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ORDERED HALLOYSITE: DIMETHYLSULFOXIDE INTERCALATE

Key Words—Dimethylsulfoxide, Halloysite, Infrared spectroscopy, Intercalation, Ordering, X-ray powder diffraction.

The halloysite minerals are similar in chemistry to kaolinite but differ by having a naturally hydrated form that contains water molecules between the silicate layers. Halloysites, either hydrated or dehydrated, intercalate relatively more easily and with a greater variety of organic molecules than do kaolinites (Theng, 1974). The interactions between the clay and the guest molecule are subtle, and an understanding of these phenomena requires knowledge of the crystal structure of the intercalated clay. Unfortunately, few examples of three-dimensionally ordered kaolin intercalates are known. Thompson and Cuff (1985) recently reported that exposure of kaolinite to heated dimethylsulfoxide (DMSO) vapor leads to a three-dimensionally ordered intercalate. They determined the crystal structure of the intercalate using the Rietveld technique. This three-dimensional ordering is not surprising because DMSO seems to interact much more strongly with the clay (Costanzo *et al.*, 1984a, 1984b; Lipsicas *et al.*, 1985) than do other organic molecules. We report here that the vapor treatment also forms an ordered intercalate with halloysite. This is apparently the first observation of long-range order in a halloysite and is most unexpected because of halloysite's tubular morphology and its high degree of disorder. The existence of a three-dimensionally ordered halloysite: DMSO intercalate is of interest because it opens up a completely new way to examine these enigmatic minerals.

EXPERIMENTAL

Two clays were used for the present study: a well-crystallized kaolinite from Georgia (KGa-1 from the Source Clay Minerals Repository of The Clay Minerals Society) and a halloysite from Spruce Pine, North Carolina (API Standards, Ward's Natural Science Establishment, Rochester, New York). The clays were treated with reagent grade DMSO from Fisher Scientific. The X-ray powder diffraction (XRD) scans were made with a GE XRD-6 diffractometer equipped with a copper tube. All samples were dried and packed into bulk sample holders to minimize preferred orientation, with the exception of one of the Spruce Pine intercalates which was examined wet as a quasi-random smear on a glass slide. The infrared spectra were recorded in the absorbance mode using a Perkin Elmer Model 683 double-beam, ratio-recording spectrometer. The samples were mixed with a fluorinated hydrocarbon and examined as a thin film between CaF_2 plates.

The amount of DMSO intercalated into kaolinite has been reported to be about 1.5 molecules per unit cell or 0.75 per formula unit (Weiss *et al.*, 1966; Jacobs and Sterckx, 1970; Adams and Waltl, 1980). The typical intercalation procedure used in the earlier studies was to disperse the clay in liquid DMSO. Using the vapor method to intercalate kaolinite with DMSO vapor leads to a different stoichiometry, one in which the ratio $Al_2Si_2O_5(OH)_4/(CH_3)_2SO$ is 1.0 rather than 0.75, and the intercalate is three-dimensionally ordered (Thompson and Cuff, 1985). During the course of our experiments, it became clear that the application of heat, at any stage of the intercalation and subsequent drying, was a crucial factor in introducing order into the intercalates. Therefore, to obtain a disordered halloysite: DMSO intercalate, halloysite was dispersed in excess liquid DMSO for 1 hr, and then most of the liquid was removed by centrifugation and decantation. Following decantation, the damp clay was either air dried at ambient temperatures for use in the IR spectrometer or it was prepared as a smear on a glass slide for XRD. The ordered intercalates were obtained by one of two methods. The first method was to expose the clay to DMSO vapor in a closed container at 60°C for 48 hr as was done by Thompson and Cuff (1985). The alternate treatment, used solely for the Georgia kaolinite, was to disperse the clay in excess DMSO at room temperature for 6 months followed by drying at 60°C. These conditions are probably not optimum for producing either a completely ordered or disordered DMSO intercalate; the possible range of conditions is large and is presently being investigated.

RESULTS

The results of the XRD experiments are shown in Figure 1. The untreated Spruce Pine halloysite has a weak 001 reflection and a broad 02,11 band (Figure 1A). The weak intensities are probably a result of the tubular morphology and the high degree of disorder. The XRD trace of the same halloysite intercalated by DMSO without heat is shown in Figure 1B. The broad XRD band stretching from about 17° to 24°2θ may reflect both the incomplete intercalation of the sample by DMSO and the presence of some remaining liquid DMSO in the sample. Incomplete intercalation is also suggested by the relatively small d(001) spacing of 10.3 Å compared to the usual spacing of 11.1 Å for a fully expanded kaolinite:DMSO intercalate. Exposure of the

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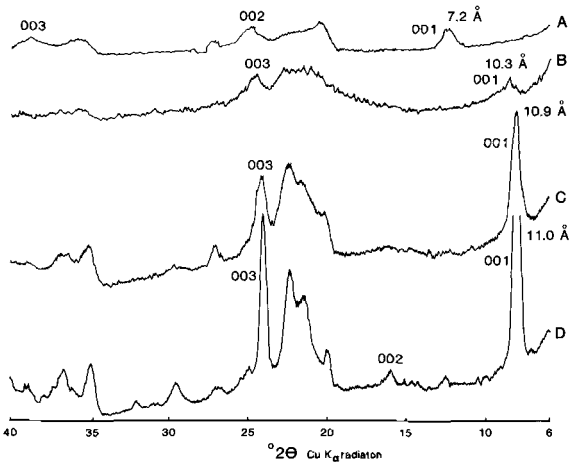


Figure 1. X-ray powder diffraction patterns of untreated Spruce Pine halloysite (A), the same halloysite treated with liquid dimethylsulfoxide (DMSO) at room temperature and run as a smear (B), the same halloysite exposed to DMSO vapor at 60°C and dried by heating at 60°C (C), and Georgia well-crystallized kaolinite soaked in DMSO for 6 months and heat dried at 60°C for 1 hr.

halloysite to warm (60°C) DMSO vapor induced a striking change in the halloysite. This is seen, first, in the very intense and narrow 001 reflection; and, second, in the relatively large amount of detail in the *hkl* reflections beginning at about 19°2θ (Figure 1C). Figure 1D is the XRD trace of the Georgia kaolinite suspended in DMSO for 6 months and then dried at 60°C. Comparison of the XRD trace in Figure 1C with that of Figure 1D shows a nearly peak-for-peak equivalence with only a few exceptions among the very weakest peaks. Although the resolution of the XRD peaks for the Spruce Pine halloysite:DMSO intercalate is not as good as the kaolinite:DMSO pattern, a degree of three-dimensional order which normally would not be expected for a halloysite is clearly present. The similarities in the *hkl* intensities of the halloysite and kaolinite intercalates indicates a fundamental equivalence in the structure of the silicate layer in both minerals. This structural equivalence is a strong argument against Edelman and Favejee's (1940) proposed structure for halloysite which has a portion of the silica tetrahedra pointing into the interlayer space.

The IR spectra of the following samples are shown in Figure 2: the untreated Spruce Pine halloysite (Figure 2A), the same halloysite intercalated and dried at room temperature (Figure 2B), the same halloysite intercalated by heated vapor and dried by heat (Figure 2C), and the Georgia kaolinite intercalated as described above (Figure 2D). The IR results yield conclusions similar to those derived from the XRD results described above. The untreated halloysite (Figure 2A) shows little detail other than two structural OH-stretching bands at 3693 and 3619 cm^{-1} and water bands at ~3400 and 1627 cm^{-1}. The origin of the band

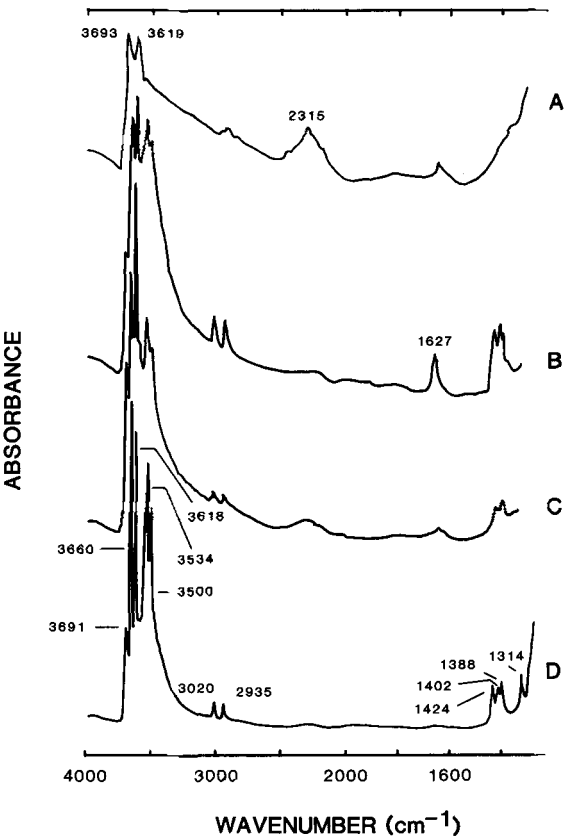


Figure 2. Absorbance-mode infrared spectra of untreated Spruce Pine halloysite (A), the same halloysite treated with liquid dimethylsulfoxide (DMSO) at room temperature for 1 hr and heat dried under ambient conditions (B), the halloysite exposed to DMSO vapor at 60°C and dried at 60°C (C), and Georgia well-crystallized kaolinite intercalated as described in Figure 1D.

at 2315 cm^{-1} is not known. Exposure of the halloysite to DMSO at room temperature, which resulted in little or no order as shown by XRD (Figure 1B), produced some ordering (Figure 2B), probably because the IR sample was dried. Water was still present in this intercalate as shown by the bending mode of water at 1627 cm^{-1}. The slowly decaying absorption on the low-frequency side of the ~3500-cm^{-1} band is indicative of some remaining disorder. Figure 2C is the spectrum of halloysite which was intercalated by DMSO vapor at 60°C followed by drying at the same temperature. It is similar to the spectrum of the well-ordered kaolinite:DMSO intercalate (Figure 2D). In fact, as in the XRD patterns (Figures 1C, 1D), there is a nearly band-for-band match. Again, the intensities are not identical, probably due to the disorder in the halloysite.

The experiments show that Spruce Pine halloysite is very sensitive to the temperature of DMSO intercalation. Modest heating for a relatively short time (~1 hr) is enough to induce a considerable degree of order.

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The fact that three-dimensional order can be created in Spruce Pine halloysite is remarkable. It is difficult to imagine how a tubular structure can have an ordered stacking of layers, as seems to be indicated by the results shown in Figures 1C and 2C. A simple explanation is that the bonding between the DMSO and the kaolin layers in the halloysite is sufficiently strong that the tubes unroll. The present study was not designed to test that hypothesis, but previous experiments have shown that platey kaolinite can, under the right circumstances, roll into tubes (Weiss and Russo, 1963; Sanchez Camazano and Gonzalez Garcia, 1970). It may not be unreasonable to expect that this change in morphology is reversible if the intercalating molecule has a strong tendency to adopt an ordered arrangement between the kaolin layers. This possibility is presently being investigated.

Previous studies of clay organic reactions have stressed the need to specify the type of clay and its properties. It appears from this study that the conditions of intercalation are very critical and, to obtain reproducible results, it may be necessary to repeat the intercalation in precisely the same way each time.

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