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A RECOMMENDED PROCEDURE FOR THE PREPARATION OF ORIENTED CLAY-MINERAL SPECIMENS FOR X-RAY DIFFRACTION ANALYSIS: MODIFICATIONS TO DREVER'S FILTER-MEMBRANE PEEL TECHNIQUE

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A Recommended Procedure For The Preparation Of Oriented Clay-Mineral Specimens For X-Ray Diffraction Analysis: Modifications To Drever's Filter-Membrane Peel Technique

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ABSTRACT

Extremely well-oriented clay mineral mounts for X-ray diffraction analysis can be prepared quickly and without introducing segregation using the filter-membrane peel technique. Mounting problems encountered with smectite-rich samples can be resolved by using minimal sample and partial air-drying of the clay film before transfer to a glass slide. Samples containing small quantities of clay can produce useful oriented specimens if Teflon masks having more restrictive areas are inserted above the membrane filter during clay deposition. Warpage and thermal shock of glass slides can be controlled by using a flat, porous, ceramic plate as a holding surface during heat treatments.

INTRODUCTION

Several methods have been used to produce oriented clay-mineral specimens for X-ray diffraction analysis. These methods include sedimentation onto a glass slide or other flat substrate (Brown, 1953; Jackson, 1956; Gude and Hathaway, 1961; Kittrick, 1961; Gipson, 1966), centrifuging onto a flat surface (Gibbs, 1965; Spoljaric, 1971), suction onto unglazed, porous ceramic tile (Kinter and Diamond, 1956; Rich, 1969; Shaw, 1972; Carlton, 1975), smearing a clay slurry onto a glass slide or other flat surface (Theisen and Harward, 1962; Gibbs, 1965), pressed clay powders (Mitchell, 1953; Cody and Thompson, 1976), and suction onto a cellulose filter-membrane (Drever, 1973) or silver membrane (Poppe and Hathaway, 1979).

Studies by Gibbs (1965) showed that although air-dried or centrifuge-sedimentation techniques produce well-oriented clay specimens, analysis of their resulting X-ray diffraction patterns may be biased by segregation of typically coarse clay-minerals, such as the kaolin and chlorite minerals, from those that are typically much finer-grained, smectites, illite, and mixed-layer phases. The technique for which I recommend modification was first suggested by Drever (1973). The method is referred to as the "filter-membrane peel" technique. The method involves a rapid deposition of a clay suspension onto a smooth, microporous membrane (cellulose, vinyl, Teflon, etc.) producing a clay film that is extremely well oriented and does not allow opportunity for size segregation. The method is well described by Drever (1973), however, no figures, diagrams or photos are included in his article, and many analysts have had some trouble producing a finished clay mount from only Drever's description. Therefore, this paper includes photographs and suggests minor modifications that may be helpful in the preparation of specimens.

MATERIALS AND APPARATUS

Filter membranes are now available from several manufacturers; however, the 47 mm, 0.45 micrometer pore size available from the Millipore Corporation (Catalog No. HAWP 04700) have a glossy-white surface and were proven to be the most durable and effective for this application. Smaller pore size membranes are available for super-fine fraction analysis (-0.5 μm). The basic filtration apparatus consists of a borosilicate glass funnel and base with a fritted-glass support for the filter, an anodized aluminum spring clamp and a neoprene stopper (Figs. 1A and B) and is available from the same manufacturer for about $46.00 (July 1981 Catalog no. XX10 04700).

Other necessary materials which are needed or useful in the preparation are as follows:

1. a 20-25 cc disposable, plastic syringe
2. standard petrographic (26 x 46 mm) or half-cut biological microscope slides (26 x 76 mm).
3. filter flask
4. vacuum tubing
5. ring stand
6. watch glass (8-9 cm diameter)
7. 1 1/4 inch (3 cm) diameter glass vial or cylinder
8. aluminum spatula
9. permanent marking pen or diamond scribe
10. 3" x 5" index cards
11. flat, porous, ceramic plate
12. vacuum source

PROCEDURE

The technique used in producing a finished, oriented, clay mount is relatively simple; however, it requires some experience to consistantly produce specimens without problems or imperfections. In my experience, the workability of the clay film deposited on the filter is dependent upon several factors. These factors include the amount of material deposited, mineralogy of the clay suspension (e.g. smectite-bearing vs. non-smectite-bearing), presence of organic material or amorphous iron, and the particle size of the clay fraction being prepared. The effects of these factors will be discussed subsequently.

The disassembled filtration apparatus and many of the materials are shown in figure 1a. The filter is mounted on the fritted-glass support of the base, shown disassembled in figure 2. The filter-flask is placed inside a metal ring stand to secure the top- heavy assembly and then connected to a fairly strong vacuum source. A piece of white paper may be placed under the filter-flask so that the filtrate may be monitored for leakage due to super-fine particles (-0.5 μm) or filter defects. In my experience, and as noted by Drever (1973), clay material passing through the filter has rarely been observed.

After fractionation of the desired clay size, the vacuum is turned on, an aliquot of the clay suspension is withdrawn using the plastic syringe and then released into the filter funnel (fig. 1b). The use of a plastic syringe aids considerably in judging the amount of suspension for each slide as well as being an effective tool for extracting the suspension (Pollastro, 1977). It is also easily cleaned between samples.

Figure 1.--(a) Disassembled filter holder and materials needed for preparing oriented clay mineral specimens using the filter-membrane-peel technique. (b) Releasing clay suspension into the assembled filtration unit using a plastic syringe.

A.

B.

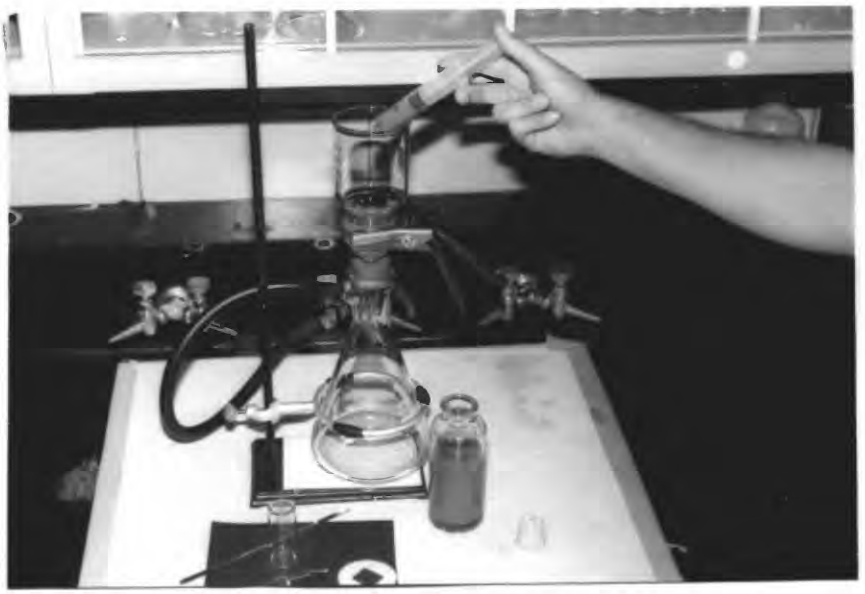

FIGURE 1.

Figure 2.--Removing the membrane filter with deposited clay film from the disassembled filtration holder. Note fritted-glass support base.

FIGURE 2.

Depending on the volume, concentration, and mineralogy of the suspension, filtration time may vary from a few seconds to several minutes, averaging about 1-3 minutes. Approximately 50 - 150 mg of clay usually produces an excellent mount (see Drever, 1973, p. 553). Less material is required for smectite-rich samples (e.g. bentonites). An excessively thick clay film may result in severe spawling during glycol or heat treatments.

After filtration is complete, the filter holder is disassembled, and the membrane, while still moist, is carefully removed from the fritted-glass support using the aluminium spatula (fig. 2). The membrane is then carefully, but firmly, wrapped around the glass cylinder with the clay film up and held by the thumb and middle or forefinger (fig. 3a). A clean and labeled glass slide is then held similarly in the opposite hand. The clay film is positioned near the glass slide, and then lightly without hesitation, quickly rolled across the slide transferring the clay film onto the glass surface (fig. 3b). Providing that there are no air bubbles or coarse particles between the clay and glass, the clay film will adhere to the glass and the membrane will separate cleanly without pitting of the film. Hesitation while transferring the film to the slide may cause rippling of the film and, therefore, disrupt preferred orientation. The specimen dries in just a few minutes and is ready for X-ray diffraction analysis. The specimen may then be exposed to glycol or heat treatments.

Figure 3.--(a) Filter membrane is wrapped tightly around cylinder with clay film up and held firmly with the thumb and forefinger. (b) Membrane filter and clay film are center-positioned near glass slide and then quickly, without hesitation, lightly rolled across slide to transfer the clay film to the slide.

A.

B.

FIGURE 3.

COMMENTS AND SUGGESTIONS

Specific problems occasionally arise in the preparation and handling of various types of samples when using the filter-membrane peel technique. The purpose of this section is to describe some of the common problems encountered and suggest corrective methods.

Warpage of glass slides during high heat treatment is a common problem. Warpage and thermal shock can be avoided at temperatures to 550°C if the slides are placed on a cool, flat, porous, ceramic plate, placed in the furnace for heat treatment, and allowed to cool slowly on the plate after removal from the furnace.

Smectite-rich samples (e.g. bentonites) are commonly hard to work with because they gel and are very slippery; it is difficult to roll the clay film onto the glass slide when the clay film is slippery. I have found it helpful to deposit a minimal amount of clay suspension onto the filter and either allow the vacuum to continue drawing air through the film after deposition, or to remove the filter and blow a light stream of compressed air across the front or under-side of the filter. This technique makes the clay film much easier to transfer.

Organic-rich samples create problems in the preparation, orientation and X-ray characteristics of clay specimens. Fine organic material forms coatings on clay particles causing them to become non-wetting. In addition, when a clay mount can be prepared, these organic particles prop the clay platelets and create poor oriented specimens. The resulting X-ray diffraction pattern has high background and weak basal reflections due to dilution, absorption and disorientation. Therefore, when a sample has minimal clay and high organic content, it is recommended that these samples be treated with a solution of 5.25 percent sodium hypochloride (household bleach) or H_2O_2.

Commonly a sample or suspension contains very little clay and, therefore, the area of the 47 mm diameter membrane filter is much too large to produce a good specimen. I have investigated several methods to prepare clay mounts when only a small amount of clay material is available. The use of a Teflon mask over the membrane filter has proven to be most effective (fig. 4). To make a mask a 47 mm diameter circle is scribed and cut from a sheet of Teflon 1/16 to 1/8 inch (1 - 2 mm) thick (fig. 5a). From this circle, an opening of any desired configuration can be cut out to confine the deposited clay film to a limited area. This maximizes the sample thickness and ease of preparation. A rectangular opening is recommended and the edges of the opening should be beveled so that the suspension is drawn into the selected area more easily (fig. 5b). The specimen should be prepared so that the clay surface can be properly mounted in the sample chamber to coincide with the diffractometer axis (fig. 5c). If the clay surface does not coincide with the diffractometer axis errors may result in the two-theta position of the peaks in the X-ray diffraction pattern and resolution may also be poor (Cullity, 1967, p. 184-188). This error may be very significant when interpreting super-order reflections from regularly interstratified clays which occur at low two-theta angles. In this region a slight error in the low two-theta values of a peak results in a relatively large error when converted to d-values.

Finally, the finished slides are easily stored by stapling a pocket to a labeled 3" x 5" index card, placing the slide(s) in the pocket and storing the card in an index card file box (fig. 6).

Figure 4.--Schematic of assembled filter apparatus showing position of Teflon mask inserted above membrane filter.

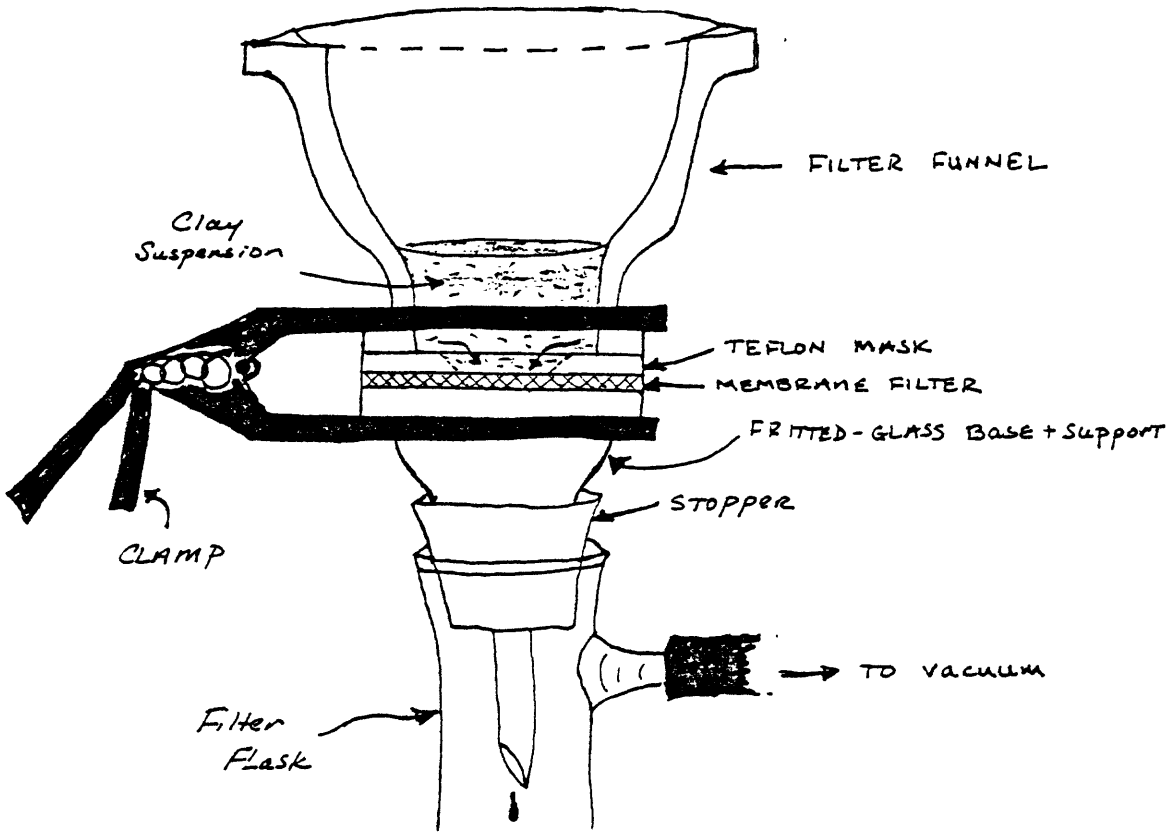
FILTER FUNNEL
Clay Suspension
TEFLON MASK
MEMBRANE FILTER
FRITTED-GLASS Base + Support
STOPPER
CLAMP
TO vacuum
Filter Flask

FIGURE 4.

Figure 5.--(a) Mask insert is prepared by cutting out a 47 mm circle from 1-2 mm thick sheet of Teflon. (b) Openings with beveled edges are then cut out of the 47 mm circle. (c) It is important that the clay film on the glass slide be of sufficient size to be mounted in line with the diffractometer axis when mounted in the sample holder of the diffractometer.

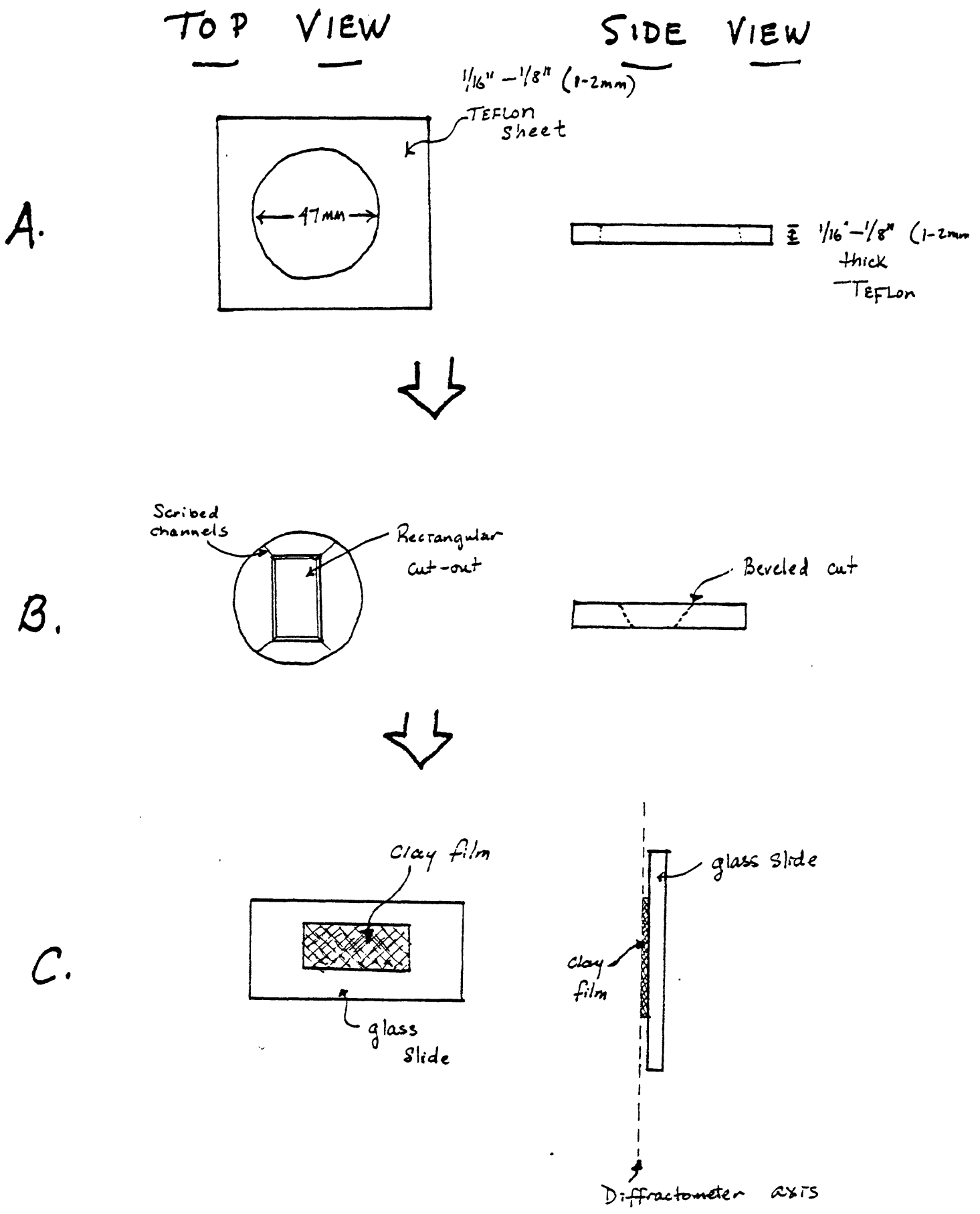
TOP VIEW
SIDE VIEW
1/16" – 1/8" (1-2mm)
TEFLON Sheet
A.
47mm
1/16" – 1/8" (1-2mm thick TEFLON
Scribed channels
Rectangular cut-out
B.
Beveled cut
C.
Clay film
glass Slide
glass Slide
Clay film
Diffractometer axis

FIGURE 5.

Figure 6.--Finished clay slides are placed in pockets attached to index cards and can be easily stored.

FIGURE 6.

SUMMARY

The filter-membrane peel technique produces extremely well oriented clay mineral specimens for X-ray diffraction analysis. The method is quick and gives representative and reproducible patterns of the clay mineral assemblages from clay-bearing samples. No particle-size segregation of clay mineral phases occurs using this method because rapid vacuum deposition does not allow time for segregation. In addition, the clay-film surface mounted in the plane of the diffractometer axis is that of the material initially deposited onto the filter. This is in contrast with other vacuum-deposition methods, which analyze the material that is deposited last.

Warpage and shock problems with the use of glass slides can be avoided by placing the clay slides on a flat, porous, ceramic plate during heat treatments and allowing the plate and slides to cool slowly after removal from heat. Problems in transferring smectite-rich samples to the glass slide can usually be resolved by partially air-drying the clay film while still on the filter. Samples containing small quantities of clay-size material can produce good oriented specimens if the suspension is concentrated using Teflon masks with a more restricted shape and area.

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