

THE MICROSTRUCTURE OF THREE Na^+ SMECTITES: THE IMPORTANCE OF PARTICLE GEOMETRY ON DEHYDRATION AND REHYDRATION

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Abstract—Recent pedological evidence of the widespread distribution of beidellites in soils indicates the need for a greater knowledge of the effect of charge location on the microstructural organization of Na^+ smectite in gels. After equilibration at a suction pressure of 3.2 kPa before and after desiccation, TEM observations showed large differences between a beidellite and both a low and high charge montmorillonite. Monolayers were rare; individual layers were instead organized in particles with larger interparticle distances. This has implication for theories relating swelling pressures to interlayer distances or surface areas and implies the need for a geometrical approach to the study of swelling in smectites. Location of isomorphous substitution in the tetrahedral sheet of smectites results in an increased lateral extension of overlapping layers. This was reflected in a greater capacity to rehydrate after desiccation. Increased number of layers in particles were found with increasing surface charge density. The geometric organization of the particles is critical to the understanding of the ability of Na^+ smectite to hold water against an applied suction.

Key Words—Beidellite, Layer charge, Microstructure, Montmorillonite, Particle, Smectite, TEM.

INTRODUCTION

Surface charge densities and the locations of isomorphous substitution in smectites play a critical role in their microstructural organization. Electron microscopic studies on the microstructure of Na^+ smectites have been limited principally to the low-charge montmorillonites (Tessier, 1993). Recently, Wilson (1987) suggested that beidellites were common in soils, while montmorillonites were more typical of geologic materials. In support of this, many recent pedologic studies offer evidence that beidellites are widespread in soils (Lim and Jackson, 1984; Badraoui *et al.*, 1987; Badraoui and Bloom, 1990; Aragonese and Garcia-Gonzales, 1991; Robert *et al.*, 1991). In order to improve our understanding of critical soil processes such as the shrink-swell potential, a comparison of the properties of montmorillonites to that of a beidellite is, therefore, warranted. Changes in water content of Na^+ smectites after a dehydration-rehydration cycle have been measured (Tessier, 1991), but no microscopic investigation of the resulting microstructures has been made.

Various theories have been proposed to explain the formation and structure of smectite gels. The double layer theory predicts a relation between swelling pressure and interlayer distances, but deviations have been observed for a Na^+ montmorillonite. These deviations are believed to be caused by the formation of particles (Lubetkin *et al.*, 1984). Double layer theory has led to a model of the microstructure of smectite layers and particles into various pH dependent geometrical arrangements such as the cardhouse structure (van Ol-

phen, 1977). The presence of such structures has been questioned previously (Callaghan and Ottewill, 1974; Tessier and Pedro, 1982; Lubetkin *et al.*, 1984; Chen *et al.*, 1990). A different theory (Low, 1980, 1987) proposes that the surface area of the smectites controls the structure of water at distances greater than three or four molecular layers of water. Both theories explicitly require the presence of smectite monolayers, which have yet to be observed in gels of natural Na^+ smectites.

Based on the above discussion, it seemed necessary to examine gels of Na^+ smectite for the presence of monolayers and for the geometric arrangement of the layers and particles. Changes in the water contents of the gels, before and after a desiccation-rehydration cycle, will be examined to determine the role of the geometry of smectite particles on this property. The effects of layer charge and location of isomorphous substitution on the microstructure and resulting water contents of the smectites will also be investigated.

MATERIALS AND METHODS

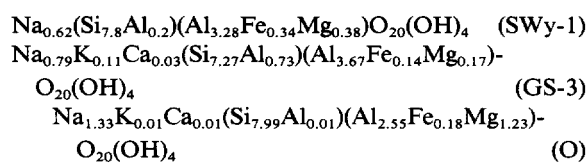
Three smectites with different charge characteristics were used in this study: a beidellite (GS-3) from DeLamar mine near Silver City, Idaho; a low-charge montmorillonite (SWy-1) from Crook County, Wyoming; and a high-charge montmorillonite from Otay, California. The three smectites were prepared by washing in sodium perchlorate solutions following the method of Sposito and LeVesque (1985) and the $<0.2 \mu\text{m}$ e.s.d. fractions were separated by centrifugation (Jackson, 1979).

Table 1. Selected physical and chemical data for the three smectites.¹

Smectite	Surface charge (mMol. kg ⁻¹)	Surface area (m ² g ⁻¹)
Beidellite	759 (46)	597 (1)
Otay	1088 (21)	825 (15)
SWy-1	748 (25)	800 (28)

¹ Data from Hetzel and Doner (1993).

The structural formulae of the SWy-1 montmorillonite (Weaver and Pollard, 1973), beidellite (GS-3) and Otay (O) montmorillonite (Hetzel and Doner, 1993) are:



The beidellite sample contains 10% kaolinite and 6% illite by weight, which is reflected in the lower specific surface of this sample. Selected data for the three smectites are given in Table 1.

The Na⁺ smectite suspensions were brought to a final equilibrium at a suction pressure of 3.2 kPa following the procedure of Tessier and Berrier (1979). Three different paths were followed to reach the final suction pressure of 3.2 kPa. The first pathway consisted of drying the suspensions, i.e., desiccation. For the second treatment, the three smectites were initially equilibrated at a suction pressure of one MPa in a pressure plate apparatus prior to rehydration to 3.2 kPa. In the third treatment, an initial desiccation humidity over a saturated solution of K⁺CH₃COO⁻, at 22% relative humidity (Robinson and Stokes, 1970) equivalent to about 200 MPa, was performed prior to rehydration to 3.2 kPa. Deionized water at equilibrium with the atmosphere was used, and all gels had a final pH below 7. The gels of the first and third treatments were selected for the TEM analysis.

Sample preparation of the smectites for TEM analysis follows the method of Tessier (1984). Briefly, the gels were carefully cut so as to preserve their orientation and placed in dissolved Agar, which helps preserve the microstructure during the ensuing solvent exchange. After solidification, the excess Agar was removed and the sample placed in a Reichert Jung Lynx el sample embedder. Water was first replaced by methanol, then propylene oxide, and finally Spurr's resin. The smectites were then placed in a 65°C oven for 24 hr to polymerize the resin. The samples maintained their original color throughout the embedding procedure, as had been previously noted for a nontronite (Stucki and Tessier, 1991). Thin sections were then cut with a diamond knife on a Reichert-Jung Ultracut E microtome

Table 2. Water content (g H₂O g⁻¹ clay) of the Na⁺ smectites at various desiccations.

Treatment	Beidellite	SWy-1	Otay
3.2 kPa drying	8.77	13.6	8.13
one MPa drying	0.53	1.17	0.95
3.2 kPa after one MPa drying	8.62	8.03	7.11
200 MPa drying	0.077	0.084	0.13
3.2 kPa after 200 MPa drying	7.56	4.56	3.16

to a thickness of 50–60 nm and a width of about 100 μm. They were then placed on colloidon coated Cu grids. Electron micrographs were obtained on a Philips model 420 transmission electron microscope (TEM).

RESULTS

The water content of the three Na⁺ smectites at equilibrium after various treatments are given in Table 2. The results at 3.2 kPa, during the first desiccation, followed the relation of layer charge with volumetric water content previously found by Tessier and Pedro (1987). Applying a suction pressure of one MPa prior to rehydration led to a decreased water content for the three smectites as compared to the initial desiccation. Increasing the desiccation stress from one MPa to 200 MPa led to a further decrease in water content after rehydration. Both dehydration treatments resulted in a layer charge-water content relationship that deviated from that found by Tessier and Pedro (1987). At a relative humidity of 22% (200 MPa), the water contents were related to the exchange capacity as expected (Quirk, 1955).

In the following, layer denotes the individual 2:1 smectite. The microstructural organization of the smectites is described in terms of particles, i.e., the assemblage of elementary layers, which are more or less ordered along the c-axis.

The three smectites showed a very different organization after the initial desiccation (Figure 1). At low magnification, it can be seen that the distribution of the size and organization of the particles for each smectite was homogeneous and that the smectites were relatively free of minerals other than phyllosilicates. The Otay montmorillonite can be described as formed of thicker particles along the c axis (10–60 nm), with a short lateral extension (0.1–0.60 μm) in the ab plane (Figure 1a). It displayed an isotropic orientation distribution. The SWy-1 montmorillonite also showed an isotropic orientation distribution, but the lateral extension of the particles (0.3–0.9 μm) was greater than for the Otay montmorillonite (Figure 1b). The increased lateral extension was complemented with a slightly thinner particle along the c axis (10–40 nm). The beidellite had a considerable lateral extension in the ab plane such that it was not quantifiable (Figure 1c) and exhibited a thickness in the c-axis of 10–50

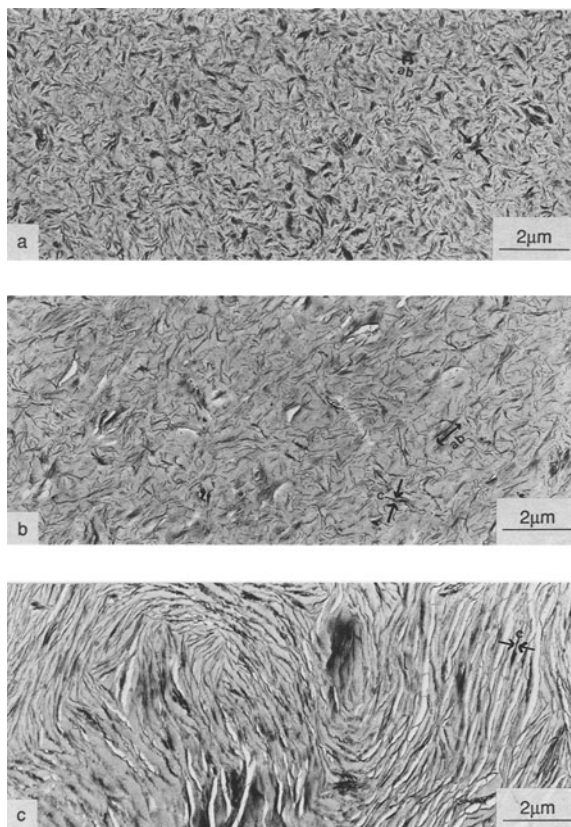


Figure 1. Low resolution transmission electron micrographs of the Na^+ smectites equilibrated at a suction pressure of 3.2 kPa, initial desiccation: a) Otay montmorillonite, b) SWy-1 montmorillonite, and c) Beidellite. *ab* denotes the length of the *ab* plane and *c* denotes the thickness along the *c* axis.

nm. The thicknesses of the SWy-1 montmorillonite and of the beidellite are likely to be overestimates due to their wavy morphologies.

Desiccation in a controlled environment of 22% R.H. (200 MPa) and subsequent rehydration resulted in a greater alignment, or anisotropy, of the particles for all three smectites (Figure 2), and each smectite maintained an homogeneous size distribution. Indirect evidence has already been presented for the alignment of montmorillonite particles after an applied suction pressure and subsequent rehydration (Warkentin *et al.*, 1957; Callaghan and Ottewill, 1974). The increase in anisotropy was accompanied by a change in the lateral extension and an increase in the thickness of the particles. For the Otay montmorillonite, the particles had larger lateral extensions (0.1–0.9 μm) and greater thicknesses (10–100 nm). The SWy-1 montmorillonite particles also had increased lateral extensions (0.4–1.5 μm) and larger thicknesses (10–60 nm). Particle thicknesses also increased for the beidellite (10–100 nm), but the extensions in the *ab* plane were smaller and could be quantified (0.7–2.5 μm).

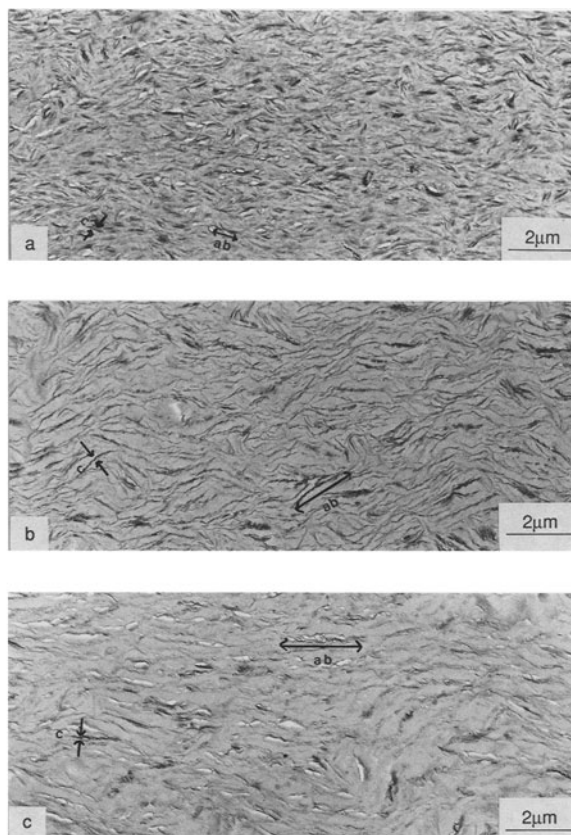


Figure 2. Low resolution transmission electron micrographs of the Na^+ smectites equilibrated at a suction pressure of 3.2 kPa after an initial desiccation at 200 MPa: a) Otay montmorillonite, b) SWy-1 montmorillonite, and c) beidellite. *ab* denotes the length of the *ab* plane and *c* denotes the thickness along the *c* axis.

The isotropic organization of the Otay montmorillonite particles after the initial desiccation can still be seen at high magnification (Figure 3a). For the SWy-1 montmorillonite, the isotropic organization of the particles was only found at lower magnifications, and for the beidellite some local order can be seen even at lower magnification (Figure 1c).

Higher magnification showed that the lateral extension of the Na^+ Otay montmorillonite after the initial desiccation (Figure 3) was only slightly longer than that of the individual layers (30–85 nm) and, after one drying and rewetting cycle, the lateral extension of the particles increased slightly. The individual layers of the Na^+ SWy-1 montmorillonite (35–90 nm) were slightly longer than those of the Otay montmorillonite, but the lateral extension was greater (Figure 4). The individual layers of the Na^+ beidellite were longer than those of the montmorillonite (100–200 nm) but, as with the SWy-1, were much smaller than the lateral extension of the particles (Figure 5). Lateral extensions of the

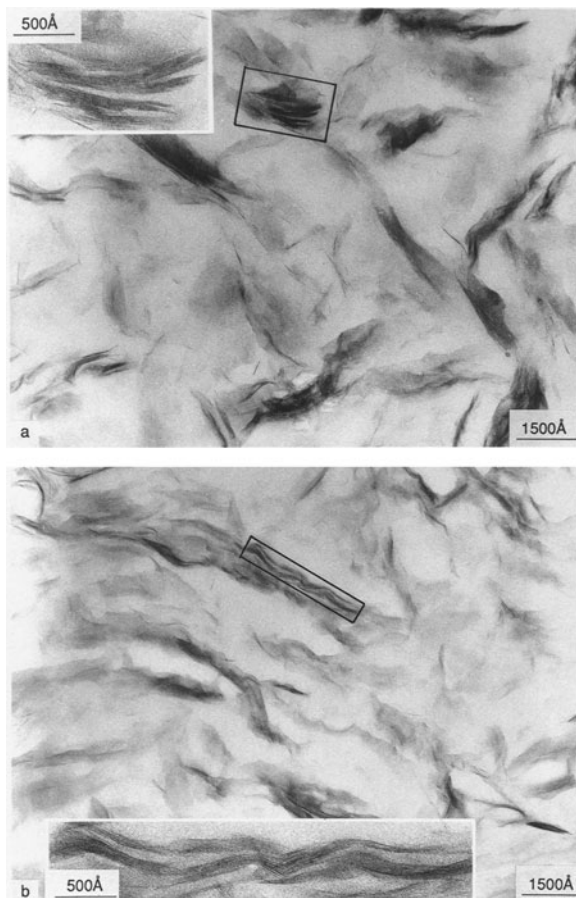


Figure 3. High resolution transmission electron micrographs of the Na⁺ Otay montmorillonite equilibrated at a suction pressure of 3.2 kPa: a) initial dehydration and b) after an initial desiccation to 200 MPa.

particle are, therefore, not a function of the size of the individual layers.

For the two montmorillonites, there were no completely collapsed smectite layers (10 Å). The presence of kaolinite was observed in the beidellite sample (Figure 5d). The individual layers of the particles for the three smectites exhibited a spacing of about 1.25 nm which is in the range expected of the Na⁺ montmorillonite-methanol system (Annabi-Bergaya *et al.*, 1980). These workers showed that the Na⁺ Camp Berteaux montmorillonite saturated with methanol had a c-spacing of 1.27 ± 0.2 nm. For all three smectites, very few monolayers were observed, and the majority of the layers were organized into particles. Particles for all three smectites comprised four to ten layers as had been previously observed (Tessier and Pedro, 1982). The presence of particles of this size has also been confirmed by small angle X-ray scattering experiments on low charge montmorillonites (Pons *et al.*, 1982; Ben Rhaïem *et al.*, 1987). For the Otay montmorillonite,

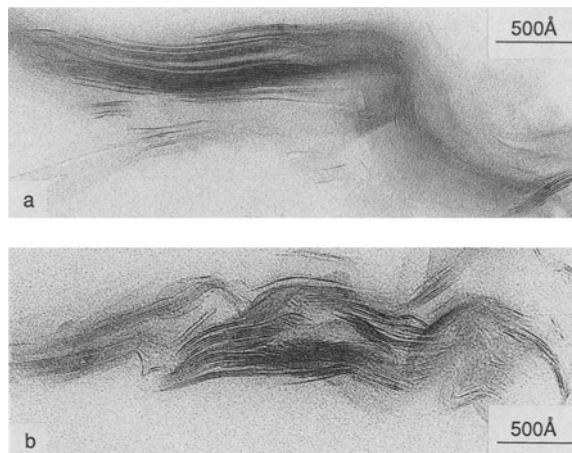


Figure 4. High resolution transmission electron micrographs of the Na⁺ SWy-1 montmorillonite equilibrated at a suction pressure of 3.2 kPa: a) initial dehydration and b) after an initial desiccation to 200 MPa.

the aggregation of these particles reached 30–35 layers; whereas, for the other two smectites, the particles were much thinner. The number of layers is smaller than the measured particle thicknesses for both the SWy-1 montmorillonite and the beidellite. This confirms the overestimation of the thicknesses measured at the lower magnification. The formation of these particles is not believed to be an artifact of the method since a similar technique was capable of isolating monolayers in colloidal suspensions (Shomer and Mingelgrin, 1978) and for a synthetic Na⁺ laponite at suction pressures similar to this study (Tessier and Grimaldi, 1993). Desiccation increased the number of layers in each particle by bringing smaller particles together.

DISCUSSION

Under the conditions imposed on the system, the water contents of these three smectites, submitted to different initial constraints, were not related to the total surface area. Rather large and flexible layers, and the geometry of the pores are critical to the concentration of water in smectites (Tessier, 1993). The degree of isotropy was inversely related to the lateral extension of the particles. As this lateral extension decreased, the disorder in the geometric organization of the particles increased. Differences in the lateral extensions of the particles were not due solely to the size of the individual layers but rather to the stacking arrangement of these layers. The charge characteristics of the smectites were, therefore, important in determining the organization of the particles. Increased numbers of layers stacked along the c-axis and shorter lateral extension of the particles were related to increased layer charge, whereas increasing tetrahedral charge resulted in a greater lateral extension. Short lateral extension and large stacks

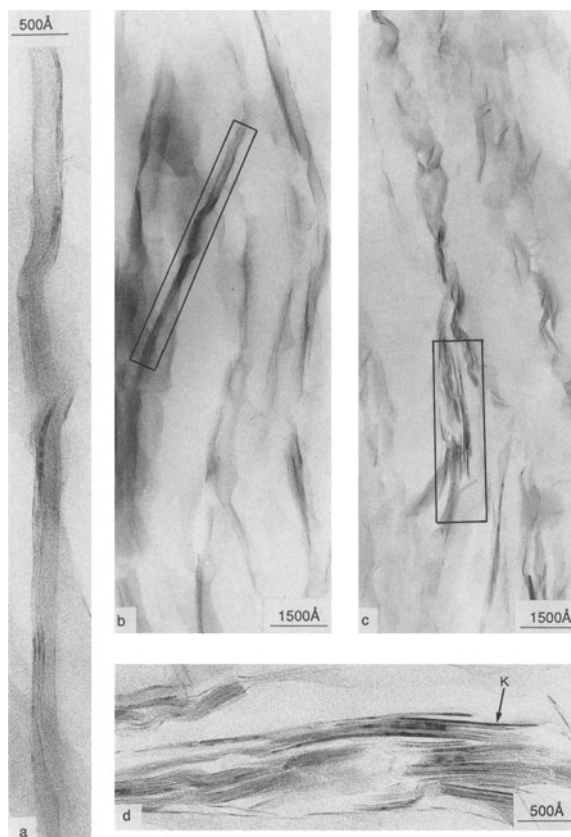


Figure 5. High resolution transmission electron micrographs of the Na⁺ beidellite equilibrated at a suction pressure of 3.2 kPa: a) initial dehydration and b) after an initial desiccation to 200 MPa.

of particles in the c-axis resulted in a decreased water content as was seen for the Otay montmorillonite. The importance of geometry and continuity of the pores on water retention can be seen in the lower water retention of the beidellite which had “infinite” lateral extension and would have been expected to swell the most.

Increased tetrahedral charge seemed to enhance rehydration. This is in agreement with the data of Foster (1953), which showed that, at a given total surface charge density, increasing tetrahedral charge enhanced the swelling potential of montmorillonites. The decrease in water content at a suction pressure of 3.2 kPa, after initial desiccation, is greater than that previously reported for low charge Na⁺ montmorillonites (Tessier, 1991) and was due to the greater desiccation stress applied. The greater rehydration of the beidellite was due to the large lateral extension in the ab plane still present after the desiccation treatment. The resistance to stacking along the c axis of the beidellite was a consequence of the greater repulsion resulting from the location of charge in the tetrahedral sheet. The observed increase in particle thickness along the c axis

for the three smectites, i.e., decrease in external surface, is not enough to explain the decrease in water content before and after desiccation. The large decrease in the water content of the two montmorillonites, along with the small increase in particle thickness, denotes the importance of the geometry and organization of the particles on the water content. The increased order in the geometric organization of the smectite particles must, therefore, be responsible to a large extent for the decrease in the water content.

In a previous study on a low charge montmorillonite, it was shown that the reduction of structural Fe³⁺ to Fe²⁺ in a Na⁺ nontronite resulted in an increased stacking along the c axis (Stucki and Tessier, 1991). They postulated that this resulted from the increase in the total charge density. Our data suggests a complimentary explanation in that the decrease in the percentage of tetrahedral charge, from 73% to 30%, enhanced the ability of the Na⁺ nontronite to stack along the c-axis. Previous work has shown that the reduction of Fe³⁺ to Fe²⁺ decreases the swelling of montmorillonites (Foster, 1953), which is compatible with the increased organization of the Na⁺ nontronite and our data for the Otay montmorillonite.

The distribution of particles with varying number of layers stacked along the c-axis, and of different lateral extensions, implies that the role of surface charge density on the organization of these layers into particles needs to be considered for a successful application of current theories to Na⁺ smectite gels. For example, water in both interparticle and interlayer spaces makes the development of the double layer theory to the study of Na⁺ smectite gels difficult. Double layer theory relating applied pressure to interlayer distances for gels of Na⁺ smectites has already been shown to deviate from experimental results (Lubetkin *et al.*, 1984). The formation of particles was suggested as being responsible for this deviation. The postulated different structural organizations (van Olphen, 1977) of Na⁺ smectites in gels both for the individual layers and the particles include: edge-face (EF), edge-edge (EE), and face-face (FF). The arrangement of these smectite layers into particles follows a FF organization, with the location of charge deficiency being crucial to the lateral extension of the particles. The absence of EF association of both the individual layers and the particles, in the acidic pH range, had been postulated before (Tessier and Pedro, 1982; Lubetkin *et al.*, 1984; Chen *et al.*, 1990) and is supported by our data.

In contrast to the double layer theory, the properties of water in montmorillonite gels may be related to the surface areas of the montmorillonites (Low, 1980, 1987). To this end, properties of clay-water systems were measured and related to the surface areas of montmorillonites (Salle de Chou *et al.*, 1980; Mulla and Low, 1983; Viani *et al.*, 1983). Changes in the molar absorptivity and the stretching frequency of the O–D

bond of deuterated water, as a function of water content, were taken to imply an effect of surface on water at distances up to 40 Å (Salle de Chou *et al.*, 1980; Mulla and Low, 1983). Parker (1986) suggested that the divergence in the infrared spectroscopic data stemmed from the presence of water near the surface still perturbed by surface, i.e., an averaging effect with the "bulk" water. The organization of the smectite layers in particles, at similar water contents as these workers, demonstrates the presence of both interlayer and interparticle water. Infrared spectroscopy, therefore, measures an average value for water interparticle and interlayer spaces, supporting the hypothesis of Parker (1986). X-ray data (Viani *et al.*, 1983) showed that applying pressure resulted in the lowering of the d-spacing down to about 40 Å where a jump to 19 Å occurred. After an initial desiccation and rehydration cycle, this jump occurred at a lower applied pressure for a low-charge montmorillonite. Again, this is consistent with our geometric argument. As an initial pressure is applied, both particles and layers need to align themselves in order to obtain a diffraction maxima at 19 Å. After an initial desiccation, the particles are already oriented (Figure 2), and only the jump to 19 Å spacings needs to occur for the diffraction maxima to be seen. Thus, any theory formulated to relate swelling potential to the surface area of smectites must first be able to distinguish between interlayer and interparticle surfaces. This is not the case for smectite surface areas measured by the use of polar molecules such as 2-ethoxy ethanol (Low, 1980). The tacit assumption made in relating swelling to surface area that nearly all the water is in interlayer pores (Odom and Low, 1978) is not substantiated by these data.

The almost complete absence of monolayers and the absence of edge-face associations, previously found for low charge montmorillonites (Tessier and Pedro, 1982), are confirmed for a high charge montmorillonite and a beidellite. Properties related to individual smectite layers do not affect water contents of gels directly. Rather, they influence the organization of the layers into particles which in turn affect water contents. The similar sizes of the smectite particles and their different geometrical organizations, after the two treatments, clearly indicate the importance of interparticle water, a function of the stacking of the particles, on the total water contents of smectite gels. These data support the hypothesis that the water content of Na⁺ smectite gels is a function of the geometry of the pores, which are themselves a function of the flexibility of the layers and their mode of stacking (Tessier, 1993).

CONCLUSION

Surface charge density and the location of isomorphous substitution is crucial in determining the stacking thicknesses along the c axis and the lateral extensions in the ab plane of Na⁺ smectites gels. This is

evidenced macroscopically by the different water contents of the gels. The geometric organization of the smectites, controlled by the lateral extension, is one of the critical factors in understanding Na⁺ smectites-water interactions. Changes in the proportion of interlayer and interparticle pores cannot explain the differences in water content at a given water suction before and after a desiccation. Lateral extension of the particles affects the water content of smectites and the ability of these smectites to rehydrate after a desiccation. The data indicate that tetrahedral charge location enhances the ability of smectites to rehydrate after a dehydration cycle. Further studies are needed to confirm this effect as little work has been performed so far on the effect of initial dehydration on the water content of Na⁺ smectites.

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