree of Na^+ saturation.

Foster's observations are fundamental and must be explained in any theory of swelling. Yet, her interpretation is unsatisfactory. For example, if swelling depends on the number of dissociated (osmotically active) cations, it is difficult to understand why it is not related to the number of cations capable of dissociation, i.e., to the cation exchange

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‡The decrease becomes more nearly linear with the omission of one relatively discrepant data point (for Santa Rosa clay).

capacity. Therefore, the authors decided to renew the study of swelling as it relates to octahedral substitution. A report of this study follows.

MATERIALS AND METHODS

Six montmorillonites were selected for this investigation. Their sources and mineralogical compositions are listed in Table 1.

fractionated by the procedure described by Tanner and Jackson (1947). The 0.04–0.1 μ fraction was freeze-dried and retained for investigation.

Cation exchange capacities of the fractionated, freeze-dried clays were determined by exchanging the adsorbed Na^+ with NH_4^+ and determining the exchanged Na^+ by means of a Jarrell Ash atomic absorption unit.

Table 1. Mineralogical compositions of the Na-montmorillonites used in this study

Clay mineral	Mineralogical composition		
Belle Fourche, S. D.	$[\text{Al}_{1.60}^{3+} \text{Fe}_{.19}^{3+} \text{Mg}_{.22}^{2+}]$	$[\text{Si}_{3.84}^{4+} \text{Al}_{.16}^{3+}]$	$\text{O}_{10} [\text{OH}]_2 \text{X}_{.35}$
Upton, Wyo. (25 b)	$[\text{Al}_{1.53}^{3+} \text{Fe}_{.15}^{3+} \text{Fe}_{.01}^{2+} \text{Mg}_{.33}^{2+}]$	$[\text{Si}_{3.91}^{4+} \text{Al}_{.09}^{3+}]$	$\text{O}_{10} [\text{OH}]_2 \text{X}_{.37}$
Polkville, Miss. (21)	$[\text{Al}_{1.41}^{3+} \text{Fe}_{.13}^{3+} \text{Fe}_{.01}^{2+} \text{Mg}_{.45}^{2+}]$	$[\text{Si}_{3.93}^{4+} \text{Al}_{.07}^{3+}]$	$\text{O}_{10} [\text{OH}]_2 \text{X}_{.53}$
Otay, Calif. (24)	$[\text{Al}_{1.35}^{3+} \text{Fe}_{.05}^{3+} \text{Mg}_{.60}^{2+}]$	$[\text{Si}_{3.98}^{4+} \text{Al}_{.02}^{3+}]$	$\text{O}_{10} [\text{OH}]_2 \text{X}_{.62}$
Cheto, Ariz.	$[\text{Al}_{1.38}^{3+} \text{Fe}_{.09}^{3+} \text{Mg}_{.54}^{2+}]$	$[\text{Si}_{3.91}^{4+} \text{Al}_{.09}^{3+}]$	$\text{O}_{10} [\text{OH}]_2 \text{X}_{.60}$
Bayard, N. M. (30 a)	$[\text{Al}_{1.46}^{3+} \text{Fe}_{.06}^{3+} \text{Fe}_{.01}^{2+} \text{Mg}_{.47}^{2+}]$	$[\text{Si}_{4.0}^{4+}]$	$\text{O}_{10} [\text{OH}]_2 \text{X}_{.48}$

The Belle Fourche and Cheto clays were those used by Leonard and Low (1964). The other clays, i.e., those followed by A.P.I. numbers in parentheses, were obtained recently from Wards National Science Establishment. Various mineralogical compositions have been reported for the different clays (e.g., Kerr *et al.*, 1951; Foster, 1951; Foster, 1953; Osthaus, 1956; Grim and Kulbicki, 1961; Schultz, 1969). However, we used the mineralogical composition reported by Foster (1953) for the Belle Fourche clay, that reported by Grim and Kulbicki (1961) for the Cheto clay and that reported by Schultz (1969) for each of the remaining clays. These mineralogical compositions were selected because, in view of the times and locations at which our samples were obtained, they seemed most representative.

A 0.1 per cent solution of "Calgon" was added to each clay (including Belle Fourche and Cheto, which were largely Na-saturated already by Leonard and Low) to make a suspension containing 1 per cent clay by weight. The resulting suspension was stirred for 24 hr. Next, sufficient NaCl was added to make its concentration 2 N. After stirring again for 24 hr, the clay was allowed to settle out, the supernatant liquid was decanted and the sediment was redispersed in 2 N NaCl solution. This procedure was repeated three times. Then deionized water was added and, by repeated stirring, centrifugation and decantation, most of the NaCl was washed out. The balance of it was removed by dialysis.

Subsequent to sodium saturation, the clays were

For the determination of free swelling (maximal swelling under no external constraint), Gooch crucibles with sintered-glass filters were employed. About 1 g of clay was accurately weighed onto the the water-saturated filter of each crucible. Then the crucibles were covered with a flexible plastic sheet perforated by a single pinhole (for the maintenance of atmospheric pressure) and placed together in the same tray of water at room temperature. Any air trapped between the filters and the water was withdrawn by means of a V-shaped tube. Thus, the clays were allowed to swell freely at atmospheric pressure without evaporative drying. To determine when equilibrium was attained, the crucibles were weighed periodically for several weeks. Finally, free swelling was expressed in terms of the grams of water absorbed per gram of clay.

Zeta potentials of the different Na-saturated clays were determined in 2 per cent suspensions by the method of Long and Ross (1965).

RESULTS AND DISCUSSION

When isomorphous substitution occurs there are two effects: (1) the clay structure becomes electrically charged if the replacing cation has a different charge than the one being replaced, and (2) the *b*-dimension of the lattice changes and, as a consequence, the silicon tetrahedra rotate alternately clockwise and counterclockwise (Radoslovich and Norrish, 1962; Radoslovich, 1962). Let us examine these two effects of isomorphous substitution on free swelling.

In Table 2 are presented experimental data for the different clays. Note that there is no relation between free swelling and the cation exchange capacity. Recall that Foster (1953, 1955) made the

Table 2. Free swelling, cation exchange capacity (C.E.C.) and zeta potential (ζ) of the montmorillonites used in this study

Montmorillonite type	Free swelling (g H ₂ O/g clay)	C.E.C. (me/100 g)	ζ (mV)
Cheto, Ariz.	6.83	96	25.7
Polkville, Miss.	11.46	63	24.3
Bayard, N. M.	13.02	127	34.2
Otay, Calif.	13.51	52	27.8
Upton, Wyoming	15.39	100	23.9
Belle Fourche, S. D.	18.38	85	21.7

same observation. But, contrary to Foster's belief, there does not appear to be any relation between free swelling and cation dissociation. This can be shown in the following way. If it is assumed that the *dissociated* cations and anions are those outside the plane of shear, the effective surface charge density inside the plane of shear, σ' , is given by

$$\sigma' = ve(N_+ - N_-) \quad (1)$$

where v is the common valence of the ions (Na⁺ and Cl⁻ in this case), e is the electronic charge and N_+ and N_- are the number of *dissociated* cations and anions, respectively, per cm² of surface. When the content of free electrolyte is low

$$\sigma' \cong veN_+ \quad (2)$$

Now, we can write (MacInnes, 1939)

$$\zeta = 4\pi\sigma'/\epsilon\kappa \quad (3)$$

where

$$\kappa = (8\pi ne^2v^2/\epsilon kT)^{1/2} \quad (4)$$

ζ is the zeta potential, ϵ is the dielectric constant, κ is the Debye-Huckel constant, n is the number of ions per cm³ beyond the electric field of the particle, k is the Boltzmann constant and T is the absolute temperature. Combination of equations (2) and (3) yields

$$\zeta = 4\pi veN_+/\epsilon\kappa \quad (5)$$

The value of κ should have been nearly the same in the different suspensions in which ζ was measured because they were all prepared by mixing salt-free, freeze-dried clay with deionized water. Since there

was no relation between free swelling and ζ (Table 2), we conclude that free swelling was not related to cation dissociation.

A more quantitative approach to the effect of surface charge (and its associated cation atmosphere) on free swelling is provided by double-layer theory (Verwey and Overbeek, 1948; van Olphen, 1963). We utilized this theory to calculate the repulsive pressure, p , when the half-distance between particles, d , had different values in excess of 100 Å. Preliminary calculations indicated that, when the half-distance exceeded this value, the electrical double layers of the particles were essentially unperturbed by each other and that, therefore, the midplane potential could be calculated by summing their individual contributions. In this calculation, the surface charge densities were determined from the cation exchange capacities and surface area (assumed to be 8×10^6 cm² per g). The ionic concentration in the external solution was the same for all clays since they were equilibrated together in the same tray of deionized water. It was arbitrarily assigned a value of 6.02×10^{16} ions per cm³, corresponding to a 10^{-4} N solution. It was found that the midplane potentials varied with d but, at any specific value of $d > 100$ Å, were essentially the same for the different clays. Hence, the values of p were also essentially the same. This conclusion is supported by the work of Low (1968) who calculated p as a function of d by using the complete double-layer theory, i.e., without approximating the midplane potential as indicated above. At maximal swelling, the values of d for our clays were, with one exception, greater than 100 Å (Table 3). These values of d were calculated by assuming a density of unity for the water in the system and dividing its weight by the surface area of the clay. They are believed to be good approximations because unpublished evidence of I. Ravina in this laboratory as well as other evidence (Norrish, 1954; Foster, Savins and Waite, 1955) indicates that, in pure water, the interlayer spacing of Na-montmorillonite is directly proportional to water content and that the interlayer water accounts for nearly all the water in the system. Therefore, according to double-layer theory, differences in surface charge density cannot account for our results.

Both theory and experiment indicate that isomorphous substitution does not affect free swelling by changing the surface charge density of the clay. The surface charge density is usually related to the repulsive force between particles. Let us now see if isomorphous substitution affects the attractive force. The only attractive force that is known to be significant at interparticle distances comparable to those reached in our experiments is the van der

Table 3. Calculated values of the surface charge density (σ), the surface potential (Ψ_0) the half-distance between particles (d), the mid-plane potential (Ψ_d) the repulsive pressure (p) and the van der Waals attractive force (f) for the different montmorillonites at maximal swelling

Montmorillonite type	σ (esu/cm ² $\times 10^{-4}$)	Ψ_0 (esu/cm $\times 10^4$)	d (Å)	Ψ_d (esu/cm $\times 10^4$)	p (dynes/cm ² $\times 10^{-3}$)	f (dynes/cm ² $\times 10^{-3}$)
Cheto, Ariz.	3.46	9.00	87	6.48	287	9.49
Polkville, Miss.	2.28	8.30	143	4.80	139	1.30
Bayard, N. M.	4.59	9.50	162	5.50	118	0.79
Otay, Calif.	1.84	7.80	169	4.22	108	0.67
Upton, Wyoming	3.62	9.10	192	3.94	88	0.40
Belle Fourche, S. D.	3.16	8.50	230	3.34	62	0.19

Waals' force. Both theory and experiment (Prosser and Kitchener, 1956; Derjaguin and Abrikossova, 1958; Black *et al.*, 1960; Tabor and Winterton, 1968) show that the magnitude, f , of this force between two parallel flat plates is related to the distance, h , which separates them ($h = 2d$) by

$$f = A/6\pi h^3 \quad (6)$$

if the force is normal and by

$$f = B/h^4 \quad (7)$$

if the force is retarded. Equation (6) with $A \cong 10^{-12}$ erg is supposed to apply when h is less than about 100 Å and equation (7) with $B \cong 10^{-19}$ erg cm is supposed to apply at larger distances. Hence, equation (7) should be applicable to the freely swollen systems of this experiment. Now, theoretically, B in this equation is supposed to depend somewhat on the atomic composition of the plates. It is conceivable, therefore, that isomorphous substitution could affect B and, thereby, interplate attraction. That this is unlikely, however, is indicated by the constancy of B for silicates of different composition. For example, it equals $1-2 \times 10^{-19}$ erg cm for quartz (Derjaguin and Abrikossova, 1958; Black *et al.*, 1960), 1.1×10^{-19} erg cm for glass (Kitchener and Prosser, 1957) and 0.87×10^{-19} erg cm for muscovite mica (Tabor and Winterton, 1968). Therefore, it appears that isomorphous substitution would have too small an effect on the van der Waals' force to account for the observed differences in free swelling.

Values of f at maximal swelling, determined by using equation (7) and the force constant for muscovite mica (which should be representative of layer silicates like montmorillonite) are recorded in Table 3. Observe that p is much greater than f . The same observation has been made by others

(Norrish, 1954; van Olphen, 1962; Norrish and Rausell-Colom, 1963; Andrews, Schmidt and van Olphen, 1967) who have explained the discrepancy by assuming that an additional attractive force exists because of positive-edge to negative-surface association. However, it has been shown that the edges of the 1:1 minerals, kaolinite and dickite, are positively charged only under acidic conditions (Schofield and Samson, 1953; Sumner, 1963; Okuda and Williamson, 1964; Follett, 1965) and that the edges of the 2:1 minerals, pyrophyllite and talc, are negatively charged even under these conditions (Okuda, Inoue and Williamson, 1969). Further, as indicated in a recent review (Low, 1968), almost all the evidence derived from electron microscopy, X-ray analysis and analysis of birefringence favors edge-to-edge or face-to-face association. Therefore, we doubt the existence of an attractive force depending on positive-edge to negative-surface association in Na-montmorillonite systems, especially since these systems have an alkaline reaction. It is more likely that the calculated magnitude of either p or f is in error. In this regard Overbeek (1966) has noted that, for colloids in general, there is a lack of agreement between experiments and theory based exclusively on van der Waals' forces and double-layer interaction. His conclusion was that the theories were either inaccurate or needed refinement. Of particular relevance to this work was his statement that "Undoubtedly, the structure of a liquid near an interface deviates from its structure in bulk. There is no doubt either that the special structure of water near the interface with particles dispersed in it will affect their stability by influencing the structure of the electrical double layer and possibly even by modifying the van der Waals forces."

Neither the repulsive force arising from the surface charge (and its associated ionic atmosphere) nor the van der Waals' attractive force appears to be primarily responsible for the differences in

swelling of the various montmorillonites. Let us turn our attention, therefore, to the effect on free swelling of changes in lattice dimensions produced by isomorphous substitution. The relation between b -dimension and isomorphous substitution in montmorillonites has been determined by Radoslovich (1962). It is

$$b_{\text{obs}} = (8.944 + 0.096 \text{ Mg}^{2+} + 0.096 \text{ Fe}^{3+} + 0.037 \text{ Al}_{\text{tetra}}) \pm 0.012 \text{ \AA}. \quad (8)$$

This relation was used to obtain the b -dimensions of the montmorillonites employed in Foster's (1953, 1955) and the present study. Then curves were drawn of free swelling versus b -dimension. In plotting the curve for Foster's data, the relatively discrepant data point representing Santa Rosa clay was omitted. Further, no distinction was made between the units of free swelling that she used (ml H₂O/g clay) and the units that we used (g H₂O/g clay) because the values in both units are essentially the same. The two curves and their appropriate regression equations are shown in Fig. 1. All data points are within experimental error (i.e., within the possible error in b -dimension) of their respective curves. Evidently, free swelling decreases linearly with increasing b -dimension.

Note from Fig. 1 that the line for Foster's data was higher and had a different slope than that for our data. Presumably, this is because her method of determining free swelling was different from ours. She dropped 1-g samples of clay into distilled water in 100-ml graduated cylinders and observed the resulting gel volumes. It is also possible that her method of clay preparation, which she did not describe, was different.

In view of equation (8) and Fig. 1, one would expect that: (1) free swelling would decrease linearly with octahedral substitution; (2) substitution of Fe³⁺ and Mg²⁺ for Al³⁺ in octahedral positions would have the same effect on free swelling; (3) substitution of Al³⁺ for Si⁴⁺ in tetrahedral positions would have little effect on free swelling, and (4) free swelling would increase when octahedral Fe²⁺ is oxidized to Fe³⁺ because this contracts the structure by decreasing ionic size and increasing ionic charge. These expectations are consistent with Foster's (1953, 1955) observations.

Conceivably, free swelling is linearly related to the b -dimension because the b -dimension is proportional to the attraction between negative surfaces and intermediate cations which prevents layer expansion (Norrish, 1954) or, alternatively, to the attraction between negative surfaces and positive edges which causes cross-linking (Norrish and Rausell-Colom, 1963; Andrews, Schmidt and van

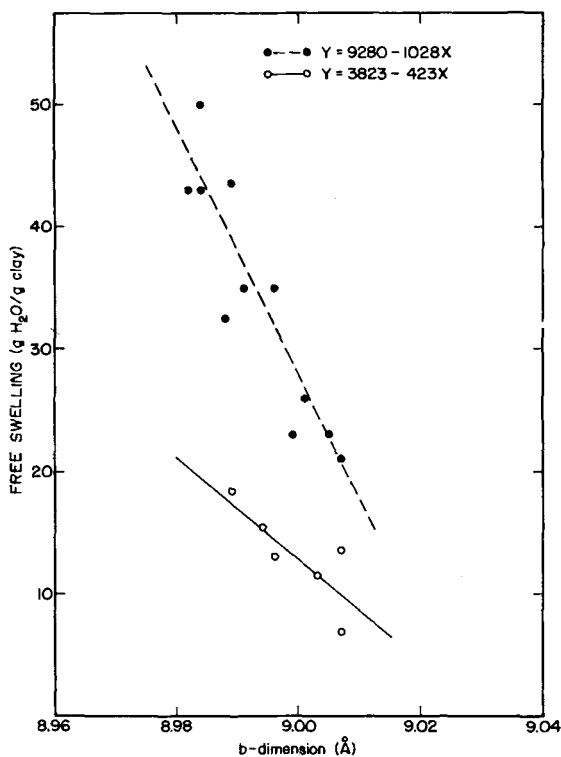


Fig. 1. The relation between free swelling and b -dimension for Na-montmorillonites. ●, Foster's data; ○, this work.

Olphen, 1967). However, both kinds of attraction, being electrostatic, depend primarily on lattice substitutions that alter electrical charge (Low, 1968), whereas, the b -dimension depends on all lattice substitutions (equation 8). In particular, substitution of Mg²⁺ for Al³⁺ would affect the surface and edge charges differently than substitution of Fe³⁺ for Al³⁺. But these substitutions have the same effect on the b -dimension. Further, free swelling is not related to cation exchange capacity, i.e., to electrical charge. We do not subscribe, therefore, to either alternative. Instead, we propose that, by virtue of the attraction between surface oxygens and adjacent water molecules, the clay surface acts as a template on which a relatively stable water structure is built. Hence, as the b -dimension adjusts to lattice substitutions, there is a corresponding adjustment in the water structure. This adjustment takes place by changes in intermolecular bond angles and distances and, in extreme cases, by changes in coordination number. Accordingly, the relative partial molar free energy of the water $\bar{F} - \bar{F}^\circ$, changes. Now, $\bar{F} - \bar{F}^\circ$ is related to the swelling pressure, π , of the clay and the relative

vapor pressure, p/p° , of the water in it by the thermodynamic relationships (Low and Anderson, 1958)

$$\bar{F} - \bar{F}^\circ = -\bar{v}\pi = RT \ln p/p^\circ \quad (9)$$

where \bar{v} is the partial molar volume of water in the clay, R is the molar gas constant and T is the temperature. Thus, changes in b -dimension lead ultimately to changes in swelling.

Our proposal is supported by the work of Nagasawa (1969) which came to our attention when the present article was being edited for publication. He found that halloysite samples could be divided into two groups based on the stability of interlayer water. The halloysite samples with the more stable interlayer water had the smaller b -dimensions. Consequently, he concluded that the b -dimension determines the stability of interlayer water.

Recall that the silicon tetrahedra in the clay structure rotate as the b -dimension changes. By this mechanism, the tetrahedral layers adjust to the dimensions of the octahedral layer. If the water is bonded to the basal oxygens of the silicon tetrahedra, as supposed, there should be some relation between free swelling and α , the angle through which these tetrahedra rotate. Now α can be calculated (Brindley and MacEwan, 1953; Radoslovich and Norrish, 1962; Bailey, 1966) from the equation

$$\cos \alpha = b_{\text{obs}}/b_{\text{tetra}} \quad (10)$$

where b_{tetra} , the b -dimension of the unconstrained tetrahedral layer, is given by

$$b_{\text{tetra}} = 9.051 + 0.254 \text{Al}_{\text{tetra}} \quad (11)$$

Equation (11) was developed from mineralogical data and geometrical considerations by Radoslovich and Norrish (1962). It gives results that are similar to those obtained by a method described by Bailey (1966). We knew the Al_{tetra} in each clay from the mineralogical composition. Therefore, we were able to calculate b_{tetra} and, consequently, α for Foster's and our clays.

As has been noted already, the difference between the two curves in Fig. 1 is believed to be due to differences in experimental procedure. Therefore, to correct for these differences, so that the two sets of data could be combined, we added to each of our observed values of free swelling an amount equal to the difference in the lines at the corresponding b -dimension. Then we plotted the corrected values, along with those observed by

Foster, against the calculated values of α . The results are shown in Fig. 2.

It can be seen from Fig. 2 that the data points for clays with similar amounts of tetrahedral substitution tend to fall on the same straight line and that, as the amount of tetrahedral substitution increases, the location of the line shifts to the right. Also, it appears that the different lines are nearly parallel to each other. Thus, a definite pattern exists. Although more work must be done before explicit

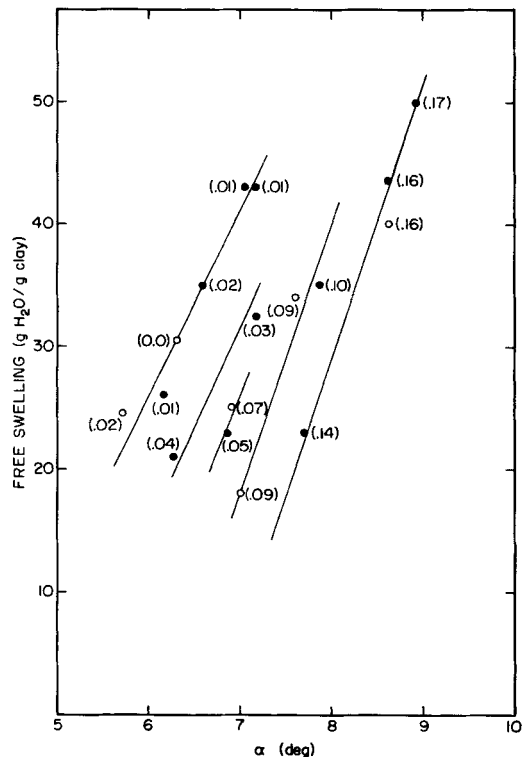


Fig. 2. Relation between free swelling and the angle of rotation (α) of the silicon tetrahedra. Figures in parentheses represent the tetrahedral Al^{3+} per unit cell. ●, Foster's data; ○, this work (corrected).

conclusions can be drawn, it appears that free swelling is influenced by α .

In summary, we have shown that clay swelling is not related to the surface charge or number of associated cations in any obvious way. Instead, it is related to the configuration of the crystal lattice of the clay. Presumably, the reason for this relationship is that the clay lattice serves as a template for the water lattice. As it changes in configuration, so does the water lattice. The result is a change in the free energy of the water and, therefore, in the swelling of the clay.

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Résumé— Incités par l'observation de Foster d'après laquelle le libre gonflement est lié à la substitution octaédrale, les auteurs ont déterminé le libre gonflement de six Na-montmorillonites avec différents volumes de substitution octaédrale et tétraédrale. Ils ont trouvé que les montmorillonites présent-

aient des différences marquées dans le gonflement libre. Ces différences n'avaient aucune relation avec celles de la capacité d'échange de cations, ni avec les différences de potentiel ζ , qui est un critère de la dissociation des cations. De plus, les calculs ont indiqué qu'elles ne pouvaient être justifiées par les différences de répulsion des couches doubles ou d'attraction de Van der Waals. Ainsi, pour déterminer si les changements dimensionnels produits par la substitution isomorphe étaient responsables, on a relevé le libre gonflement selon la dimension b de la structure argileuse calculée à partir de sa composition minéralogique. Le résultat était une ligne droite avec une pente négative. Un résultat similaire a été obtenu à partir des données de Foster. De plus, on a effectué un relevé du gonflement libre d'après le degré de rotation tétraédrale dans la structure argileuse, également calculé à partir de sa composition minéralogique. Le résultat a donné une famille de lignes droites presque parallèles qui se distinguaient les unes des autres par la quantité de Al^{3+} tétraédrale dans les argiles identifiées avec elles. Ces résultats ont conduit à la proposition d'après laquelle la surface argileuse agit en tant que gabarit pour la structure de l'eau adjacente et que la structure de l'eau change avec les modifications de la configuration de surface. Ceci entraîne une modification de l'énergie libre de l'eau et, ainsi, du gonflement de l'argile.

Kurzreferat—Angeregt durch die Beobachtung von Foster, dass eine Beziehung besteht zwischen freier Quellung und oktaedrischer Substitution, bestimmten die Autoren die freie Quellung von sechs Na-Montmorilloniten mit verschiedenen Ausmassen von oktaedrischer und tetraedrischer Substitution. Sie fanden, dass die Montmorillonite deutliche Unterschiede in der freien Quellung zeigten. Diese Unterschiede standen in keinem Verhältnis zu Unterschieden in der Kationenaustauschkapazität. Auch konnte kein Zusammenhang mit Unterschieden im ζ Potential, das ein Kriterium für Kationendissoziation darstellt, festgestellt werden. Rechnungsmässig zeigte sich ferner, dass sie nicht auf Grund von Unterschieden in Doppelschichtabstossung oder van der Waalsscher Anziehung zu erklären waren. Um daher herauszufinden ob dimensionelle, durch isomorphe Substitution hervorgerufene, Veränderungen verantwortlich waren, wurde die freie Quellung gegen die b -Dimension der Tonstruktur, die aus dessen mineralogischer Zusammensetzung errechnet wurde, aufgetragen. Das Ergebnis war eine Gerade mit negativer Neigung. Ein ähnliches Resultat wurde mit den Messwerten von Foster erhalten. Darüber hinaus wurde die freie Quellung gegen das Ausmass tetraedrischer Drehung in der Tonstruktur, das ebenfalls aus der mineralogischen Zusammensetzung des Tons berechnet wurde, aufgetragen. Das Ergebnis war eine Schar beinahe paralleler Gerader, die sich durch die Menge von tetraedrischem Al^{3+} in den mit ihnen identifizierten Tönen von einander unterschieden. Diese Ergebnisse führten zu der Anregung, dass die Tonoberfläche als Schablone für die Struktur des benachbarten Wassers wirkt, und dass bei Veränderung in der Konfiguration der Oberfläche, eine entsprechende Veränderung in der Wasserstruktur eintritt. Dadurch erfolgt aber eine Änderung in der freien Energie des Wassers und folglich in der Quellung des Tons.

Резюме— Авторы, побуждаемые наблюдениями Фостер о существовании зависимости свободного набухания от октаэдрических замещений, предприняли определение свободного набухания шести образцов Na-монтмориллонита с различной степенью октаэдрических и тетраэдрических замещений. При этом было установлено, что монтмориллониты обнаруживают заметные различия свободного набухания. Эти различия не связаны с различиями в катионно-обменной емкости. Не связаны они также и с различиями дзета-потенциала, который является критерием диссоциации катионов. Подсчет показал, что они не могут быть обусловлены различиями в силах отталкивания или ван-дер-ваальсовского притяжения двойных слоев. Поэтому, для выяснения того, влияют ли на процессы набухания изменения в размерах слоев, обусловленные изоморфными замещениями, значения степени свободного набухания были нанесены на график ее зависимости от размеров b , которые были вычислены с учетом минерального состава. Результат выражался прямой линией с отрицательным наклоном. Аналогичный результат был получен с использованием данных Фостер. Кроме того, значения степени свободного набухания были нанесены на график ее зависимости от степени разворота тетраэдров, которая также была подсчитана с учетом минерального состава. Результирующий график представлял собой семейство примерно параллельных прямых линий, отличающихся друг от друга количеством тетраэдрического Al^{3+} в соответствующей глине. Полученные результаты приводят к предположению, что поверхность глины действует как шаблон, определяющий структуру смежного слоя воды и что вследствие изменения поверхности происходит изменение структуры воды. Это вызывает изменение свободной энергии воды, и следовательно, способности к набуханию глин.