Examination of core samples from the Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope: Effects of retrieval and preservation

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Abstract

Collecting and preserving undamaged core samples containing gas hydrates from depth is difficult because of the pressure and temperature changes encountered upon retrieval. Hydrate-bearing core samples were collected at the BPXA-DOE-USGS Mount Elbert Gas Hydrate Stratigraphic Test Well in February 2007. Coring was performed while using a custom oil-based drilling mud, and the cores were retrieved by a wireline. The samples were characterized and subsampled at the surface under ambient winter arctic conditions. Samples thought to be hydrate bearing were preserved either by immersion in liquid nitrogen (LN), or by storage under methane pressure at ambient arctic conditions, and later depressurized and immersed in LN. Eleven core samples from hydrate-bearing zones were scanned using x-ray computed tomography to examine core structure and homogeneity. Features observed include radial fractures, spalling-type fractures, and reduced density near the periphery. These features were induced during sample collection, handling, and preservation. Isotopic analysis of the methane from hydrate in an initially LN-preserved core and a pressure-preserved core indicate that secondary hydrate formation occurred throughout the pressurized core, whereas none occurred in the LN-preserved core, however no hydrate was found near the periphery of the LN-preserved core. To replicate some aspects of the preservation methods, natural and laboratory-made saturated porous media samples were frozen in a variety of ways, with radial fractures observed in some LN-frozen sands, and needle-like ice crystals forming

in slowly frozen clay-rich sediments. Suggestions for hydrate-bearing core preservation are presented.

Introduction

Natural gas hydrates, hereafter called "hydrates", are a class of clathrate compounds formed when water molecules encapsulate small gas molecules (Sloan, 1998). These compounds typically form at relatively high pressures and low temperatures where water and guest molecules (e.g., methane, ethane, propane) are present. Gas hydrates are studied for a variety of reasons including flow assurance in pipelines, energy recovery, climate change, geohazard and drilling safety, and gas storage/transportation. Recent estimates of the volume of hydrocarbons (predominantly methane) contained in gas hydrates span a large range (from 1 to 5×10^{15} m^3 (Milkov, 2004) to 120×10^{15} m^3 at standard temperature and pressure (Klauda and Sandler, 2005)).

Acquisition and analyses of gas hydrate-bearing core samples is critical to advancing our understanding of the occurrence and behavior of gas hydrates in nature. Scientific and engineering observations and physical property measurements on these samples provide important insights into the characteristics and behavior of hydrate bearing sediments (HBS) and hydrate-bearing reservoirs. Ideally, samples would be collected without thermal, mechanical or chemical disturbance, (i.e. the samples would remain at *in-situ* pressure, effective stress, chemical conditions, and temperature). Obtaining pristine HBS samples is difficult because of the behavior of hydrates in the sediment and the differences in conditions between the in-situ sample and the earth surface.

Hydrate is stable only within a specific temperature and pressure range, and this range is affected by the (possibly evolving) pore fluid chemistry during core acquisition and handling. By a combination of decreasing pressure, increasing temperature, or increasing salt (or inhibitor) concentration, hydrate dissociates into gas and either water or ice. Conventional coring imparts significant pressure, thermal, and chemical perturbations to the HBS samples, therefore attempts are made to retrieve and preserve the samples as

quickly as possible (Tulk et al., 1999) to minimize sample changes. In the arctic setting, cold ambient temperatures may help preserve hydrate, particularly if the drilling mud is chilled.

Hydrate can be present in a number of configurations in HBS. These include disseminated (which could be either pore-filling, grain-cementing, or a combination), part of the structural frame of the medium, in veins, nodules, and in massive layers (Sloan, 1990). Depending on its configuration, hydrate may either comprise a significant portion of the HBS providing a large portion of the mechanical, thermal, chemical, or physical properties of interest, or it may be limited to filling available pore space, having a very different impact on the overall HBS properties.

In this paper we describe HBS core retrieval from the BPXA-DOE-USGS Mount Elbert Gas Hydrate Stratigraphic Test Well (Mount Elbert Well) during drilling and coring operations that occurred from February 3 to 18, 2007. Eleven samples from 131 meters of conventional (non-pressure) wireline-retrieved core were preserved onsite and distributed to a number of laboratories for detailed study. Seven of these samples were placed in LN immediately after retrieval and description. Four others were initially preserved in methane-pressurized vessels and later depressurized and transferred to liquid nitrogen (LN). We describe methods used to handle the core and preserve samples. In addition, we consider the mechanical forces, depressurization, heating, chemical changes, repressurization, and freezing mechanisms that disturb HBS. We show results from analytical tests and x-ray computed tomography (CT) scanning of a number of core samples to describe these cores, interpret the impact of handling procedures on core condition and gas hydrate occurrence, and recommend procedures for future gas hydrate core handling and preservation in sand-rich systems.

Core Retrieval and Core Disturbance at the Mount Elbert Well

The Mount Elbert Well was drilled from ground surface to a casing depth of 594.4 m (1,950 ft) using a 12¼ inch bit and water-based drilling fluids. At that point, a 9 5/8-inch

casing was set, and drilling proceeded to a depth of 606.5 m (1,990 ft) using a custom mineral-oil-based chilled drilling fluid. This fluid was used throughout the coring program, enabling on-site mud chillers to circulate subfreezing drilling fluid to mitigate down-hole gas hydrate dissociation and associated hole destabilization. In addition, the oil-based drilling fluid used during coring ensured that all water subsequently extracted from core samples was original pore waters. The well was continuously cored using a Doyon 14 rig to a depth of 760 m (2,494 ft) with the ReedHycalog *Corion* wireline-retrievable coring system. Over this 153.5 m section, the 23 deployments of the system successfully recovered 131 m (430 ft) of high-quality 7.6 cm (3-inch) diameter core (85% recovery efficiency). Coring took place over 2 and a half days.

Extracted cores were laid out on the floor of the pipe shed at ambient arctic temperatures ranging from about -20°C (-4°F) to -7°C (20°F). From each coring run, the two 3.7 m (12 ft) sections of slotted aluminum core barrels were marked and cut into sections roughly 1 m (36 inches) in length. The individual sections were loaded into wooden boxes, and then transported via forklift approximately 11 m (~35 ft) to the unheated core examination trailer where the cores were laid out. Temperatures inside the trailer varied, but ranged typically from about -20°C (-4°F) to -7°C (20°F) during processing of the gas hydrate-bearing sections. The aluminum liners were cut open and the cores examined, described, and subsampled. The estimated time from when the core was cut into sections to when the samples were stored varied from 20 to 45 minutes. Further details on the coring and core sampling programs are provided in Hunter et al. (this volume) and Rose et al. (this volume).

Infra-red (IR) imaging has been used in many marine gas hydrate coring programs to identify “cold spots” that may indicate locations of endothermic cooling from gas hydrate dissociation. IR imaging was not employed in this program due to the very cold ambient temperatures and the use of aluminum liners that spread temperature anomalies over a large area.

Cores were initially scraped to remove the rind of oil-based drilling fluids. Zones that were thought to be potentially gas-hydrate bearing at the time of sub-sampling were recognized via three primary methods; 1) temperature probes were inserted into the core approximately every two meters and ongoing temperature decline indicated the endothermic effect of gas hydrate dissociation; 2) small samples were taken and placed in liquid water, with visual release of gas bubbles indicating gas hydrate presence; and 3) gas-hydrate bearing zones were commonly observed to be well consolidated (would ring when struck with a hammer) as opposed to non gas-hydrate-bearing zones, in which the sediments (particularly the sands) were often very poorly consolidated.

The cores were then sub-sampled according to a pre-established sampling plan. Small samples from inferred gas hydrate bearing zones were placed in syringes to collect gas samples (see Lorenson et al., this volume). Eleven whole-round samples collected from sediments determined to be gas-hydrate bearing *in situ* were preserved in either pressure vessels ("HYPV", 10-inch samples) or in immersed in LN ("HYLN", 5-inch samples).

Four samples were cut to 10-inch lengths (Table 1), scraped clean, wrapped in aluminum foil, placed in pressure vessels (Parr Instruments, Moline, IL), and pressurized to 5.52 MPa (800 psi) with 99.99% pure methane gas. The vessels were then kept frozen at temperatures ranging from -40°C to -4°C. Prior to shipping from the well site, the vessels were inspected and it was noted that pressures had decreased to 4.48, 4.76, 4.83, and 5.17 MPa (650, 690, 700, and 750 psi), which is still above the stable methane hydrate stability pressure at 0°C of about 2.62 MPa (380 psi). This decrease in pressure can be explained by cooling, small gas leaks in the vessel seals or valves, or by hydrate formation, as the samples were maintained at pressures well within the hydrate stability zone. As a result of the pressure decline and the desire to maintain the samples within the stability zone, the vessels were further pressurized to 6.20 MPa (900 psi) then shipped overland to Anchorage, Alaska. Temperatures during transportation in late February ranged from -40 to -10 degrees C. After arrival in Anchorage, core samples were stored in a refrigerated container maintained at -7°C. On May 2, 2007, the pressure vessels, having pressures ranging from 4.48 to 5.17 MPa (650 to 750 psi.), were rapidly

depressurized (in about 1 minute), the samples removed, labeled, and placed into cloth bags and immersed in LN (taking 3-6 minutes), before shipment for CT scanning prior to shipment to other laboratories for further analysis.

The seven whole-round core samples placed directly in liquid nitrogen at the site (Table 1) were cut to 12.7 cm (5-in) lengths, wrapped in aluminum foil, placed in cloth bags, and put into liquid nitrogen dewars. These dewars were stored out doors and shipped to Anchorage, and then shipped along with the four original HYPV samples.

Comparison of the hydrate sample collection depth with log data (Table 1; Figure 1) shows that six of the samples were clearly taken within zones of high gas hydrate concentration (HYPV-1, HYPV-2, HYLN-1, HYLN-2, HYLN-3, and HYLN-4). The remaining four samples were taken at depths close to gas hydrate-water contacts within the C unit. Potential uncertainties in core to log depth correlations make it difficult to conclusively determine the likely in situ gas hydrate content of these samples from the logs, however it is possible that several samples (particularly samples HYPV-3, HYPV-4, HYLN-6, and HYLN-7) were taken from zones that are primarily water-bearing *in situ*.

Effects of Sample Collection, Retrieval, and Preservation Processes on HBS

We briefly describe some of the many possible effects of core collection, recovery, and preservation on HBS. To retrieve core, it is first mechanically separated from the surrounding media by the bit or core barrel, relieving the overburden stress, and damaging the core sides. This results in a number of effects that have been studied over the last several decades for samples without hydrate; interpretation of these effects to HBS is considered in Waite et al., 2009 . The core barrel and sample will be in contact with the drilling mud as it is retrieved, and temperature and pressure changes will occur as the sample is brought to the ground surface. Temperature changes will occur from hydrate dissociation in the sample causing cooling where dissociation occurs. Heat transfer between the core and the mud will also affect the core temperature from the outside in, with the rate being governed by thermal conductivity of the medium and heat

absorbed by dissociation. At the Mount Elbert Well, the mud was chilled, cooling the core from its *in-situ* temperature. Pressure changes will be transferred very rapidly through the sample. At the Mount Elbert Well, pressure coring was not used, thus the core was depressurized upon ascent. Drilling mud chemistry can also affect hydrate stability if hydrate-inhibiting chemicals are present in the mud. The oil-based mud used at the Mount Elbert Well should not have chemically impacted the hydrate in the core to a large extent.

Core handling at the surface exposes the sample to atmospheric pressure at the examination location temperature until preservation occurs. Systems have been developed to manipulate and test pressure cores maintained under pressure (Yun et al., 2006), but most cores are processed at atmospheric pressure, as were the Mount Elbert Well cores. Minimizing the duration of these operations is critical to maintaining sample quality. Preservation of gas hydrate-bearing samples is typically performed by either submerging samples in LN, or placing the samples in pressure vessels that are subsequently pressurized with either dissociated gas or methane from another source and maintained in a temperature-controlled environment.

Gas hydrate sample storage in LN has been an effective method for preserving hydrate chemical properties studies (Lu et al., 2005; Lu et al., 2007; Udachin et al., 2007). With HBS it is critical to stabilize samples rapidly to minimize dissociation. Although preserving the chemical nature of the hydrate, preservation by freezing in liquid nitrogen may have several effects on the sample. First, water in the sample expands when freezing and this can cause grain separation altering the sample fabric and affecting the results of subsequent measurements. Second, freezing water excludes and concentrates solutes. These may then precipitate and thawing may not reconstitute pore water with the same chemistry. Third, freezing induces stresses in all media, particularly water-containing media. Most solids tend to contract when temperature is decreased described by the coefficient of thermal expansion. When the outer boundary of an object is cooled, a temperature gradient from the inside to the outside of the object is created, inducing mechanical stresses (Timoshenko and Goodier, 1970). If the temperature gradient is

severe, a cylinder may form radial cracks due to the thermal stress (Figure 2a). Freezing water in the outer layer of a core sample of porous medium containing water may initially expand on freezing, and then contract upon further cooling. The expansion upon freezing may cause spalling (commonly seen in concrete) due to the unbalanced forces (Figure 2b.).

Preservation of HBS by pressurization also affects the sample. Waite et al. (2008) investigated the effects of depressurizing and repressurizing an HBS core. Their premise was that for many measurements, even a pristinely collected pressure core would have to be briefly depressurized to be placed into many testing systems, and the sample would then be repressurized. Their findings showed for an initially partially saturated hydrate-bearing laboratory-formed sand sample, (akin to a partially dissociated sand sample) a brief depressurization caused hydrate dissociation on the outside of the sample. Water resulting from the dissociation then migrated towards the center of the core driven by a capillary pressure gradient, where hydrate formed upon repressurization. This reformed hydrate and its distribution affects the properties of the sample, because less hydrate present at the sample surface and more present in the sample center.

Observations and Investigations

CT scanning was performed on the Mount Elbert cores to provide information on the variation within and between the eleven Mount Elbert preserved whole-round core samples. X-ray CT scanning is a non-destructive technique that provides information on the three-dimensional density distribution of an object. In an attempt to understand some of the CT observations, a limited laboratory investigation was performed to examine the effects of various freezing methods on sandy and clay-rich media. Finally, a detailed comparison of the methane hydrate saturation and the methane isotopic compositions of subsamples of LN-preserved and repressurized-LN preserved samples is presented.

X-ray Computed Tomography Scanning of Mount Elbert Cores

The Mount Elbert Well samples (Table 1) were received in dry-ship dewars at the normal LN boiling temperature (-196°C), and the dewars were filled with LN upon arrival. For scanning, the cores were removed from the shipping dewars and placed in a Styrofoam shipping cooler partially filled with liquid nitrogen, and the cooler was closed to hinder warming. Two or three cores were scanned simultaneously. When two cores were scanned, they were placed side-by-side and both were submerged in LN. When three cores were scanned, the lower two were placed side-by-side and submerged in LN, and the other core was placed on a shelf resting on the two lower cores (Figure 3), not submerged in LN, but kept cold by the slowly evaporating LN in the cooler as occurs in a dry-ship dewar. CT scanning was performed without removing the samples from their bags or removing the aluminum foil covering the samples. Following scanning, the cores were replaced in the dewars.

The CT scanning was performed using a modified Siemens Somatom HiQ medical x-ray CT scanner, set to scan the samples in 3 mm thick slices with a voxel (prismatic region for which the density is computed) size of 393 microns × 393 microns × 3 mm (perpendicular to the core axis × perpendicular to the core axis × parallel to the core axis). The scanning parameters were selected to minimize scanning time, while providing reasonable resolution. Because of the LN present in the Styrofoam cooler, the samples remained very near -196°C, which is well below the methane hydrate stability point at atmospheric pressure. After scanning the cores, a set of standards with known density and diameter were scanned for density and spatial calibration.

Observations

Density

The calibrated density of the samples from the x-ray CT includes all phases present within a voxel including mineral, ice, hydrate, other natural phases, and the nitrogen (liquid or gas) present in pore spaces within the samples. During scanning, three of the samples (HYLN1, HYLN2, and HYLN7) were not submerged in LN (Figure 3), thus their densities reflect that there is less LN is present in the pore space. Our primary goal

was to examine differences within a single core, and secondarily to compare cores. The maximum impact of the LN on density for a completely dry sample having the highest observed porosity would be 0.37 g/cm^3.

The CT-estimated densities of the recovered samples are lower than the densities presented in the log (Table 1). From these density measurements alone, it is not possible to quantify the amount of hydrate lost on recovery for several reasons. First, all of these samples contained methane hydrate (as indicated by the log data and observations). When some of the hydrate dissociates during the core recovery, gas and water are produced. Gas produced will displace some water, reducing the density of the recovered sample. Second, LN is less dense than either hydrate or water; therefore it cannot raise the density to completely compensate for the loss of either water or hydrate. Third, the two methods for computing density are based on different measurements and involve different assumptions, producing slightly different results.

The three-dimensional density maps provided by CT are useful for understanding the structure of the samples. Laminations, fractures, vugs, bioturbation, hydrate nodules, and other features can be observed. Sub-voxel scale features such as disseminated hydrate are not easily detectible by CT at the scale it was applied, but changes in a sample from disturbances may be detected resulting in inferences of sub-voxel scale processes. Several of these will be discussed below.

Core Disturbance

Several types of disturbance were observed in the Mount Elbert cores using CT. Because the exact initial condition of the cores is unknown, core disturbance described below is somewhat speculative, but constrained by observations, core geometry, and understanding of the processes that occurred in the core. Depressurization occurred in all of these samples during core recovery, onsite processing and subsampling. Some cores show signs of depressurization, while others show signs of thermal processes as well. A CT cross section of a fairly uniform core (HYPV3) is presented in Figure 4a. This cross section shows the uniformity of the sample, as well as some of the artifacts of the

scanning. The apparent density of the sample seems to decrease from the outside in (brighter on the outside than the center). This is the result of beam hardening, in which the "softer" lower energy frequencies of the polychromatic x-ray beam are selectively more strongly attenuated in the outer regions. There are also artifacts from scanning two (or more) cores side-by-side (labeled as "1." in the figure). In Figure 4a, these artifacts appear as lower-density lines pointing towards the core that was located to its right during scanning. The circular low-density bands on the left of Figure 4a (labeled as "2." in the figure) are the result of two x-ray detectors not functioning properly.

Figure 4b is another cross section of the same core sample located several centimeters from the scan in Figure 4a. In it, however, we see low-density zones (LDZ) resembling fractures (labeled as "3." in the figure) that approximately "parallel" the circular surface of the core. These fractures are not likely to be natural because of their approximate cylindrical geometry and could be due to a number of processes including mechanical damage during coring releasing the effective stress, or the result of a strong temperature change such as freezing in LN. A freezing sample would be most strongly affected at its perimeter, and the freezing front would move from the outside in, changing properties of the sample as it moved. At a certain point, the differential stresses from the shrinking (or expanding) outer layer and the more-slowly shrinking (or expanding) inner zone could cause this spalling type of fracturing.

Figure 4c shows hydrate-bearing sample HYLN4, which that has radial fractures. These fractures, which extend axially through the core (e.g. axial cross sections in Figure 6), were not observed at the ends of cores prior to preservation, but are visible after preservation not only in CT scans, but in saw-cut cross sections as well (Figure 5). It is likely that rapid freezing and shrinking of the medium caused the fractures. Cracks in the samples observed in the CT scans of all the cores were compared. Cracks were qualitatively assigned three values (slight, medium, and extreme) and these were compared to the sample density (both log and CT), the standard deviation of the sample density (CT), the preservation technique, and the hydrate saturation from the log. No correlation was apparent.

Figure 4d shows a cross section of an apparently heterogeneous sample (HYLN2). We assume that the sample was originally fairly uniform like the center ("5.") although we don't know the exact initial sample conditions. Thermal or mechanical alteration probably resulted in the damaged zone on the outside of the core ("6.") because the density is lower as would occur upon hydrate dissociation or dilation. The inside of the sample, with the exception of a large linear fracture similar to those seen in the laboratory freezing tests described below, may be the least disturbed part. The high-density streaks ("7.") in the outer region may be the result of drilling mud containing barite having a significantly higher density than most minerals in the sample (see Torres et al., this issue) that invaded the disturbed sample.

Figure 5 compares photos of the ends of a core sample with CT scans from near those locations (within 1 cm.), and photos of nearby saw-cut surfaces. Although some cracks are visible at the core ends, they are not as obvious as observed in the CT scans. However, upon sawing the end off the core sample, the fracture pattern is clearly visible to the naked eye. Cross sections from the CT scans of the eleven samples are presented in Figure 6 from the shallowest depth to the deepest. In each, an axial cross section is presented with two or three cross sections perpendicular to the axis. The densities appear more smeared in the axial direction, due to the CT slice thickness being 0.3 cm.

Laboratory Investigation of the Effects of Sample Freezing

To gain a preliminary understanding of the effect of freezing cylindrical sand and clay-rich samples, tests were performed in which natural and prepared samples were frozen a number of ways to simulate sample preservation.

Fine Sand Samples

Five sand samples (F110 silica sand; US Silica; Berkeley Springs, WV; ~110 micron median grain size) were prepared by dropping aliquots of sand into plastic bottles containing water. The samples were densely packed by vibration, and sand was added until there was no free water. One sample was directly immersed in LN (~-196°C) to

rapidly freeze it, one placed in a chest freezer (~-20°C) for slower freezing, one was frozen in a freezer and then immersed in LN, one was frozen in a freezer, partially thawed, and then immersed in LN, and one was not frozen. After one day, the three samples were examined using x-ray CT scanning. The CT scans showed only one crack in the center of the LN-frozen sample that can be attributed to the freezing process, and no fractures in either the unfrozen or freezer-frozen samples. In the freezer-frozen/partially-thawed/LN-frozen sample (thought to be akin to a disturbed HBS sample preserved in LN), however, numerous redial fractures were observed (Figure 7) that extended axially for some distance similar to those seen in the Mount Elbert samples. Packing artifacts including bubbles and density differences formed at layer interfaces in all three samples, presumably due to fining on grain settlement, were observed (Figure 7).

Clay-Rich Samples

Although fine sand deposits are primarily being investigated in the Mount Elbert well, much of the world's natural gas hydrate exists in much finer-grained marine sediments. To examine the effect of freezing on these clay-rich sediments, oceanic core sediment samples were frozen 1) in a freezer, 2) in a pressure vessel in a freezer, and 3) in LN. We used three different imaging techniques to ascertain the effect of freezing on the resulting structure: visual observation, Xradiography, and CT scanning.

The structure of clay-rich sediment at refrigerated (+4°C), normal freezer (-21 to -23°C), and liquid nitrogen (-196°C) temperatures are strikingly different. The refrigerated sample showed little cracking or disturbance. Both samples slowly frozen in the freezer showed extensive cracking throughout (Figures 8 and 9) with the sample frozen in the pressure vessel having an increase of 4.7% in length. Close-up examination of the sediment revealed a complicated network of ice-filled cracks. In contrast, the sample frozen in LN has few fractures except for a fracture along the axis in the center similar to the fracture observed in the LN-frozen sand and Mount Elbert HBS samples. The upper portion of sediment, which was not submerged in LN, was fractured away from the rest of the sample. From this, it appears that both the rate of freezing and the applied temperature gradient appear important to sample preservation. In these clay-rich

sediments, slow freezing caused cracking throughout, and the rapid freezing caused less-extensive fracturing.

Comparison of Methane Pressure-Stabilized and LN-Stabilized Cores

Two Mount Elbert Well samples, one preserved in LN, the other initially repressurized with methane and subsequently preserved in LN (HYPV4 and HYLN7) were used in this study. Both samples were light gray to dark gray uniform massive medium-grained sandstone and were taken from Core #9, Section #1. These samples are coarser-grained than most of the other Mount Elbert Well hydrate-bearing regions which are typically very fine to fine-grain sands. HYPV4 was sampled from the depth interval of 663.89 - 664.14 m below ground surface, and HYLN7 was taken from the nearby interval of 664.50 - 664.63m. After sampling, HYPV4 was maintained under pressurized CH_4 gas for 80 days before it was transferred into liquid nitrogen for preservation, while HYLN7 was placed in liquid nitrogen after retrieval. The hydrate saturation distribution in these cores was measured and is reported in Lu et al. (this volume). The surface layer (up to ~5 mm from core surface) of HYLN7 contained no hydrate, while the surface layer of HYPV4 had a pore-space hydrate saturation of 40%. The center portion of HYPV4 had a hydrate saturation of 86%; significantly higher than that estimated from logging results in the same interval (47 to 63%).

Differences in both the $\delta^{13}C$ and the δD exist between the CH_4 from the Mount Elbert gas hydrate and the methane gas used for stabilization. Lorenson et al. (this volume) show that secondary hydrate formed in Mount Elbert samples has a mixed isotopic composition. Figure 10 shows the $\delta^{13}C$ and the δD of the methane extracted from hydrate in core subsamples at varying distances from the core surface. The distributions of both the $\delta^{13}C$ (-48.6‰) and the δD (-239 ~ -253‰) are in a narrow range, almost homogeneous through HYLN7 and very similar to the methane isotopic values ($\delta^{13}C$: ~ -49‰, δD: ~ -245‰) from gas hydrates recovered from other sediment sections of the Mount Elbert well (Lorenson et al., this issue). A different isotopic distribution pattern was found with HYPV4, however. Both the methane $\delta^{13}C$ and δD increase near the core

surface. The methane $\delta^{13}C$ and δD values in the surface layer (up to ~ 5mm) are almost the same as those of the methane gas that was used to pressurize HYPV4. This, along with the anomalously high gas hydrate saturation indicates the formation of secondary methane hydrate from the pressurizing gas.

Because HYPV4 was retrieved from about 30 cm above HYLN7 and the isotopic compositions of methane in hydrates are nearly homogeneous throughout the Mount Elbert Well, the isotopic compositions of methane in hydrate in HYPV4 should be similar to those in HYLN7. However, the isotopic compositions in HYPV4 show much different characteristics from those in HYLN7, gradually shifting away from those of the pressurizing methane gas and toward (but still different from) the hydrate nearer the core center (Figure 10). This implies that secondary methane hydrate formed throughout the whole core with the contributions of pressurizing gas being different from the surface to the center of HYPV4. As shown in Figure 11, 100% of the methane hydrate in the surface layer was from pressurizing gas, while the fraction of pressurizing gas in hydrate decreased to about 40% near the core center.

The hydrate saturation in HYPV4 would not be expected to significantly exceed the saturation estimated from logging results (~63% Table 1, also Collett et al. this volume). However, the pore space hydrate saturation in the central portion of HYPV4 was determined to be about 86% (Lu et al. this volume). For hydrate to form, both water and gas are needed. Pore water was naturally present in the sample, and dissociating hydrate left additional water. Waite et al., (2008) showed that for a partially hydrate-saturated, core-shaped sample, that brief depressurization and repressurization resulted in a decrease in hydrate saturation at the outside of the sample, and an increase in hydrate saturation in the center, similar to what was observed here. The formation of secondary methane hydrate altered the original core structure and physical properties from the natural condition.

The isotopic compositions in HYLN7 are almost homogeneous through the core and almost the same as those of hydrates in other samples (see Lorenson et al., this issue), so

this confirmed that preserving HBS in liquid nitrogen preserves the chemical nature of the hydrate, consistent with the results obtained for the preservation of gas hydrate samples from Cascadia (Lu et al. 2005, 2007).

Discussion

Understanding the distribution, characteristics, and behavior of hydrate-bearing reservoirs is critical for identifying and solving gas production, safety, and mechanical stability issues related to HBS. Retrieving pristine HBS useful to gaining this understanding is difficult and challenging because of the properties of both gas hydrate and HBS, and the realities associated with core collection and retrieval. In spite of the difficulties and challenges, observations and measurements made on natural samples of HBS tremendously improve our understanding and improve conceptual models of hydrate-bearing reservoirs, therefore the need for sampling persists.

In spite of the difficulties in retrieving HBS samples, coring at the Mount Elbert well was successful in retrieving hydrate-bearing core. Some hydrate dissociation occurred in samples collected and preserved from the Mount Elbert Well during core recovery and processing, as shown by their density being lower than the host sediment, and the lack of hydrate in the outer layer of a preserved sample. Dissociation occurred when the samples were retrieved from depth and depressurized as the sample was brought to the surface, and also during handling prior to preservation. Samples also show signs of disturbances from the handling and preservation techniques used, including immersion in LN and preservation in methane-charged pressure vessels.

Comparing the two preservation techniques, immersion in LN after retrieval, and immersion in LN after repressurization we see a number of effects. No secondary hydrate formation was identified in the LN-preserved sample, whereas significant secondary hydrate formation occurred in the repressurized/LN-preserved sample. During repressurization, the samples were overpressurized to keep the hydrate well within the stability field. Hydrate can form from ice under the proper conditions, but will form faster

if liquid water is present. Because hydrate formation is an exothermic process, some self-warming could occur causing some thawing, especially for warmer regions of samples. In spite of the storage temperatures being below freezing, pressures in the samples declined, indicating possible gas leakage from the vessels, and/or secondary hydrate formation in the overpressurized samples over ~80 days of storage.

Although preservation in LN effectively stops hydrate dissociation, it affects HBS samples by freezing the water in the sample possibly separating grains, and can cause thermal shock that can result in cracking. Water freezing in a thawed outer layer can result in spalling, however we did not see that in our laboratory tests. Spalling or radial fracturing, as well as mechanical fracturing or damage from the coring operations will affect sample hydrologic, geophysical, and geomechanical properties of HBS samples. The effects of spalling and surface damage can be handled by subsampling if fractures do not penetrate through the sample, however radial fractures cannot easily be avoided by subcoring, particularly if larger samples are needed to include the heterogeneity in a sample. Sample fracturing occurred in all samples, however it was less prevalent in the samples originating from the water-bearing units (Table 1, and Figure 6 Samples HYLN5 and deeper). No differences in fracturing were apparent between the repressurized-LN-preserved/LN-preserved samples. This could be because the temperatures of both types of samples were about the same at the time they were immersed in LN.

Hydrate dissociation requires heat input. Initially, the heat will come from the sample itself lowering the sample temperature. At atmospheric pressure, the dissociating hydrate could theoretically lower its temperature to a minimum of ~-80°C (Stern et al., 2001), establishing a thermal gradient causing heat flow. In an analysis of hydrate dissociation on core retrieval, Moridis and Kowalsky (2005) considered the effects of core dimensions (0.0635 m [2.5 inch] and 0.085 m [3.345 in] diameter), time of ascent (20 or 30 minutes), drilling mud temperature (0.2, 3, 6°C), type of dissociation (equilibrium and kinetic), intrinsic sample permeability ($3x10^{-14}$ m^2 [30 mD], $3x10^{-13}$ m^2 [300 mD], $1x10^{-12}$ m^2 [1000 mD]), initial sample temperature (10 and 13.5 ^{o}C), and hydrate saturation (25 and 50%) on the final hydrate content in the recovered core. They concluded that for the 50%

hydrate saturated core, about 46% of the original hydrate in place in the 0.085 m diameter core would be present after the 20-minute ascent, with only about 40% remaining in the smaller diameter core. Only about 22% of the original hydrate was predicted to remain in the smaller core for the 30-minute ascent. Factors increasing the amount of hydrate remaining in the sample were 1) larger diameter, 2) higher hydrate saturation, 3) shorter ascent time, 4) lower permeability, and 5) colder mud. Although the initial hydrate temperature and pressure are different than those from the Mt. Elbert site, their conclusions are applicable here because the core temperature rapidly approached the mud temperature prior to dissociating. In the Mount Elbert Well, collecting large-diameter cores, retrieving the cores quickly, and using a hydrate-inert chilled mud, optimized the factors enhancing hydrate recovery. Other optimizations might be possible in future operations.

Data presented herein and by Lu et al. (this volume) indicate that the coring method and surface handling caused hydrate dissociation in the recovered samples, and preservation further changed the cores. Although more difficult to employ, pressure coring may have significantly reduced this hydrate loss and preservation-related damage. Some handling and some preliminary tests can also be performed on pressurized samples without depressurizing, as is done in the Instrumented Pressure Testing Chamber (Yun et al., 2006). While it would be ideal to conduct characterization under *in-situ* conditions, further development of measurement techniques to perform these types of analyses are needed.

The retrieval and preservation methods used at Mount Elbert were selected to quickly and safely acquire maximum amount of core while most rapidly impeding hydrate dissociation. These methods optimized collection but applied strong gradients to the samples, resulting in sample cracking and secondary hydrate formation. An alternate method might be considered in which retrieved samples (whether pressurized or not) are repressurized to the equilibrium pressure for the core (or mud) temperature. This would immediately stabilize much of the sample. Moderate temperature gradients (far less severe than those caused by immersion in LN) in the sample would still be present, thus

perfectly balancing pressure and temperature along the hydrate stability curve cannot be attained at every location in a sample. Following this, the samples could be cooled at a moderate rate, while reducing methane gas pressure accordingly, until the samples could be stored in LN.

The converse problem is important as well. Returning a sample from an LN-preserved state to the reservoir state (or other state of interest) for laboratory measurements must also be carefully approached. Again, extreme gradients need to be avoided. A proposed method would be to perform any needed machining (subsampling/plugging, sawing off ends) near the LN boiling temperature. Following that, the sample might be placed in the measurement device and warmed such that the LN is removed but not beyond about -80°C. This warming should be gradual so that only a moderate temperature gradient is present to avoid spalling. Once the sample is warmed to an average temperature of about -80°C, methane gas pressure should be applied and increased along the equilibrium curve while slowly warming the sample to the desired point. Particular care needs to be taken at temperatures near 0°C and above, as ice melting will occur and then liquid water will be available to rapidly form hydrate if the methane pressure is higher than the hydrate equilibrium pressure for the temperature and chemical conditions.

Conclusions

The collection, retrieval, and preservation of HBS and subsequent reestablishment of *in situ* conditions for laboratory examination and testing are difficult processes. Each step requires careful planning and execution. Eleven whole-round hydrate-bearing cores were collected and preserved from the BPXA-DOE-USGS Mount Elbert gas hydrate stratigraphic test well. All eleven were CT scanned and features relating to core disturbance were identified. These features primarily include radial and spalling-type fractures. The radial fractures are thought to be the result of rapid freezing by immersion in LN as occurred in the freezing tests. The spalling-type fractures could be the result of mechanical stresses, or from water freezing in the outer part of the core when immersed in LN.

The hydrate distribution from two proximal Mount Elbert Well hydrate-bearing samples preserved differently was investigated. The sample originally preserved onsite in LN-preserved sample had no hydrate in the outer layer, but hydrate remained in the inner parts of the core (~ 40% saturation vs. *in-situ* saturation of 47- 63%). The repressurized core sample (later preserved in LN) had abundant hydrate and secondary hydrate formation that was confirmed by isotopic measurements of the evolved gas and repressurization gas in addition to the hydrate saturation exceeding the saturations from wireline log estimates. Freezing tests were performed on sand and clayey samples, with rapid freezing causing fracturing in the core center, and slow freezing causing massive ice-filled fractures to form in the clay-rich sediment. LN freezing of a partially thawed saturated sand sample resulted in radial fractures in the sample similar to those observed in many Mount Elbert Well samples.

Field programs seeking to recover gas hydrate bearing samples that most closely reflect in-situ conditions should utilize pressure coring. However, sample transfer techniques need further development to allow for the transfer of pressure cores to experimental test cells with minimal or no damage to the samples.

Applying large driving forces to hydrate-bearing samples (low or high pressures, extreme temperatures, chemistry) will dramatically impact the samples, affecting their overall properties. The application of smaller driving forces over longer times may be effective in reducing some of the disturbances that were observed in Mount Elbert cores. Consideration of the medium (sand, silt, clay) is important however, as slow freezing (lower driving force) had significantly different effects on sandy and clay-rich samples. In clay-rich samples, many fractures and ice lenses formed throughout the sample. The sandy samples were not significantly impacted by the slow freezing. Rapid freezing left fractures in the sandy samples, but not in the clay-rich samples.

Working with HBS in the lab or field is always challenging. Preliminary tests and modeling of coring and handling should be performed prior to field expeditions to improve techniques of sample handling and preservation.

Acknowledgements

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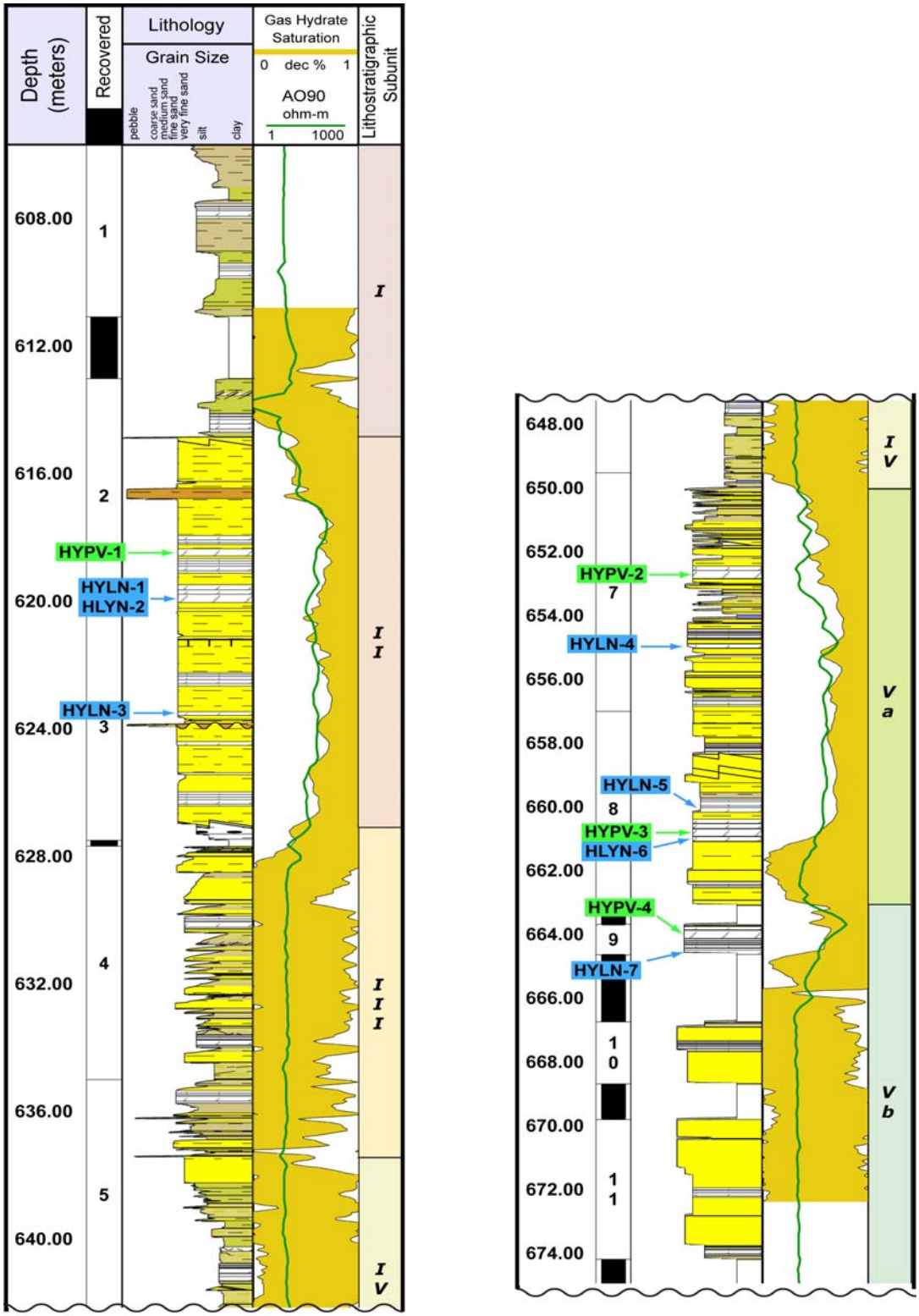
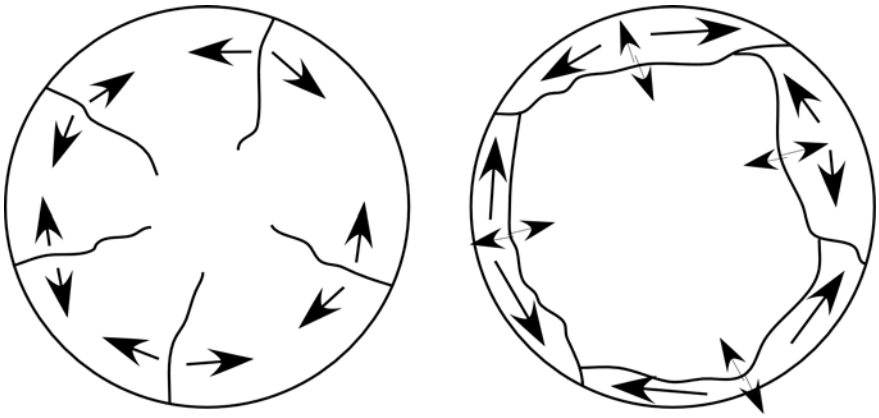


Figure 1. Depth, lithology, and hydrate saturation showing the original location of the samples.



(a) (b)

Figure 2.(a). Radial fracturing due to shrinkage from rapid cooling; (b) Spalling from water expanding upon freezing.

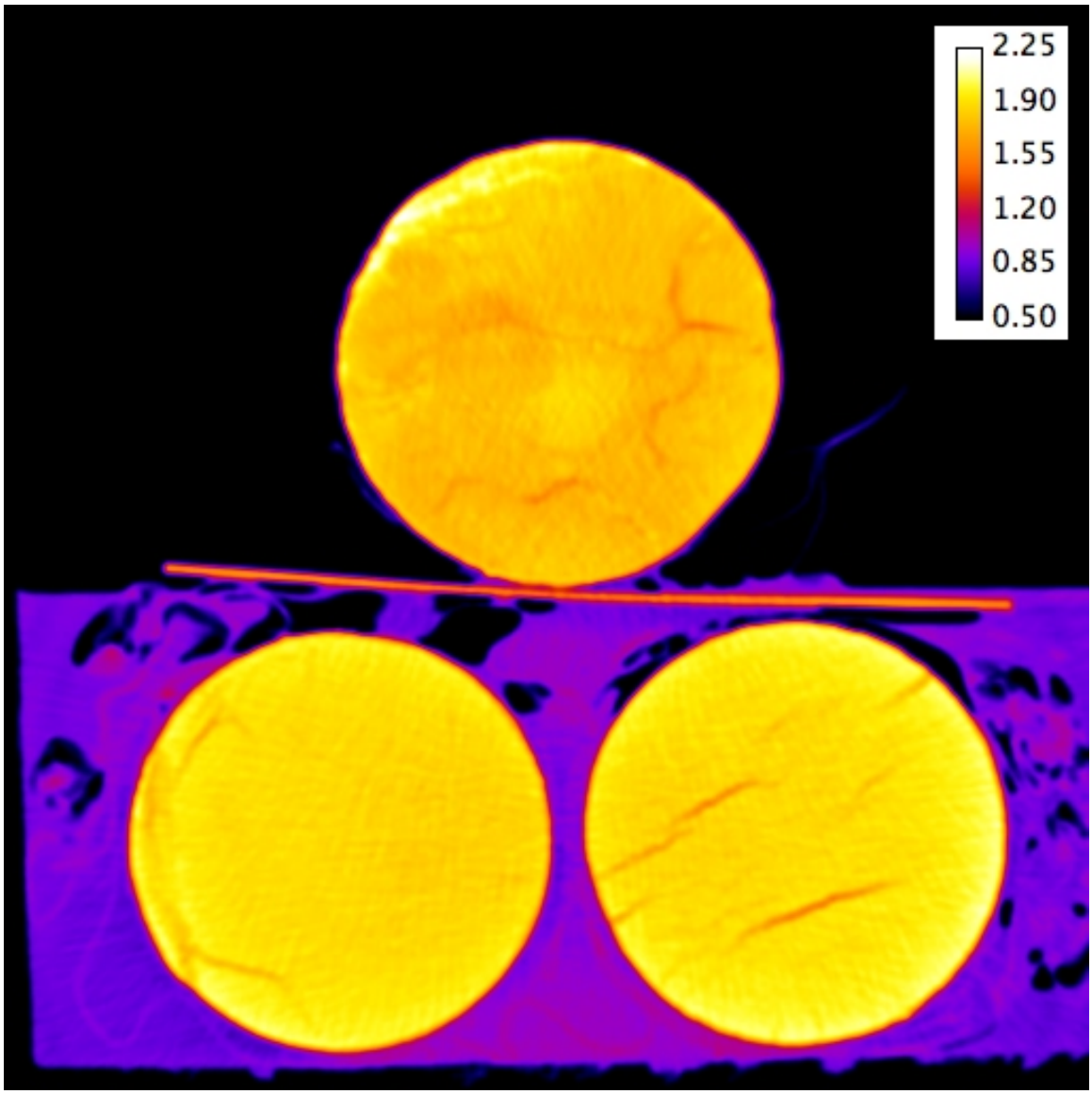


Figure 3. CT scan of three core samples with two submerged in LN and the other on a shelf. Core density variations from fractures are clearly visible. Scale is density in g/cm^3.

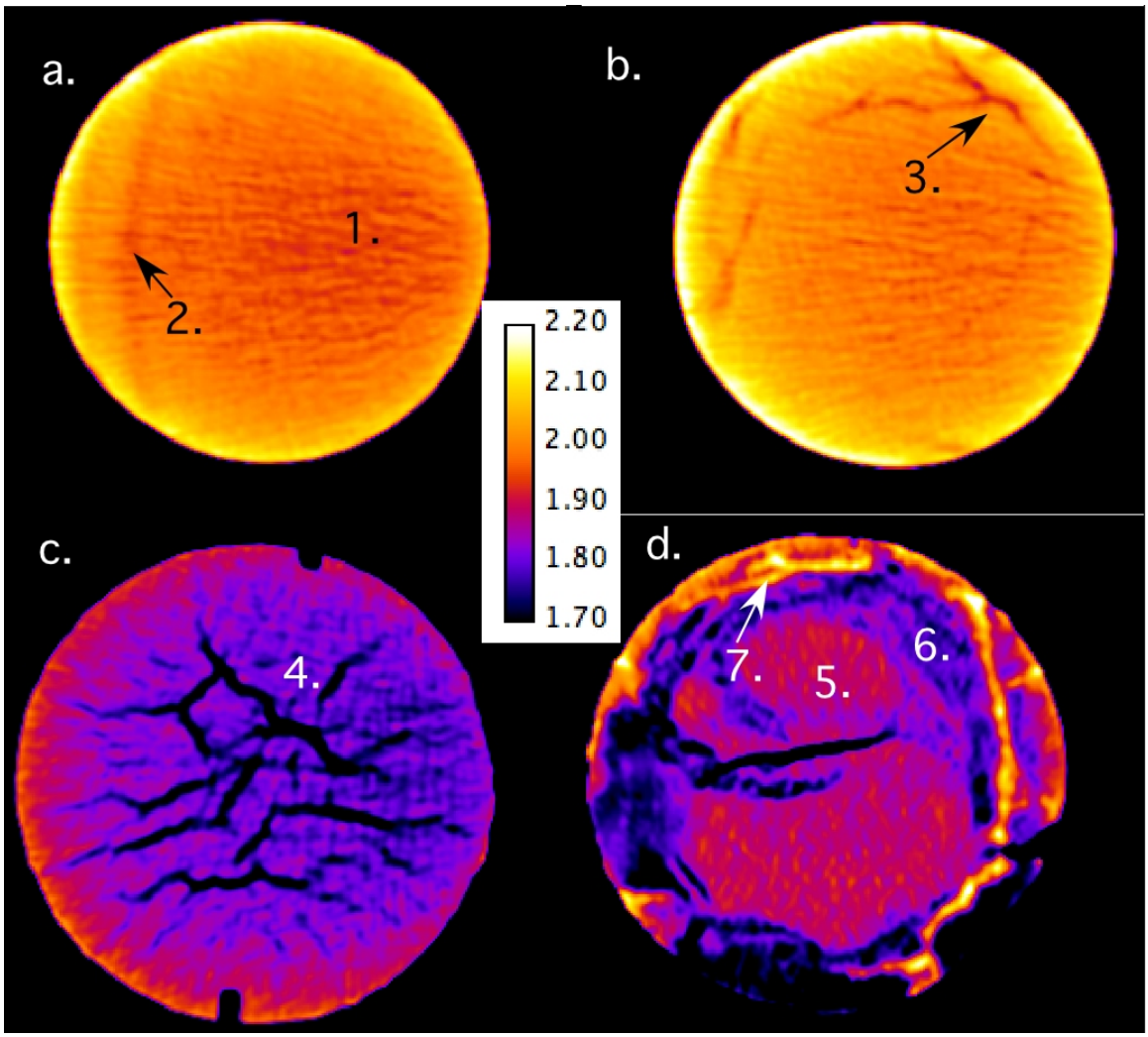


Figure 4. Four cross sections of three Mt. Elbert core samples. a. Fairly uniform slice (HYPV3), b. slice showing some damage, probably as a result of a thermal shock, c. slice showing dissociation, probably from depressurization (HYLN4), d. slice showing dissociation from sample heating, and sample refreezing on the periphery (HYLN2).

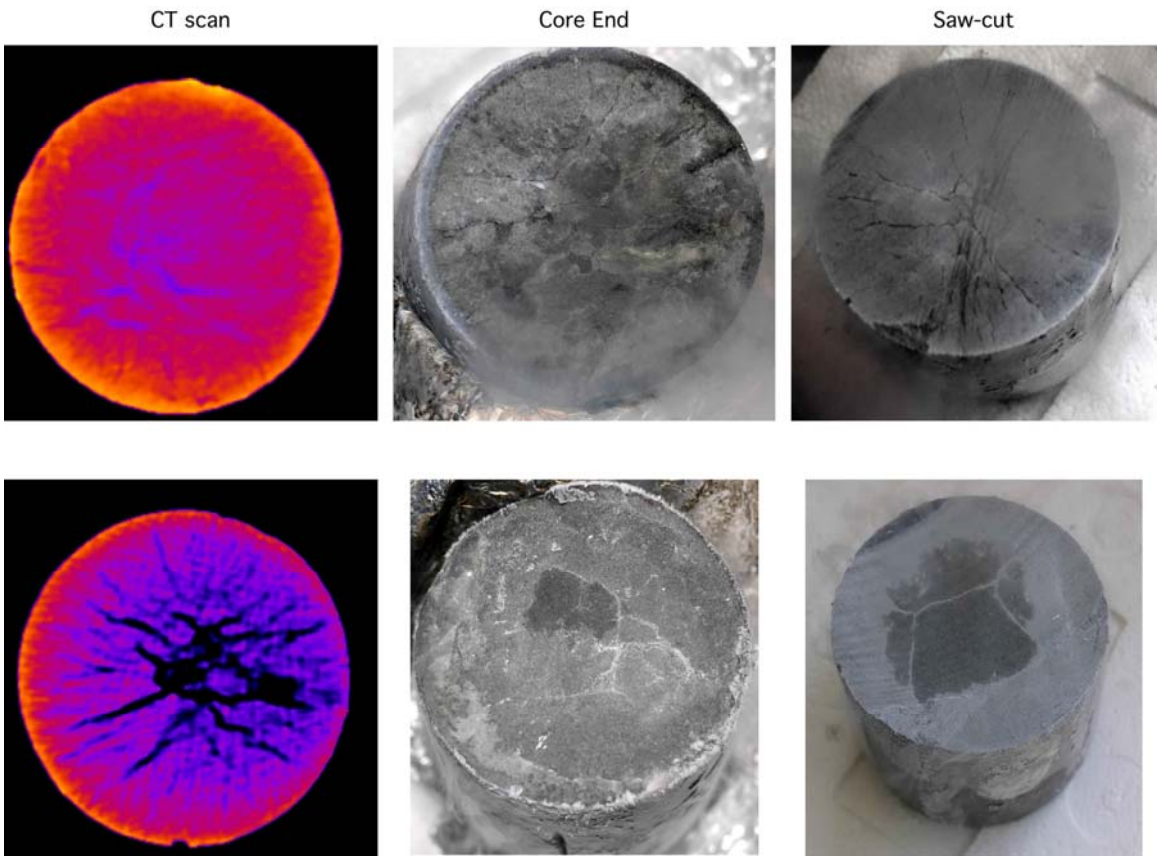
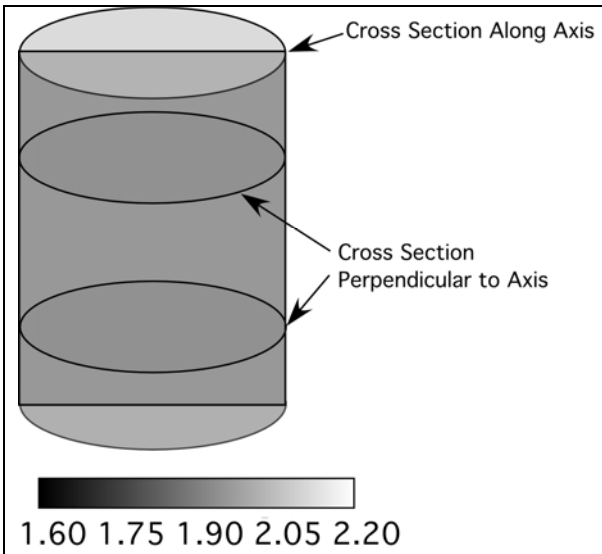
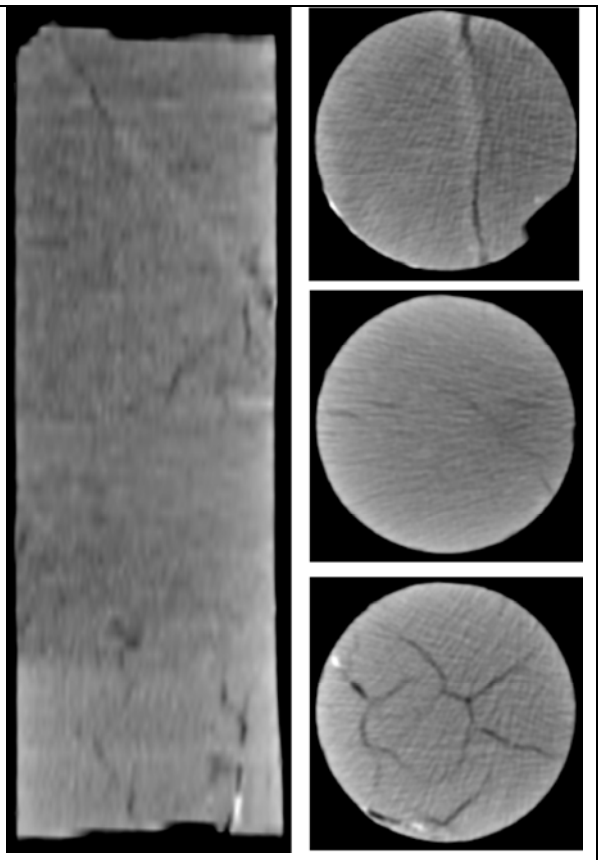
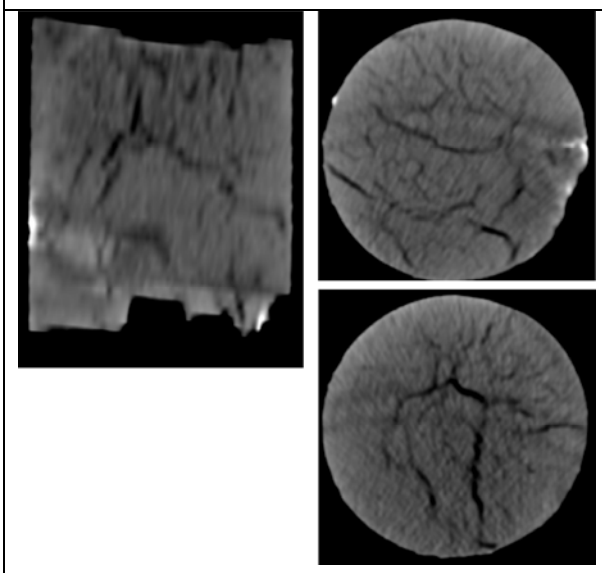


Figure 5. Near-end CT scans, photo of the end of HYLN4, and saw-cut core.

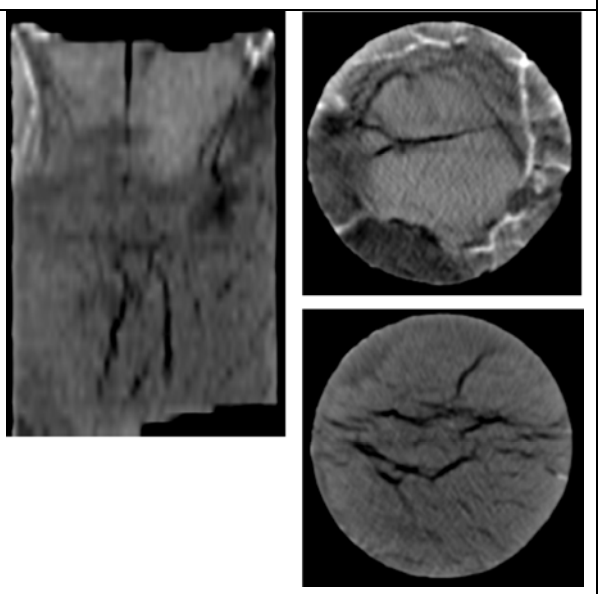




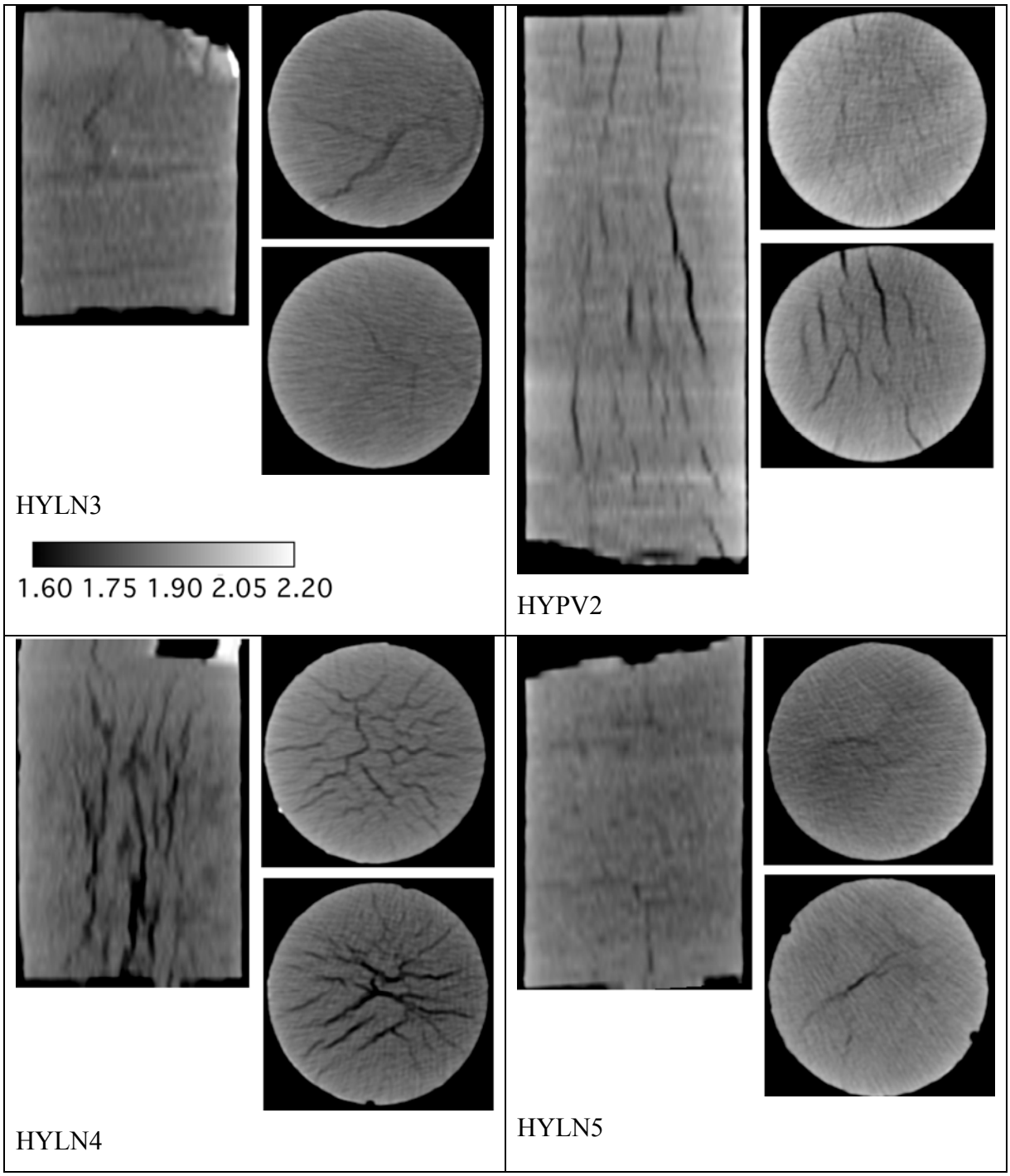
HYPV1

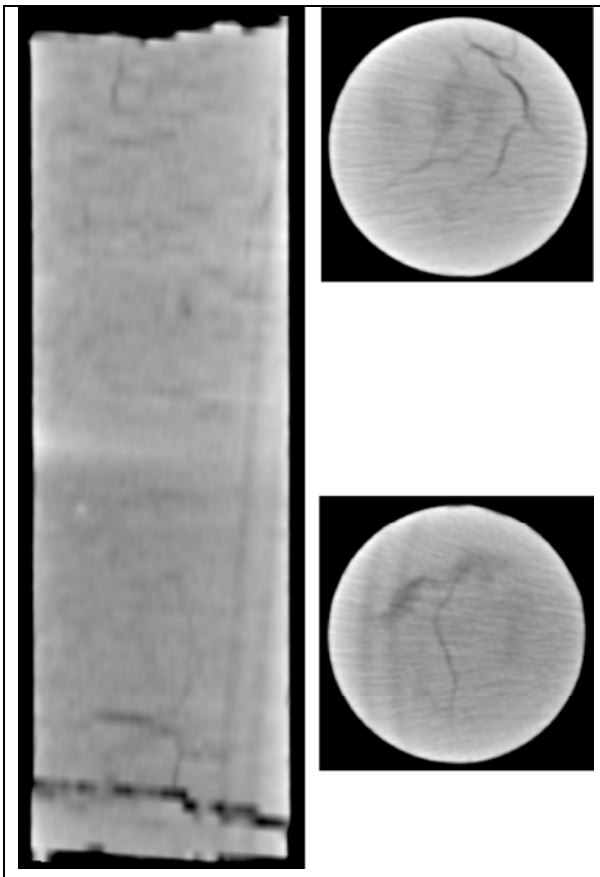


HYLN1

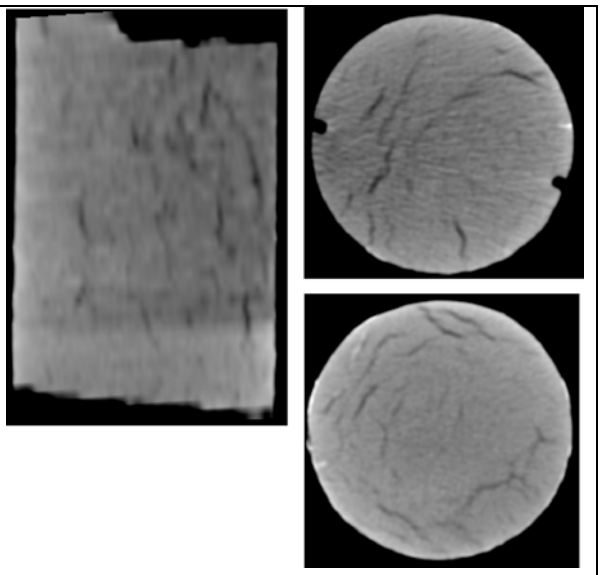


HYLN2

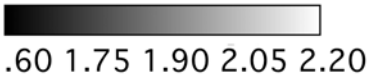

HYLN3
1.60 1.75 1.90 2.05 2.20
HYPV2
HYLN4
HYLN5



HYPV3



HYLN6



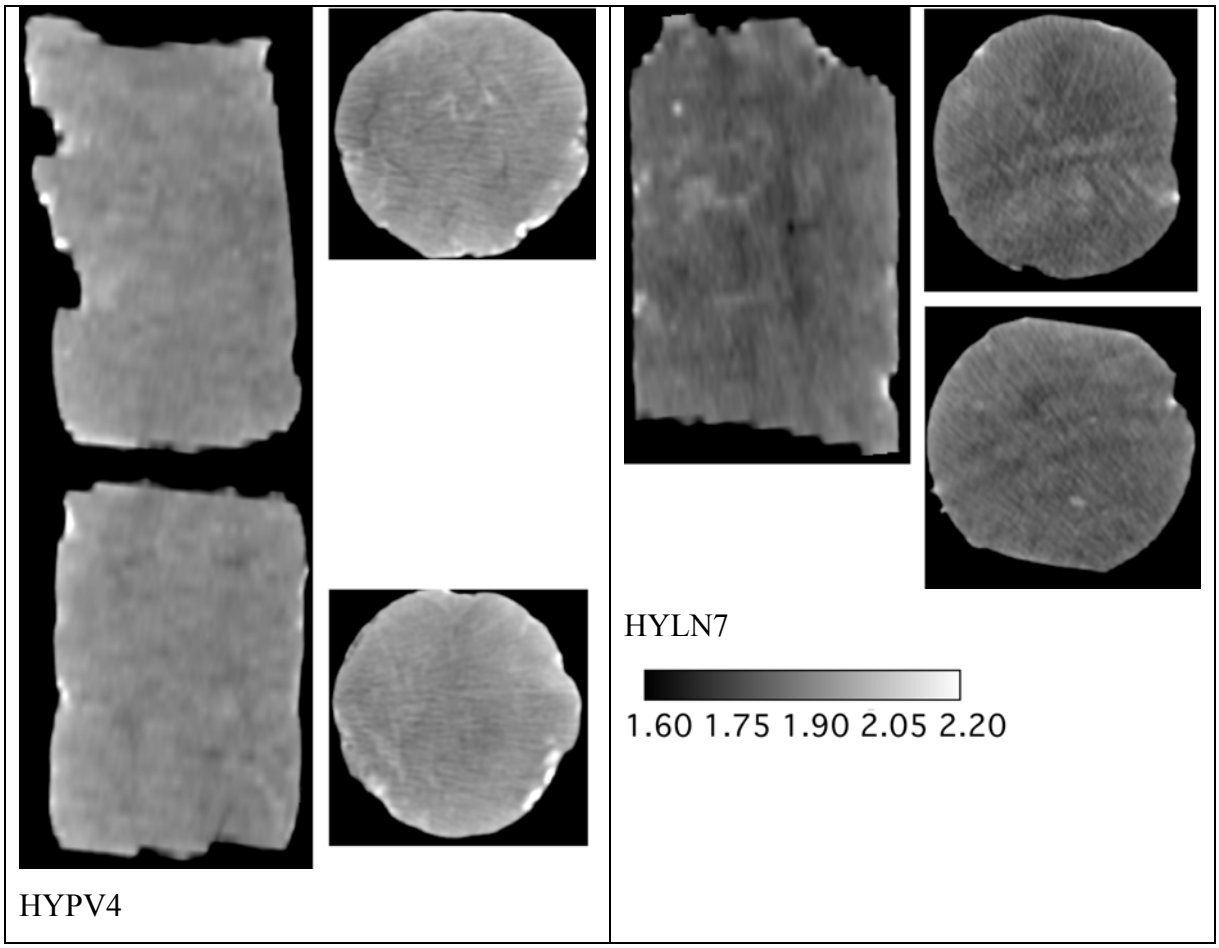


Figure 6. Cross sections from CT data for samples in order of increasing depth HYPV1, HYLN1, HYLN2, HYLN3, HYPV2, HYLN4, HYLN5, HYPV3, HYLN6, HYPV4, and HYLN7 (left to right, top to bottom). The calibration scale is the same for all.

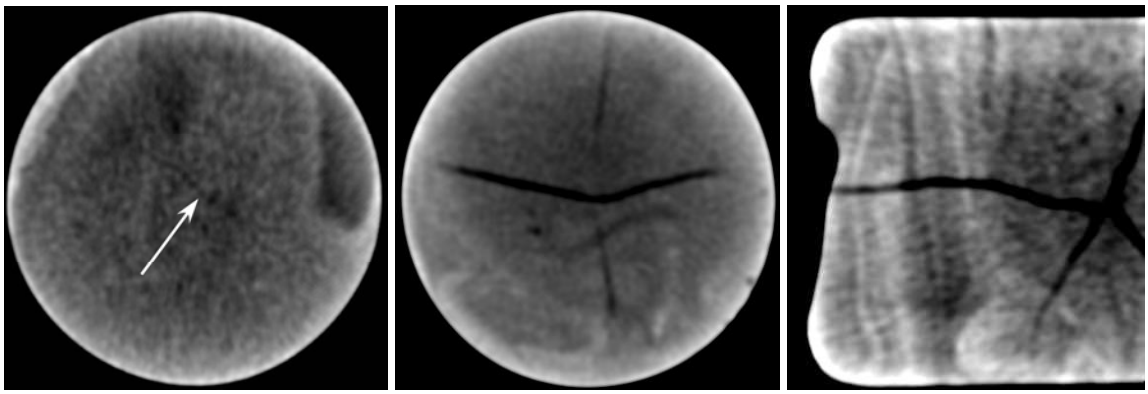


Figure 7. X-ray CT scans of LN-frozen water-saturated sand samples. Left - Water-saturated sand frozen in LN. Arrow shows the location of the crack in center of the sample. Center – Radial fractures in freezer frozen, partially thawed then LN-frozen sample. Right – same as center but axial cross section. Peripheral brightness is due to x-ray beam hardening, and other density variations are attributable to packing.

Figure 8. Cracks present throughout the clay-rich sample frozen in a pressure vessel in a freezer.

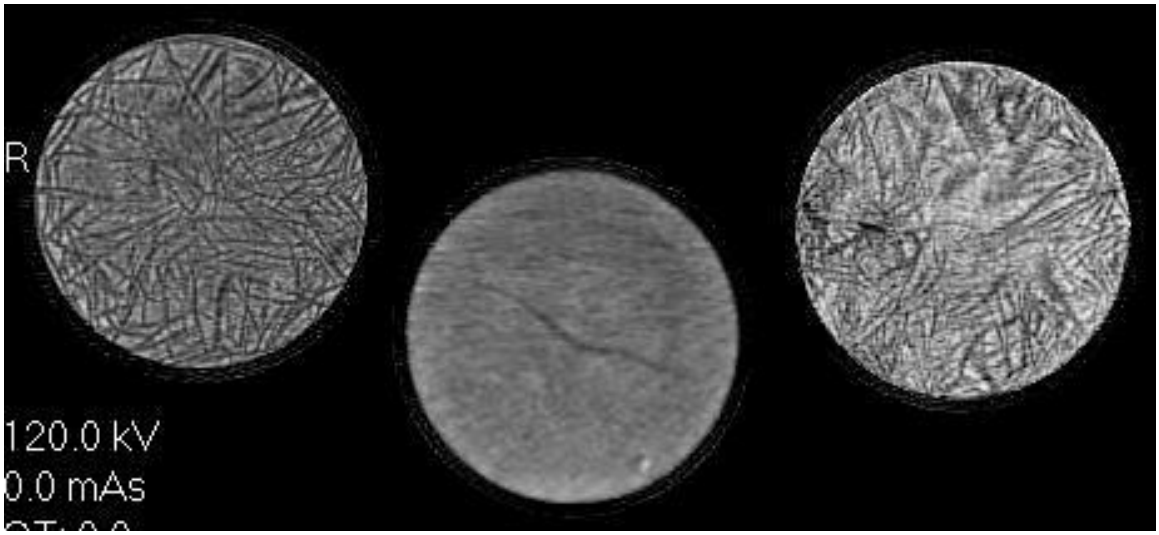


Figure 9. CT scan showing cracks in freezer-frozen clay-rich samples (outer samples) and relative lack of cracks in LN-frozen sample (center).

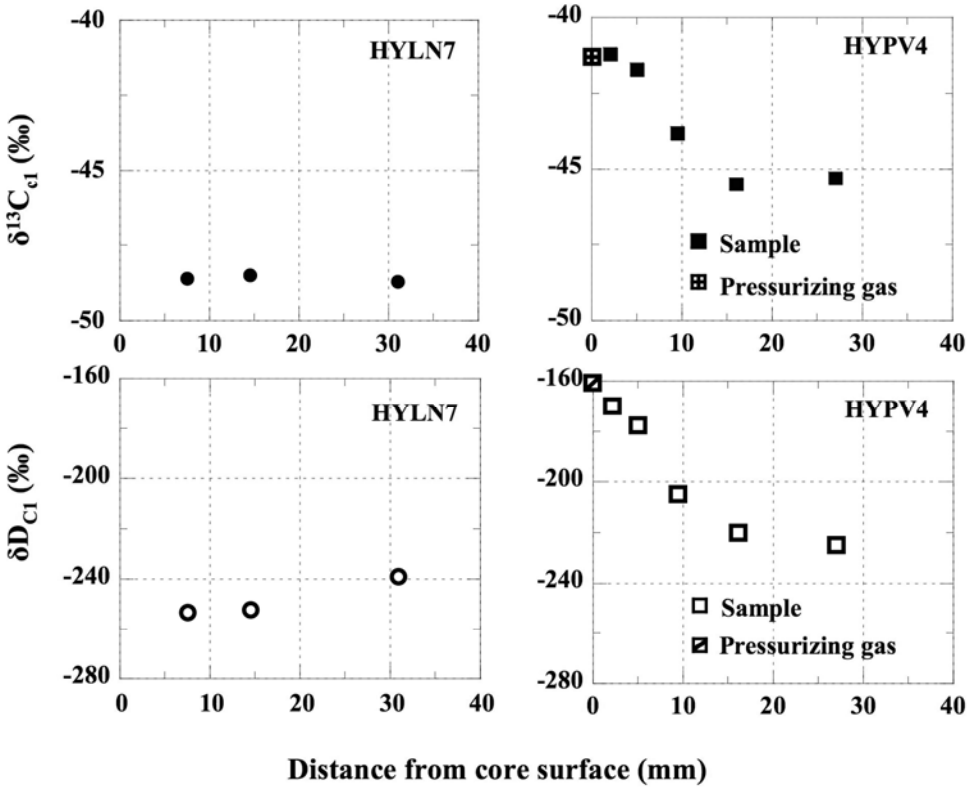


Figure 10. The distributions of $\delta^{13}C$ and δD in HYLN7 and HYPV4

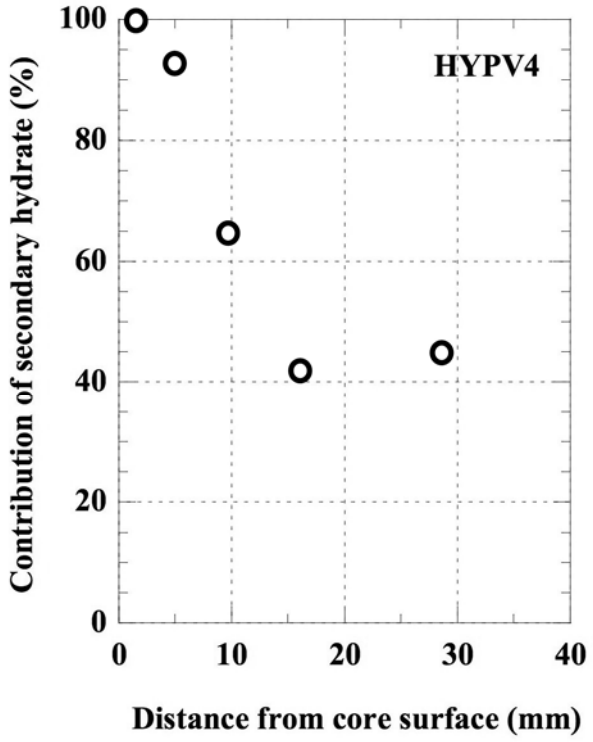


Figure 11. The contribution of secondary formation of methane hydrate to hydrate saturation in HYPV4. Core radius is ~3.8 cm.

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