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CHARACTERIZATION OF CLAY FABRIC USING CRITICAL POINT DRYING TO PRESERVE CLAY TEXTURE AND MORPHOLOGY

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Abstract

Critical point drying is a sample preparation technique that minimizes damage to some clay fabrics in reservoir rocks. In this technique, the original pore fluids in a sample are replaced successively with acetone, liquid carbon dioxide and air without allowing a high energy meniscus to pass through the sample. Acetone replacement is accomplished in a diffusion dehydration system. SEM micrographs show striking differences between critical point dried clay samples and air dried samples.

KEY WORDS: Critical point drying, diffusion, dehydration, smectite, illite, clay fabric.

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Introduction

Critical point drying is a sample preparation technique for reservoir rock samples that reduces distortion of the clay fabric due to sample desiccation. Mechanical damage to clay fabric is caused by a high energy liquid/vapor meniscus passing through the sample as the water in the sample evaporates (Pallatt, et al., 1984). When laboratory measurements of physical properties of rock, such as permeability, are taken on critical point dried samples, the results are closer to in situ measurements than those taken on air dried samples (Heaviside, et al., 1983). The degree of clay fabric distortion is a function of the types of textures of clay minerals. Structurally stable clay minerals, such as chlorite, are not affected by the passage of a high energy meniscus. Smectite fabric is moderately to severely affected, while illite fabric shows severe damage. Critical point dried Gulf Coast samples often show large platelets of smectite with thin wisps of smectite/illite "whiskers" tailing from the edge of the platelets. In air dried samples, these "whiskers" are rarely identifiable, and the smectite platelets are often congealed into nondescript mats, coating grains and filling pore space. In the scanning electron microscope (SEM), these mats can usually be identified as "clay" by their distribution in pores and around grains and by using energy dispersive X-ray analysis (EDS). Occasionally, poorly defined platelets of smectite can be recognized in air dried samples from Gulf Coast rocks. Delicate illite fabric suffers greatly during sample desiccation (Pallatt, et al., 1984; Heaviside, et al., 1983; McHardy, et al., 1982), and some of the most spectacular differences between air dried samples and critical point dried samples are seen in illite-rich samples. A series of experiments was conducted to illustrate the application of the critical point drying technique as a tool to better understand clay fabric seen in SEM micrographs. This study incorporates diffusion dehydration techniques as part of the sample preparation.

Sample Collection and Preparation

Samples recovered while drilling for oil which are intended for critical point drying must be collected and processed at the well site. The ideal situation is to collect the sample as soon as it is exposed to air and store it in fluid from the same formation. Samples may be stored in .1 molar potassium chloride (KCl) solution if formation fluid is not available. Samples must not be allowed to dry before being stored in formation fluid or KCl solution.

Samples chosen for comparisons between air dried and critical point dried techniques in this study were prepared so that surfaces investigated in the SEM were adjacent to each other. The original sample was split and the SEM-size pieces were chosen where each fragment had a face in common with its corresponding fragment. This procedure was followed so that comparison photos were taken from areas as close to one another as possible. Splits for air drying were placed in small petri dishes, labeled and allowed to sit in a hood for 24 to 48 hours. Splits to be critically point dried were immediately placed in the diffusion dehydration system. Samples for critical point drying were never allowed to dry.

Critical Point Drying Process

Critical point drying is the process whereby liquid converts to a vapor without allowing a high energy meniscus to pass through the sample. This is accomplished by confining the liquid and heating it above its critical point. This process can be done with water-saturated samples, but the high temperature and pressure (374°C at 221.2 bar [3,208 psi]) would significantly alter the characteristics of the rock. In order for critical point drying to be carried out under less severe conditions, it is usually accomplished using liquid carbon dioxide (CO_2). Liquid CO_2 has a critical temperature of 31.09°C at a pressure of 71.95 bars (1,043.6 psi). These conditions do not significantly alter the texture of the rock samples. The process of critical point drying includes the following major steps:

a. Miscible replacement of pore fluid with acetone,

b. Miscible replacement of acetone with liquid CO_2,

c. Increasing the temperature of the liquid CO_2 to 40°C,

d. Return to room conditions.

Step a. is done in a diffusion dehydration system contained in a vacuum desiccation vessel. Steps b. through d. are carried out in a critical point drying pressure vessel.

Diffusion Dehydration

Because liquid CO_2 is not miscible with formation brines, the brine in the pore space must be replaced with a fluid that is miscible with both the brine in the pores and liquid CO_2. Several types of intermediate fluids can be used, and acetone is most commonly used. The stepwise replacement of water in samples can take several days and is labor intensive. It is accomplished in a series of steps where successive mixtures of intermediate fluid are flowed through the sample until all of the water is removed from the sample.

We used a diffusion dehydration procedure which is satisfactory and fast on small, SEM-sized samples (Figure 1).

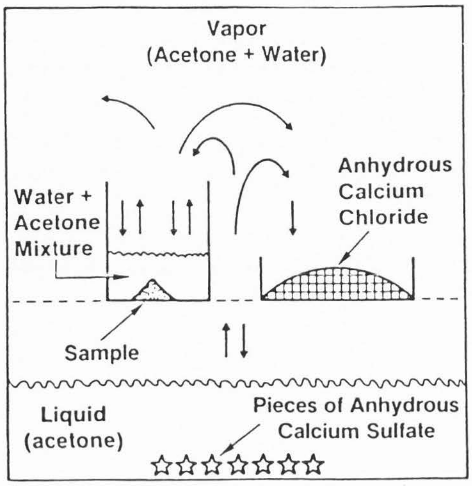

Figure 1:
Schematic of a diffusion dehydration system designed to replace formation brines in a SEM size (less than cm^3) sample with acetone, in a period of a few hours. Arrows indicate movements of acetone and water molecules.

The sample is placed in a beaker in a mixture of 20% acetone + 80% .1M KCl brine. The well in the desiccator is filled with acetone and a few chips of anhydrous calcium sulfate are added to absorb any water in the acetone. The beaker with the sample is placed over the acetone-filled well beside a petri dish containing anhydrous calcium chloride ($CaCl_2$) powder. The lid is placed on the desiccator, a vacuum is drawn on the jar until the acetone boils, and the system is sealed and allowed to stand 12 to 48 hours. Over time, the water contained in the sample beaker diffuses and mixes with the acetone. As the acetone/water system approaches equilibrium, water vapor contacts the $CaCl_2$ and is tied up hydrating the $CaCl_2$ crystals. This procedure usually removes all of the free water from the system and leaves the sample saturated with pure acetone within 12 to 48 hours. This process has also been used to prepare biological specimens (Sitte, 1962).

Critical Point Drying

A Polaron critical point drying vessel was used for these experiments. It consists of a high-pressure rated stainless steel cylinder with a glass (2.54 cm thick) window at one end and the sample entrance/exit port at the other. The chamber is surrounded by a water jacket which is used to regulate chamber temperature. The chamber is connected to a liquid CO_2 bottle by a flexible, high-pressure hose. Liquid CO_2 inlet and outlet valves and gas outlet valve are located on the body of the chamber. Attached to the top of the cylinder are a thermometer and a pressure gauge. The chamber is cooled by circulating ice water through the water jacket and is heated by circulating hot water through the water jacket.

As the samples are removed from the diffusion dehydration system, they should immediately be placed in the critical point pressure chamber. This transfer should be done while the chamber is at room temperature. If the sample loading is done while the chamber is cold, the door will be extremely difficult to open at the end of the drying process. When the samples are in place, the chamber is sealed, and the temperature is lowered to a range between 5°C and 10°C. This facilitates the transfer of liquid CO_2 from the bottle to the pressure chamber.

Acetone is flushed out of the acetone-saturated sample by manipulating liquid flow in order to allow liquid CO_2 to flow through the chamber. Samples are covered with liquid CO_2 during this procedure. After 2 to 5 minutes of active flushing, the chamber is filled with liquid CO_2 and allowed to stand for 30 minutes (or longer if necessary). This allows any remaining acetone to mix with the liquid CO_2. When the acetone is completely flushed from the sample, the pressure chamber is sealed and the chamber temperature is elevated above the critical point of CO_2. As the temperature increases, several observations can be made:

a. The pressure steadily increases;

b. Boiling occurs in the liquid;

c. As the critical temperature is passed, the meniscus disappears.

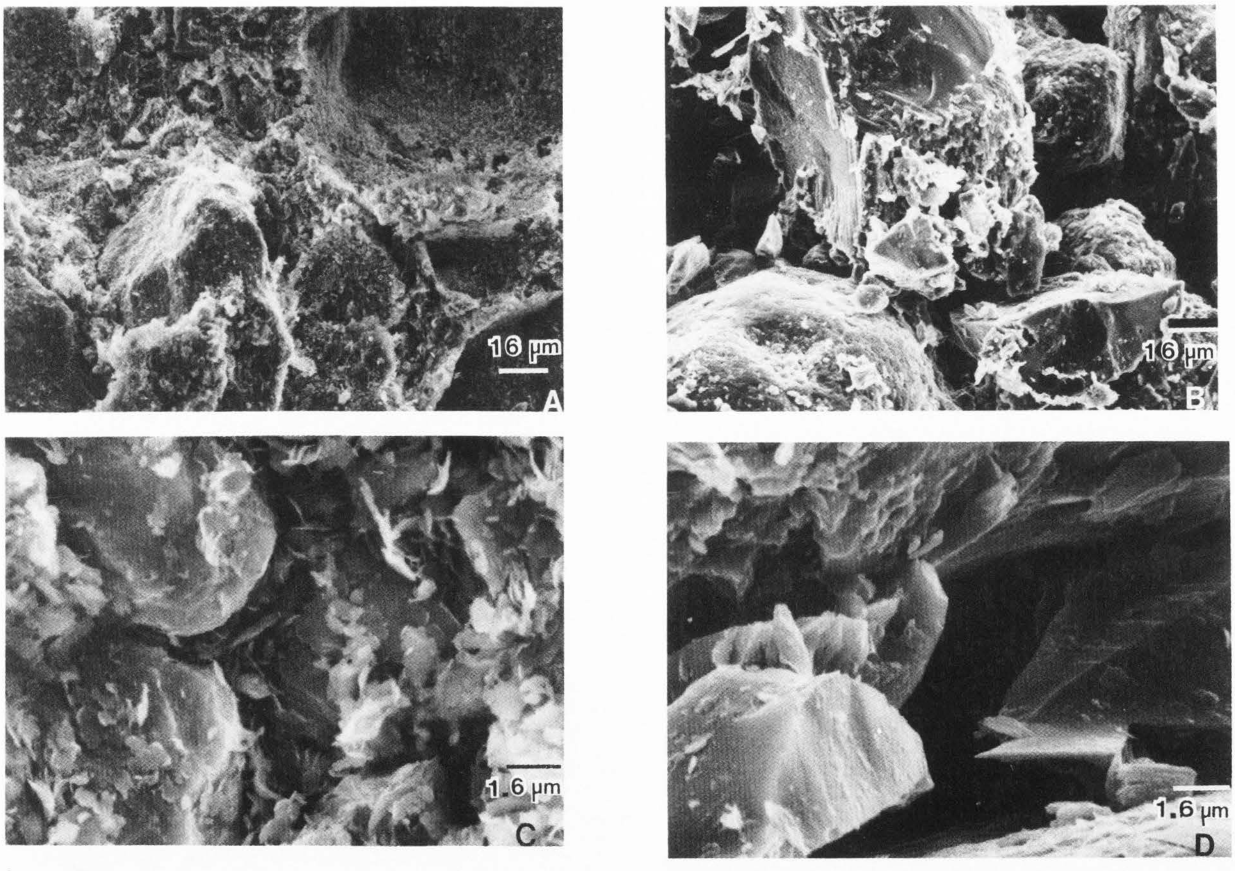

Figure 2:
Comparisons of critical point dried (a,c) and air dried (b,d) smectite. Sample is an intermediate depth (7000') Gulf coast shaley sand. Contrast abundance of macroporosity seen in air dried samples with the microporosity seen in the critical point dried samples.

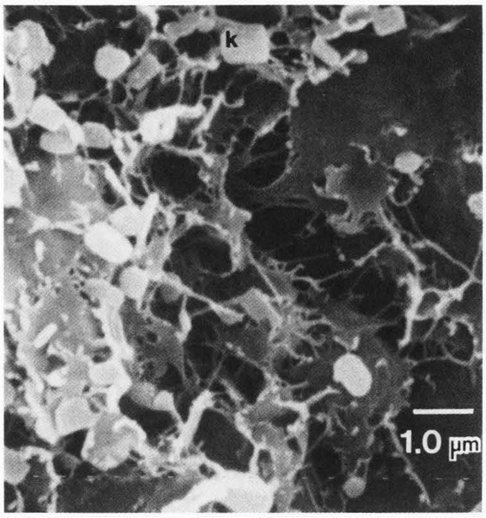

Figure 3:
Critical point dried sample from a deep (11000') Gulf Coast shaley sand. Notice the lath-like "whiskers" of smectite/illite growing from the edges of the smectite platelets. White cubic crystals (K) are potassium chloride.

The chamber is maintained at 40°C for 30 minutes so that equilibrium conditions are reached throughout the chamber.

Samples are then returned to room conditions by slowly allowing supercritical vapor to escape from the chamber while the chamber temperature is maintained above the critical temperature. This must be done slowly because if the supercritical vapor is vented all at once, adiabatic cooling of the escaping gas could cause some of the liquid to recondense inside the chamber and rewet or mechanically damage delicate clay fabrics.

Sample Preparation for SEM

When samples are critical point dried, the clays are very fragile and must be handled carefully. Samples investigated in these experiments were attached to standard SEM mounts with diluted silver paint. The samples were coated with a 40/60 AuPd alloy, using a sputter coater. The clays tended to charge in the SEM, even at low acceleration voltages. The SEM work was done at an acceleration voltage of 15 to 20 kV and an emission current approximately 100 microamps. The SEM inspection should be done as quickly as possible after sample preparation because the sample coatings crack easily causing sample charging and samples disaggregate because the clays are not strong enough to hold the sample together. A wide variety of samples were studied using this preparation technique: Samples containing illites, smectites and chlorites; well-indurated samples and unconsolidated sediments; samples from reservoir water zones and from reservoir oil zones; and samples from geographic locations as diverse as the Cook Inlet, Alaska, Alberta, the Los Angeles Basin and the San Joaquin Valley in California, and the Louisiana Gulf Coast.

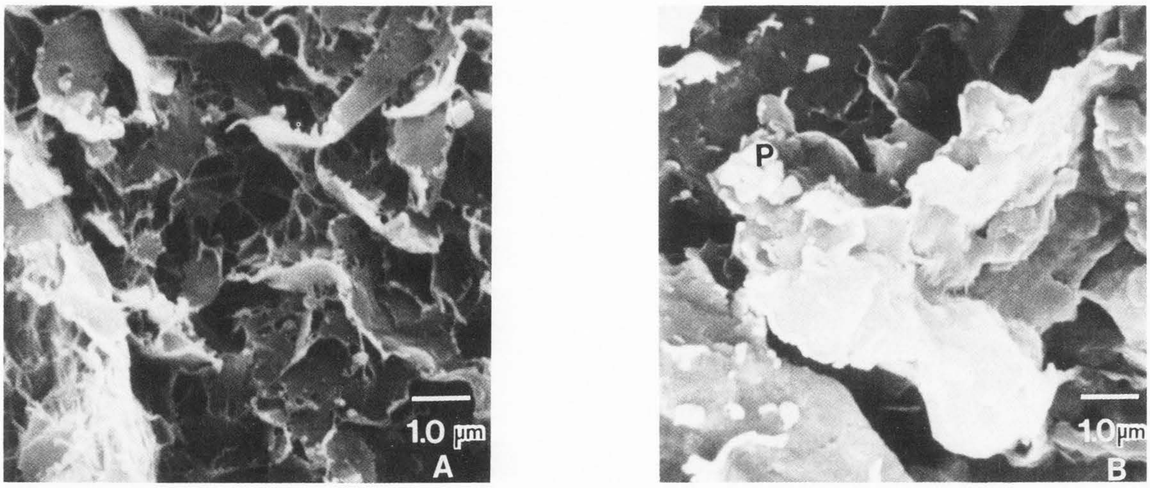

Figure 4:
Comparison of critical point dried (a) and air dried (b) samples from a deep (11000') Gulf Coast shaly sand. Notice the lath-like "whiskers" of illite/smectite protruding from the smectite platelets in the critical point dried sample. The air dried sample shows the indistinct morphology created by the drying process. P = pyrite.

Observations

Smectite and mixed layer smectite/illite fabrics are moderately to severely damaged during air drying. Differences in the clay texture in an air dried and critical point dried sample from approximately 7,000' in the Gulf Coast is shown in Figure 2. The air-dried sample exhibits large pore spaces which are not evident in the critical point dried sample. The critical point dried micrograph shows distinct smectite platelets filling the pore spaces between very fine sand and silt-sized grains. Figure 3 shows a typical Gulf Coast smectite which has been critical point dried. Figure 4 compares air dried and critical point dried smectite fabric from a deep (11,000') Gulf Coast sample. This is an example of moderate damage to the clay fabric caused by air drying. The air dried sample shows some "clumping" of the smectite platelets, but the platelet morphology can still be identified. The critical point dried micrograph shows distinct smectite platelets and interconnecting laths of smectite or smectite/illite connecting the platelets throughout the pores (see Figure 5).

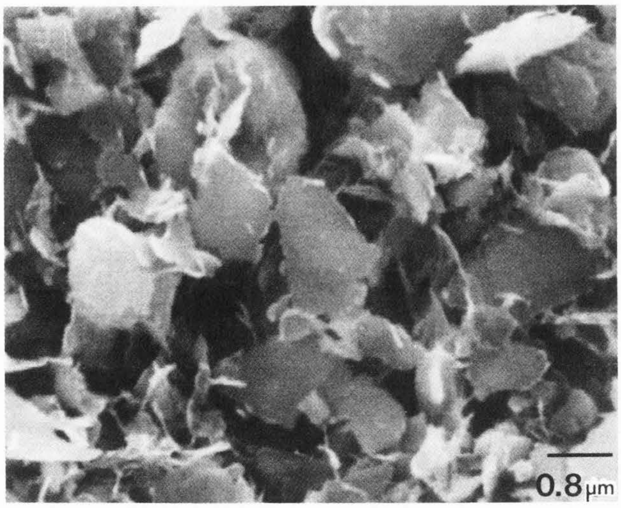

Figure 5:
Critical point dried smectite from an intermediate depth (7000') Gulf Coast shaley sand.

Illite fabric is always severely rearranged and deformed during air drying of samples. McHardy, et al (1982), Heaviside (1983) and Pallatt, et al (1984) show numerous examples of this in their study of reservoir rocks in the Magnus Field, North Sea. In all of the illite-bearing samples we investigated, there were major differences between air dried samples and critical point dried samples. Figure 6 compares differences in the fabric of air-dried and critical point dried samples containing pore-bridging illite from a sample from Cook Inlet, Alaska. The air dried sample has a shrunken, matte appearance with more macroporosity than the "whisker"-filled pore seen in the critical point dried sample. Figure 7 shows illite habits seen in rock samples from northern Alberta. These delicate fibrous morphologies are lost when the samples are allowed to air dry.

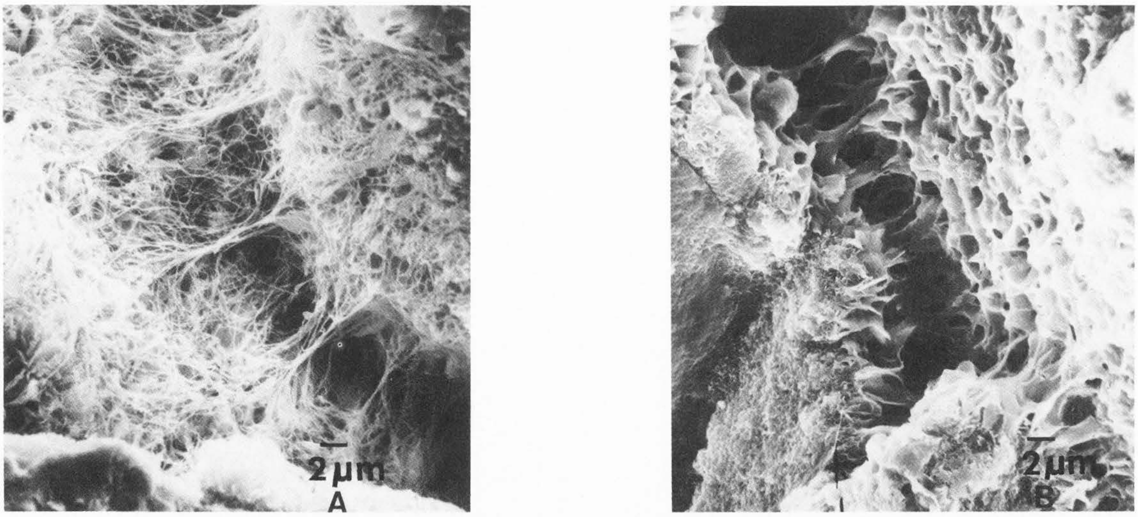

Figure 6:
Comparison of critical point dried (a) and air dried (b) pore-bridging illite from Cook Inlet, Alaska. Permeability characteristics are different because of the greater macroporosity that is created by the air drying process. (Refer to paper by Heaviside et al, 1983.)

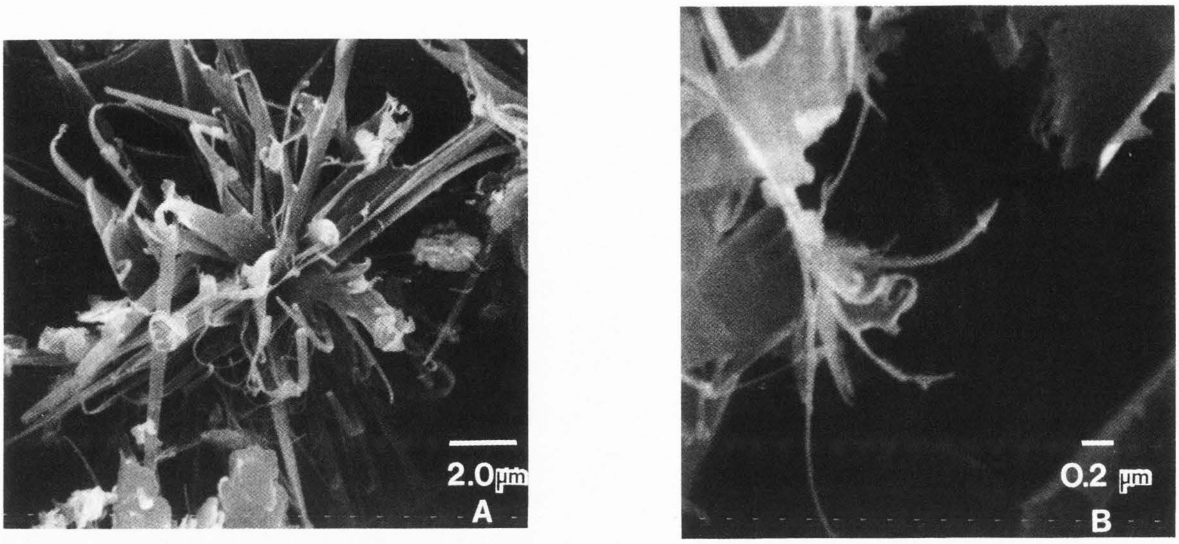

Figure 7:
Critical point dried illites from a reservoir sand, northern Alberta. Note delicate structure preserved by critical point drying.

Conclusions

Critical point drying is the best way to preserve the clay fabric for SEM assessment of the distribution and location of clays in pores. This is especially true if the clays are illite or smectite. Critical point drying can only be done on carefully preserved samples. The diffusion dehydration step is more efficient and works well for SEM size samples. Correct assessment of clay mineral fabric is essential for the accurate understanding of rock properties such as permeability.

Acknowledgements

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Discussion with Reviewers

A. L. Cohen: Specimens might be preserved in 1% osmium tetroxide in 0.1M KCl to stabilize the structure and then rinsed in distilled water. While this suggestion contradicts the conventional wisdom that OsO_4 is useless for most inorganic materials, nevertheless, minerals are often coated with a thin reducible organic film which may be stabilized (and hence act as a binder) with OsO_4 treatment. OsO_4, being weakly polar, might bind to even the mineral surfaces. Osmium treatment might also decrease the excessive charging you noticed. Please comment.

Authors: This is an interesting observation and one approach that we did not try.

A. L. Cohen: Although preserving the ionic environment is at least theoretically preferable, have you tried comparing distilled water washed specimens with those in which the KCl is left in the specimen?

Authors: We made this comparison on several samples. The most obvious damage was seen in samples from the Gulf Coast which contained a high percentage of smectitic clays.

S. Z. Levin: Since the salts in the brine or in the 0.1M KCl are insoluble in acetone, they must precipitate out during your liquid replacement step. Could they constitute some of the differences you see (e.g., some of the "whiskers") between critical point drying and air dried specimens?

Authors: It could be a possibility; it is interesting to note that the "whiskers" were only seen in samples that were preserved in KCl solution, but we are not prepared to suggest KCl is the cause of the "whisker" morphology on the smectitic clay platelets.

W-A Chiou: How do you check if the formation fluid or KCl brine has been totally replaced by acetone or intermediate fluids?

Authors: By smell. If we could smell acetone as we removed the samples from the critical point dryer, we assumed the replacement was incomplete and processed another suite of samples.

W-A Chiou: Will clay fabric be destroyed by intense liquid CO_2 boiling and why?

Authors: The clay fabric is inherently delicate and we would expect some damage to the fabric by intense boiling. This is one reason the critical point of CO_2 should be approached by slowly heating the critical point dryer to about 37-40°C.

W-A Chiou: Have you considered the effect of pressure change on clay fabric?

Authors: Since the pressure applied to the sample in the vessel is from all directions with the same force, we think the clays will not be significantly disturbed by the pressure. The delicate nests of illite fibers seen filling pore spaces in some of the Cook Inlet samples (Figure 6b) support this view.

W-A Chiou: Have you proven that the low molarity KCl brine can be used to replace formation fluid and have no side effect?

Authors: The ideal situation is not to have to replace the formation fluids. But in the cases where there was no formation fluid to store the samples in, we tried several options, including high salinity brines, low molarity NaCl solutions, water and 0.1M KCl solution, and in our judgment, the least damage occurred to samples stored in 0.1M KCl solution.

W-A Chiou: What is the difference between fibrous and platey illite in terms of their structure and surface texture/morphology and why?

Authors: It has been suggested the difference between fibrous and platey illite is the occurrence of unfilled potassium sites in the illite structure which causes fibers to form instead of plates.

A. L. Cohen: There is an early reference to critical point drying of clays: T.G. Naymik, The effects of drying on clay-rich soil texture. Proc. 32nd EMSA Meeting, Claitor's Publ. Div., Baton Rouge, LA,466-467, 1974.

Authors: Thank you for bringing this abstract to our attention.