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A NEW METHOD OF DEHYDRATION FOR PURE CLAY MATERIALS USING PELDRI II

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Abstract—A new chemical, Peldri II, is evaluated as a compound for drying soft clay materials. Peldri II, a fluorocarbon (1,1-difluorotetrachloroethane), is a solid at room temperature and is a liquid above 25°C. Clay gels are embedded in Peldri II by immersing them in the liquid and allowing it to solidify. Once solidified, Peldri II will sublime, with or without vacuum, to a dry specimen, probably without introducing surface tension. Wyoming montmorillonite saturated in 10^{-3} M NaCl and 1 M $CaCl_2$ solutions has been examined to compare preservation of its initial structure after Peldri II, critical point, and freeze drying techniques. Transmission electron microscopy of ultrathin sections, scanning electron microscopy, and mercury intrusion porosimetry techniques were used. No differences were detected between Peldri II and critical point drying methods. Peldri II appears to be a significant improvement as an alternative drying agent for clay materials in studies of their structural properties. It is also very convenient for drying large numbers of samples.

Key Words—Critical point drying, Freeze drying, Mercury porosimetry, Montmorillonite, Peldri II, SEM, TEM.

INTRODUCTION

One of the basic problems that needs to be solved in the preservation of clay structure during the drying process is how to remove water from the sample while minimizing structural modifications. Many methods have been described in the literature for the drying of clay specimens to preserve the initial organization of clay particles. Most of these methods are based on removal of meniscus at the solid-liquid-gas interface without allowing the development of capillary forces. These forces play a major role in the reorganization of the dehydrated clays (Tessier, 1987). The two techniques for moisture removal that have been most commonly employed and are regarded as the most promising are freeze drying (FD) and critical point drying (CPD).

Several workers have confirmed that structural changes have taken place in freeze-dried clays and clay gels (Norrish and Rausell-Colom, 1962; Tovey, 1971; Greene-Kelly, 1973). Norrish and Rausell-Colom (1962), working with montmorillonite and nontronite, found that during freezing there was a rapid redistribution of pore water. X-ray analysis showed a decrease in basal spacing of the clay minerals corresponding to the withdrawal of interlamellar water. Particle rearrangement involving larger structural units was found by Tovey (1971) who freeze-dried clay soils and observed samples during the sublimation stage with a scanning electron microscope. Greene-Kelly (1973) and Lawrance *et al.* (1979) also conducted freeze drying experiments on clay soils and concluded that the technique was not satisfactory. Although FD of swollen clay materials often leads to only small losses of the total porosity, some doubts have been raised concerning the validity of the resultant pore size distribution. These problems are summarized in a review article by Lawrance (1977). Some workers (Thompson *et al.*, 1985; Jongerius and Heintzberger, 1975) found that ice crystals altered the porosity, particularly in the center of frozen specimens. FD may also cause artifacts in the form of fissures due to water migration (Murray and Quirk, 1980) or the formation of cracks due to thermal gradients (Gillott, 1980). Others have claimed that FD does give satisfactory results very similar to those obtained by the CPD technique (Diamond, 1970; Mitchell, 1956).

The CPD of fine-textured soil has so far been restricted to samples containing either water or liquid carbon dioxide. Diamond (1970) and Sridharan *et al.* (1971) have both conducted CPD of wet clay samples and found little or no sample shrinkage. Lawrance *et al.* (1979) concluded that FD and CPD of clay soils leads to some shrinkage. As with FD techniques the CPD method also has inherent limitations. Possible causes of fabric damage include thermal and pressure stresses in the sample, and possibly also the effects of fluid movements (Gillott, 1980). Nevertheless, it appears that the CPD method modifies the initial structure less than the FD method (Bruand and Tessier, 1987).

Therefore, there is a need to explore the possibilities of some alternative, faster and comparable drying techniques to preserve the initial microstructure of clay materials.

The present report describes the application of a new

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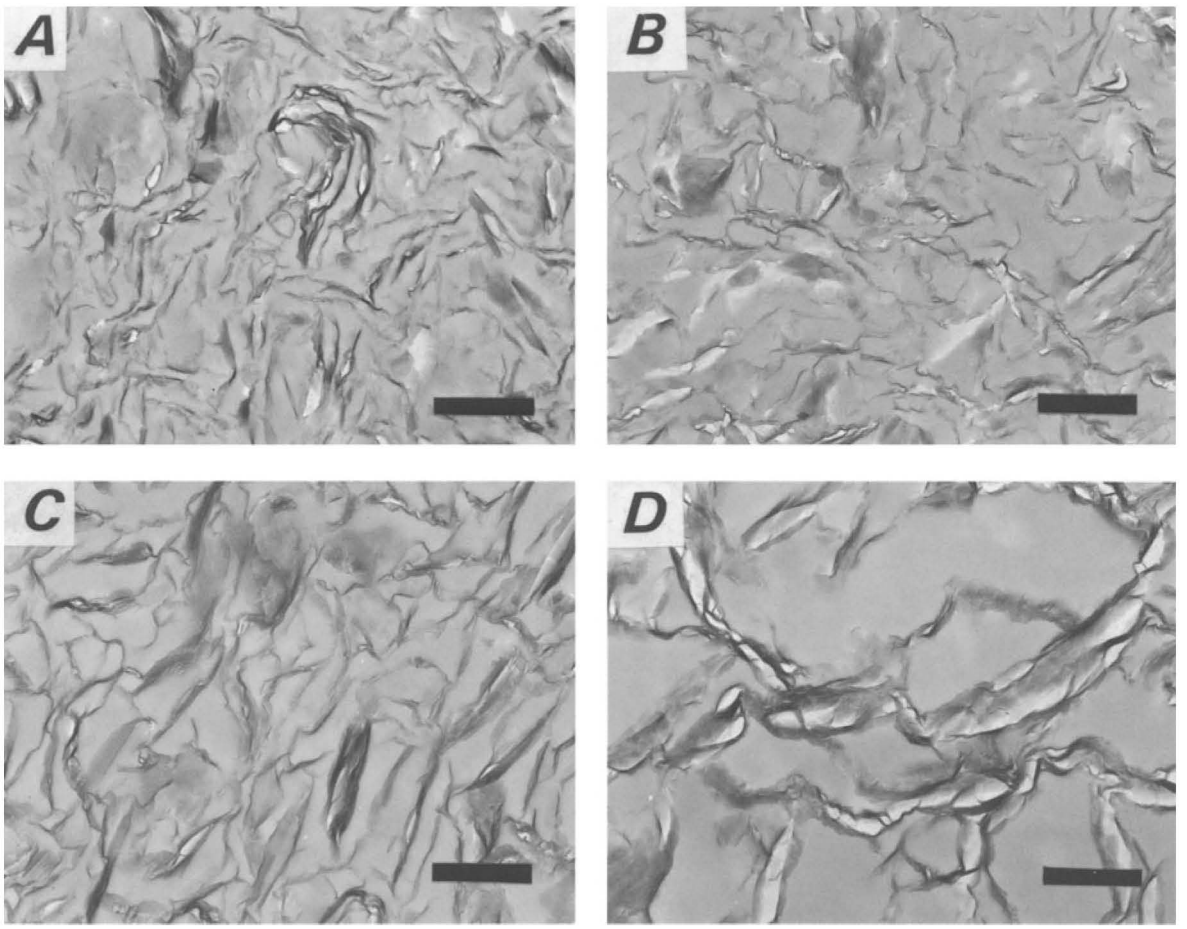


Figure 1. Transmission electron micrographs of ultrathin sections of Wyoming montmorillonite saturated at 10^{-3} M NaCl after: (a) dehydration with acetone, (b) Peldri II drying, (c) critical point drying, and (d) freeze drying. Marker = 1 μm.

fluorocarbon (1,1-difluorotetrachloroethane) compound—Peldri II (U.S. Patent No. 4,735,794) as a medium for drying soft clay specimens. The first application of Peldri II for drying biological tissue offers the same capabilities provided by CPD techniques (Kennedy *et al.*, 1989). Peldri II is a solid at room temperature and can be liquefied above 25°C. Once solidified it will sublime, with or without vacuum, to a dry material without producing surface tension changes. In this paper we examine drying by sublimation with Peldri II (PLD) and compare it with CPD and FD as a technique for microstructure study using transmission and scanning electron microscopy (TEM and SEM). As a supplement to this submicroscopic investigation we use the mercury intrusion porosimetry method.

MATERIALS AND METHODS

The clay material used for the present experiments was Wyoming montmorillonite No. 25 from Upton, Wyoming. From this clay in the sodium form, a <2-μm fraction was prepared by suspending the clay in water, followed by repeated cycles of sedimentation, siphoning, and resuspension. Both Na- and Ca-saturated suspensions were prepared in 10^{-3} M NaCl and 1 M $CaCl_2$ solutions, respectively, and homogenized by mechanical stirring. The nature and concentration of cations were chosen to obtain a different arrangement and internal structure for the tactoids of montmorillonite. In low-sodium concentration we expected to obtain a loose, remarkable open-type of structure. Saturation of montmorillonite with high concentrations of calcium would lead to the formation of a dense, compacted structure (Tessier and Pedro, 1982; Ben Rhaïem *et al.*, 1987 and Stawiński *et al.*, 1990). Water retention at 0.5 bar suction pressure was obtained in a filtration cell, as described by Tessier and Barrier (1979). Excess liquid was expelled from the samples through a porous membrane filter (0.025 μm pore diameter) at the bottom of the pressure cell, forming clay gels on the membrane surface. Water in the clay gels was replaced by solvent exchange with 100% acetone using the method described by Murphy (1985).

Small portions of acetone-saturated clay gels, de-

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hydrated but not dried, were prepared for ultramicrotomy by replacement of acetone first with propylene oxide, then with Spurr's hard epoxy resin (Spurr, 1969). After the resin had hardened, ultrathin sections (about 90 nm thick) were cut with a diamond knife and examined in a Philips 300 TEM operated at 100 kV. Other portions of acetone-saturated clays were dried by CPD techniques using liquid CO_2 as a transitional fluid in a Polaron E 3000 apparatus following the method described by Greene-Kelly (1973).

The remaining aliquots of acetone-saturated clays were dried with Peldri II. The melting point of this compound is in the range of 24–25°C. It is nonflammable, but can cause skin irritation, pulmonary edema, and conjunctivitis after prolonged exposure. It should be used in a fume hood with rubber gloves. Our procedure for the use of Peldri II is as follows: a bottle of Peldri II was placed in a beaker of water maintained at 40–45°C on a slide warmer, also at 40–45°C. Pipettes used to exchange solutions were also heated by placing them on the warming table. Vials containing clay gels in 100% acetone were placed on the warming table. An equal volume of liquid Peldri II was added to each vial, and the vials were tightly capped. After 4 hours the mixture of Peldri II and acetone was removed and fresh, pure liquid Peldri II was added. After 4 hours a second exchange of Peldri II was made. The vials containing Peldri II and the specimens were then placed in a refrigerator at about 0°C. The vials with solidified Peldri II and the clay aggregates were then placed, without caps, in a vacuum desiccator attached to vacuum pump and evacuated until all visual evidence of Peldri II was gone and the specimens were fully exposed. There is insufficient information about the destructive influence of this fluorocarbon compound on the ozone layer, but for ecological and economical reasons we recovered the Peldri II by cooling its vapor with solid CO_2 in a U-tube placed between the desiccator and the vacuum pump.

For purposes of comparison another sample of wet clay gels was dried by the FD technique as follows: slices 1–2 mm thick were taken from wet clay gels and were rapidly frozen by immersing them in a beaker of Freon-22 (−140°C). These were transferred to liquid nitrogen and the ice was evaporated at −30°C and 2 × 10^{-3} Pa for 3 days. Dry samples were stored in a desiccator.

After each method of drying (CPD, PLD or FD) the small, dry aggregates were immersed first in propylene oxide and then in Spurr's resin. The microstructure of the clay samples was examined in ultrathin sections using TEM. CPD, PLD and FD clays vacuum-coated with gold were also observed with a JSM-840A (JEOL) SEM operated at 20 kV.

Additionally, differently-dried clay samples were examined by the mercury intrusion porosimetry method as described by Diamond (1970). This technique was used for determining changes in the total cumulative volume of pores (TCV), the bulk density of aggregates (BD), and the pore size distribution (PSD) of differently dried clays. A Carlo Erba Porosimeter model 2000 instrument was used.

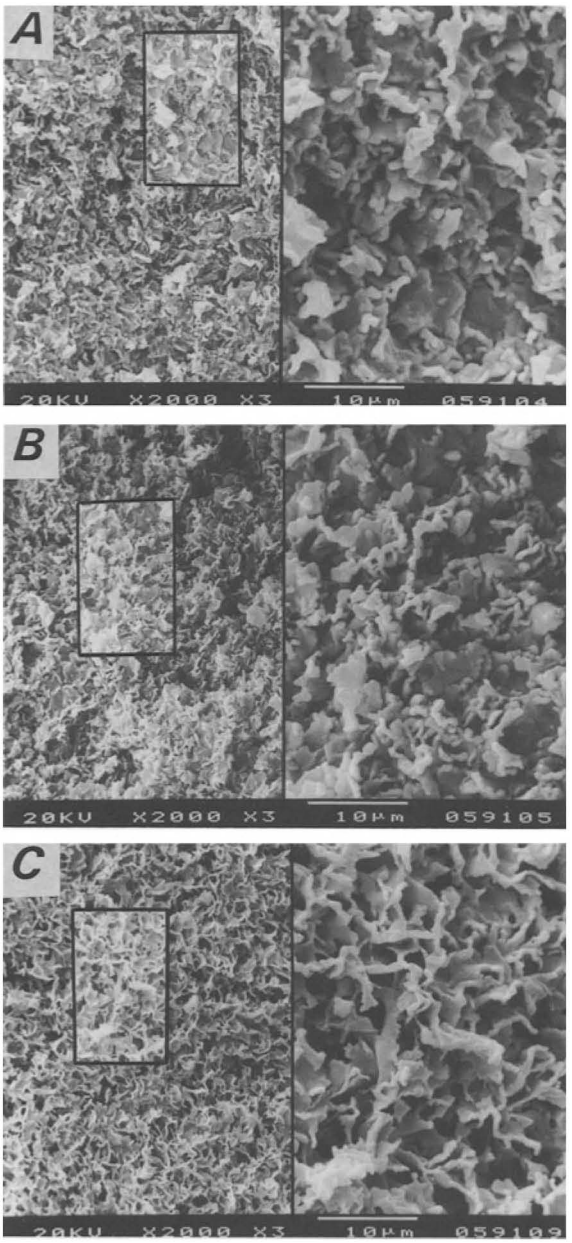


Figure 2. Scanning electron micrographs of Wyoming montmorillonite saturated at 10^{-3} M NaCl after: (a) Peldri II drying, (b) critical point drying, and (c) freeze drying.

RESULTS

Electron microscopy

The TEM micrographs of ultrathin sections of montmorillonite dehydrated, but not dried, PLD, CPD and

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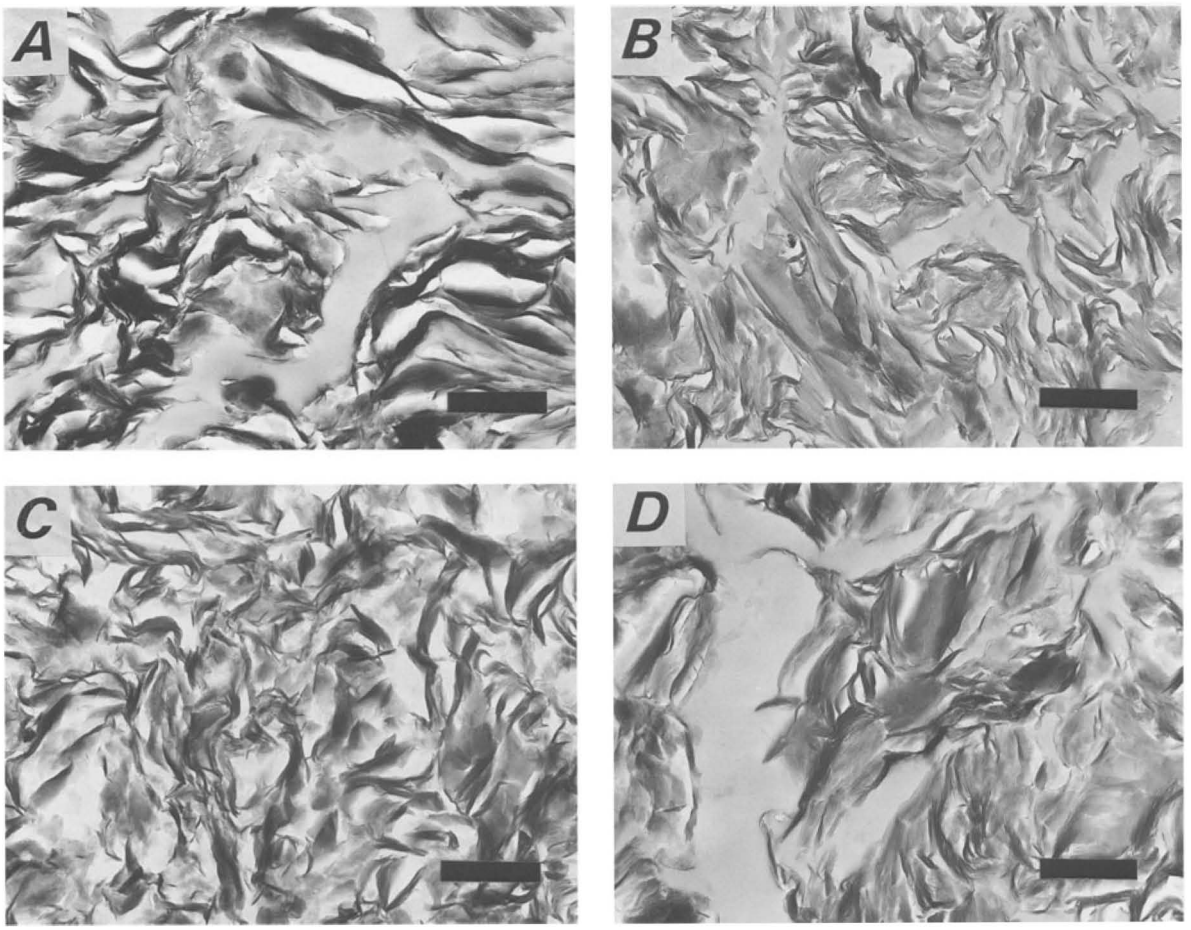


Figure 3. Transmission electron micrographs of ultrathin sections of Wyoming montmorillonite saturated at 1 M $CaCl_2$ after: (a) dehydration with acetone, (b) Peldri II drying, (c) critical point drying, and (d) freeze drying. Marker = 1 μm.

FD in two microstructural arrangements are presented in Figure 1 for montmorillonite saturated at 10^{-3} M NaCl, and in Figure 3 for montmorillonite saturated at 1 M $CaCl_2$.

Figure 1a shows the microstructure of the dehydrated but undried clay. Note that the clay particles are grouped closely in large, thick, curved particles that are comparable to the quasicrystals described by Aylmore and Quirk (1971). The quasicrystals lead to the formation of isometric networks with edge-to-face and face-to-face contacts between them. The voids between quasicrystals have a relatively small (<0.5 μm) diameter. Figure 1b shows the microstructure of the PLD clay. We observed that the arrangement and internal structure of the clay particles and quasicrystals was very similar to the type of microstructure noted in the dehydrated but undried clay (see Figure 1a). After drying the clay with the CPD technique we did not observe the very distinct differences in the type of microstructure formed (Figure 1c). However, the quasicrystals seemed to be longer, the contacts between them more frequent, and the network appeared more continuous. In comparison to the dehydration by acetone and the drying by PLD and CPD, the microstructure after the FD method showed distinct differences (Figure 1d). Note that the clay particles are grouped closely in elongated quasicrystals about 1–4 μm in length with dominant face-to-face contacts between them. The quasicrystals form stepped clusters or chains, creating a loose, interconnecting framework with oblique edge-to-face contacts, and with relatively large voids about 1–3 μm in diameter between them. This fabric is related to the honeycomb-type structure of clays.

The microstructure resulting from PLD, CPD and FD techniques was examined with the SEM (Figure 2; Na-montmorillonite). After PLD- (Figure 2a) and CPD-treatment (Figure 2b) the SEM micrographs show the same type of microstructure. Note that the clay microaggregates form a relatively dense network with small pores about 0.5 μm in diameter. The orientation of microaggregates that make up the network seems to be isotropic. However, after FD (Figure 2c) the general organization of the system is similar and the network formed keeps its isotropic character. Some distinctive

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Table 1. Mercury intrusion porosimetry data.

Method of drying	Na-montmorillonite TCV (cm^3/100 g)	Na-montmorillonite BD (g/cm^3)	Ca-montmorillonite TCV (cm^3/100 g)	Ca-montmorillonite BD (g/cm^3)
CPD	185.3	0.32	54.9	0.70
PLD	214.9	0.33	61.0	0.75
FD	279.9	0.29	64.0	0.59

differences were, however, observed. The arrangement of microaggregates of Na-montmorillonite after FD demonstrates the typical honeycomb structure that is formed by sheet-like and elongated plate-like microaggregates with dominant edge-to-face contacts. Isometric, large cell-like pores predominate here.

The TEM micrographs of ultrathin sections of dehydrated but undried, and PLD, CPD, and FD montmorillonite saturated in 1 M $CaCl_2$ are presented in Figure 3. Note that after each mode of drying (PLD, CPD and FD) and after dehydration by acetone the general organization of the clay particles is very similar. In high concentrations of Ca the particles of montmorillonite are made up of sheet-like microaggregates with predominantly face-to-face and edge-to-edge contacts. These form a continuous, very dense, fine-cellular structural network resembling the sponge microstructure described by Sergeyev *et al.* (1980). Pore space is made up of interaggregate pores, microcracks and intermicroaggregate pores of anisometric shape. However, we observed that the FD technique led to the formation of wider (about 1 μm in diameter) interaggregate pores or microcracks (see left part of Figure 3d).

Mercury intrusion porosimetry

The total cumulative volume and bulk density of the samples after different drying techniques are given in Table 1. For montmorillonite saturated at 10^{-3} M NaCl and saturated at 1 M $CaCl_2$ the TCV of pores after CPD was always lower. On the other hand, in FD-treated samples we observed the highest value of TCV. The PLD clays demonstrated an intermediate value of TCV. The bulk density values were very similar for both the CPD and PLD mode of drying. Minimum BDs were obtained for FD clays.

The pore size distribution data (PSD) are presented in the form of cumulative pore radius distribution curves. The changes in PSD following different drying techniques are presented in Figure 4 for Na-montmorillonite and in Figure 5 for Ca-montmorillonite. It is apparent from Figures 4 and 5 that for both systems there were marked differences in pore size distribution among the drying treatments. For example, most of the porosity in FD Na-montmorillonite was derived from pores in the 0.3–0.7 μm equivalent pore radius (epr) range (Figure 4). In the PLD sample the porosity

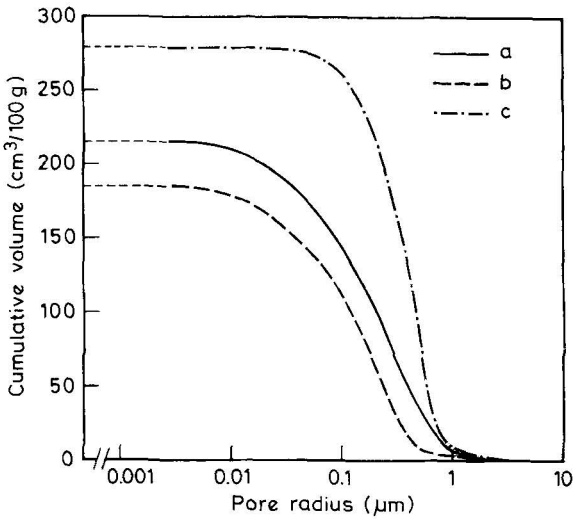


Figure 4. Pore size distribution curves for Wyoming montmorillonite saturated at 10^{-3} M NaCl after: (a) Peldri II drying, (b) critical point drying, and (c) freeze drying.

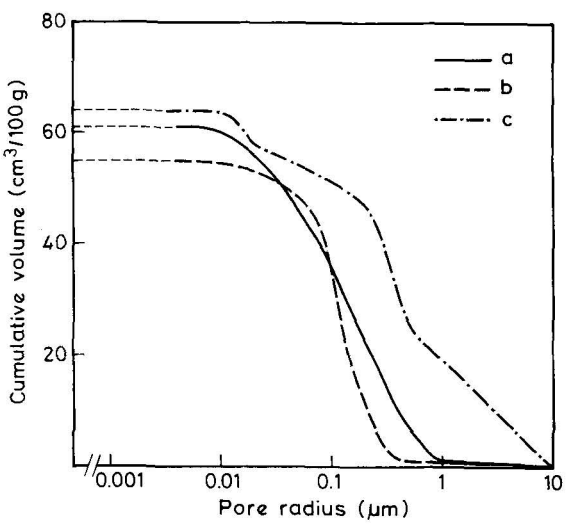


Figure 5. Pore size distribution curves for Wyoming montmorillonite saturated at 1 M $CaCl_2$ after: (a) Peldri II drying, (b) critical point drying, and (c) freeze drying.

was contributed by pores in the 0.15–0.40 μm epr range. The CPD sample had similar PSD to the PLD samples and porosity ranged from 0.15–0.35 μm epr.

The FD of Ca-montmorillonite (Figure 5) resulted in a more evenly distributed porosity. Most of the porosity in this sample was derived from pores in the 0.3–0.6 μm range and less in the 3.2–5.5 μm and 0.01–0.016 μm epr range. In the PLD samples the porosity was greatest in the 0.1–0.25 μm epr range. The CPD sample had porosity similar to the PLD sample range from 0.08 to 0.2 μm.

Generally, in both the Na- and Ca-montmorillonite,

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the effects of CPD and PLD on pore size distribution are very similar. Based on the presumption of no collapse during mercury intrusion (Diamond, 1970 and Lawrance *et al.,* 1979) we assume that this similarity in pore size distribution for CPD and PLD suggests that either the techniques do not alter very small pores much or that pores are altered similarly by both techniques. On the other hand, FD resulted in a higher porosity with a greater range of pores than did any other drying method. However, taking into account the probability of shrinkage during mercury intrusion (Murray and Quirk, 1981), the results of the porosimetry analysis permit us to maintain that after CPD and PLD the clays have very similar microstructures and/or mechanical resistance that differ from the FD montmorillonites.

DISCUSSION AND CONCLUSIONS

It is evident from these studies that freeze drying techniques lead to the alteration of the structure of montmorillonite gels. This structural damage is almost certainly due to the growth and migration of ice crystals. Even if water in the samples had frozen quickly into small crystals upon initial submersion in liquid nitrogen, there may have been recrystallization of ice crystals (Thompson *et al.,* 1985). Meryman (1957) observed recrystallization at 203 K; crystals of 1-μm diameter formed in only 30 seconds. Under the conditions employed in our study, the recrystallization of ice may have not only increased the volume of pores compared with the original porosity before drying but also caused microcracks about 1 μm in diameter (see Figures 1d, 3d). Tessier and Quirk (1979) have examined electron micrographs of illitic materials frozen at similar rates and have also observed discontinuities (about 1 μm) of the type described here.

Electron microscopy demonstrated that the arrangement of quasicrystals of montmorillonite for samples dehydrated in acetone (but not dried), and those critical point dried was very similar. For the Peldri II-dried samples, the arrangement was essentially identical. Moreover, the soft montmorillonite floccules prepared for TEM, SEM, and mercury intrusion porosimetry through sublimation of Peldri II do not appear to present any significant differences in microstructure and pore size distribution as compared to specimens prepared with critical point techniques. Furthermore, when large numbers of samples must be processed, the sublimation procedure can be carried out either under house vacuum in a vacuum desiccator or overnight without vacuum in a fume hood.

The use of Peldri II is an alternative method for the drying of clay materials. This method provides the same quality of structural preservation obtained with critical point drying techniques and eliminates most of the problems associated with the use of a CP dryer. A large number of samples may be processed more rapidly.

The applicability of this method to other clays and soil materials is being tested and the results will be published in due course.

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REFERENCES

Aylmore, L. A. G. and Quirk, J. P. (1971) Domains and quasi-crystalline regions in clay systems: *Soil Sci. Soc. Am. Proc.* **35,** 652–654.

Ben Rhaïem, H., Pons, C. H., and Tessier, D. (1987) Factors affecting the microstructure of smectites: Role of cation and history of applied stresses: in *Proc. Int. Clay Conf., Denver, 1985,* L. G. Schultz, H. van Olphen, and F. A. Mumpton, eds., The Clay Minerals Society, Bloomington, Indiana, 292–297.

Bruand, A. and Tessier, D. (1987) Etude de l'organisation d'un matériau argileux en microscopie: Modifications interrenant lors de la deshydratation: in *Proc. VIIth Int. Working Meeting, Soil Micromorphology, Paris, 1985,* N. Fedoroff, L. M. Bresson, and M. A. Courty, eds., AFES, Paris, 31–35.

Diamond, S. (1970) Pore size distributions in clays: *Clays & Clay Minerals* **18,** 7–23.

Gillott, J. E. (1980) Use of scanning electron microscope and Fourier methods in characterization of microfabric and texture of sediments: *J. Microscopy* **120,** 261–277.

Greene-Kelly, R. (1973) The preparation of clay soils for determination of structure: *J. Soil Sci.* **24,** 277–283.

Jongerius, A. and Heintzberger, G. (1975) Methods in soil micromorphology. A technique for the preparation of large thin sections: in *Soil Survey Papers No. 10,* Netherlands Soil Survey Institute, Wageningen, p. 48.

Kennedy, J. R., Williams, R. W., and Gray, J. P. (1989) Use of Peldri II (a fluorocarbon solid at room temperature) as an alternative to critical point drying for biological tissues: *J. Electron Microscopy Technique* **11,** 117–125.

Lawrance, G. P. (1977) Measurement of pore sizes in fine-textured soils: A review of existing techniques: *J. Soil Sci.* **28,** 527–540.

Lawrance, G. P., Payne, D., and Greenland, D. J. (1979) Pore size distribution in critical point and freeze dried aggregates from clay subsoil: *J. Soil Sci.* **30,** 499–516.

Meryman, H. T. (1957) Physical limitations of the rapid freezing method: *Proc. R. Soc. Lond. Ser. B,* **147,** 452–459.

Mitchell, T. K. (1956) The fabric of natural clays and its relation to engineering properties: *Proc. Highway Res. Board* **35,** 693–713.

Murphy, C. P. (1985) Faster methods of liquid-phase acetone replacement of water from soils and sediments prior to resin impregnation: *Geoderma* **35,** 39–45.

Murray, R. S. and Quirk, J. P. (1980) Freeze-dried and critical-point dried clay: A comparison: *Soil Sci. Soc. Am. J.* **44,** 232–234.

https://doi.org/10.1346/CCMN.1992.0400212 Published online by Cambridge University Press

Murray, R. S. and Quirk, J. P. (1981) Letter to the editor. Comments on recent work with critical point dried soils: *J. Soil Sci.* **32,** 161–164.

Norrish, K. and Rausell-Colom, J. (1962) Effect of freezing on the swelling of clay minerals: *Clay Miner. Bull.* **5,** 9–16.

Sergeyev, Y. M., Grabowska-Olszewska, B., Osipov, V. I., Sokolov, V. N., and Kolomenski, Y. N. (1980) The classification of microstructures of clay soils: *J. Microscopy* **120,** 237–260.

Spurr, A. R. (1969) A low-viscosity epoxy resin embedding medium for electron microscopy: *J. Ultrastr. Res.* **26,** 31–43.

Sridharan, A., Altschaeffl, A. G., and Diamond, S. (1971) Pore size distribution studies: *J. Soil Mech. Fdns. Div. Am. Soc. Civ. Engrs.* **97,** 771–787.

Stawiński, J., Wierzchoś, J., and Garcia-Gonzalez, M. T. (1990) Influence of calcium and sodium concentration on the microstructure of bentonite and kaolin: *Clays & Clay Minerals* **38,** 617–622.

Tessier, D. (1987) Validite des techniques de deshydration pour l'etude de la micro-organisation des sols—Apport des matériaux argileux purs: in *Proc. VIIth Int. Working Meeting, Soil Micromorphology, Paris, 1985,* N. Fedoroff, L. M. Bresson, and M. A. Courty, eds., AFES, Paris, 23–29.

Tessier, D. and Barrier, J. (1979) Utilisation de la microscopie électronique à balayage dans l'étude des sols. Observation de sols humides soumis à différents pF: *Science du Sol* **1,** 67–82.

Tessier, D. and Quirk, J. P. (1979) Sur l'apport de la microscopie électronique dans la connaissance du gonflement de matériaux argileux: *C. R. Acad. Sci., Paris* **288,** 1375–1378.

Tessier, D. and Pedro, G. (1982) Electron microscopy study of Na smectite fabric—Role of layer charge, salt concentration and suction parameters: in *Proc. Int. Clay Conf., Bologna, Pavia, 1981,* H. van Olphen and F. Veniale, eds., Elsevier, Amsterdam, 165–176.

Thompson, M. L., McBride, J. F., and Horton, R. (1985) Effects of drying treatments on porosity of soil materials: *Soil Sci. Soc. A. J.* **49,** 1360–1364.

Tovey, N. K. (1971) Stress strain behaviour of soils: in *Proc. of the Roscoe Memorial Symposium, Cambridge,* R. H. G. Parry, ed., Foulis and Co. Ltd., Henley, Oxon, 116–120.

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