

# Oil & Natural Gas Technology

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## Topical Report

# Characterization of Methane Hydrate Bearing Sediments and Hydrate Dissociation Kinetics

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Pacific Northwest National Laboratory  
Richland, WA 99352

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## Project 45133

# NGHP-01 Hydrate Samples High-Pressure X-Ray Diffraction Results Letter Report October 2007

H. Todd Schaefer and B. P. McGrail  
Pacific Northwest National Laboratory

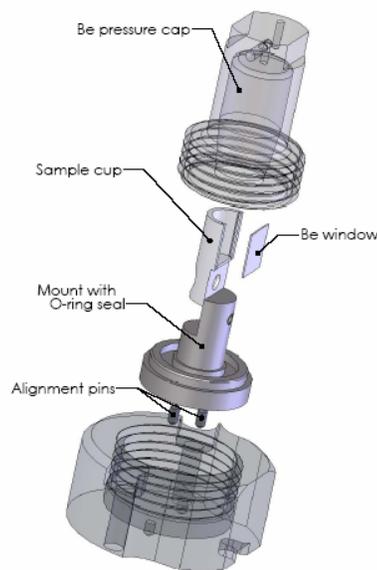
### Introduction

In this letter report, high-pressure x-ray diffraction (HXRDX) analyses were conducted on samples collected during the Natural Gas Hydrate Expedition 01 (NGHP-01) off the eastern coast of India. During the drilling operations, core samples were characterized by infrared imaging, allowing the identification of endothermic reactions associated with the dissociation of natural gas hydrate. Often these “cold spots” were isolated from the 10 m core by cutting out a 12 to 25 cm section and immediately preserving in liquid nitrogen (LN<sub>2</sub>) for post cruise analysis. Upon completion of NGHP-01, samples were shipped under cryo-conditions to PNNL for testing and characterization. As part of the post characterization activities, HXRDX was conducted to verify the presence of methane gas hydrate in the sediment and corresponding dissociation parameters such as pressure and temperature.

Gas hydrated sediment samples representing five separate boreholes were prepared for HXRDX. Some core samples contained visible signs of gas hydrate while others only displayed sediment color variations. The cores represented samples collected off the eastern coast of India in the Krishna-Godhavari Basin, Mahanadi Basin, and one location near the Andaman Islands. The objective of this study was to develop HXRDX techniques that can be used in examination of natural gas hydrate sediments under high pressure and sub-ambient temperatures.

### Experimental Setup and Cell Temperature Verification

Characterization of the hydrate core samples was accomplished with a Bruker-AXS Discover 8 x-ray diffraction (XRD) unit equipped with a custom built temperature stage (-110° to 225°C), rotating Cu anode (18 kW), and a real time 2-dimensional area detector. The instrument, designed to analyze gas hydrate samples under reservoir conditions, uses x-ray transparent high-pressure beryllium cells as pictured in Figure 1. The bottom portion of the cell and the insert are all composed of stainless steel or aluminum. A small window on the sample cup is either beryllium or Kapton. Rubber gaskets are used to seal between the beryllium pressure cap and the base. Pressurization is accomplished through the bottom of the cell. Initially the cell is chilled in an ice bath prior to placing a small

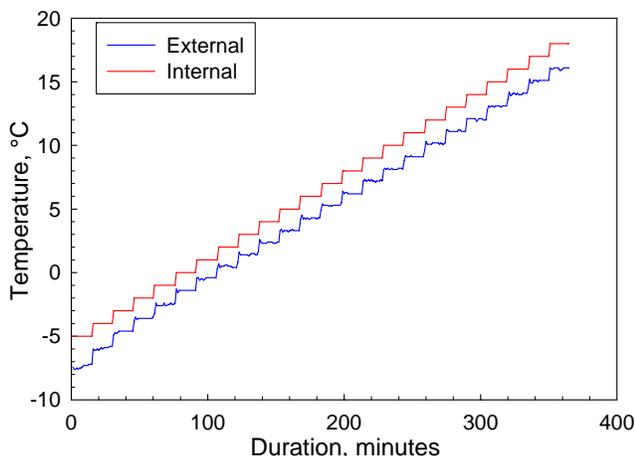


**Figure 1.** High-pressure XRD beryllium cell with internal sample cup.

piece of sediment inside the sample cup. Dry liquid nitrogen vapor is constantly allowed to flow over the sample cup to maintain cryo temperatures. The beryllium pressure cup is placed onto the cell before pressurization with CH<sub>4</sub>.

Verification of the internal temperature of the pressure cell, close to the sample cup, was also part of the instrument calibration process. Through prior observations of the unit, the cell temperature, which is measured externally in the top of the beryllium pressure cap (Figure 1), corresponded to the set point.

Internal cell temperature was verified by placing a micro transducer inside the pressure cell through the pressurization port. These tests were conducted under vacuum. Using the automated programming feature of the HXRD unit, the cell temperature was dropped to -5°C and increased by 1°C every 30 minutes up to 20°C while under vacuum (Figure 2). The internal temperature of the cell was determined to be 2°C lower than the temperature measurements taken externally in the top of the beryllium cell. Adjustments were made to the HXRD software changing the temperature set point for internal cell monitoring to compensate for the 2°C temperature offset.

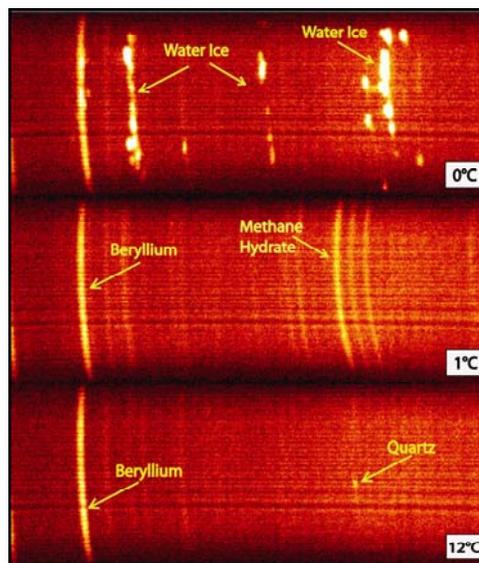


**Figure 2.** Temperature profile of beryllium cell.

### Standards Analysis

Synthetic methane hydrate with crushed quartz sand was used to establish cell alignment and instrument parameters such as stage height, cell orientation, exposure time, and beam energy requirements. Initially the holder was loaded with a small amount of finely ground quartz, creating a layer at the bottom of the sample cup (Figure 1), which was then filled with de-ionized water. By focusing the beam on the small layer of crushed quartz in the bottom of the sample cup, calibration of the cell position was established.

Methane hydrate was synthesized by adding water to the sample cup (Figure 1) and pressurizing the cell with CH<sub>4</sub> to 1000 psig while lowering the temperature to -2°C. After maintaining these conditions for several hours, cell temperature was increased to 0°C and HXRD analysis revealed the formation of coarse grained water ice, as shown in the top of Figure 3. The primary reflections associated with hexagonal water ice, detailed in PDF # 16-0687, were detected in the pattern collected at 0°C and are marked in Figure 3. Increasing the cell temperature to 1°C destroyed water ice and revealed reflections for methane hydrate, which are identified in the middle of Figure 3. Powdered diffraction data for a structure I (sI) methane hydrate provided by (BERTIE and JACOBS, 1982) includes reflections at 25.99° (I=35%), 27.08° (I=55%), and 28.12° 2θ (I=100%), which match reflections on the pattern collected at 1°C (Figure 3). The presence of sII clathrate



**Figure 3.** HXRD scans collected of synthetic methane hydrate at three temperatures (0°, 1°, and 12°C) and a pressure of 1000 psig.

hydrate in a sample is difficult to ascertain due to similar diffraction tracings between the sI and sII clathrate hydrates. Although sI clathrate hydrates are most common, there is some evidence for the existence of sI and sII clathrate hydrates coexisting in nature (HALPERN et al., 2001). Reflections produced by the beryllium cell are positioned at high  $2\theta$  and did not interfere with the analysis (Figure 3). Complete dissociation of methane hydrate occurred at  $10^{\circ}\text{C}$ . The primary reflection for quartz ( $26.64^{\circ} 2\theta$ ) was detected; no reflections corresponding to methane hydrate were observed above  $10^{\circ}\text{C}$ . A dissociation temperature observed via the HXRD corresponds almost exactly with the equilibrium temperature for  $\text{CH}_4$  hydrate of  $10.1^{\circ}\text{C}$  at 7 MPa pressure (1000 psig).

### High Pressure X-Ray Diffraction Results

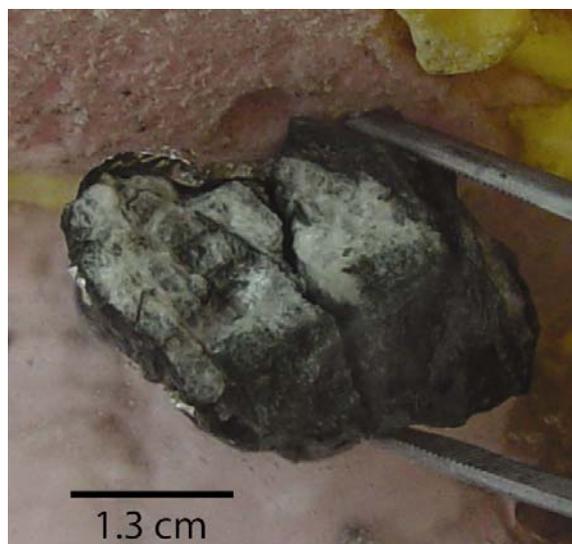
Sample collection protocol during India's NGHP-01 was designed to identify and preserve hydrated sediment during core retrieval. After arrival on the catwalk, typically each 10 m core was positioned in the core rack and imaged by scanning infrared cameras. Computer displays positioned throughout the catwalk allowed researchers to identify areas of the core thermally altered by dissociation of gas hydrate as the analysis was ongoing. These regions, often 10's of centimeters in length, were removed and preserved in  $\text{LN}_2$  as 5cm whole rounds. Following the conclusion of NGHP-01, core samples were provided to eight research institutions. Pacific Northwest National Laboratory received nine cryo-preserved natural gas hydrate samples, which are listed in Table 1 along with the corresponding borehole, depth (mbsf), and type of sediment. Out of the five boreholes represented in the sediment samples (Table 1), three different types of hydrated sediment are identified: 1) massive hydrate nodules or vein fill (M), 2) hydrate disseminated in fine sand or silt (DS) and 3) hydrate disseminated in volcanic ash (DA). Each sample was photographed and sub-sampled prior to characterization by HXRD.

Initially, NGHP-01 hydrate sample 11, representing core 10B at 42 mbsf, was dissected under liquid nitrogen ( $\text{LN}_2$ ), exposing laminated layers of gas hydrate (white) in dark fine grained sediment (Figure 4). Gas hydrate crystals were readily visible and easily discernable from the dark host sediment. Two separate types of samples were prepared, a bulk unaltered sample and one that was crushed. To conform to the Be-

**Table 1.** Natural gas hydrate samples collected during India's NGHP-01 and preserved in  $\text{LN}_2$

Sample ID	Borehole	Depth mbsf	Type
11	10B	42	M
27	10B	93	M
32	10B	113	M
45	10D	45	M
57	10D	65	M
94	14A	103	DS
113	17A	465	DA
122	17A	588	DA
126	21A	75.7	M

M-massive, DS-disseminated in sand or silt  
DA-disseminated in volcanic ash

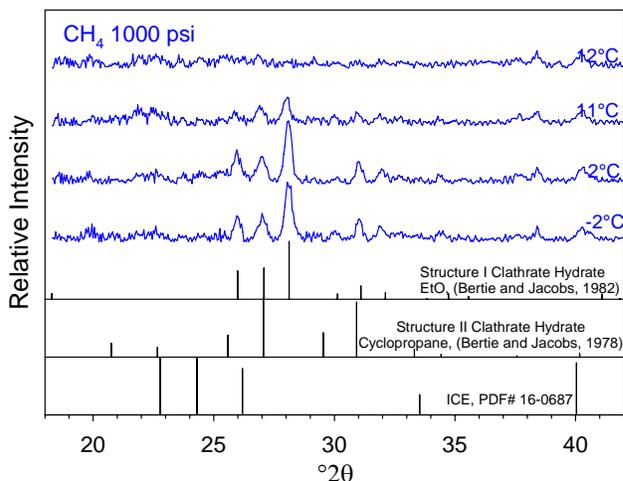


**Figure 4.** Core sediment sample 11, collected from Borehole NGHP-01-10B at 42 (mbsf) showing thin layer of natural gas hydrate.

hydrate bearing sediment was selected to fit inside the sample cup (Figure 1). The gas hydrate bearing portion of the sample was positioned flat against the beryllium window, allowing for maximum exposure to the x-ray beam. Additionally, more gas hydrate rich pieces of sediment (sample 11) were transferred under LN<sub>2</sub> to a mortar and pestle containing LN<sub>2</sub>, and crushed to a fine powder, then later transferred into the sample cup for analysis. After samples (bulk or crushed) were placed into sample cups (under LN<sub>2</sub>), they were inserted into the pre-chilled beryllium pressure cell, the cell was evacuated under vacuum, and then pressurized with CH<sub>4</sub> to 1000 psig. Initially, scans were collected at -2° to 12°C at 1°C increments for 200 seconds with a range of 7 to 42° 2θ. Sample temperature was equilibrated for one hour prior to data collection. During the analysis, methane gas pressure was held constant at 1000 psig.

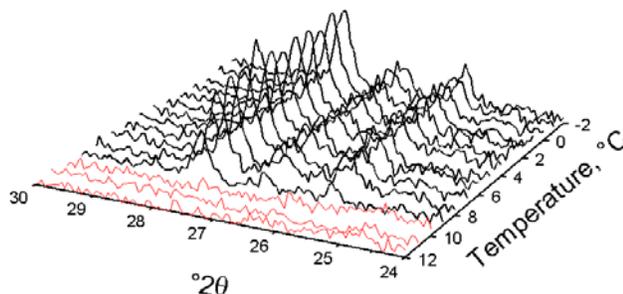
Select results from the HXRD analysis of bulk gas hydrate sediment from borehole NGHP-01-10B are presented in Figure 5 and for comparison, representative diffraction graphs of water ice (PDF# 16-0687), structure I (sI) clathrate hydrate (Bertie and Jacobs, 1982), and structure II (sII) clathrate hydrate (Bertie and Jacobs, 1978) are shown. The initial scan, collected at -2°C, shows no evidence of water ice but only sI clathrate hydrate. The primary reflections for sI methane hydrate are positioned at 25.99°, 27.08°, and 28.12° 2θ. As the temperature increased (1°C per 30 minute), primary hydrate reflections remained constant in position and intensity. Peak intensity appeared to decrease as the temperature approached 11°C. Reflections corresponding to methane hydrate completely disappeared at 12°C, indicating dissociation of sI clathrate. No other reflections were observed at temperatures above 12°C (Figure 5).

Similar high-pressure XRD results for sample 11 were obtained from the technique utilizing crushed sediment. Structure I clathrate hydrate was identified as the primary crystalline material in sample 11 at temperatures between -2° and 11°C. Water ice was also detected in the sample, but not significantly and was likely related to the sample preparation. Results from both types of sample mounts showed the sediment did not contain reflections above 11°C. Additional HXRD scans were collected from two other locations on core sample 11. The temperature range was between (-2° to 13°C) and CH<sub>4</sub> gas pressure was held constant at 1000 psig. Complete dissociation of methane gas hydrate in the sample occurred above 11°C each time. Similar HXRD results were obtained from sediment sample 27, which was collected at a depth of 93 mbsf in the same borehole (NGHP-01-10B).



**Figure 5.** XRD Results from sediment sample #11 (NGHP-01-10B) with stick graphs of water ice (PDF# 16-0687), structure I clathrate hydrate (BERTIE and JACOBS, 1982), and structure II clathrate hydrate (BERTIE and JACOBS, 1978).

From the same borehole, NGHP-01-10B, a small piece of hydrated sediment representing 113 mbsf was extracted from sample 32. The whole round core was broken during sample handling exposing a small vein of brownish grey gas-hydrate rich layer. Unlike previous samples, this one contained hydrate that was discolored and appeared as distinct individual gas hydrate layers. Visual observations were difficult in the presence of LN<sub>2</sub> and a thorough examination of the sample was not feasible. After careful selection, a small sample was loaded into the chilled beryllium cell and pressurized. Parameters used during the HXRD were -2° to 12°C at a constant CH<sub>4</sub> pressure of 1000 psig. The HXRD results are summarized in Figure 6 as a function of temperature. Only methane gas hydrate was detected at -2°C; reflections corresponding to water ice were not detected. Intensity for reflections associated with sI clathrate hydrate decreased slightly at higher temperatures (9°C), before completely disappearing at 10°C. Some evidence of partial dissociation was observed at 8°C and 9°C.



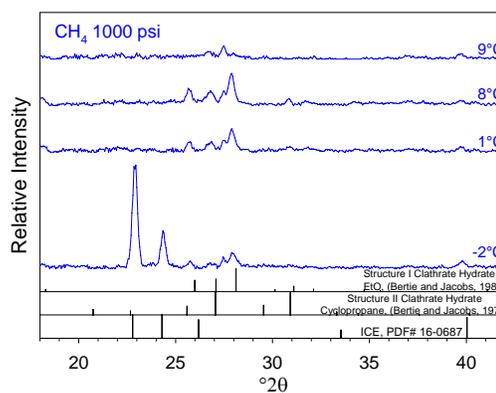
**Figure 6.** HXRD of sample 32 (NGHP01-10B) collected from -2° to 12°C at a constant CH<sub>4</sub> gas pressure of 1000 psig.



**Figure 7.** Partial sample from whole round core (sample 57), collected from borehole NGHP-01-10B (65 mbsf) and preserved in LN<sub>2</sub>.

Located in the KG basin next to borehole NGHP-01-10B was borehole NGHP-01-10D, which is represented by two sediment samples: 45 and 57 (Table 1). Core sediment from depths of 45 mbsf (45) and 65 mbsf (57) were sub-sampled under LN<sub>2</sub>. Displaying an abundant amount of vein filled gas hydrate, sediment sample 57 was an excellent choice for HXRD. Shown in Figure 7 is part of the core that split open during examination, revealing a delicate layer of gas hydrate. Although the layer is thin, it does appear to occur in a vein dissecting the core. Additional laboratory testing indicates sample 57 is 52% water.

Small pieces of sediment were easily removed for analysis. Confirmation of methane gas hydrate was obtained by HXRD for both samples, 45 and 57. Results indicated minor differences in sample 45 compared to sample 57 and samples from nearby borehole NGHP-01-10B. The thermal dissociation limit measured for sample 45 appears slightly lower, by as much as 2°C. For example, HXRD showed complete dissociation of gas hydrate in sample 45 after increasing the temperature above 8°C (Figure 8). No reflections were observed corresponding to gas hydrate sI in sample 45 above 8°C. Note in Figure 8 the large reflection at 22.78° 2θ, which is the primary reflection associated with water ice. The



**Figure 8.** HXRD results collected from sample 45 (NGHP-01-10D, 45 mbsf) over a range of temperatures (-2° to 9°C) and constant CH<sub>4</sub> pressure of 1000 psig.

presence of water ice indicates partial dissociation of the gas hydrate prior to preservation in LN<sub>2</sub>. These HXRD results were typical for sample 45 as well.

Representing borehole NGHP-01-14A is sample 94, collected 103 mbsf and classified as having gas hydrate disseminated in sand and silt. Physically, the core sample appears homogeneous and fine grained. No textural features were noted during sub-sampling for HXRD. Results collected from -2° to 13°C at 1000 psig of CH<sub>4</sub> contain no reflections for methane gas hydrate. Minor amounts of quartz were detected during the HXRD analysis, which supports the earlier classification of sand or silt. A number of sub-samples were examined by HXRD and no methane gas hydrate was detected. Factors such as gas hydrate concentration, sub-sample location,

and core handling times on the catwalk should be considered as an explanation for not detecting methane gas hydrate in this sample.

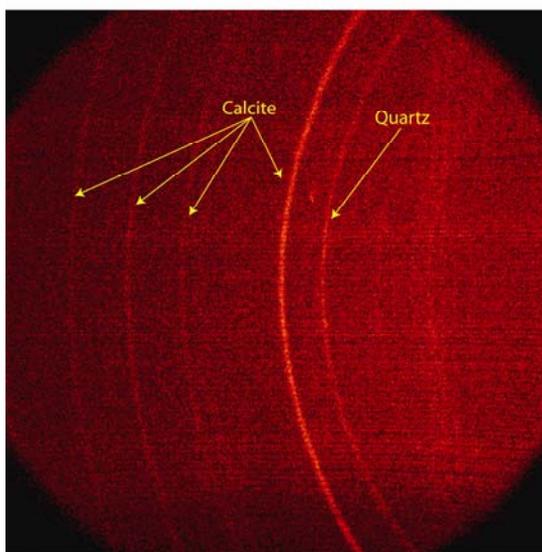
Cored sediment retrieved from borehole NGHP-01-17A was designated as ash with disseminated gas hydrate. Two samples, 113 (465 mbsf) and 122 (588 mbsf), represent some of the deepest sediment samples collected during NGHP-01 (Table 1). No visible difference was noted between the two samples. Both cores appeared green and homogeneous; no visible signs of gas hydrate (Figure 9). Moisture content, ~50%, was similar for both samples. At room temperature the samples appeared waxy and fine grained, very similar to smectite, a sheet layer clay mineral.

Bulk powder XRD shows calcite as the dominant crystalline phase along with minor amounts of quartz (Figure 10). Calcite reflections (23.05, 29.40°, 35.97°, 39.40°, 43.16° 2θ) observed in the pattern matched to calcite PDF# 47-1743. A single weak reflection at 26.64° 2θ was assigned to quartz, based on quartz PDF# 46-1045. No reflections associated with clay minerals were detected. However, bulk powder mounted sample techniques are not typically valid for detection of clays, especially swelling clays such as smectite.

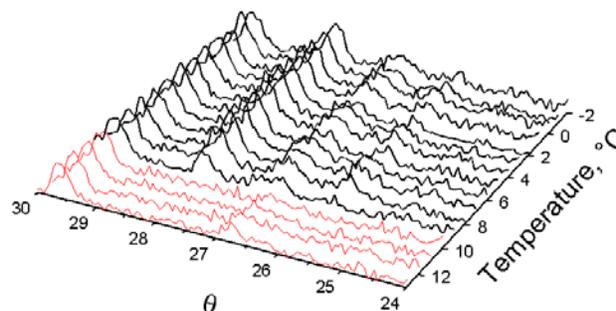
Examination of sample 122 (NGHP-01-17A, 588 mbsf) by HXRD confirmed the presence of methane gas hydrate (Figure 11). As with previous scans, sample 122 was analyzed over the temperature range -2° to



**Figure 9.** Whole round core, samples 122, collected from borehole NGHP-01-17A (588 mbsf) and preserved in LN<sub>2</sub>.

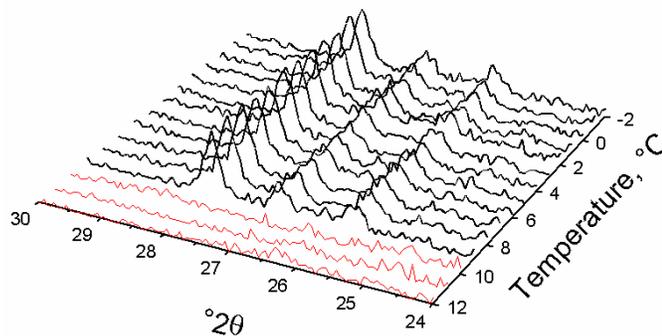


**Figure 10.** Bulk powdered XRD results collected from sample 122 (NGHP-01-17A, 588 mbsf) at room temperature and atmospheric pressure.



**Figure 11.** HXRD of sample 122 (NGHP-01-17A) collected from -2° to 13°C at a constant CH<sub>4</sub> gas pressure of 1000 psig.

13°C while under a constant pressure (1000 psig) with CH<sub>4</sub> gas. Reflections positioned at 25.99°, 27.08°, and 28.12° 2θ, were assigned to sI clathrate hydrate (Figure 11). The primary reflection corresponding to calcite (29.40°2θ) was detected throughout the entire temperature range (-2° to 13°C).



**Figure 12.** HXRD of sample 126 (NGHP-01-21A) collected from -2° to 12°C at a constant CH<sub>4</sub> gas pressure of 1000 psig.

Core material collected from borehole NGHP-01-21A was categorized as containing nodules and vein filling gas hydrate. However, during sub-sampling of sample 126, very little gas hydrate was visibly evident. The whole round core, measuring 25 cm in length, was broken into several pieces revealing a fresh center with minor amounts of localized gas hydrate. From these small areas, several slivers were selected for HXRD. Scans were collected as described previously. Figure 12 shows tracings collected at different temperatures (-2° to 12°C) while maintaining a constant CH<sub>4</sub> pressure of 1000 psig. Three primary reflections were detected originally at -2°C. Positioned at 25.99°, 27.08°, and 28.12° 2θ were reflections consistent with sI clathrate hydrate. By increasing the cell temperature from -2° to 12°C, 1°C every 30 minutes, a complete thermal dissociation profile of gas hydrate in sample 126 was developed (Figure 12). As the sample temperature increased from 9°C to 10°C, all detectable methane gas hydrate dissociated, apparent by the absence of reflections 10°C (Figure 12). No other reflections were detected during the analysis.

## Conclusion

Deep marine core sediments collected during the NGHP-01 Expedition (summer 2006) were examined by HXRD. Core samples, representing five boreholes from two basins off eastern India were preserved in LN<sub>2</sub> shipboard. As part of an extended research team, PNNL was selected to conduct basic characterization activities on several of these sediment samples post cruise. A variety of core samples were received at PNNL representing three forms of gas hydrated sediment: 1) nodules and vein filling, 2) disseminated in sand and silt, and 3) disseminated in volcanic ash. Successful development of a high-pressure beryllium cell designed to accommodate temperature sensitive samples, made it possible to examine natural gas hydrated sediment by XRD. Most importantly, this type of in situ measurement most closely emulates reservoir conditions for gas pressure and formation temperature.

Each sample was visually examined under LN<sub>2</sub>, photographed, and sub-sampled. Subsequent examination by HXRD confirmed the presences of natural gas hydrate in each core sample, with the exception of sample 94 (NGHP-01-14A). Identification of gas hydrate was determined by comparing HXRD results with published sI clathrate hydrate from Bertie and Jacobs, (1982). Synthetic methane gas hydrate was characterized and used as a comparison pattern. Hexagonal water ice was also identified on several samples, but was notably absent in most hydrate sediments examined. Thermal stability limits were measured for each sample and ranged between 8°C and 11°C while under a constant CH<sub>4</sub> pressure of 1000 psig.

## References

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## **National Energy Technology Laboratory**

626 Cochrans Mill Road  
P.O. Box 10940  
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road  
P.O. Box 880  
Morgantown, WV 26507-0880

One West Third Street, Suite 1400  
Tulsa, OK 74103-3519

1450 Queen Avenue SW  
Albany, OR 97321-2198

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