

Electron microscopy of smectites prepared by low temperature freeze-drying

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Abstract

A low temperature freeze-drying method for the preparation of clay samples for transmission electron microscopy is described. After depositing a carbon film on freshly cleaved mica, the sample is freeze-dried, shadowed and a second carbon film deposited. Electron micrographs obtained of dispersions of smectites and organosmectites prepared by this method show pronounced "stringing" or end-to-end association of the clay particles.

Introduction

For many years there has been an interest in studying various methods of clay sample preparation for electron microscopy, so as to better visualize the particle-particle interrelationships of dispersions. For transmission electron microscopy the sample preparation methods have generally centered about the use of freeze-drying and critical-point drying methods (Bates, 1958; Corbet *et al.*, 1956; Hofmann *et al.*, 1962; Jernigan *et al.*, 1975; McKee *et al.*, 1977; Mering *et al.*, 1971.) In a recent paper (McAtee *et al.*, 1979), a modified freeze-drying procedure was described that reduced the amount of curling and aggregation of clay platelets which resulted in electron micrographs that better illustrated the shapes of individual clay particles, and the delicate morphology of aggregates.

In 1966, Claesson *et al.* described a freeze-drying method for the study of gel particles and other super molecular structures in solution. An adaptation of the procedure by Claesson has been made for our vacuum evaporator so that this method could be used for the study of clay dispersions in both water and organic fluids. It is believed that the procedure described in this paper is an improvement over previous clay sample preparation methods since it better shows the particle-particle interaction and the morphology of the clay particles.

Experimental

A variety of smectites, including Wyoming and southern montmorillonites and hectorites, were examined by electron microscopy. In addition, several of the samples were complexed with various

organic quaternary ammonium cations so that the resulting organo-clays could be dispersed in organic fluids.

The organo-clays were prepared by adding the quaternary ammonium salt to a dilute suspension of smectite while stirring at high speed in a Waring blender. After the addition of approximately one hundred milliequivalents of quaternary cation per hundred grams of clay, the stirring was continued for fifteen minutes and then the dispersion allowed to sit overnight. It was then filtered, washed with distilled water, and dried at 105°C. The resulting organo-clay complex was dispersed in a small beaker of benzene-methanol by means of a Sonifier Cell Disrupter (Model W185). The Sonifier was kept at constant energy setting (50 watts) for approximately fifteen minutes for the preparation of all samples. Smectites dispersed in water were prepared in a similar manner, but the Sonifier was operated at slightly less energy of 40 watts for five minutes.

The apparatus used to prepare the electron microscope grids was built according to the principles of Claesson *et al.* A schematic view of the apparatus is given in Figure 1 where the bell jar and heat-radiation shields have been omitted for simplicity. The specimen can be kept at any temperature from that of approximately liquid air to room temperature (measured by a thermocouple). The vacuum in the vacuum evaporator is about 10^{-5} mm Hg.

Sample preparation

Samples are prepared as follows: (1) Carbon electrodes are prepared and placed about six cm above the copper sample stage and then a piece of

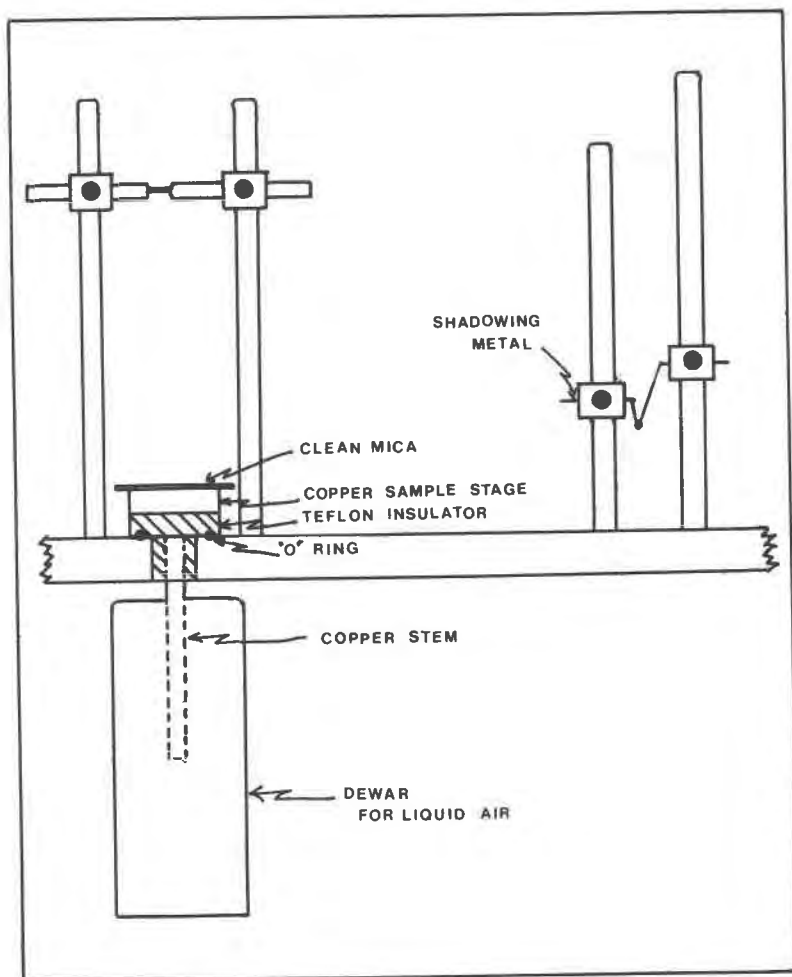


Fig. 1. Sketch of low temperature freeze-drying apparatus.

freshly cleaved, clean mica is placed on the stage. (2) Before closing the bell jar, a suitable shadowing material is placed on the second pair of electrodes and positioned to give about a twenty degree shadow angle. The general layout is shown in Figure 1. (Tungsten oxide and gold were used for shadowing materials in these studies.) (3) A thermocouple for measuring the temperature of the stage is positioned into a cavity in the copper sample stage. The bell jar positioned, and the system evacuated to 10^{-5} torr. (4) A thin carbon film is evaporated onto the mica surface. (5) Liquid air in a Dewar is positioned so that the stem of the copper sample stage is inserted into the liquid air (Fig. 1) and the stage is allowed to cool to the desired temperature, usually to -80°C or less. (6) While the sample stage is cooling, the dispersion to be studied is prepared in a spray device such as a DeVilbiss Atomizer so that a dilute

suspension of sample can be atomized onto the cold stage immediately upon letting clean, dry air into the chamber. (7) The operation of opening the bell jar and spraying the sample must be carried out as rapidly as possible so that condensation does not freeze on the carbon coated mica. It was observed that the sample freezes on the surface of the mica in about a second. (8) The bell jar is replaced and evacuated to start the freeze-drying process. As soon as a vacuum of about 10^{-5} torr is reached, the liquid air is removed. (9) After the thermocouple indicates the sample has returned to room temperature, the sample is lightly shadowed with the shadowing material. (10) After shadowing, a second thin carbon film is placed on the sample, thus producing a "sandwich" of shadowed sample between the carbon films. (11) Dry, pure air is slowly admitted, the mica removed and the carbon film is floated

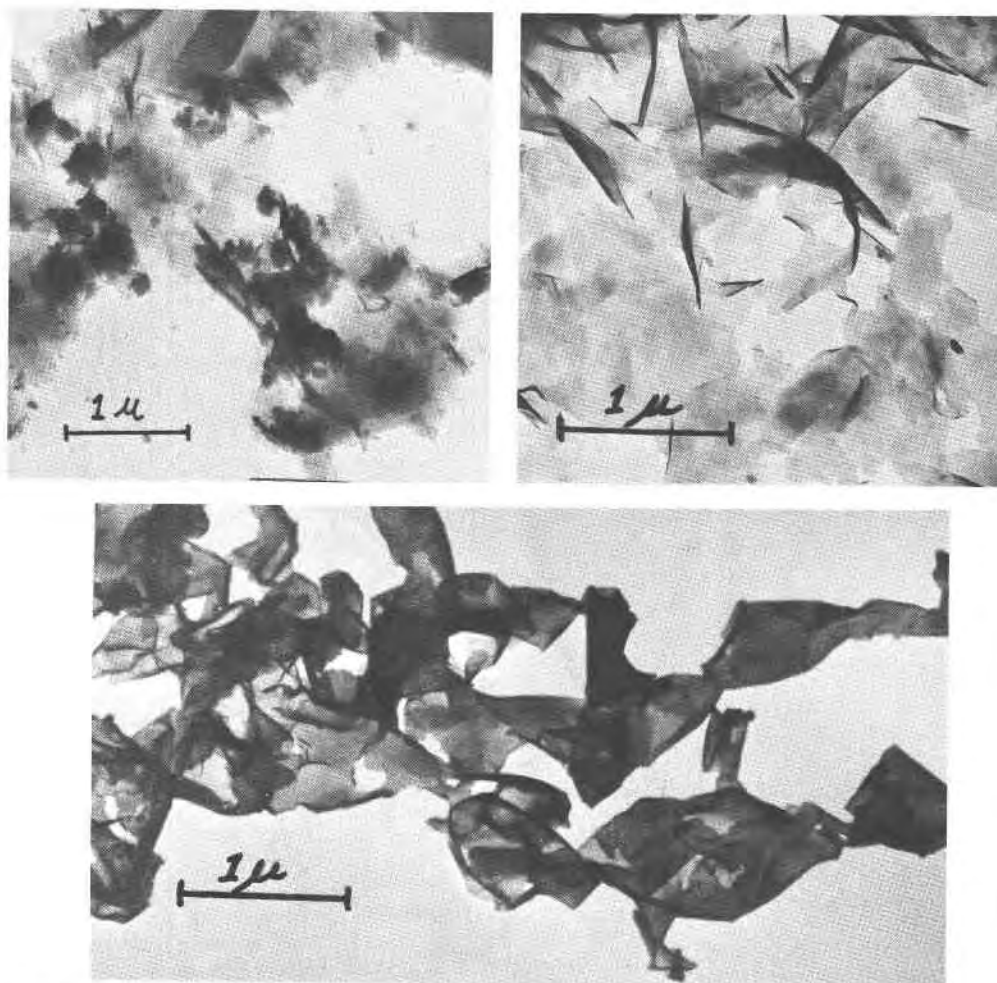


Fig. 2. Wyoming Na-smectites prepared by several different methods for electron microscopy: (a) dispersion sprayed onto carbon coated grid with atomizer; (b) critical point dried dispersion; (c) low temperature freeze-drying method.

onto the surface of clean, distilled water. (12) The resulting carbon film is then lowered onto electron microscope grids in the conventional manner and allowed to dry.

The samples were examined in a Hitachi HU-11A electron microscope at acceleration voltages of 50 and 75 kV. Magnification was calibrated by means of polystyrene latex spheres obtained from Ladd Research Industries, Inc.

Results and discussion

The main purpose of this paper is to describe the equipment used and procedure for preparation of clay samples for transmission electron microscopy. Many clay samples have been prepared and examined by TEM, and almost all show much greater detail of morphology and particle-particle relation-

ships than other methods used in our laboratories.

In order to illustrate the value of this method of sample preparation for transmission electron microscopy, several different smectites and organo-smectites have been examined. The different smectites represented in the electron micrographs were mined in the Wyoming area from several different mines and geological areas. All of the clays were predominately sodium-type clays and were dispersed in the "as received" condition. The organo-smectites illustrated were prepared as discussed previously.

Figure 2 compares electron micrographs of a Wyoming Na-smectite prepared by several different methods. This clay when prepared by conventional atomizer spray on a carbon coated grid is shown in Figure 2a, while Figure 2b shows the same clay

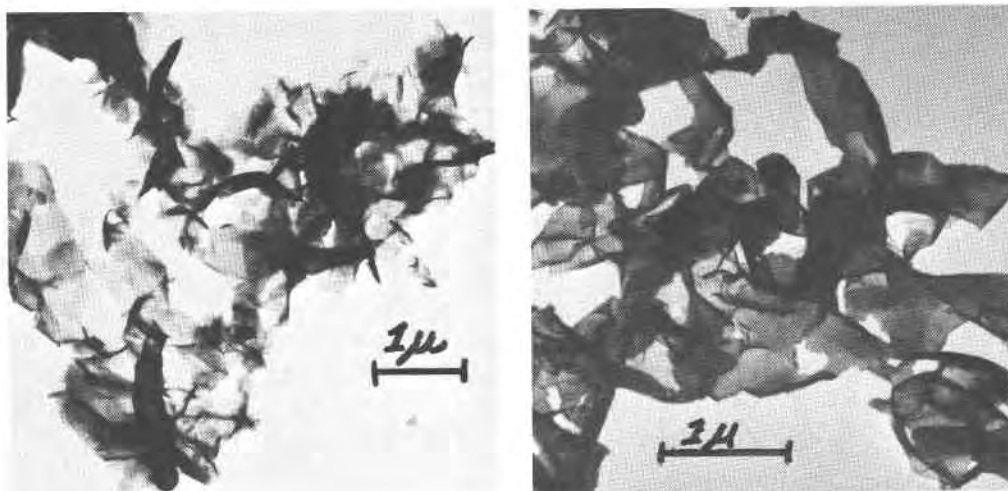


Fig. 3. Wyoming Na-smectites prepared by the low temperature freeze-drying method.

prepared by critical point drying. Figure 2c illustrates this smectite prepared by the freeze drying-shadowing method described in this paper. These figures clearly show how the freeze drying-shadowing sample preparation yields improved definition of particle size and shape and particle-particle interaction.

Figure 3 shows two different Wyoming smectites illustrating an open network of clay particles that results from this method of sample preparation. It can be seen in these micrographs that the individual clay particles appear to be aligned predominantly end-to-end with the "strings" of clay particles randomly aligned similar to electron micrographs of linear polymeric materials. Examination of the electron micrographs shows that individual clay particles appear to be possibly overlapping one another slightly on their basal faces. Figure 4 illustrates a typical electron micrograph observed from an organo-clay that has been dispersed in benzene-methanol solution. The figure again illustrates the end-to-end particle association observed in the smectites.

If the end-to-end particle relationship illustrated by these electron micrographs can be postulated as to the type of particle-particle interaction of the smectites in a dispersed state, it would help to explain the sensitivity of these clays to various dispersants and flocculants. For example, it is well known that anionic materials such as lignosulfonates and tannates act as thinning agents in drilling mud and that very small amounts of them can change very readily the viscosity and other rheolog-

ical properties of clay dispersants. If the smectite particles indeed have an end-to-end association, then it would be very apparent as to why small quantities of such anionic organic reagents would cause such large changes in the rheology of the clay dispersions.

Future work with this method of sample preparation will include higher resolution photographs with a different electron microscope so as to better determine the type of particle-particle interaction. Samples prepared from dispersions of smectite to



Fig. 4. Dimethyldioctadecyl ammonium smectite dispersed in benzene-methanol solutions and freeze-dried.

which various flocculants and dispersants have been added also will be examined to determine whether the effect of these additives on the particle-particle relations can be shown.

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