

# The Limited Crystalline Swelling of Smectites in $\text{CaCl}_2$ , $\text{MgCl}_2$ , and $\text{LaCl}_3$ Solutions

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The limited crystalline swelling, or transition of the basal spacings from  $\sim 15.5$  to  $\sim 19.0$  Å, has been studied for some well-defined Mg-, Ca-, or La-saturated montmorillonites equilibrated with corresponding salt solutions. The swelling occurs over a range of salt concentrations depending upon the magnitude and structural origin of the clay's surface charge. The higher its charge, the lower the salt concentration at which the clay swells. Ca-saturated smectites with high surface charges, developed principally from  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  substitutions in tetrahedral sites, have restricted swelling in water. The swelling phenomenon involves a balance between cation hydration forces and interlayer electrostatic forces. The transition from 15.5 to 19.0 Å spacings can be considered an osmotic process; this is discussed. © 1991 Academic Press, Inc.

## INTRODUCTION

This paper concerns the limited crystalline swelling of smectite clay minerals. Smectites belong to the larger group of 2:1 layer lattice aluminosilicates which also includes the micas and the vermiculites. The description 2:1 refers to the fact that each elementary silicate layer of  $\sim 10$  Å thickness is made up of two sheets of silicon-oxygen tetrahedra, one either side of an aluminum-oxygen octahedral sheet. The minerals have various ionic substitutions such as  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sites and, for example,  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in the octahedral sites. These substitutions cause the crystal lattices to be negatively charged, but the negative lattice charge is balanced by interlayer materials, including hydrated cations, individual cations, and hydroxide groups. The smectites have a range of substitutions so that the various members of the group have a lattice charge deficiency ranging from about 0.6 to about 1.2 electrons per unit cell composing an anionic framework of  $\text{O}_{20}(\text{OH})_4$ . Their lattice

charges are neutralized by exchangeable hydrated cations. When the substitutions occur in the tetrahedral sites, the lattice charge deficiency has its origin  $\sim 2.0$  Å from the surfaces of the silicate layers but when the substitutions are in the octahedral sites the origin is  $\sim 4.7$  Å from the surfaces. The best known and most extensively investigated smectite is the montmorillonite from Upton, Wyoming. The charge of Wyoming montmorillonite not only is at the lower end of the range but also is largely generated from octahedral substitutions.

The expansion of montmorillonites with charges balanced by polyvalent ions, such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , or  $\text{La}^{3+}$ , is limited to basal spacings of 19 Å or less. This behavior contrasts with that of montmorillonites with charges balanced by monovalent, alkali metal ions such as  $\text{Li}^+$  and  $\text{Na}^+$ . In solutions more dilute than about 0.25 M, the latter montmorillonites exhibit extensive crystalline swelling. For instance Na-montmorillonite (Wyoming) expands to give a basal spacing of 43 Å in 0.25 M NaCl. In more dilute solutions it expands to higher spacings which are a linear function

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of the reciprocal of the square root of the concentration Norrish (1). Such swelling is sometimes referred to as macroscopic swelling.

The swelling of smectites depends upon their structures, their chemical compositions, and the properties of enveloping electrolytes. In turn, smectite swelling influences the dispersability, the permeability, and the engineering properties of soils and consequently it is of great practical importance. Furthermore, some smectites are important for a number of industrial processes, notably oil drilling where the thixotropic character of an aqueous suspension of the Na-saturated mineral can help suspend solids in the drilling mud when drilling ceases. Smectites have also been used in the clarification of beer and in foundry sands.

The nondispersion of montmorillonite-rich soils from Queensland was attributed by Norrish and Tiller (2) to very high electrostatic interactions between the clay layers. These interactions resulted from extensive substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sites of the clays' crystal structure.

Quirk (3, 4) showed, from permeability measurements, that Na- and Ca-saturated montmorillonite behaved very differently; Na-montmorillonite expanded at low electrolyte concentrations and so lost permeability, while Ca-montmorillonite did not swell as much and maintained high permeabilities, even in distilled water.

That Ca-montmorillonites are restrained in their swelling by the existence of a potential minimum, when the particles are separated by a distance of  $\sim 10 \text{ \AA}$ , is an important phenomenon. This has been discussed by Quirk (5) in relation to soil behavior and in particular the management of sodium affected soils under irrigation.

Clay swelling is broadly of two kinds and each can cause damage to man-made structures. Crystalline swelling, the first kind, results from the hydration of exchangeable cations. Macroscopic swelling, the second kind which may proceed from crystalline swelling, was analyzed by Norrish (1) in terms of the inter-

action of diffuse double layers as discussed by Langmuir (6) and Verwey and Overbeek (7). However, Low (8) has pointed out that structural forces make a major contribution to the swelling pressures exerted by Na- and Li-montmorillonites in very dilute solutions. Crystalline swelling occurs in steps, corresponding to from one to four sheets or layers of water between the silicate layers, and pressures, due to such swelling can be very large: between 10 and several hundred megapascals. Pressures due to macroscopic swelling, although much smaller ( $\sim 2 \text{ MPa}$ ), act over greater distances.

Posner and Quirk (9) examined the crystalline swelling of a *single* montmorillonite (Wyoming) variously saturated with Li, Na, K, Ca, Mg, Sr, or Ba ions and in equilibrium with corresponding salt solutions over the range in concentration from around 0.5 *m* to saturation. Within this range the basal spacings varied from between about 19 and approximately 15.5  $\text{ \AA}$ . Recently, Slade *et al.* (10) measured the crystalline swelling of *various*, differently charged, smectites in equilibrium with NaCl solutions having concentrations between 0.25 and 2.5 *m*. The more highly charged smectites, especially those with significant tetrahedrally derived components to their charges, swelled differently from the lower charged ones. In contrast to Wyoming montmorillonite, highly charged Na-montmorillonites neither swelled to 19  $\text{ \AA}$  nor swelled macroscopically ( $>43 \text{ \AA}$ ), even in distilled water.

The present paper examines the extent of crystalline swelling shown by differently charged Mg-, Ca-, or La-saturated montmorillonites in equilibrium with corresponding salt solutions over a range of concentrations.

## EXPERIMENTAL

### *Materials*

Mg-, Ca-, and La-chloride solutions, with concentrations ranging 0.25–2.0, 0.25–2.55, and 0.05–3.2 *m*, respectively, were prepared from analytical grade salts.

Baes and Mesmer (11) give the first hydrolysis product of  $\text{La}^{3+}$  as  $\sim 10^{-10}$ . Since the pH measured for a 1 *m*  $\text{LaCl}_3$  solution was 3.5, the ratio of  $[\text{La}(\text{OH})^{2+}]/[\text{La}^{3+}]$  present will be  $\sim 10^{-6.5}$ . Under these circumstances, and the concentrations used for the  $\text{LaCl}_3$  solutions, hydrolysis was not likely to have been significant.

The smectites used for this work were part of the group whose swelling, in  $\text{NaCl}$  solutions, was described by Slade *et al.* (10). Source localities and compositions were given by these authors. From the compositions the total and the tetrahedrally derived charges were calculated and are respectively given in parentheses in the following: Nibost (1.14, 0.74), Drayton (1.06, 1.02), Otay (1.04, 0.06), Wyoming (0.74, 0.08), and Hectorite (0.70, 0.04).

Initially, approximately 1-g portions of the  $<2\text{-}\mu\text{m}$  fractions of each Na-saturated smectite were Ca-saturated by suspension and centrifugation in molar  $\text{CaCl}_2$  solution. The process was repeated four times and the clay was then washed twice with distilled water and finally with ethanol until free of chloride ions. The Mg- and La-saturated clays were prepared from the Ca-clays.

### Methods

*Control of swelling and X-ray diffractometry.* The methods used for these aspects of the work have been described by Slade *et al.* (10).

*Calculation of  $p/p_0$  values and osmotic pressures.* Where the relative vapor pressures for the various solutions were not available, they were calculated from osmotic coefficients with the following equation from Robinson and Stokes (12),

$$\ln a_A = \ln \frac{p}{p_0} = - \frac{\nu m W_A}{1000} \phi, \quad [1]$$

where  $a_A$  is the activity of the solvent (water),  $\nu$  is the number of moles of ions formed from 1 mole of electrolyte,  $m$  is the molarity of the solution,  $W_A$  is the molecular weight of solvent (water), and  $\phi$  is the molal osmotic coefficient.

The  $p/p_0$  values were transposed into equivalent osmotic pressures ( $P$ ) by the relationship

$$P = \frac{RT}{V_{\text{H}_2\text{O}}} \ln \frac{p}{p_0} \quad [2]$$

in which  $R$  is the gas constant,  $T$  the kelvin temperature, and  $V_{\text{H}_2\text{O}}$  molal volume of water.

### RESULTS AND DISCUSSION

Figures 1, 2, and 3 show the basal spacings respectively of the Ca-, Mg-, and La-saturated clays plotted against the concentrations of corresponding electrolytes.

These figures broadly show that the concentrations of electrolyte at which changes to higher spacings occur differ from sample to sample within each group of homoionic clays. The most highly charged clays such as the Drayton and Nibost montmorillonites, with total charges of 1.06 and 1.14 electrons per unit cell, respectively, swell at the lowest concentrations, but even then not to the same extent as the lower charged Wyoming montmorillonite. There are other aspects of the swelling which are specific to the ionic modification of each clay and to its enveloping electrolyte. A discussion of the details follows.

#### Swelling in $\text{CaCl}_2$

In calcium chloride solutions, the basal spacings of the more highly charged clays in-

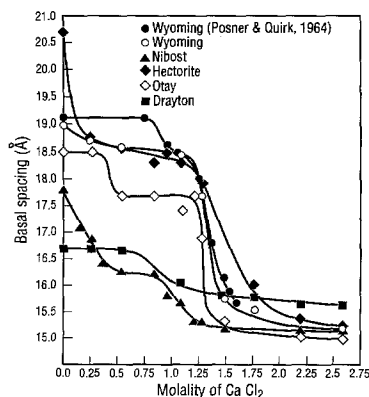


FIG. 1. Basal spacings ( $\text{\AA}$ ) of Ca-saturated montmorillonites as a function of  $\text{CaCl}_2$  concentration in enveloping electrolyte.

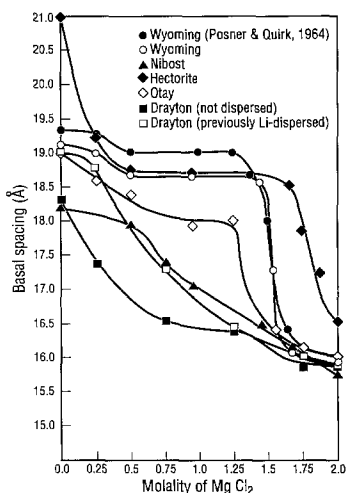


FIG. 2. Basal spacings (Å) of Mg-saturated montmorillonites as a function of MgCl<sub>2</sub> concentration in enveloping electrolyte.

clude not only values characteristic of two or three interlayer water sheets ( $\sim 15$  and  $\sim 18.5$  Å) but also values which probably correspond to small rearrangements of these basic packing arrangements. In Fig. 1 note as examples the final plateau in the swelling curve at 16.7 Å for Drayton montmorillonite, and also the steps in the swelling curves at 17.7 Å for Otay, and 16.25 Å for Nibost montmorillonite, respectively. For each of these three given basal spacings a rational set of four or more 001 reflections was observed.

Figure 1 also shows the basal spacings obtained by Posner and Quirk (9) for Wyoming montmorillonite in CaCl<sub>2</sub> solutions. Over a substantial part of the concentration range, the agreement between the former and the present work on the Wyoming clay is good. However, the new study shows a progressive increase in swelling from 18.5 to 19.0 Å, rather than the previously reported sharp increase. Such a small difference may simply result from experimental error.

#### Swelling in MgCl<sub>2</sub>

The swelling curves (Fig. 2) for the Nibost or Drayton montmorillonites in magnesium

chloride solutions do not have any distinct steps and the curve for Otay montmorillonite has a less well defined one at 18 Å. The high surface density of charge for Otay montmorillonite results chiefly from octahedral substitutions but the high surface charges for the Nibost and Drayton samples include substantial, tetrahedrally derived components. Apparently, for these three highly charged smectites, the hydration energy of Mg<sup>2+</sup> is barely sufficient to overcome the electrostatic attractive forces and consequently homogeneous crystallites with three sheets of interlayer water do not form. A set of ill-defined, interstratified, structure units seem to coexist instead.

The enthalpy values of hydration, reported by Bernal and Fowler (13), for the Mg<sup>2+</sup> and the Ca<sup>2+</sup> ions, are 490 and 410 kcal/g ion, respectively. The difference results in the basal spacing of a Mg<sup>2+</sup>-montmorillonite being greater than the value for the corresponding Ca<sup>2+</sup>-montmorillonite at a given electrolyte concentration.

Highly charged, Mg-saturated smectites have their crystalline swelling limited to less than 19 Å. This value is intermediate between that found for smectites with a lower charge on the one hand and Mg-vermiculites on the other. The latter do not swell beyond the two-water sheet state, whereas the structures of the former readily swell to include three sheets of water between their silicate layers. Compared with smectites, all vermiculites have signifi-

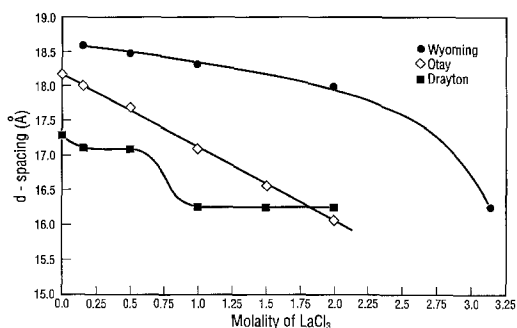


FIG. 3. Basal spacings (Å) of La-saturated montmorillonites as a function of LaCl<sub>3</sub> concentration in enveloping electrolyte.

cantly greater tetrahedral substitutions. These produce intense electrostatic attractions which restrict crystalline expansion to the limiting structure incorporating two interlayer water sheets, except for low-charge, Li-saturated, vermiculites in water which give spacings greater than 40 Å (Norrish and Rausell-Colom (14)).

Figures 1 and 2 show that in  $\text{CaCl}_2$  or  $\text{MgCl}_2$  solutions, with concentrations below 0.25 *m*, hectorite swells more than Wyoming montmorillonite. This difference results from hectorite having a lower charge (0.70 overall, 0.04 tetrahedral) than Wyoming montmorillonite (0.74 overall, 0.08 tetrahedral). The larger maximum spacing of Mg-hectorite (21.0 Å) than of the Ca-clay (20.7 Å) follows from the enthalpy of hydration of  $\text{Mg}^{2+}$  being greater than that of  $\text{Ca}^{2+}$ .

#### Swelling in $\text{LaCl}_3$

The three montmorillonites selected for the swelling experiments in  $\text{LaCl}_3$  solutions had contrasting charges: Wyoming, low (octahedrally derived); Otay, high (octahedrally derived); and Drayton, high (tetrahedrally derived). Figure 3 indicates that the swelling of each of these clays is substantially influenced by its charge. Although trivalent ions have high enthalpies of hydration, 768 kcal/g ion for  $\text{La}^{3+}$  (Bernal and Fowler (13)), local electrostatic attractive forces involving such interlayer ions are also high, and consequently the swelling of the three La-smectites in water is more restrained than that of their  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  counterparts. For instance, the low charged Wyoming montmorillonite attains a spacing of only 18.5 Å in water but the more highly charged Otay and Drayton montmorillonites attain spacings of 18.2 and 17.2 Å, respectively. The lower basal spacing for the Drayton sample can be attributed to the fact that virtually all its charge is developed in the tetrahedral sites.

A further effect of the competition between the hydration energy of the saturating ions and the attraction due to surface charges can be

seen by comparing the basal spacing of Wyoming montmorillonite with the spacings of the more highly charged clays in the 2 *m*  $\text{LaCl}_3$  solution. At this concentration, the spacing of Wyoming montmorillonite is already 18 Å but the spacing of the more highly charged clays is 16 Å. It is noteworthy that none of the divalent ion clays reached 18 Å at such a high electrolyte concentration for which the osmotic pressure of the enveloping solution is 25 MPa. By contrast, the transitions for Mg- and Ca-Wyoming montmorillonite are virtually complete when the osmotic pressures of the enveloping solutions are 15 and 10 MPa, respectively (Fig. 4). This phenomenon emphasizes the effect of the high hydration energy of the  $\text{La}^{3+}$  ions. When the concentration of the  $\text{LaCl}_3$  solution was increased to 3.2 *m*, the basal spacing of La-Wyoming montmorillonite fell to 16.2 Å. Information on the solution properties of  $\text{LaCl}_3$  is not available for this higher concentration, but an extrapolation of the data from 2 *m* indicates that its osmotic pressure approaches 100 MPa.

Figure 3 shows that the La-Otay montmorillonite displays a progressive increase in spacing, rather than a sharp transition. This, in conjunction with its maximum swelling to only about 18 Å, indicates that the nature of its swelling is significantly different from that which occurs with other ions. The smoothness

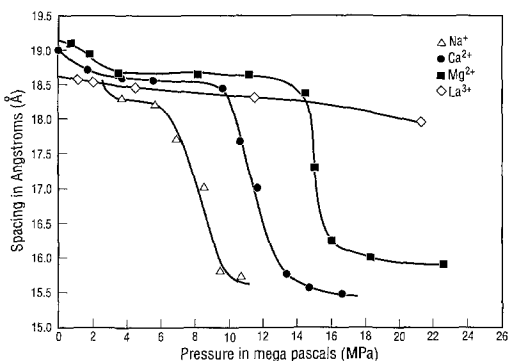


FIG. 4. Basal spacings (Å) of Na- (data from (10)), Ca-, Mg-, and La-saturated Wyoming montmorillonite in relation to the osmotic pressures (MPa) of corresponding electrolytes.

of the swelling curve probably reflects a marginal balance between attractive and swelling forces at a given concentration. This allows a number of ill-defined interlayer arrangements, perhaps including randomly interstratified layers, to coexist for all but the highest and the lowest concentrations.

*Limited Swelling Considered as  
an Osmotic Phenomena*

The crystalline swelling of various ionic modifications of montmorillonite has already been briefly commented on in relation to the osmotic pressures of enveloping solutions. However, Murray and Quirk (15) have pointed out that the swelling phenomenon involves an osmotic equilibrium between the bulk solution and the electrolyte within the interlayer spaces. Previously, Posner and Quirk (16) had shown that salt does not enter the interlamellar region until the 19- to ~15.5-Å transition has taken place and hence the movement of water from the interlamellar space can be regarded as an osmotic effect. The spacing of ~15.5 Å is sustained to very high concentrations even though the osmotic pressure of the bathing solution increases markedly.

Figures 1 and 2 extend the information on Na-smectites to Ca- and Mg-smectites and reveal the wide range of swelling behavior due to variation in surface density of charge and to its structural source. A more detailed discussion of the reasons for these variations follows.

The swellings of Wyoming and Otay montmorillonites with respectively low and high charges, arising principally in the octahedral sites, are contrasted in Table I; some general conclusions emerge. The osmotic pressure of the solution at which the transition is half-complete is lower for the material with the higher surface charge. For instance, for Na-Otay montmorillonite the pressure is 4.0 MPa and for Na-Wyoming montmorillonite it is 8.2

TABLE I

Crystalline Swelling of Wyoming and Otay Smectites in Relation to Osmotic Pressure, Relative Vapor Pressure, and Exchangeable Cation

Ion	Pressure midway between ~15.5 Å and final spacing (MPa)	Relative vapor pressure ( $p/p_0$ )	Final spacing (Å)
Wyoming smectite			
Na	8.2	(0.943)	18.3
Mg	15.2	(0.894)	18.6
Ca	11.4	(0.920)	18.5
Otay smectite			
Na	4.0	(0.974)	18.8
Mg	12.5	(0.912)	18.0
	2.1	(0.983)	19.0
Ca	10.8	(0.923)	17.7
	3.2	(0.980)	18.5

MPa. Similar, but less marked, differences exist for the other ions. This behavior can be explained in general terms by reference to the treatment of Norrish (1).

When the exchangeable interlayer ions and the charged silicate surfaces are regarded as condenser plates, the attractive potential is given by

$$E_A = \frac{2\pi\sigma^2 D}{\epsilon}, \quad [3]$$

in which  $\sigma$  is the surface density of charge,  $D$  is the half-distance of separation of the plates, and  $\epsilon$  is the dielectric constant. The repulsive potential arising from the hydration of the ions is given by

$$E_R = \frac{2U\sigma}{zeN} \quad [4]$$

in which  $U$  is the hydration energy of an ion,  $z$  is valency,  $e$  is the electronic charge, and  $N$  is Avogadro's number.

From Eq. [3] it may be noted that the attractive potential varies as the square of the surface density of charge, whereas from Eq. [4], it can be seen that the repulsive potential increases linearly with charge density. As a result, the transitions of the basal spacings from  $\sim 15.5$  to  $\sim 19.0$  Å for clays with higher charge densities require greater differences in osmotic pressure between solutions in the interlamellar spaces and enveloping solutions to overcome the larger attractive potentials. To have a greater difference in osmotic pressure between the interlamellar spaces and the bulk solution, the latter must be more dilute.

The same qualitative arguments apply to the effect of hydration energy and cation valency on the transition. The repulsive potential is, from the above equation, related to  $U/z$  which for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  takes the values 114, 205, and 245 kcal/g ion, respectively. The osmotic pressures of the enveloping solutions at which the transitions take place, as indicated in Figs. 4 and 5 and Table I, are in the order  $\text{Mg} > \text{Ca} > \text{Na}$ . For any given smectite, the transition between 15.5 and 18.5 Å occurs in a salt solution at a concentration dependent upon the ion's  $U/z$  value; the higher  $U/z$ , the higher the salt concentration. This occurs because at higher values of  $U/z$ , the differences in the osmotic pressures re-

quired to effect the transitions are less. Norrish (1) suggested that where the interlayer cations are far from one another, as they will be when the interlayer cations have a high charge, the relationship of an ion to the silicate surface may more appropriately be considered a point charge adjacent to a thick plane conductor. This contrasts with the situation just discussed when a condenser model was used. For the point charge model Norrish (1) has defined the ratio of the swelling potential to the attractive potential as equal to  $U\epsilon/z^2$ , with symbols as defined in Eqs. [3] and [4]. If, for example, the La-Otay montmorillonite is compared with the Mg-modification, then  $U$  has only changed from 490 to 768 kcal/g ion for  $\text{Mg}^{2+}$  and  $\text{La}^{3+}$ , respectively (Bernal and Fowler (13)). The attractive potential, as reflected in  $z^2$ , however, has changed from 4 to 9, an increase of 2.25 times, whereas the hydration potential has increased by only 1.6, when  $\text{Mg}^{2+}$ -ions are exchanged for  $\text{La}^{3+}$ -ions.

Table I shows that the transition to 18.5 Å for Ca-Wyoming montmorillonite is one-half complete at an osmotic pressure of  $\sim 12$  MPa. For the more highly charged Ca- and Mg-Otay montmorillonite, the transition occurs in two stages at 10–12 MPa and at 2–3 MPa. These steps probably correspond to metastable interlayer water structures which occur when the ordered structure at 18.5 Å can be reached only with difficulty, because of the high attractive potential.

The attractive forces between clay particles arising from ion-ion correlations have been calculated from the primitive model of electrolyte solutions by Kjellander *et al.* (17). They reported that such attractive forces for divalent ions are approximately five times larger than the traditional van der Waal forces and increase with increasing surface density of charge. The potential minimum, i.e., the particle separation, also decreased with increasing charge density. These findings are in accordance with the results presented here in that as the surface charge density increases,

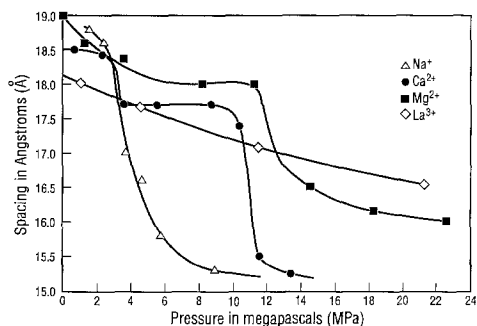


FIG. 5. Basal spacings (Å) of Na- (data from (10)), Ca-, Mg-, and La-saturated Otay montmorillonite in relation to the osmotic pressures (MPa) of corresponding electrolytes.

the attractive forces assist the osmotic pressure in effecting the transition. The transition therefore takes place at the smaller osmotic pressure differential and so at a lower concentration in the enveloping solution.

In a recent paper, Quirk and Pashley (18) have reported measurements of structural forces between two isolated, molecularly smooth, Ca-muscovite surfaces. The work has indicated that the swelling of Ca-clays involves (i) an interplay of repulsive structural forces in slit-shaped pores (Murray and Quirk (19)) when the surfaces are separated by more than 10 Å, and (ii) attractive ion-correlation forces in regions of particle overlap, where the surfaces are separated by less than 10 Å. The nature of the structural forces has been discussed by Pashley and Quirk (20).

The present paper, in focusing on the limited crystalline swelling of montmorillonites, has shown that the magnitude and origin of the structural charge markedly influences the interaction of clay crystals separated by less than 10 Å.

#### CONCLUSION

The method of using enveloping salt solutions to produce crystalline swelling in clays is an especially convenient way to establish the relative vapor pressure, or activity of water, necessary to cause the 15.5- to 18.5-Å transition. Other workers, notably Mooney *et al.* (21) and Glaeser and Méring (22), used adsorption from the vapor phase but were not able to determine the vapor pressure for the transition because of the necessity to have precise temperature control near saturation. The relative vapor pressures for the transitions shown by the clays discussed here are shown in Table I.

Montmorillonite minerals occur commonly in soils and are dominant in the black earths which are widely distributed in Australia, India, and the southern United States, princi-

pally Texas. The present work demonstrates that it is not appropriate to consider that soil montmorillonites will generally behave like Wyoming montmorillonite. For example, a black earth soil from the Emerald Irrigation Area in Queensland contains 70% montmorillonite (Murray *et al.* (23)), with a charge similar to that of Nibost. As expected, the swelling of this Queensland clay resembles that of Nibost rather than that of the very different Wyoming montmorillonite. The Drayton montmorillonite is also a major component of another Queensland soil. This clay carries both high total and tetrahedral charges (1.06 and 1.02 electrons/cell, respectively) and, in its field state, is largely Ca-saturated. Here, it has been shown that such a material exhibits very restricted swelling. This property is in accordance with the subplastic character reported for the whole soil by Norrish and Tiller (2).

Since soil clays so strongly influence the physical properties of soils, the variability of smectite clays and consequently their swelling behavior is emphasized by the present study.

#### ACKNOWLEDGMENT

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