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NOTES

TECHNIQUE FOR TRANSMISSION ELECTRON MICROSCOPY AND X-RAY POWDER DIFFRACTION ANALYSES OF THE SAME CLAY MINERAL SPECIMEN

Key Words—Hydrobiotite, Sample preparation, Spurr resin, Transmission electron microscopy, Vermiculite, X-ray powder diffraction.

Techniques involving X-ray powder diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) are often used to characterize clay-size phyllosilicates. The XRD approach is particularly well suited for determining the distinctive basal spacings of clay minerals. The information provided by XRD analyses, however, can be complicated by interstratification, because the combined effects of various basal spacings are not easily distinguished from those due to particle size, morphology, and orientation (Brindley, 1980). On the other hand, HRTEM is an excellent method for studying the arrangement of both the particles within clay specimens and the layers within clay particles. Clearly, a combination of the two methods can provide a better understanding of the fabric of clay specimens than either method alone. The various techniques, however, of preparing clay specimens for HRTEM and XRD analyses (Jackson, 1985; McKee and Brown, 1977; Rich and Barnhisel, 1977) are substantially different, and it is not clear to what extent these techniques influence the fabric of the clay specimens. The following procedure was therefore developed to obtain XRD and HRTEM results for the same clay mineral specimen.

MATERIALS AND METHODS

South Carolina vermiculitic material (a mixture of vermiculite, hydrobiotite, and biotite), obtained from the Zonolite Company (now a part of W. R. Grace and Company), was dry-ground and fractionated first by sieving and then by sedimentation to obtain a sample (~150 mg) of the <1-μm material. This sample was washed in 25-ml aliquots of 1 M NaCl three times and then with distilled water until free of $AgNO_3$-detectible Cl^-. Next, the sample was thoroughly mixed with 5 ml of 0.5 M octylamine hydrochloride and incubated at 60°C for 24 hr. The incubation procedure was repeated with a fresh aliquot of the octylamine hydrochloride solution, and the sample was then washed free of Cl^- with 95% ethanol.

An oriented specimen of the octylamine hydrochloride-treated sample was prepared by first attaching a sheet of Teflon film to a glass microscope slide with double-stick tape and then spreading a viscous slurry of the clay in ethanol over the Teflon surface with a spatula. The specimen was dried at 60°C for 24 hr in a vacuum oven (−26 kPa) and then analyzed by XRD in a desiccated atmosphere. Several drops of Spurr embedding resin (Spurr, 1969) were spread over the surface of the specimen and allowed to interact with the mineral. After 20 min, excess resin was removed with a tissue, and the specimen was placed in a 60°C oven for 24 hr and then analyzed by XRD. All XRD analyses were performed with CuKα radiation using a General Electric XRD-6 diffractometer equipped with a focusing monochromator.

To prepare a portion of the resin-treated specimen for HRTEM analyses, a strip (~1 × 10 mm) of the specimen was first separated from the Teflon film with a razor blade. This strip was then placed on a layer of cured resin and covered with uncured resin. This resin-clay-resin sandwich was incubated at 60°C for 24 hr to cure the added resin and then sliced with a microtome to obtain ultrathin (~500 Å) cross sections of the embedded specimen. These sections were mounted on 400-mesh copper grids and analyzed with a JEOL JEM-100CX II transmission electron microscope operated at 100 kV.

RESULTS AND DISCUSSION

In this study, the clay specimen was analyzed by XRD while mounted on Teflon both before and after an embedding-resin treatment. Therefore, XRD peaks associated with the Teflon and the resin had to be accounted for in the interpretation of XRD patterns. The Spurr embedding resin exhibited no XRD reflections between 2° and 20°2θ, however, the Teflon film produced a sharp peak at 18.1°2θ (Figure 1). Fortunately, this Teflon peak did not interfere with the basal reflections of the octylammonium-treated South Carolina vermiculitic material (Figure 2).

It was necessary to saturate the clay mineral speci-

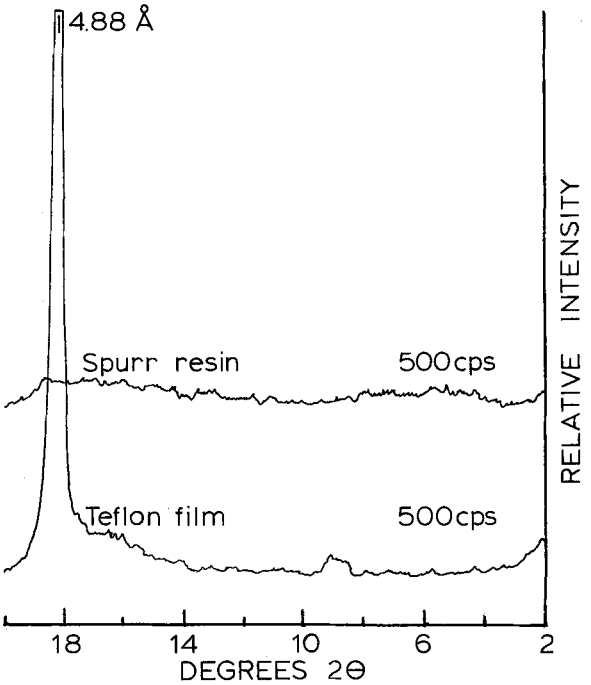

Figure 1. X-ray powder diffraction patterns of Teflon film and block of cured Spurr embedding resin. CuKα radiation.

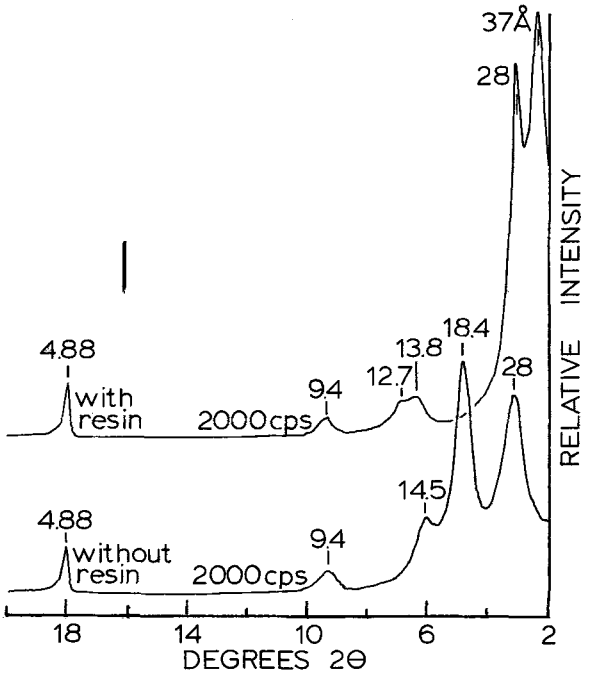

Figure 2. X-ray powder diffraction patterns of the octylammonium-saturated specimen of South Carolina vermiculitic material before and after embedding-resin treatment. CuKα radiation.

men with octylammonium cations to avoid the effects of drying during pretreatments for the HRTEM analysis. The XRD results for this octylammonium-treated material before the Spurr treatment (Figure 2, without resin) indicated basal spacings of 9.4, 18.4, and 28 Å, which identified the presence of a fully contracted phase (biotite), an expandable phase (vermiculite), and a regularly interstratified phase (hydrobiotite), respectively. When the same specimen was treated with the embedding resin, the fully contracted phase did not change, whereas the basal spacings of the expandable and the regularly interstratified phases increased to 28 and 37 Å, respectively (Figure 2, with resin). These results corroborate the observation by Vali and Köster (1986) that the embedding resin may penetrate the interlayer space of the expandable parts of vermiculitic material. In similar experiments, the Spurr embedding resin expanded octadecylammonium-smectite and partly expanded oven-dried K-smectite, but it had no effect on the basal spacings of kaolinite, chlorite, or naturally contracted micaceous minerals. Clearly, the expanding effects of embedding resins on phyllosilicates should be considered when clay mineral specimens are prepared for HRTEM analyses. The effects also emphasize the importance of using the same specimen for XRD and HRTEM comparisons.

The results of the HRTEM analysis for the same octylammonium-treated mineral sample verified the existence of the three mineral phases identified by XRD. Typical of these results are the lattice-fringe images of particles of the fully contracted and regularly interstratified phases in Figure 3 and the expandable phase in Figure 4. The HRTEM micrographs, however, revealed three aspects of the layer-layer organization of the South Carolina vermiculitic material not detected

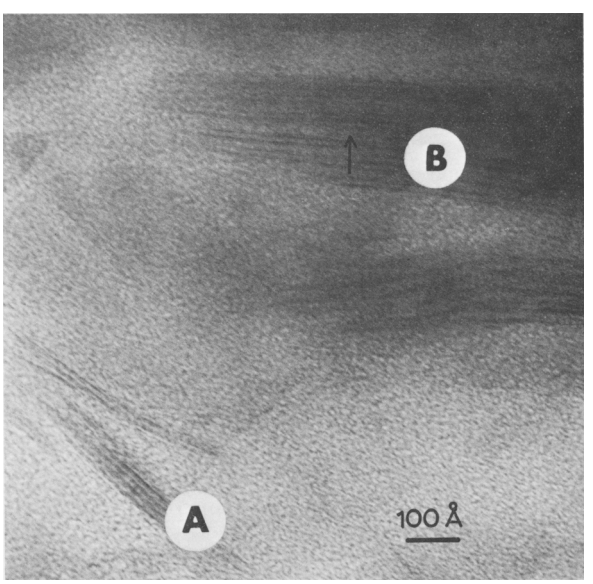

Figure 3. Lattice-fringe images of fully contracted (A) and regularly interstratified (B) phases with estimated fringe widths of 10 and 28 Å, respectively. A layer termination within the regularly interstratified phase is marked with an arrow.

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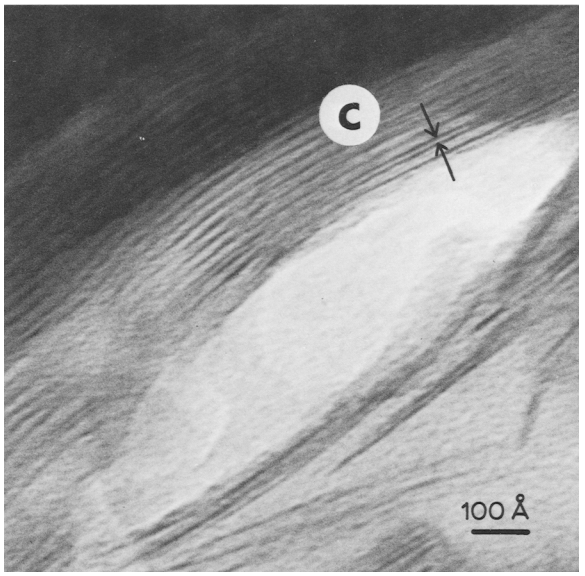

Figure 4. Lattice-fringe image of vermiculite phase (C) with estimated fringe width of 18 Å. A contracted layer (identified by the arrows) is interstratified with the expanded layers.

by XRD: (1) Most of the clay particles were dominated by one of the three phases rather than by mixtures of phases, but a few particles contained both the expandable and regularly interstratified phases. (2) Defects within layer sequences were common [e.g., a layer termination (Figure 3) and the existence of a contracted layer in a sequence of expanded layers (Figure 4)]. (3) No layers containing contiguous expanded and contracted regions were observed (i.e., individual layers were either fully contracted or fully expanded).

The HRTEM analysis also revealed that the fabric of the mineral specimen was considerably disoriented (Figure 5). The fabric of the ultrathin section shown in Figure 5 may have been altered when the section was cut, but no visible evidence of alterations was observed. Instead, micrographs indicated that the section was devoid of tears and that most of the voids between the clay particles were filled with resin. Furthermore, numerous other ultrathin sections from this specimen were found to have similarly disoriented fabrics. Therefore, Figure 5 probably illustrates the fabric of the specimen at the time the XRD analyses (Figure 2) were performed. If so, only a very small part of the specimen was properly oriented to account for the coherently diffracted radiation depicted by the XRD peaks in Figure 2.

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Figure 5. Transmission electron micrograph illustrating fabric of specimen of South Carolina vemiculitic material. Plane of "preferred orientation" is perpendicular to plane of micrograph and parallel to specimen-resin contact, evident on left side of micrograph.

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