EXPANSION OF SMECTITE BY LAURYLAMINE HYDROCHLORIDE: AMBIGUITIES IN TRANSMISSION ELECTRON MICROSCOPE OBSERVATIONS[1]

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Abstract—Treatment of smectite with laurylamine hydrochloride was verified to cause expansion of d(001) which may be retained and observed in ion-milled samples by transmission electron microscopy. The spacings between layers as observed in lattice fringe images, however, are variable and may be as small as 10 Å. The method therefore produces ambiguities in differentiating between some smectites and illites, similar to those that have been found for untreated samples; e.g., on this basis, expanded layers may be inferred to be smectite, but layers with d-values approaching 10 Å may be either illite or smectite. Expansion also destroys the original rock texture, which, therefore, must be observed using only untreated samples.

Key Words—Expansion, Illite, Lattice fringe images, Laurylamine hydrochloride, Smectite, Transmission electron microscopy.

INTRODUCTION

One of the major difficulties in transmission electron microscopy (TEM) of smectites is the potential for dehydration and collapse of layers to an interplanar spacing of about 10 Å. Such damage may be caused by at least three factors: (1) heating of the specimen by absorption of electron beam energy; (2) exposure of the specimen to the vacuum of the electron microscope; and (3) exposure of the specimen to the vacuum of an ion-thinner. Phyllosilicates are generally characterized by TEM largely on the basis of their 001 diffraction patterns and resultant 001 lattice fringe images. Because illite has d(001) = 10 Å, it may not be differentiated from collapsed smectite solely on the basis of such observations. Because illite and smectite also occur as mixed-layer structures (as implied by X-ray powder diffraction data), which may be either disordered or ordered in stacking sequence, it is especially important to be able to distinguish between these two clay minerals. Ahn *et al.* (1983) and Ahn and Peacor (1984) inferred that smectite or illite give rise to characteristic lattice fringe images that permit identification of one or the other in Gulf Coast sediment samples. Furthermore, they suggested that smectite and illite occur as separate packets of layers in these samples. Illite layers, however, have not yet been proven to exist within areas having the characteristics of smectite. Indeed, the existence of mixed-layer illite/smectite can only be ab-solutely proven by direct observation. It is therefore imperative to be able to discriminate between illite and smectite layers by TEM.

Page and Wenk (1979) showed that smectite from Butte, Montana, gave rise to lattice fringe images with d-values >10Å. Our own observations, as well as those of Ahn *et al.* (1983), Ahn and Peacor (1984), and Freed and Peacor (1984) for Gulf Coast samples, and the extensive imaging of Wyoming bentonites by Peacor *et al.* (1984), have been inconsistent. Experiments in this laboratory show that the d(001) of well-defined Wyoming bentonite (commercial product, Envirogel), as observed by TEM, is variable, but approaches 10 Å. Moreover, many layers (or portions of a single layer have d-values as large as 14 Å and average values of 12.9 Å. These values were found to vary from specimen to specimen and even locally within a single specimen. Such behavior, however, may actually be a useful and significant measure of chemical and structural heterogeneity in ways that cannot be assessed at this time. For present purposes, the variability implies that individual layers having d-values of about 10 Å cannot be unequivocally identified as either illite or smectite, if such layers occur within areas of the specimen that have the characteristic appearance of smectite (Ahn *et al.*, 1983; Ahn and Peacor, 1984).

Yoshida (1973) showed that smectite treated with laurylamine hydrochloride gave rise to layer expansion that apparently is retained during TEM observations. He observed expanded layers only on the curled edges of individual crystals. Nevertheless, such treatment appears to be a means of solving the problem of the collapse of smectite layers. Klimentidis and Mackinnon (1984), on the other hand, reported that the expansion of smectite by dodecylamine hydrochloride
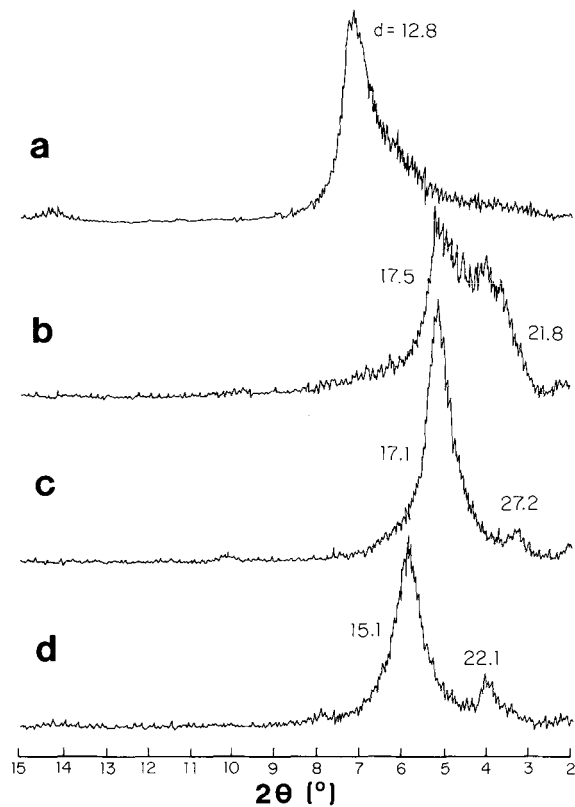
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Figure 1. X-ray powder diffraction patterns of Wyoming bentonite (commercial product Envirogel). (a) untreated, air-dried bentonite (<2 μm in size); (b) after complete treatment with laurylamine hydrochloride; (c) after washing for 1 day with alcohol and water solution; (d) after washing for 3 days with alcohol and water solution. Patterns b, c, and d correspond to treatment sequence numbers 5, 6, and 8 in Table 1.
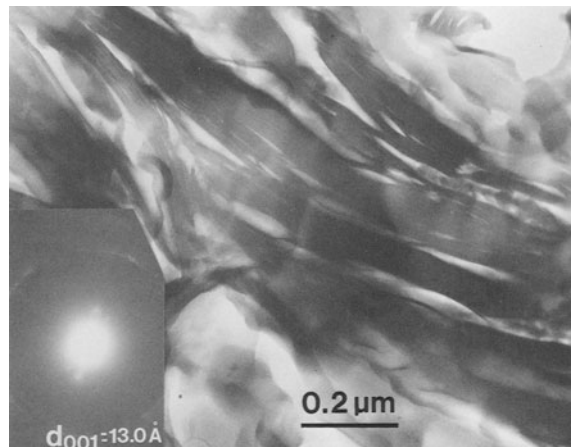

Figure 2. Transmission electron micrograph of untreated Wyoming bentonite embedded in epoxy. Lattice fringes of smectite layers are apparent in darker areas; most areas with lighter contrast are epoxy. Inset electron diffraction pattern has d(001) = 13.0 Å. Random distribution of smectite layers is indicated by diffraction pattern.

show nearly 100% smectite and rare euhedral crystals of what appear to be feldspars or zeolites.

The XRD patterns showed a relatively sharp 001 peak (d = 12.5 Å) which is diffuse toward lower 2θ values. Saturation with ethylene glycol resulted in the expansion of d(001) to 16.6 Å, as a single, relatively sharp peak.

Laurylamine hydrochloride expansion

Laurylamine hydrochloride was used to expand the smectite according to the method of Yoshida (1973). The smectite was placed in a 0.1 N laurylamine hydrochloride solution first for 24 hr at 65°C with frequent stirring, and then for one month at room tem-
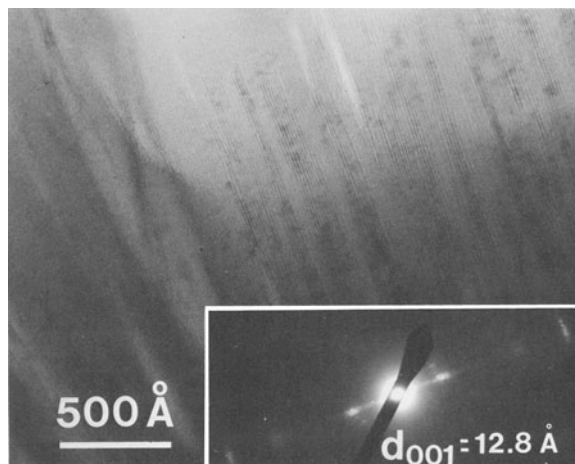
(equivalent to laurylamine hydrochloride) gave non-permanent expansion, and that the results depended in part on ambient TEM conditions. Because such expansion data appear to be ambiguous or inconclusive, we have attempted to clarify the situation by expanding smectite with laurylamine hydrochloride.

EXPERIMENTAL

Material

The smectite used in these studies was a commercial Wyoming bentonite having the trade name Envirogel. This material has been extensively characterized (see, e.g., Peacor *et al.*, 1984) and shown to consist of about 95% smectite, partly on the basis of X-ray powder diffraction (XRD) data. Quartz, calcite, and a well-ordered 10-Å phyllosilicate were detected as impurities. An X-ray fluorescence analysis is consistent with nearly 100% smectite, implying that contaminating non-crystalline phases (volcanic glass, poorly crystalline cristobalite, etc.) cannot be present to a significant degree. Scanning electron microscope observations, including energy dispersive analyses of selected areas,

Figure 3. Lattice fringe image of untreated and epoxy-embedded Wyoming bentonite. Average value of d(001) = 12.8 Å is displayed by lattice fringe image and electron diffraction pattern in inset.
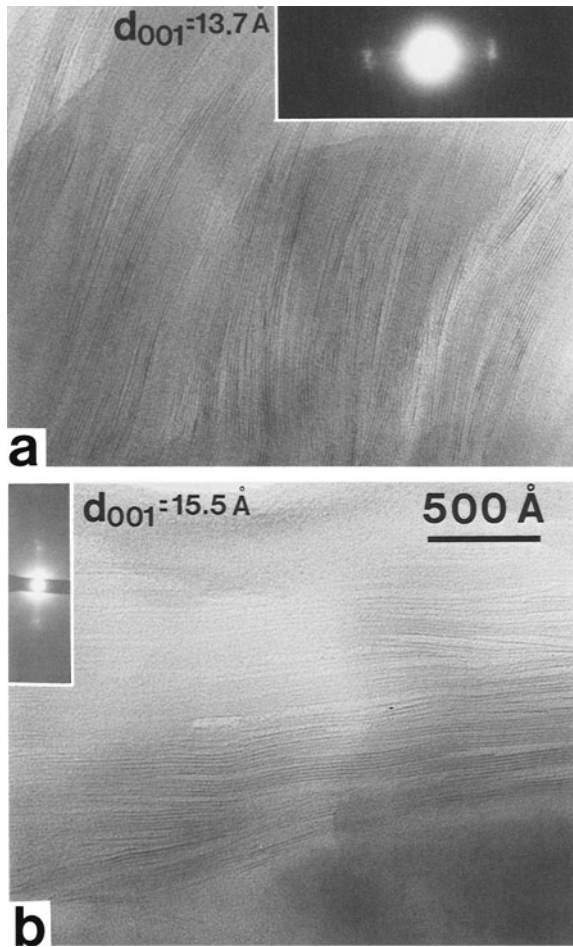
Figure 4. Transmission electron microscope lattice fringe images of Wyoming bentonite treated with laurylamine hydrochloride: (a) d(001) = 13.7 Å, (b) d(001) = 15.5 Å as indicated by lattice fringes and electron diffraction patterns. Samples are embedded in epoxy.
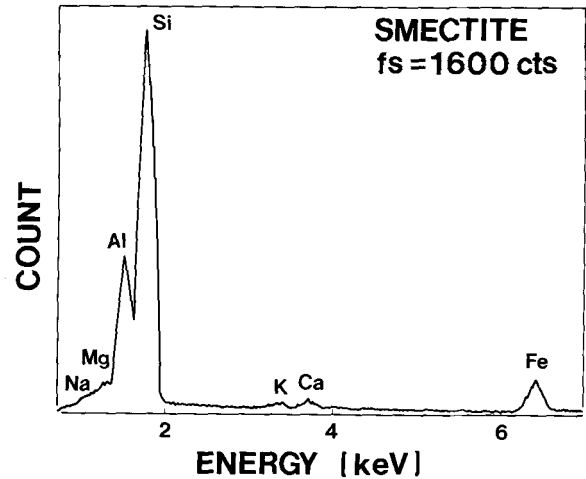

Figure 5. Energy dispersive X-ray spectrum of Wyoming bentonite. Peak intensities are not directly proportional to the concentrations of the corresponding elements.

in the solution, outer layers began to expand and spall off, until only a powdered sample remained. The stresses caused by expansion of smectite thus destroyed the original texture of the sample. Even if the treatment had not disintegrated the original sample, such stresses probably altered the original texture.

Transmission-analytical electron microscopy

Smectite powders (both treated and untreated) were embedded in a casting resin by allowing grains to settle in alcohol onto a solidified layer of resin. Another layer

perature with occasional stirring. The clay was decanted and washed several times with a 1:1 solution of water and alcohol. It was then treated with the laurylamine hydrochloride solution for one week with occasional stirring, and finally washed with a water/alcohol solution. Every 24 hr, the solution was replaced until no further changes were observed in the XRD patterns obtained at each step. It was only then assumed that a permanent expansion had occurred whose magnitude would not change with further treatment. Table 1 lists values for d(001) for various stages of treatment; Figure 1 shows portions of selected XRD patterns. In general, two 001 peaks were observed, with the peak at the higher d-value generally having an intensity less than that of the other.

Well cuttings of smectite-rich Gulf Coast argillaceous sediments were also treated with laurylamine hydrochloride; however, as soon as a sample was placed

Table 1. Intensities and d-values of 001 smectite peaks as a function of treatment.

Sequential treatment conditions	d (Å)	Relative peak height
1. Initial 4-week expansion with laurylamine hydrochloride	24.2	55
	17.5	55
2. 1st day wash with alcohol + water	23.3	70
	17.9	55
3. 2nd day wash with alcohol + water	—	—
	17.9	—
4. 3rd day wash with alcohol + water	21.8	15
	16.1	35
5. 1-week additional treatment with laurylamine hydrochloride	21.8	33
	17.5	45
6. 1st day wash with alcohol + water	27.2	7
	17.1	60
7. 2nd day wash with alcohol + water	22.6	10
	15.8	34
8. 3rd day wash with alcohol + water	22.1	10
	15.1	40
9. 4th day wash with alcohol + water	23.1	5
	14.9	30
10. 5th day wash with alcohol + water	20.8	10
	14.7	43
11. 6th day wash with alcohol + water	20.8	20
	15.0	100

of resin was then added to form a package in which smectite grains had preferred orientation. Thin sections were prepared with the smectite layers normal to the section. Following optical examination, sections were separated from the slide and thinned in an ion mill. All TEM observations were obtained using the University of Michigan JEOL JEM-100CX scanning-transmission electron microscope. Methods of observation were described, for example, by Lee and Peacor (1983).

To determine the composition of smectite grains directly, untreated samples were qualitatively analyzed using energy dispersive X-ray techniques (EDX) as detailed by Isaacs *et al.* (1981). These techniques allowed resolution of about 300 Å. Crushed grains mounted on Be grids were first characterized by TEM techniques and found to be identical to those imaged in Figures 2 and 3.

RESULTS

Figures 2 and 3 are images of untreated smectite at different magnifications. The electron diffraction pattern leading to these lattice fringe images gave d(001) about 13.0 Å, in good agreement with the average XRD value, and verifying that layers had not collapsed significantly. Considerable diffuseness, however, was noted paralleled to c* in the electron diffraction patterns and was consistent with the variation in spacing.

Figure 2 shows typical lattice fringe images of smectite layers. The images are severely distorted and imperfect in a variety of ways. Figure 3 is a lattice fringe image at higher magnification. The lines shown are images of the layers of the structure, having a spacing of several Ångstroms; they are typical of all smectites that have been observed in this laboratory. Different layer spacings can be seen. Most spacings are about 13.0 Å, consistent with a normal, hydrated smectite, but others are as small as 10 Å. The smaller d-values are presumably due to the collapse of an original 13-Å layer of the smectite upon loss of water in the vacuum of the TEM. They could, however, also be interpreted as being due to local heterogeneities in the original chemistry and/or structure.

Figure 2 shows structural imperfections that typify natural, untreated smectites (see, e.g., Lee *et al.,* 1985). What appears to be, to the first approximation, a single smectite crystal, is actually a mosaic of subparallel domains. Where such domains meet, the intersection resembles a small-angle grain boundary. In general, individual layers terminate in a series of edge dislocation-like features along these boundaries. Such layer terminations resemble classic images of edge dislocation and are common, even within the domains of structure which at first sight appear to be relatively perfect.

Figures 4a and 4b show typical images of the expanded smectite. The electron diffraction patterns leading to these images have d(001) = 13–16 Å, consistent with expanded layers as measured by XRD. The same doubled 001 reflections visible in XRD patterns are present; significant streaking parallel to c* is present and indicates structural and/or chemical differences between layers.

Figures 4a and 4b also show individual layers, most of which have spacings of 14–16 Å; a few, however, approach 10 Å. These spacings further verify the permanent expanding ability of laurylamine hydrochloride. The layers show the same high degree of imperfection as shown in Figures 2 and 3. The correspondence of average d-values as determined by TEM is particularly significant in that several days had passed between specimen preparation and the TEM observations, during which time the sample was ion-milled. Thus, the expansion appears to be permanent, at least for epoxy-embedded samples.

Representative EDX spectra (Figure 5) show that the principal interlayer cation of the smectite is Na, as expected, with minor Ca. A trace of K is present, as was commonly observed in spectra from other areas of the sample. The average smectite grain, as typified by Figure 5, has Al as the dominant octahedral cation. Significant amounts of Fe and Mg are also present apparently in octahedral sites, although the Al, Mg, and Fe contents vary considerably. Thus, even this relatively ideal, well-characterized bentonite is heterogeneous in composition at the sub-micrometer level.

CONCLUSIONS

Laurylamine hydrochloride causes expansion of smectite layers that is detectable by electron diffraction and lattice fringe imaging; however, the expansion is variable and inconsistent even for adjacent layers. Therefore, the technique does not permit unambiguous differentiation between smectite and illite layers. The existence of two 001 peaks for expanded smectite remains unexplained. Because laurylamine hydrochloride treatment destroys the original texture of the sample, it should be used cautiously and selectively. It may then be useful to identify layers having spacings >10 Å as smectite; however, layers with spacings of about 10 Å cannot be positively identified. Treatment by laurylamine hydrochloride thus appears to be of minimum aid for the unambiguous characterization of mixed-layer illite/smectite clays.

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