

ORDERED INTERSTRATIFICATION OF DEHYDRATED AND HYDRATED Na-SMECTITE

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Abstract—The 001 spacing of Na-smectite was found to vary from 9.6 Å at 0% relative humidity (RH) to 12.4 Å at 60–65% RH. The 9.6-Å spacing corresponds to dehydrated Na-smectite, and the 12.4-Å corresponds to Na-smectite with one water layer. A regular series of intermediate values resulted from ordered interstratification of the 9.6- and 12.4-Å units. Ordered interstratification was confirmed by the presence of a 001 spacing of $9.6 + 12.4 \text{ Å} = 22 \text{ Å}$. This peak appeared under experimental conditions at about 35% RH. It appeared for calculated simulations of ordered stacking of 50/50 mixtures ($\pm 10\%$) of 9.6- and 12.4-Å units. The 004 peak of this 22-Å spacing interacted with the 002 of the 9.6-Å spacing of ordered mixtures of more than 50% 9.6-Å units and with the 002 of the 12.4-Å spacing of ordered mixtures of more than 50% 12.4-Å units. The result of this interaction was a complex peak, the position of which was a function of the ratio of 9.6- and 12.4-Å units. This complex peak was noted for experimental and for calculated conditions. Calculated tracings assuming ordered stacking matched the experimental tracings closely, whereas those assuming random stacking did not.

Ordering was apparently due to the interaction of the positive charge of the interlayer cation repelling the positive charge of the hydrogens of the hydroxyl ions, one above and one below, closest to the interlayer space. The collapse of a single interlayer space (dehydration) brought the interlayer cation closer to the hydrogens of the hydroxyls causing the hydroxyls to rotate such that the hydrogens shifted toward the adjacent interlayer spaces. Collapse of these two interlayer spaces was therefore more difficult. This same mechanism helps explain ordering in illite/smectite. The difference is that hydration/dehydration is quick and reversible, whereas the change from smectite to illite is slow and irreversible.

Key Words—Hydration, Hydrogen positions, Illite, Interstratification, Smectite, Water, X-ray powder diffraction.

INTRODUCTION

The 001 spacing recorded on X-ray powder diffraction profiles of oriented aggregates of Na-smectite varies between 11 and 15 Å depending on the ambient relative humidity (RH). Changing the RH in a controlled environment can change this spacing from 9.6 Å at 0% RH to 18 Å at 100% RH. Some samples examined at about 35% RH yield a diffraction peak having a spacing of about 24–25 Å. Figure 1A shows the diffraction pattern of an oriented specimen of the <1- μm fraction of Wyoming bentonite recorded at about 35% RH. This diffraction pattern, as will be demonstrated below, results from the 1:1 regular interstratification of 9.6- and 12.4-Å layers. Ordered interstratification of these units persists between 12 and 65% RH. It will be argued that the ordered interlayering occurs because the collapse of one interlayer space increases the energy needed to collapse the adjacent interlayer spaces. The increased resistance to collapse is due to change in the orientation of hydroxyls of the octahedral sheet. It will be shown that the $d(001)$ of Na-smectite is a continuous function of RH; that calculated diffraction profiles duplicate experimental tracings only when ordered interstratification is assumed;

and that the 001 series of the 22-Å spacing in experimental tracings and calculated profiles is logically explained as the sum of the 9.6- and the 12.4-Å spacings.

Historical background

Ross and Shannon (1926) were the first to suggest that smectite swells because water enters the structure between the 2:1 silicate layers. Nagelschmidt (1936) and Bradley *et al.* (1937) demonstrated that the 001 spacing of smectite increases in distinct steps as the amount of water in the environment is increased. The latter workers suggested that the steps represented the formation of distinct hydrates containing one, two, and three layers of water molecules.

From the time of Bradley *et al.* (1937), the relation between the RH (or partial pressure of water vapor) and the 001 spacing of smectite has been conceptualized in two ways. Hendricks *et al.* (1940) advocated that the layer spacing varies continuously, but not uniformly, with water content, apparently as an averaging effect from various hydrates. Mooney *et al.* (1952) on the other hand, asserted that the most significant feature of the X-ray powder diffraction data from smectite is the *absence* of spacings representing mixes of hydrates, i.e., a plot of RH vs. $d(001)$ shows only discrete steps. The currency of this idea can be seen in papers

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by Keren and Shainberg (1975, 1979, 1980) and Glaeser and Méring (1968, in MacEwan and Wilson, 1980, p. 206).

A consideration of the nature of ordered interlayering of units of differing thickness in smectite should begin with the comment by Hendricks *et al.* (1940) that the 001 spacing represents an averaging effect. Walker (1956) suggested that the dehydration of Mg-vermiculite results in alternation of a dehydrated layer and a hydrated layer with one water layer. Bassett (1959) recognized the formation of hydrobiotite from biotite with regular interlayering of biotite and vermiculite. He suggested that the regularity was the result of the replacement of an unhydrated K by a hydrated Ca or Mg, decreasing the bonding of that layer but increasing the bonding in the adjacent layers still occupied by unhydrated K, making these potassium ions less susceptible to replacement by hydrated cations than other potassium cations. Sawhney (1967), for the reverse of the formation of hydrobiotite from biotite, showed that Ca-vermiculite forms a 1:1 regularly interstratified mica/vermiculite with the partial replacement of Ca^{2+} by K^+ . He suggested that alternate layers remain hydrated because the effective negative interlayer charge of the tetrahedral sheet adjacent to a hydrated interlayer space is reduced when the adjacent interlayer is dehydrated. He attributed the charge reduction to an increase in the electrostatic force between the K^+ and the tetrahedral sheet adjacent to the hydrated interlayer space, accompanied by a consequent decrease in the effective negative charge of this tetrahedral sheet. This decrease means that a K ion is less likely to enter this interlayer space displacing a hydrated Ca ion and more likely to enter an interlayer space bounded by unaffected tetrahedral sheets.

For smectites, no one has suggested, to the best of the authors' knowledge, regular interstratification of two states: one dehydrated and one with a single water layer in the interlayer space. Current thinking is illustrated by: "... this variation [of $d(00l)$] results from a random interstratification of two (or more) successive hydrates" (MacEwan and Wilson, 1980, p. 202).

EXPERIMENTAL

The material studied was Na-saturated smectite, SWy-1, from Crook County, Wyoming, obtained from the Source Clay Repository of The Clay Minerals Society. X-ray powder diffraction (XRD) analyses were made of $<0.5\text{-}\mu\text{m}$ material sedimented onto glass slides. The procedure produced effectively infinite thicknesses as verified by comparison with the intensity values for the 00 l series given by Reynolds (1965). A Philips-Norelco diffractometer with Cu-target tube and a Ni filter was used. All samples were scanned at $1^\circ 2\theta/\text{min}$ from 2° to $32^\circ 2\theta$. For ten selected samples at different RHs, scans at $1/4^\circ 2\theta/\text{min}$ were made from 11° to $21^\circ 2\theta$ to study the complex peak $002_{9.6}/004_{22.0}/002_{12.4}$. Basal

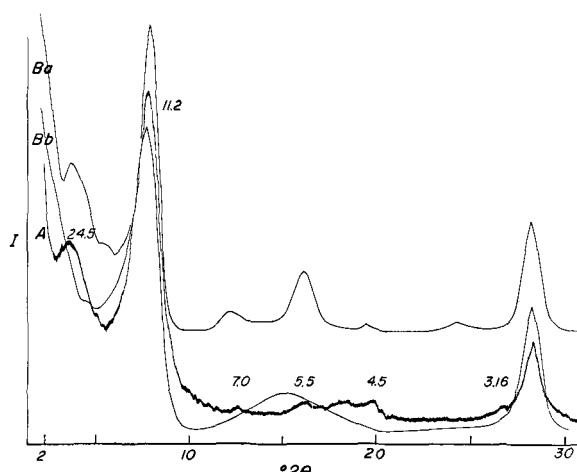


Figure 1. Experimental (A) and calculated (Ba and Bb) X-ray powder diffraction tracings for Na-smectite. Tracing A is $<1\text{-}\mu\text{m}$ clay sedimented on a glass slide and run at a RH of about 35%. Conditions for calculations for tracings Ba and Bb are 56% collapsed layers and from 2 to 8 unit cells stacked in coherent scattering arrays. Tracing Ba assumes an ordering probability of .975, i.e., ordered stacking, and Bb assumes an ordering probability of .56, i.e., random stacking. See text for discussion. Values above or next to peaks on the experimental tracings are in Å. The $d(001)_{9.6+12.4}$ peak for ordered stacking is at 11.2 Å (Ba) and at 11.5 Å (Bb) for random stacking.

spacings were calibrated by comparison of the $d(001)$ value of a pegmatitic muscovite with that of dehydrated Na-smectite. The $d(001)$ of the muscovite was taken to be 10.01 Å.

Two media were used to regulate RH: an H_2SO_4 -water mixture and a series of three-phase salt solutions. Slides were held in atmospheres of controlled RH for at least 24 hr before they were examined by XRD. RH was controlled also during diffraction by two techniques, one dynamic and one static. RH was controlled dynamically by bubbling a stream of air through two successive fluid-filled, 1-liter washing bottles, through a flow gauge, and then through a port in the shield around the sample, the shield having been sealed with Mylar film. In the static method, RH was controlled by plugging the port in the shield and placing a 75-ml half-cylinder in the shield beneath the sample. In both methods, either the washing bottles or the half-cylinder was filled with the desired H_2SO_4 -water mix or three-phase salt solution. These two methods did not always yield the same results.

Calculated XRD profiles of basal spacings were produced using a modification of Reynolds and Hower's (1970) method. Each unit cell (a 2:1 layer, one layer thick) was assumed to contain 12 oxygens; from 2 to 8 unit cells were stacked in coherent scattering arrays. The 12.4-Å unit had one molecule of water in the interlayer space, both the 9.6- and 12.4-Å units had an average of 0.3 Na^+ in the interlayer space, and both had 0.3 equivalents of layer charge.

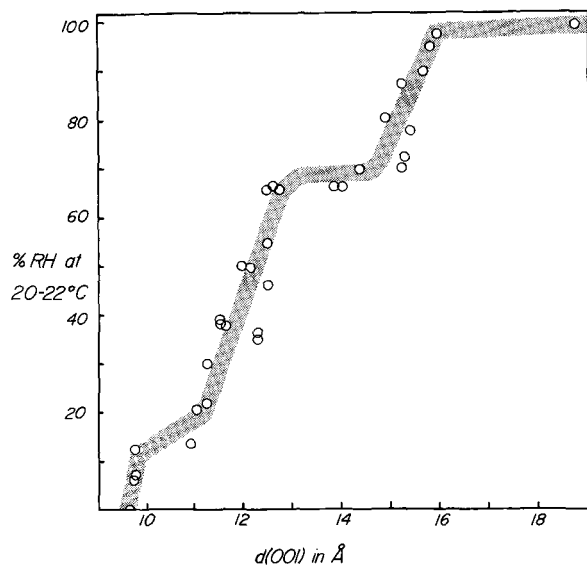


Figure 2. Experimental values of $d(001)_{9.6+12.4}$ vs. relative humidity (RH) as high as about 65% RH; of $d(001)_{12.4+15.2}$ from about 65 to 98% RH; and of $d(001)_{15.2+18}$ from about 98 to 100% RH. The scatter of points represents, for the most part, imperfect control of RH.

RESULTS

Figure 2 shows experimental values of 001 plotted against RH. Ordered interlayering was studied between 12 and 65% RH. Figure 3 shows the spacings which could be involved in combined reflections for either experimental or calculated tracings. The integral series of peaks shown for a 22-Å spacing, or their contribution to shifting peaks would be present *only* if 9.6- and 12.4-Å units were stacked in an ordered, regularly al-

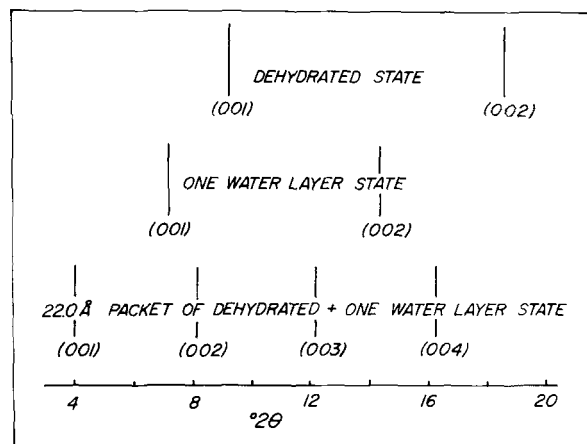


Figure 3. 2θ values for possible reflections from the 9.6- and 12.4-Å Na-smectite units in either ordered or random stacking. $\text{CuK}\alpha$ radiation. Reflections from a 22.0-Å unit possible only if 9.6- and 12.4-Å units are stacked in a regular, alternating manner.

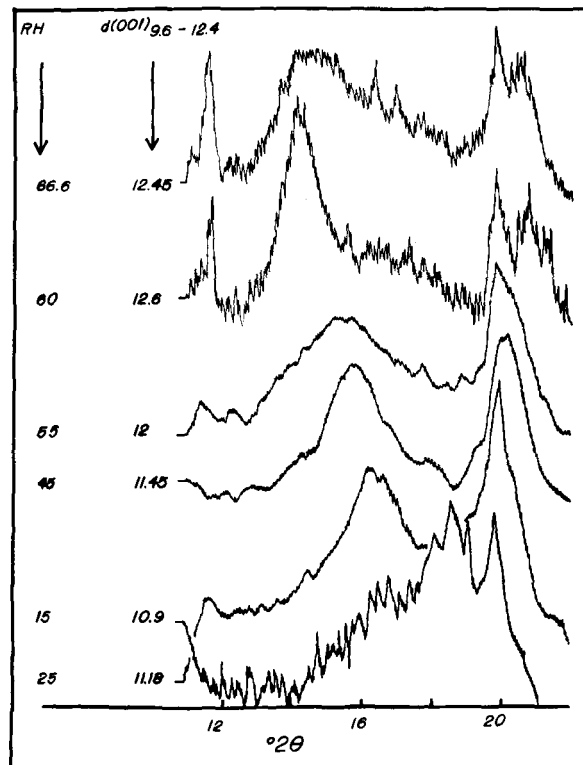


Figure 4. Experimental peak representing the $002_{9.6}/004_{22} + 004_{22}/002_{12.4}$ shifting from $18.5^\circ 2\theta$ for 15% RH to $14^\circ 2\theta$ for 60% RH (cf. Figure 3). At 66.6% RH the regular shift is no longer evident. The value for $001_{9.6}/001_{12.4}$ at 60% RH is anomalous and probably represents lack of control of RH. These tracings were recorded at $1/4^\circ 2\theta/\text{min}$. $\text{CuK}\alpha$ radiation.

ternating array. The 001 peak for the 22-Å spacing was resolved only when the RH was about 35% (Figure 1A).

Figure 4 shows a peak whose position is a function of RH for values from 15 to 60%. It shifts from $18.5^\circ 2\theta$ at low RH to $14^\circ 2\theta$ at high values. Figures 5 and 6 show profiles calculated for this same 2θ interval. The profiles in Figure 5 were calculated assuming that the 9.6- and 12.4-Å units were interstratified in an ordered, alternating fashion, whereas the profiles in Figure 6 assumed random stacking. The percentages used in these illustrations are the percentage of collapsed (% C) or 9.6-Å units.

INTERPRETATION AND DISCUSSION

From Figure 2, it can be seen that discrete hydrates of Na-smectite form as a function of the amount of water available. The peak which shifts from 9.6 Å at 0% RH to 12.4 Å at about 65% RH represents continuously changing proportions of 9.6- and 12.4-Å units. The shift is not linear, but S-shaped. From 0 to 10% RH Na-smectite does not appear to hydrate. At RH > 60–65%, the data are not precise enough to support speculation beyond suggesting by analogy that two more

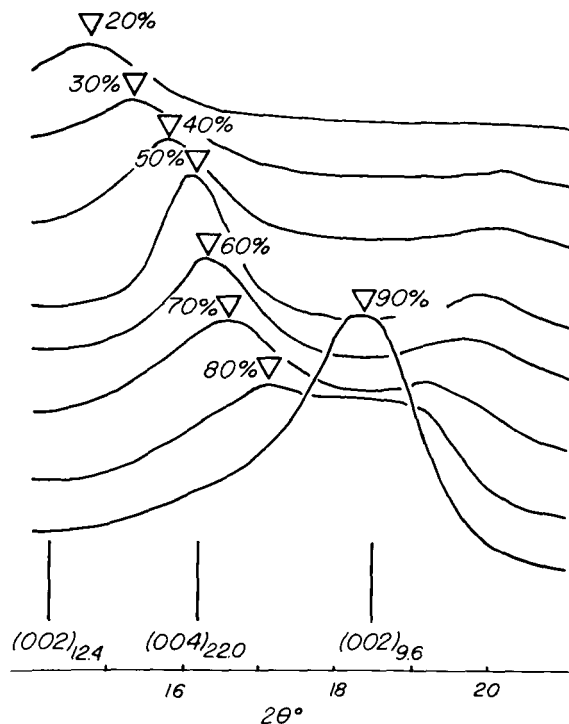


Figure 5. X-ray powder diffraction profiles calculated for a series of 9.6- and 12.4-Å units with different percentages of collapsed (9.6-Å) units. The two units are assumed to be stacked in an ordered, alternating fashion. The Bragg spacings involved are shown at the bottom. Inverted triangles indicate maximum intensity.

S-shaped curves are present: one from 65 to 98% RH representing the peak shifting between Na-smectite with one water layer to that with two layers [$d(001) = 15.2$ Å]; and, the other representing the shift from the 15.2-Å unit to that with three water layers [$d(001) = 18$ Å], all occurring between 98 and 100% RH.

RH could not be controlled with satisfactory precision. The estimated margin of error was $\pm 5\%$. Therefore, although the general trend was quite clear, the details are tentative concerning the relation between RH (or partial pressure of water vapor) and the ratio of any two states of hydration of Na-smectite. The dynamic and static methods for controlling RH agreed only roughly. The dynamic method seemed better for lower RH, whereas the static one seemed better for higher RH. This relation held for both the H_2SO_4 -water mixes and the three-phase salt solutions. Attempts to improve precision included keeping a record of temperature in the laboratory and making runs as long as three days (72 hr). During this time, the sample remained on the diffractometer under RH conditions controlled by one of the methods and the position of the 001 peak was checked regularly. No improvement in precision was obtained. Hysteresis in the hydration dehydration process (see, e.g., adsorption isotherms of

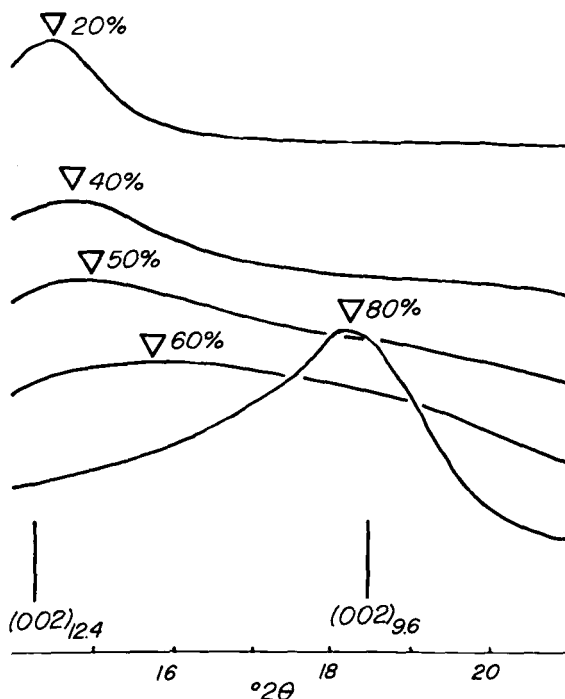


Figure 6. X-ray powder diffraction profiles calculated for a series of randomly interstratified 9.6- and 12.4-Å units with different percentages of collapsed (9.6-Å) spacings. The Bragg spacings involved are shown at the bottom. Inverted triangles indicate maximum intensity.

Keren and Shainberg, 1980) may play a role in lowering precision, and/or some physical factor in the two methods for controlling RH may not be understood.

The 9.6- and 12.4-Å units appear to be stacked in an ordered, alternating manner as evidenced by reflections from the 22-Å packet that results from an ordered combination of the 9.6- and 12.4-Å units. Because the 001 reflection for the 22-Å spacing was observed only twice experimentally, other 00 l reflections are the primary evidence. A distinct 001 reflection of the 22-Å spacing appeared in calculated patterns only between values of 40 and 60% 9.6-Å units. Between 14° and $18.5^\circ 2\theta$, the presence of the 004 reflection of the 22-Å spacing also established the interstratification as being ordered. The 004 reflection of the 22-Å spacing interacts with the 002 reflections of both the 9.6- and 12.4-Å spacings, thereby allowing the proportions of these units to be estimated on experimental tracings (see Figure 4). Patterns calculated assuming that the 9.6- and 12.4-Å units are ordered (Figure 5), show the results of the interaction of the 004₂₂ reflection with the 002_{9.6} reflection at lower RH, and with the 002_{12.4} reflection at higher RH. In contrast, Figure 6 shows only very broad, weak peaks in the 2θ region between the 002_{9.6} and 002_{12.4} reflections with no evidence for the interaction of the 004₂₂ spacing. These reflections were calculated assuming random stacking of the 9.6-

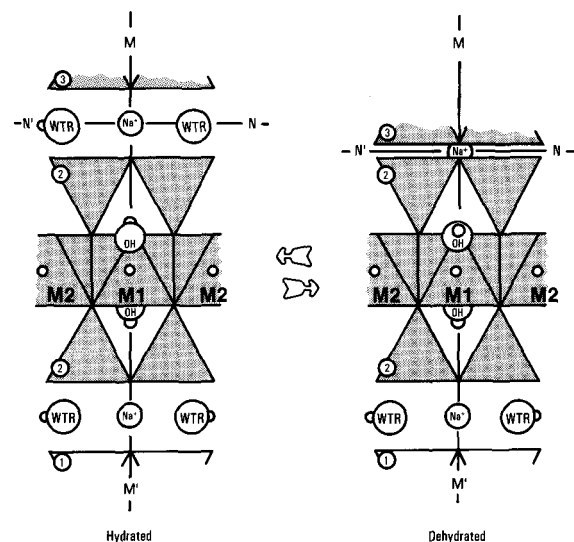


Figure 7. Sketch illustrating the change in orientation of hydroxyls as layers collapse. MM' and NN' are mirrors or pseudomirrors. Circled numbers designate the 2:1 layers. M1 and M2 are the octahedral sites. Waters are labelled WTR.

and 12.4-Å units. Comparison of these calculated patterns (Figures 5 and 6) with experimental results (Figure 4) indicates that the interlayering has maximum ordering over the compositional range of 30 to 80% 9.6-Å layers.

As a further confirmation of ordered compared to random interstratification, Figure 1B shows two patterns, *a* and *b*, calculated for interstratified 9.6- and 12.4-Å units, both with 56% 9.6-Å layers and all other characteristics the same except the degree of ordering. Pattern *a* was calculated assuming that the stacking is highly ordered, whereas pattern *b* assumed random stacking. Both patterns produced a strong reflection for the combined intensities from the $001_{9.6}$ and $001_{12.4}$ spacings; for the ordered arrangement the resultant peak is at 11.2 Å, whereas for the random arrangement, it is at 11.5 Å. The calculated profile assuming ordered interstratification (Figure 1Ba) reproduces more faithfully the other features of the experimental pattern (Figure 1A) including the reflection at $24.5^\circ 2\theta$. This peak position, if adjusted for displacement caused by the Lorentz factor, gives a true spacing of 22 Å. The experimental pattern shows a small peak corresponding to a 4.8-Å spacing. This peak is the 002 reflection from stacks of 9.6-Å units that are not involved (or have not yet become involved) in the interlayering and may be acting as a third phase (personal communication, R. C. Reynolds, Jr., Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire, 1983).

Why ordered rather than random stacking? Ordering is probably a function of the interaction of the interlayer cation (IC) and the hydroxyl ions of the flanking silicate layers. Giese (1971), Giese and Datta (1973),

and Giese (1977, 1979, 1980) carried out electrostatic energy calculations that explain observed hydroxyl orientations in 1:1 and 2:1 layer silicates. Their calculations involved minimizing the electrostatic potential energy as a function of hydroxyl orientation (Giese, 1971). Giese's (1979) results show a large change in the orientation of the hydroxyl axis for a dioctahedral mica with and without interlayer K^+ . With K^+ present, the hydroxyl axis tilts 14.3° toward the adjacent interlayer space, i.e., it is only 14.3° from being parallel with the (001) plane. Without K^+ , the tilt is 53.2° . These calculations show the important effect of the IC on redistributing electrostatic charge within the 2:1 layer.

Figure 7 shows the re-orientation of hydroxyls during dehydration. Note first that the ICs, both hydroxyls, and the M1 site (vacant in dioctahedral layer silicates) are on the mirror or pseudomirror plane (MM'). Imagine another mirror plane (NN') perpendicular to the first, parallel to (001), and bisecting the IC. Three silicate layers are shown indicated by the circled numbers 1, 2, and 3. When collapse or dehydration occurs, the ditrigonal cavity in the basal plane of oxygens above and below close around the IC. This closing has the effect of bringing the hydroxyls of layers 2 and 3, which are centered in the ditrigonal cavities, closer to the IC. In turn, the hydrogen end of the hydroxyl axis rotates (in the plane of the vertical mirror MM') away from the IC and toward the empty octahedral site, M1. This brings the hydrogen end of the upper hydroxyl in layer 2 closer to the hydrogen end of the hydroxyl below it in the same layer (Figure 7, dehydrated). The mirror image of this operation takes place simultaneously in layer 3 across the mirror NN' . As a consequence, the hydroxyl axes of the lower hydroxyl ion in layer 2 and the upper one in layer 3 (not shown) require a slightly greater force to cause them to rotate away from approaching ICs. The effect of this greater resistance to approaching ICs is that after one interlayer space (e.g., between layers 2 and 3) has collapsed, the two adjoining interlayer spaces (between layers 1 and 2 and layers 3 and 4), are slightly more difficult to collapse, whereas the next two adjoining spaces are not. On the basis of preliminary calculations, R. F. Giese (Department of Geological Sciences, State University of New York at Buffalo, Amherst, New York, personal communication, 1981) suggested that regular interstratification is energetically more stable than random interstratification.

Ordered interlayering of illite/smectite may be explained, at least in part, by this same mechanism. The additional K^+ added in the interlayer space during the formation of illite from smectite amplifies the effect of re-orienting hydroxyl axes. This concept could be tested by calculating electrostatic potential energy as a function of the number of ICs per formula unit. One major difference between the interstratification of hydrated and dehydrated smectite and the interstratification of

illite and smectite is that hydration-dehydration reaction is rapid and reversible, and the conversion of smectite to illite is neither of these. Interstratified hydrated/dehydrated smectite is ordered over a broad compositional range because it equilibrates with ease. In the process of layer dehydration any "mistakes" in the ordered sequence that arise can be corrected. Thus, the energetically preferred regular alteration of hydrated and dehydrated layers is manifest throughout the entire sequence. By contrast, the conversion of smectite to illite through an interstratified sequence during progressive diagenesis, is effectively irreversible. Initially formed illite layers remain illite layers even though they may eventually disrupt the regular sequence when sufficient additional illite layers form. Therefore, illite/smectite does not display ordered interstratification until more than half of the smectite layers have been converted to illite.

CONCLUSIONS

The basal spacing of Na-smectite is a function of relative humidity. For RHs between about 12 and 65%, the basal spacing results from the interstratification of the 9.6-Å dehydrated unit and the 12.4-Å one-water-layer hydrated unit. These two forms of Na-smectite are stacked in a regular, as opposed to a random manner. For X-ray powder diffraction tracings, the consequences of ordered interstratification are a 001 reflection that shifts as a continuous function of RH and, when very close to a 50-50 mix of 9.6- and 12.4-Å units, the appearance of a reflection for a 22-Å spacing. The ordered arrangement is more stable than the random arrangement and results from the interaction of the interlayer cation with the hydroxyl ions in the plane of atoms shared by the octahedral and tetrahedral sheets. The collapse of one interlayer space brings the interlayer cation closer to the hydrogens of the hydroxyl groups making collapse of adjoining interlayer spaces more difficult. This same reasoning may be applicable to the ordering of illite and smectite layers in interstratified illite/smectite.

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