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# THE STRUCTURE OF HYDRATE BEARING FINE GRAINED MARINE SEDIMENTS

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## ABSTRACT

Recent advances in pressure coring techniques, such as the HYACINTH and IODP PCS pressure cores deployed during Expedition 1 of the India National Gas Hydrate Program using the JOIDES Resolution have enabled the recovery of fine grained sediments with intact gas hydrates contained within the sediments. This has provided the opportunity to study the morphology of gas hydrates within fine grained sediments which until now has been hindered due to the long transit times during core recovery leading to the dissociation of the gas hydrates. Once recovered from the seafloor, rapid depressurization and subsequent freezing of the cores in liquid nitrogen has enabled the near complete fine fracture filling nature of the gas hydrates to be largely preserved. High resolution X-ray CT (computer tomography), which has a pixel resolution of approx. 0.07mm, has been used to provide detailed images showing the 3-dimensional distribution of hydrates within the recovered fine grained sediments. Results have shown that in fine grained sediments gas hydrates grow along fine fracture faults within the sediment. Although the fractures were predominantly sub-vertical and continuous through the cores, stranded fractures were also observed suggesting that hydrate formation is episodic. However, within the cores open voids were observed which were not evident in low resolution CT images taken before the depressurization step suggesting that during depressurization either finely disseminated gas hydrate was dissociated or that gas exsolving from solution created these voids in the sample prior to freezing in liquid nitrogen. These detailed observations of gas hydrate in fine grained sediments will help us understand the differing morphology of gas hydrates in sediments. They also show that sample disturbance is still a major concern and further techniques are required to restrict these effects so that meaningful laboratory tests can be undertaken on recovered samples.

*Keywords*: gas hydrates, X-ray CT, pressure cores, depressurization

## INTRODUCTION

During the recent Indian National Gas Hydrate Program (NGHP) 01 Expedition [1] a number of pressure cores were retrieved, at in-situ pressures, containing fine grained hydrate bearing sediments. Initial onboard physical characterization was undertaken prior to some of the cores being rapidly depressurized, sub-sectioned and stored in liquid nitrogen. As part of

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the post cruise science investigation, five sub-sections of these cores were shipped to the University of Southampton for testing in the Gas Hydrate Resonant Column apparatus, which it was hoped would help provide dynamic geophysical properties of these hydrate bearing samples.

As part of the initial examination of the cores, prior to testing, high resolution X-ray CT (computer tomography) images were obtained. This paper reports on observations made from the images on the structure of hydrate within these samples. Comparisons are made between the initial low resolution X-ray images obtained on the pressurized core prior to sub-sectioning and depressurization and those obtained subsequently. Effects of depressurization and subsequent freezing are identified suggesting that the depressurization and freezing procedure seriously alters the structure of the sediment although the gas hydrate may not be altered.

## PRESSURE CORING - BACKGROUND

Historically the recovery of gas hydrate bearing sediments from deep water marine environments has been problematic due to the thermobaric nature of gas hydrates, which leads to dissociation of the hydrate as the hydrostatic pressure is reduced and the temperature is increased during core recovery. In addition, methane solubility reduces significantly with reducing pressure causing free gas to exsolve from solution. Therefore the physical characterization of intact naturally occurring gas hydrate bearing sediments, and the quantification of the hydrate present, has not been possible using conventional coring techniques.

This has led to the development of pressure coring systems which enable gas hydrate bearing sediment samples to be recovered under in-situ pressures. Careful recovery and handling procedures can further reduce temperature induced gas hydrate instability so that minimal disturbance occurs to the structure of the sediment sample which would normally occur during hydrate dissociation.

Several alternative pressure coring systems have been developed in recent years such as the IODP Pressure Core Sampler (PCS), the HYACINTH Fugro pressure corer (FPC) and the HYACE Fugro rotary pressure corer (FRPC) [2]. All these systems allow recovery of a sediment core, under in situ hydrostatic pressures (PCS has a maximum hydrostatic pressure limit of 69MPa, the FPC and FRPC are limited to 25MPa). With the FPC and FRPC the core is contained in an inner plastic liner which allows the core to be transferred to other chambers for analysis.

The PCS was developed first and was first deployed on ODP Leg 131 [3] and successfully deployed on ODP Leg 164 on the Blake Ridge [4] to measure in-situ gas concentration from gas hydrate bearing sediment [5]. Unfortunately the PCS core barrel must be depressurized to get access to the sample and therefore no physical characterization of the sediment can be undertaken under in-situ pressure conditions, although recent modifications have allowed X-ray images to be obtained. The FPC and the FRPC were subsequently designed so that limited non-destructive testing of the sample could be undertaken at in-situ-pressures, but also the sample could be sub-sectioned for more detailed analysis, such as chemical and microbial analyses, at these in-situ pressures. All three systems have been deployed on numerous drilling programs such as the Ocean Drilling Program (ODP) Leg 204 [6], International Ocean Drilling Program (IODP) Expedition 311 [7]. Indian National Gas Hydrate Program (NGHP) 01 Expedition [1] with the FPC and RFPC also being deployed on the recent South Korean Ulleung Basin Gas Hydrate Expedition 1 (UBGH1) [8].

With the FPC and RFPC systems, once the tool is recovered to the surface the pressurized core barrel is transferred under pressure into the Geotek Pressure Core Analysis and Transfer System (PCATS) [9]. Geophysical properties of the intact sediment under hydrostatic pressure, as well as the spatial variation of the hydrate within a sample, can be determined using the MSCL-P (Multi Sensor Core Logger –Pressure) which is a component of the PCATS. This provides X-Ray images of the cores as well as detailed ultrasonic P-wave velocity and gamma density profiles. Additional physical properties have also been measured on cores retained under pressure using the Instrumented Pressure Testing Chamber [10], developed by Georgia Tech to interface with the PCATS. However at present, advanced laboratory apparatus currently in use for testing gas hydrate bearing sediments, such as tri-axial shear strength apparatus [11], or the Gas Hydrate Resonant Column (GHRC) apparatus [12] cannot directly interface with the core transfer system.

## SAMPLE DESCRIPTION

In total five sub-sectioned lengths of core were shipped to Southampton for proposed testing in the GHRC. Four sections of core came from Site No. NGHP-01-10B with a further section of core coming from Site NGHP-01-21C. Both sites were located in the Krishna-Godavari Basin on the Eastern Margin of India [1] in a water depth of 1049 metres below sea level.

Core NGHP-01-10B-08Y was recovered using the FPC corer with a total length of 86cm being recovered from a depth of 50.1 metres below sea floor (top of core). This core was notionally sub-sectioned into four lengths of 6-26cm, 26-46 cm, 46-66cm and 66-86cm for testing. Core NGHP-01-21C-02E was recovered using the RFPC corer with a total length of 110mm being recovered from a depth of 56.5 metres below sea floor (top of core). One section of the core from 23-46cm was sectioned for testing.

Both cores were rapidly depressurised and sub-sectioned, wrapped in aluminium foil, placed in a canvas bag prior to being stored in liquid nitrogen. The sub-sectioned samples were only exposed to atmospheric pressure for a maximum period of 90 seconds before freezing.

## X-RAY COMPUTED TOMOGRAPHY IMAGING

All X0ray images of frozen sample were obtained using a X-Tek Benchtop CT 160Xi which uses a 160kV, 60 Watt 'micro-focus' X-ray source. The X-rays are detected using a CMOS flat panel detector (1248x1248 pixels) with a maximum scan area of 100 mm x 100 mm. A movable stage allows the object to move closer to the X-ray source (and further from the detector panel) therefore increasing resolution down to a voxel size of 5 microns; however for samples of 100 mm voxel size is ~80 microns. With X-ray computer tomography computer software is able to compile a 3-dimensional image from a number of 2-dimensional X-ray images. With the X-Tek the object is rotated through 360° while X-ray images are acquired at set rotation angles. The quality of the 3-D X-ray CT scan, and the scanning time required, is dependent on numerous factors such as the number of rotation steps for one revolution, the number of X-ray shots per rotation step and time of exposure for each X-ray shot. To limit the scanning time required per core section (the sample would be out of the liquid nitrogen during CT imaging and would warm up, destabilizing the gas hydrate), the number of rotation steps, number of X-rays per step, and exposure time were set to 901, 1 and 2 ms, respectively producing a scan time of approx. 1hr. The use of a polystyrene container limited the rise in sample temperature, during the scan, from -196°C to -80°C, thus limiting any potential hydrate dissociation.

As part of the immediate post cruise analysis, X-ray CT scans were also obtained on various pressure cores whilst under in-situ pressure using a 16-slice Philips Mx8000 with a voxel resolution of ~ 0.5 mm. This was undertaken at the Gleneagles Hospital in Singapore. The scans conducted were obtained prior to the core being depressurised, sub-sectioned and stored in liquid nitrogen for future analysis.

### Hydrate structure

Figure 1 compares the raw X-ray images, obtained from a single shot scan at one rotation point for all samples obtained from core NGHP-01-10B-08Y, with those X-ray images obtained from onboard measurements in the MSCL-P for the same core before depressurization and

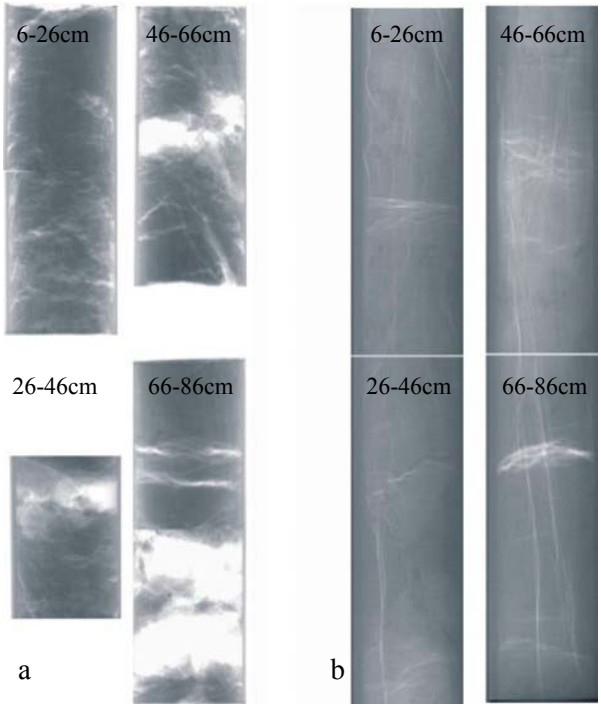


Figure 1. a) Single shot X-ray images of core sections for core NGHP-01-10B-08Y after freezing. b) X-ray images taken within the MSCL-P for the same core.

freezing. During preparation for the land based X-ray imaging the plastic core liner of each sub-section, where no sediment was evident, was trimmed. Therefore for sub-section 08Y-26-46 cm only ~ 8 cm of core was present.

The orientation of the cores during imaging for the two datasets are not similar therefore direct comparison of structure between the two datasets is not possible. It can be seen within both core sections horizontal and sub-vertical thin wispy lines throughout the core, which are inferred as veins of hydrate. The large white cloud-like areas, within the imaged core for Figure 1a, are the result of large voids within the core section, which is not evident in the MSCL-P X-ray images. This suggests that the depressurization and freezing cycle produced extensive voiding within the core either as a result of gas hydrate dissociation or the exsolving of gas from the pore water. Although not shown the section from core NGHP-01-21C-02E showed a similar pattern

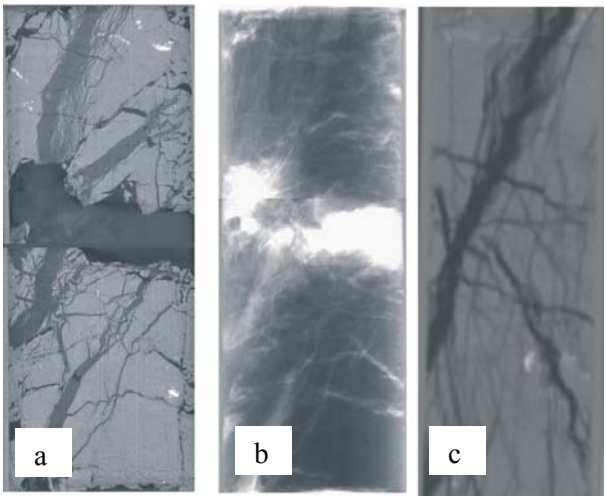


Figure 2. a) Vertical slice through centre of core section NGHP-01-10B-08Y-46-66 cm using X-Tek CT 160Xi. b) Single shot image for same core. c) Horizontal slice for core section using Phillips Mx8000.

The X-ray images presented in Figure 1 represent the average intensity of X-rays passing through the sample and so volumetric estimation of hydrate content or detailed structure of the hydrate is not possible. Figure 2a shows a vertical slice from the 3-dimensional X-ray CT scan for core section 46-66 cm of core NGHP-01-10B-08Y using the X-Tek CT 160Xi, computed using the 901 single shot X-rays from each rotation step. As the maximum size of sample imaged is only 100mm, the derived image is obtained by combining scans for the bottom half and top half of the section. Figure 2b is the single shot X-ray image for the same section, with Figure 2c obtained using the Phillips Mx8000 machine.

The CT scans in Figures 2a and 2c highlight greater detail of the structure of the gas hydrate, within the fine grained sediment, than evidenced using a single shot X-ray image (Fig 2b). The scan shows many predominantly near vertical hydrate veins, with many existing in sub-parallel groups. It is also apparent that there are more than one group of hydrate veins existing in this section of core. Within the core section occasional horizontal veins also exist which appear to be cross cutting the vertical veins.

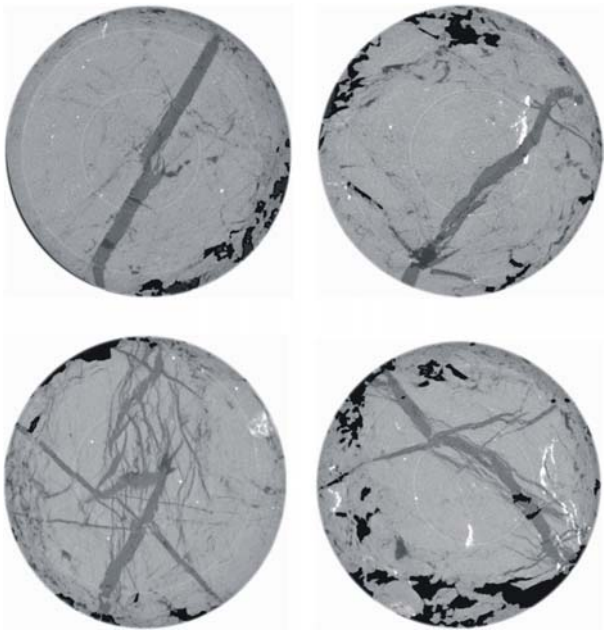

Figure 3. Horizontal slices through section core section NGHP-01-10B-08Y-6-26 cm using the X-Tek CT 160Xi.

The observations would support the hypothesis that hydrate formation in fine grained marine sediments can, at least sometimes, be dominated by fracturing of the sediment. The fracture initiation angle, assuming Coulomb criteria [13], would occur at a fixed angle (based on the friction angle of the sediment) perpendicular to the direction of principal stress (for normally consolidated sediment this can be

considered vertical). Therefore based on strength measurements undertaken on sediments from the same borehole [1] the fracture angle would be between 50° - 56° to the horizontal, which corresponds to many of the observed hydrate veins. As the principal effective stress may not always be vertical, due to such factors as increases in pore pressure during gas migration, tectonic activities, etc., the fracture angle will change and at the extreme can even become horizontal, as observed.

The hydrate growth pattern within the sediment suggests that hydrate formation may sometimes be episodic and occur under varying stress conditions. Figures 3 and 4 shows horizontal slices taken from the 3-dimensional X-ray CT scan for core section 6-26 cm of core NGHP-01-10B-08Y at different depths within the section using the X-Tek and Phillips X-ray CT, respectively. Due to the expansion of the core the slice position for the images in Figure 3 may not correspond with those in Figure 4, but are chosen based on the similarity of the hydrate pattern with those slices in Figure 4.

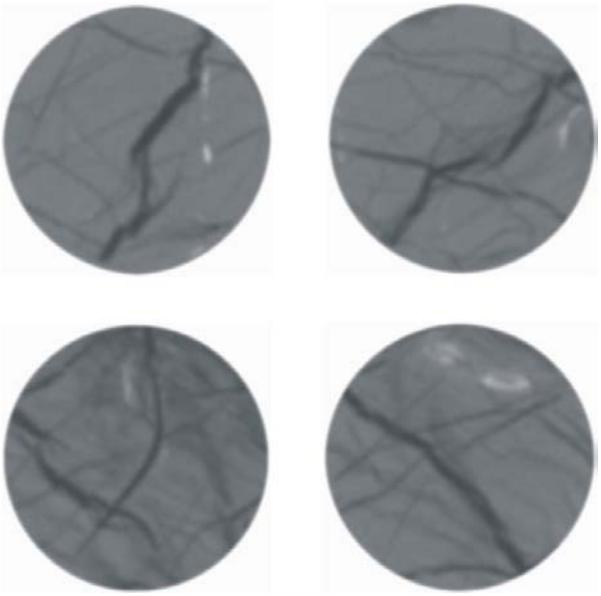

Figure 4. Horizontal slices through section core section NGHP-01-10B-08Y-6-26 cm using the Phillips Mx8000

It can be seen that although qualitative differences exist between the hydrate and sediment in Figure 3 & 4, as a result of the depressurization and subsequent freezing cycle, quantitatively both datasets show that the orientation of the hydrate veins and the number of veins alter significantly even in a short section of core. This suggests that the fracture mechanics of marine sediment induced by gas hydrate growth is very complex. The variability in volume and distribution of hydrate over a short distance will have major implications for hydrate quantification which are usually based on remote geophysical data or downhole resistivity data. The observations may lead to alternative models being developed for quantifying gas hydrate volume than are currently used.

Comparing Figures 2a & 2c and Figures 3 & 4 it can be seen that although there are minor differences between the orientations of hydrate veins between the two datasets, the volume of hydrate and number of hydrate veins appears similar. In fact the higher resolution X-Tek CT scans enables greater detail to be observed showing millimetric sized hydrate veins identified in the Phillips Mx8000 scan appearing to be formed of many sub-parallel hydrate veins. Figure 5 highlights the difference in resolution by comparing a section of a horizontal slice obtained from the 3-dimensional X-ray CT scan for core section 46-66 cm of core NGHP-01-10B-08Y. The upper scan is obtained from The X-Tek CT 160Xi scan whilst the lower image is from the Phillips Mx8000.

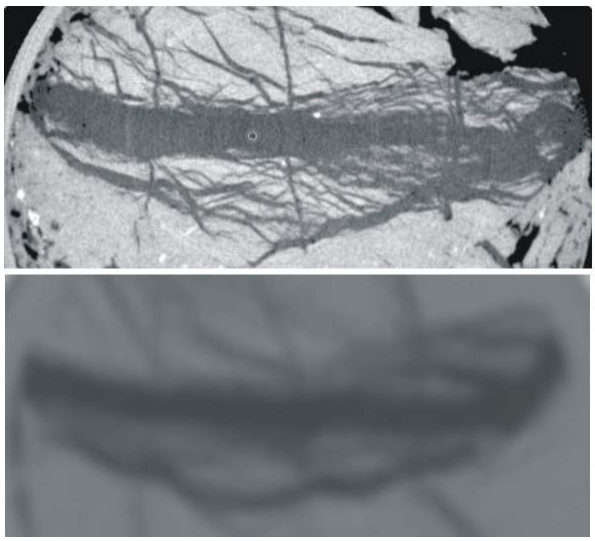

Figure 5. Comparison of scan resolution between the X-Tek derived scan (upper image) and that from the Phillips Mx8000 (lower image).

The multitude of sub-parallel veins in the high resolution image may suggest that these large veins are formed from many episodic events with

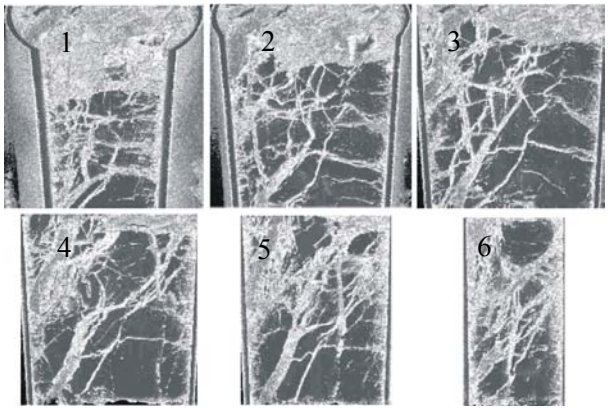


Figure 6. Sequence of vertical slices for the bottom of core section NGHP-01-10B-08Y-46-66 cm. Image 1 is obtained from the front of the section and numbered sequentially moving towards the back

Figure 7. 3-D X-ray CT scan for the bottom of core section NGHP-01-10B-08Y-6-26 cm.

future repeat fractures initiating between existing hydrate veins and the sediment. Changes in principal stress and the strength of the hydrate/sediment bond possibly give rise to subtle changes in the fracture angle leading to observed multiple veins. Close inspection of the fine vein structure also show that many veins have a limited lateral extent giving rise to a root like structure. The variability in structure of the hydrate veins within a core can be clearly seen in both Figure 6, which shows a sequence of different vertical slices taken from the 3-dimensional X-ray CT scan for the bottom part of core section NGHP-01-10B-08Y-46-66 cm, and Figure 7 showing a 3-D section for the bottom of core section NGHP-01-10B-08Y-6-26 cm. The slices in Figure 6 are taken at different distances from the front of the section, with the top left hand image (1) being the first slice near the front and moving sequentially towards the back.

**Sample disturbance**

It has been shown, through the X-ray images, that the depressurized and subsequently frozen core sections exhibit a large degree of disturbance when compared to the initial X-ray scans. This will have a major impact on interpreting the results of any physical testing that may be performed on these samples. Therefore, understanding the nature of the disturbance will help develop improvements to the handling sequence to help reduce this effect.

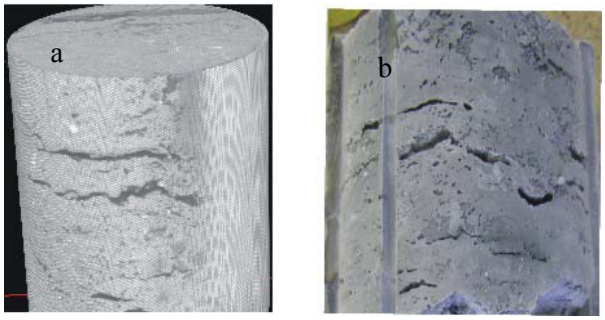


Figure 8. a) 3-D X-ray CT scan for section of core NGHP-01-10B-08Y-46-66 cm. b) digital image of same core section depicted in (a).

An important question is whether the disturbance of the sediment structure is related to hydrate dissociation or some other factor within the depressurization and subsequent freezing cycle. As can be observed in Figure 5, the fine veins of gas hydrate present in the initial image appears to survive the rapid depressurization. Although it is not possible to observe the difference between ice and hydrate in an X-ray image, due to them having similar density, subsequent dissociation tests on the hydrate bearing sediment produced significant volumes of methane gas. This would suggest that a large proportion of the gas hydrate survived being outside its stability region. This 'self-preserving' behaviour for gas hydrates, caused by the

endothermic nature of gas hydrate dissociation, is well known.

Considering the horizontal slices shown in Figure 3, it can be seen that the voids are predominantly located on the outside perimeter of the core section. Figure 8 shows a 3-D X-ray CT scan of a section of core NGHP-01-10B-08Y-46-66 cm alongside a digital image for the same core taken after the CT scan. The large vertical line in Figure 8b is caused by the disc blade when cutting away the plastic liner. Both images show the degree of surface disruption to the core, but also that they manifest themselves as horizontal fractures within the sediment. If dissociation of hydrate was a likely cause of the disruption, it would be expected that the depressurization induced fracturing would follow along the hydrate orientation, since the gas would be evolving along the surface of the hydrate leading to a weakened area at this interface, or migrating along this surface to a point of weakness. Figure 9 shows a vertical slice for the same section of core obtained from the 3-D CT scan. It can be seen clearly that the depressurization induced fracture is cross-cutting the gas hydrate vein and not following any hydrate fracture. There is also very little observable gas expansion zones located next to any hydrate veins. The lack of any gas forming at the interface of the sediment and hydrate would suggest that this interface is stronger than the normal sediment fabric. It can therefore be concluded that the sample disturbance is primarily caused by the expansion of free gas coming out of solution in the pore water, although some hydrate dissociation can not be discounted. This has major implications for laboratory testing of these sediments. The exsolving of gas during the pressure reduction leads to a porous material which is liable to collapse when any total stress is applied. Therefore alternative techniques must be developed to prevent wide spread sample disturbance occurring prior to testing

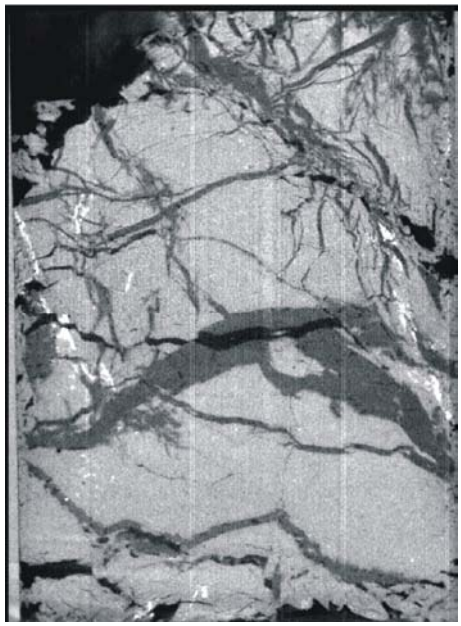

Figure 9. Vertical slice from 3-D X-ray CT scan for the bottom of core section NGHP-01-10B-08Y-46-66 cm. Large horizontal fracture cross-cutting gas hydrate vein can be observed in centre of image.

## CONCLUSIONS

This paper has reported on the structure of naturally occurring methane gas hydrate within fine grained sediments from cores recovered (under in-situ pressures) from the Krishna-Godavari Basin off the Eastern margin of India during the recent NGHP1 gas hydrate research cruise.

The in-situ structure of hydrate bearing sediments was observed using a range of different X-ray imaging system. Single scan 2-D X-ray images highlighted high angle, sub parallel veins within the recovered sediments. These were seen as white wispy clouds on the X-ray image. The use of 3-D computer tomography scans, which are able to show the internal structure of the core sections, highlighted a vastly more complicated structure than at first suggested by the 2-D scan. The observations from the CT scans showed that in this location gas hydrates occurred as fracture filling veins throughout the core. The hydrate veins were variable in thickness with many sub-parallel veins in any given group. It was also evident that more than one grouping of hydrates veins was present even in short sections of core. The fracture orientation was predominantly sub-vertical, although orientations were variable with occasional horizontal fractures being evident. High resolution CT scans where pixel resolution of 0.74mm could be obtained showed that some thick millimetric hydrate veins were composed of many, sub-millimetric veins with subtle variations in fracture angle. This suggests that hydrate formation was episodic in nature and subject to minor, although sometimes major, changes in the stress regime.

It was also observed that during rapid depressurization, and subsequent freezing using liquid nitrogen, the structure of the cores became heavily disturbed. Comparisons of hydrate volume and structure between the recovered cores under in-situ hydrostatic stress conditions and those once depressurized and frozen show that the reduction in pressure did not lead to wholesale dissociation of the hydrate veins. Instead, the expansion of gas coming out of solution, due to the reduction in total pressure was the most likely major cause for the disturbance. This observation suggests that physical characterization of gas hydrate bearing fine grained sediments can only be conducted whilst the core section remains under in-situ stress conditions if realistic values are to be obtained.

## ACKNOWEDGEMENTS

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