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NOTES

WET-TO-DRY TRANSITION OF SMECTITE AS REVEALED BY HUMIDITY-CONTROLLED ELECTRON MICROSCOPY

Key Words—Humidity control, Morphology, Smectite, Transmission electron microscopy, Wet-to-dry transition.

The loss of topsoil by wind and water erosion is currently one of the greatest global problems. The World Watch Institute has estimated that topsoil is being lost at a rate of 0.7% per year (Brown and Wolf, 1984). The erosion process depends, in part, on the micro-structure of fine particulates, which are easily mobilized by wind and rain. Soils at high latitudes appear to be particularly sensitive due, in part, to the high wind velocities (Fyfe, 1985). Previously, Tazaki et al. (1988) described the formation of aerosol size (100 Å) particles in smectites by structural damage induced by freezing. In the present study, a transmission electron microscope (TEM) equipped with a humidity-control chamber was used to study the influence of drying on the micro-structure of smectite.

The objectives of the investigation were (1) to observe directly the morphological and structural changes of smectite under humidity-controlled wet-to-dry environment, (2) to compare wet-dry cycles of smectite with freeze-thaw cycles, and (3) to discuss possibility of wind erosion of topsoil in polar regions in which intensive climatic change, such as the frozen dry condition, prevail.

In the present study high-resolution, humidity-controlled TEM was used to show that simple air-drying of smectite or placing a smectite in dry environment or a vacuum decreased the basal spacings and also produced aerosol-size fine particles.

MATERIAL AND METHODS

The material used, a Na-smectite from the Black Hills, South Dakota, was obtained from Ward's Natural Science Establishment, Rochester, New York, and was saturated with $(CH_3COO)_2Mg$.

Both Na- and Mg-saturated smectite was studied by X-ray powder diffraction (XRD) using a Rigaku goniometer equipped with a cryo-facility at liquid-nitrogen temperatures and CuKα radiation and operated at 50 kV and 120 mA. The samples were analyzed at 20° and −35°C.

Grains (<2 μm) were collected by hydraulic elutriation and pipeted onto specimen-support micro-grids for transmission electron microscopy (TEM). The wet specimen was inserted into an environmental cell in the humidity-controlled facilities. The same specimens examined by cryo-TEM by Tazaki *et al.* (1988) were examined by humidity-controlled TEM in humid air and in vacuum. The humidity-controlled TEM equipped with a film-sealed, high-resolution environmental cell was developed by Fukami and Katoh (1972). A JEOL-2000 EX TEM (side-entry type), equipped with humidity-control facilities (environmental cell), was used at an accelerating voltage of 200 kV in saturated water vapor with a carrier gas (air) at 50–60 Torr. The film-sealed high-resolution environmental cell consisted of a layering of gaskets, copper disks with apertures, and a specially prepared sealing film (275 Å in thickness), and a spacer (50 μm in thickness) (Figure 1). The experimental procedures are similar to those described by Kohyama *et al.* (1978, 1982).

RESULT AND DISCUSSION

The basal spacing of 15.2 Å of the air-dried Na-smectite decreased to 12.2 Å by freezing (Figures 2A and 2B), whereas the wet Mg-smectite showed a decrease from 20.3 to 15.9 Å by freezing (Figures 2C and 2D). The shrinkages of 20–22% of the basal spacing (001) of smectite were due to the formation of ice in the clay. The decrease in basal spacings of the smectite was also caused by dehydration in cold air-dry, in vacuum, and in freeze-dry conditions.

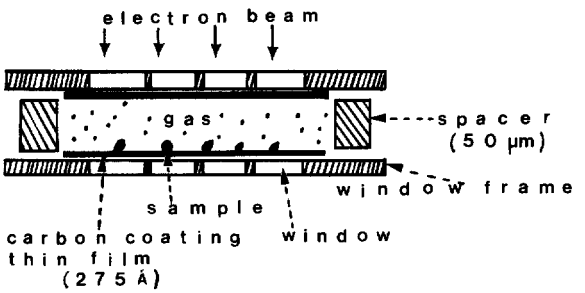

Figure 1. Specimen chamber of film-sealed environmental cell containing water vapor or carrier gas (air).

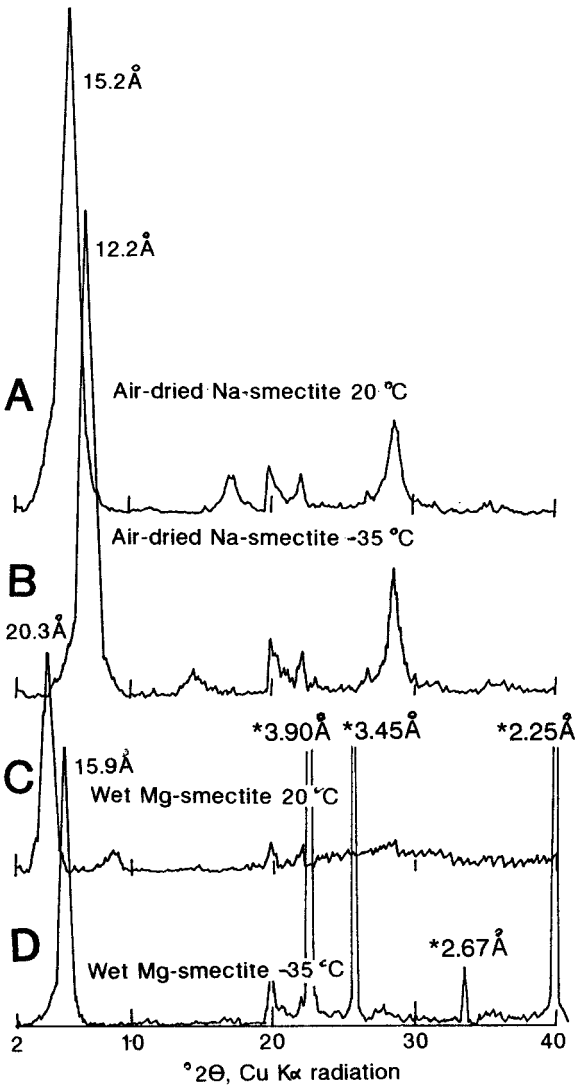

Figure 2. X-ray powder diffractograms of (A) air-dried Na-smectite analyzed at 20°C, (B) air-dried Na-smectite analyzed at −35°C, (C) wet Mg-smectite analyzed at 20°C, (D) wet Mg-smectite analyzed at −35°C. * = peaks of ice crystal.

The humidity-controlled TEM at 25°–70°C showed not only basal-spacing changes, but also the presence of cavities. As the individual layers of smectite separated, particles of aerosol dimensions were produced, similar to those observed in earlier cryo-TEM studies (Tazaki *et al.,* 1988). The basal spacing of 16.0 Å of Mg-smectite in humid air decreased to 12.8 Å by air-drying in vacuum (10^{-3}–10^{-4} Torr) (Figures 3 and 4). As shown in Figure 3 (left side), a flat, smooth lamella structure was present in the humid-air environment of 60 Torr, whereas after evacuation for 1 hr (Figure 4), the lamellar structure was not found, the sample showing the presence of domains and cavities (Figure 4, arrow).

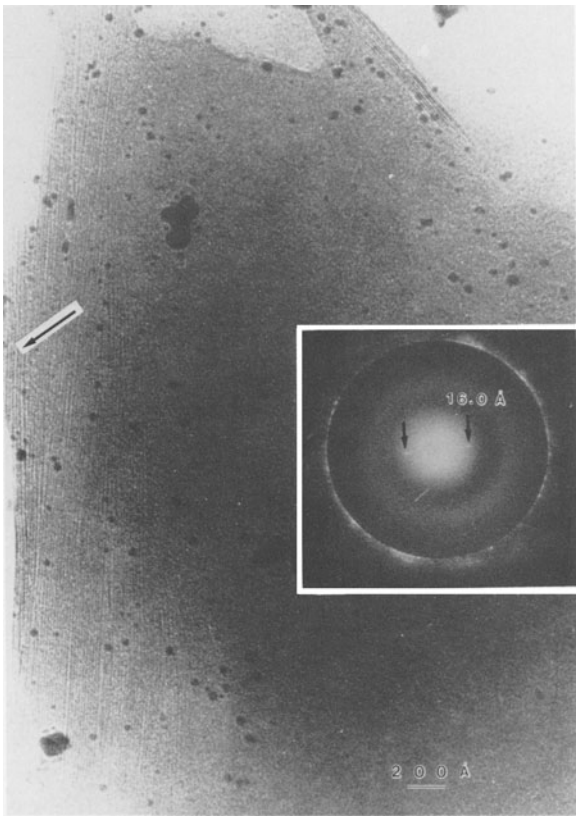

Figure 3. Humidity-controlled transmission electron micrograph and electron diffraction pattern of hydrated Mg-smectite showing a flat, smooth lamellar surface having a 16.0-Å basal spacing. Humid-air environment at 60 Torr.

The basal spacing of the Na-smectite changed from 15.5 to 12.2 Å on dehydration, separation, and dislocation caused by air-drying (Figure 5). Parts of the edges of domains were ruptured into small fragments (Figure 5B, at the top of the right corner, arrow). Typical changes in clay spacings (15.5 → 12.2 Å) represents a 21% shrinkage in vacuum of the basal spacing of the Na-smectite, at the center of the particle. The change of basal area of the Na-smectite (680 → 560 Å^2) represents an 18% shrinkage in the dry air environment after evacuation (Figure 5).

Frozen-hydrated Na-smectite showed a 32–26% shrinkage from 17 to 11.6 and 12.5 Å in contact with ice crystals (Tazaki *et al.,* 1988), suggesting that the wet-dry modification produced less shrinkage than the freeze-thaw modification.

Both the Mg- and Na-smectite showed a decrease in basal spacing from 16.0–15.5 Å to 12.8–12.2 Å by the wet-to-dry transition, which agrees well with the shrinkage of Ca-beidellite reported by Kohyama *et al.,* (1982). The Ca-beidellite in vacuum showed a decrease in basal spacing from 15.6 to 12.7 Å after evacuation for 30 min. Thus, the wet-to-dry transition produced

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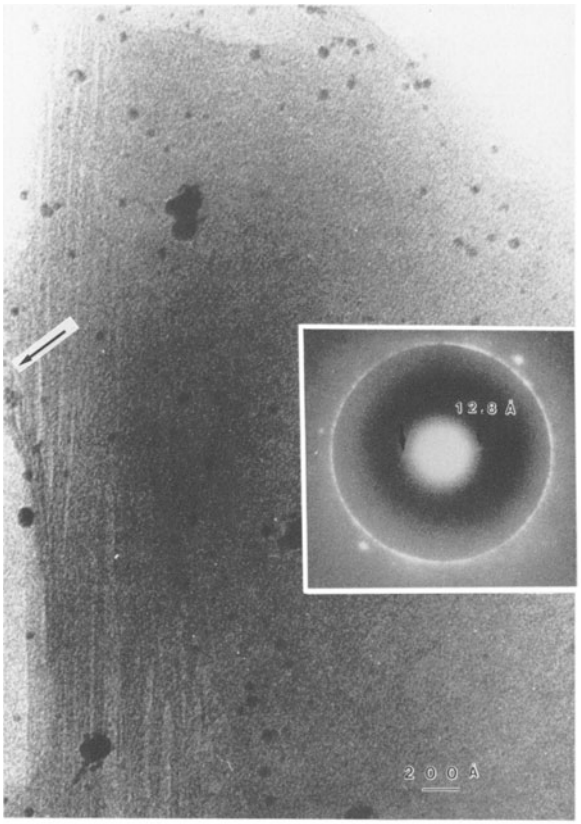

Figure 4. Transmission electron micrograph of the same particle as in Figure 3 in vacuum after evacuation for 1 hr, showing the presence of cavities (arrow) and an air-dried interlayer spacing of 12.8-Å, smaller than that of humid-air environment (16.0-Å).

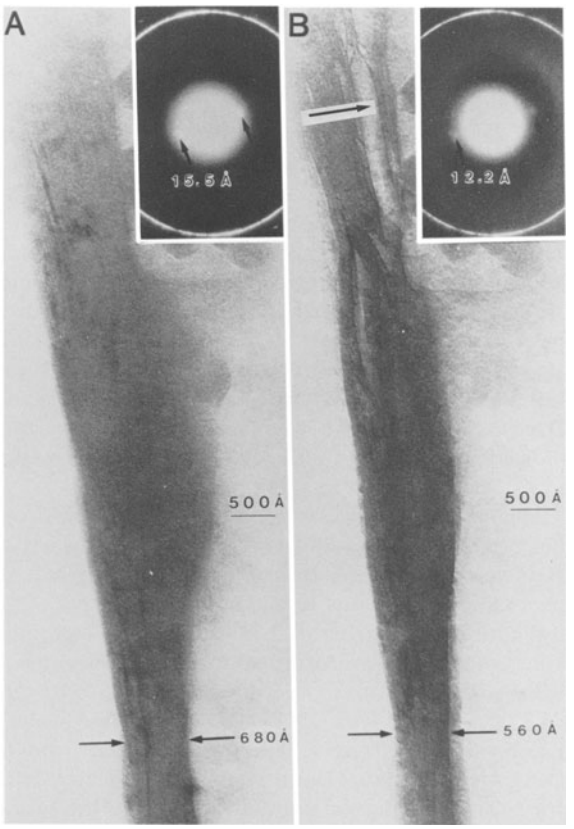

Figure 5. Humidity-controlled transmission electron micrographs of hydrated Na-smectite (A) in a humid-air environment at 60 Torr and (B) the same particle in a dry-air environment at 50 Torr, after evacuation for 1 hr at 25–70°C. Micrographs show differences in morphology and of interlayer spacing and presence of aerosol-size fine particles produced by air-drying (arrow).

Table 1. Basal spacing (Å) of Na- and Mg-smectite samples in air-dried, wet, and frozen-hydrated environments.

	Na-smectite		Mg-smectite
Cryo-X-ray powder diffraction			
Air-dried (20°C)	15.2		
Air-dried (−35°C)	12.2		
		Wet (20°C)	20.3
		Wet (−35°C)	15.9
Shrinkage	20%		22%
Humidity-controlled transmission electron microscopy			
In wet air	15.5	In wet air	16.0
In dry air (after evacuation)	12.2	In vacuum (after evacuation)	12.8
Shrinkage	21%		20%
Cryo-transmission electron microscopy[1]			
Frozen-hydrated	17–14		
Smectite in contact with ice	12.5–11.6		
Shrinkage	32–26%		

[1] Data from Tazaki *et al.* (1988).

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almost same shrinkage of basal spacings, regardless of the nature of exchangeable cation.

The basal spacings of the Na- and Mg-smectite samples in the various states using cryo-XRD, humidity-controlled TEM, and cryo-TEM are summarized in Table 1. The frozen-hydrated state (at −263° to −265°C) showed the largest shrinkage of the spacing because of the formation of ice in the clay. Smart and Tovey (1982) described degree of shrinkage of soils in six different dry conditions, if swelling clays were present. The air-dried soil shrank less than the freeze-dried soil, which agrees with the results of the present study. Rapid cooling and repeated freeze-wet-dry cycles induces cracking and the development of large pores in soils (Smart and Tovey, 1982). Cryo-SEM of freeze-dried Na-smectite showed high-porosity and card-house structure with edge-to-face contacts (Tazaki *et al.,* 1988).

The card-house structure of aerosol-size fine particles produced by freeze-drying and the cavities of domains produced by air-drying are perfect wind-catchers. In the polar regions, temperatures can reach −80°C, and commonly reach −40°C. Note that the saturated water vapor pressures dropped steeply at low temperature <0°C; in mm Hg, 0.0004 at −80°C, 0.0966 at −40°C, 4.579 at 0°C, 23.756 at 25°C (liquid water). The lowest water vapor pressure used in the present study was about 26.74 mm Hg at 27°C. Clearly, both drying and freezing can dramatically change the nature of smectite in soils. The aerosol fine particles of smectite produced through freeze-drying environment may be highly susceptible to wind erosion.

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