

2. OCCURRENCE, STRUCTURE, AND COMPOSITION OF NATURAL GAS HYDRATE RECOVERED FROM THE BLAKE RIDGE, NORTHWEST ATLANTIC¹

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ABSTRACT

Ocean Drilling Program (ODP) Leg 164 recovered a number of large solid gas hydrate from Sites 994, 996, and 997 on the Blake Ridge. Sites 994 and 997 samples, either nodular or thick massive pieces, were subjected to laboratory analysis and measurements to determine the structure, molecular and isotopic composition, thermal conductivity, and equilibrium dissociation conditions. X-ray computed tomography (CT) imagery, X-ray diffraction, nuclear magnetic resonance (NMR), and Raman spectroscopy have revealed that the gas hydrates recovered from the Blake Ridge are nearly 100% methane gas hydrate of Structure I, cubic with a lattice constant of $a = 11.95 \pm 0.05 \text{ \AA}$, and a molar ratio of water to gas (hydration number) of 6.2. The $\delta^{18}\text{O}$ of water is 2.67‰ to 3.51‰ SMOW, which is 3.5‰–4.0‰ heavier than the ambient interstitial waters. The $\delta^{13}\text{C}$ and δD of methane are –66‰ to –70‰ and –201‰ to –206‰, respectively, suggesting that the methane was generated through bacterial CO_2 reduction. Thermal conductivity values of the Blake Ridge hydrates range from 0.3 to 0.5 W/(m·K). Equilibrium dissociation experiments indicate that the three-phase equilibrium for the specimen is 3.27 MPa at 274.7 K. This is almost identical to that of synthetic pure methane hydrate in freshwater.

INTRODUCTION

Natural gas hydrate was suspected to occur extensively in hemipelagic sediments of the Blake Outer Ridge on Deep Sea Drilling Project (DSDP) Leg 11 (Hollister, Ewing, et al., 1972). Since then marine gas hydrate has been attracting a growing interest in the field of geosciences as well as in resource industries. Enormous amounts of hydrocarbon gases are expected to be trapped in gas hydrates in marine sediments, and dissociation of gas hydrates could possibly cause a sudden and dramatic change in the environment of the earth. Natural gas hydrate samples have been recovered from a number of deep-sea sites by DSDP and Ocean Drilling Program (ODP) drilling (e.g., Kvenvolden and Barnard, 1983; von Huene, Aubouin, et al., 1985; Westbrook, Carson, Musgrave, et al., 1994) and from surface sediments of marginal seas and inland seas by Brooks et al. (1991), Ginsburg et al. (1993), and others. However, our knowledge of fundamental properties of natural gas hydrate, including the composition of gas and water, molecular ratio of gas to water, structure, and crystallography is surprisingly low because of the scarcity of well-preserved gas hydrate samples. During ODP Leg 164, a number of gas hydrate samples were recovered from three locations—Sites 994, 996, and 997 on the Blake Ridge. Upon recovery, the gas hydrate samples were carefully cut and collected from the sediment cores on the catwalk and stored either in pressure vessels or in liquid nitrogen

for shore-based experiments and later transported to Tokyo by air. Hydrate samples were often observed as small fragments contained in highly disturbed sediment cores and were collected in bulk phase, but a large, nearly pure, hydrate sample from Site 997 was collected from whole-round cores.

The samples were first measured by X-ray computed tomography (CT) imagery at the Technology Research Center (TRC) of Japan National Oil Corporation (JNOC). Nuclear magnetic resonance (NMR) measurements were carried out on crushed/powdered hydrate samples at Research Center of Japan Petroleum Exploration (JAPEx) in January 1996. Water and gas from selected samples were analyzed for molecular and isotopic composition at Tokyo University and JAPEx. Well-preserved samples were sent to Hokkaido University for the low-temperature, X-ray diffraction analysis and to Hokkaido National Industrial Research Institute (HNIRI) for Raman spectroscopy in August 1996. Also, thermal conductivity was measured at the Fundamental Research Laboratory (FRL) of Osaka Gas and the equilibrium dissociation experiment was conducted at Frontier Technology Research Institute (FTRI) of Tokyo Gas from August through October of 1996.

The results of this series of analyses and measurements are reported in this article. These data improve our ability to estimate the amount of gas hydrate trapped in sediments and to quantify the potential importance of marine gas hydrate as a future natural gas resource.

OCCURRENCE OF GAS HYDRATE AT THE BLAKE RIDGE

ODP Leg 164 drilled holes at seven sites on the eastern margin of the United States and recovered a number of massive gas hydrate samples from Sites 994 and 997 on the Blake Ridge and from Site 996 on an active vent on the Blake Ridge Diapir (Fig. 1). Blake Ridge hydrates were white, lucent, solid materials of a few centimeters to more than 35 cm in length, whereas those from the diapir site occurred as fizzing and friable veins, a few millimeters thick and >10 cm long, filling nearly vertical to inclined fractures (Paull, Matsumoto, Wallace, et al., 1996). After a brief inspection (<10 min.) on the

¹Paull, C.K., Matsumoto, R., Wallace, P.J., and Dillon, W.P. (Eds.), 2000. *Proc. ODP, Sci. Results*, 164: College Station, TX (Ocean Drilling Program).

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ODP Leg 164 (Gas Hydrate Drilling)

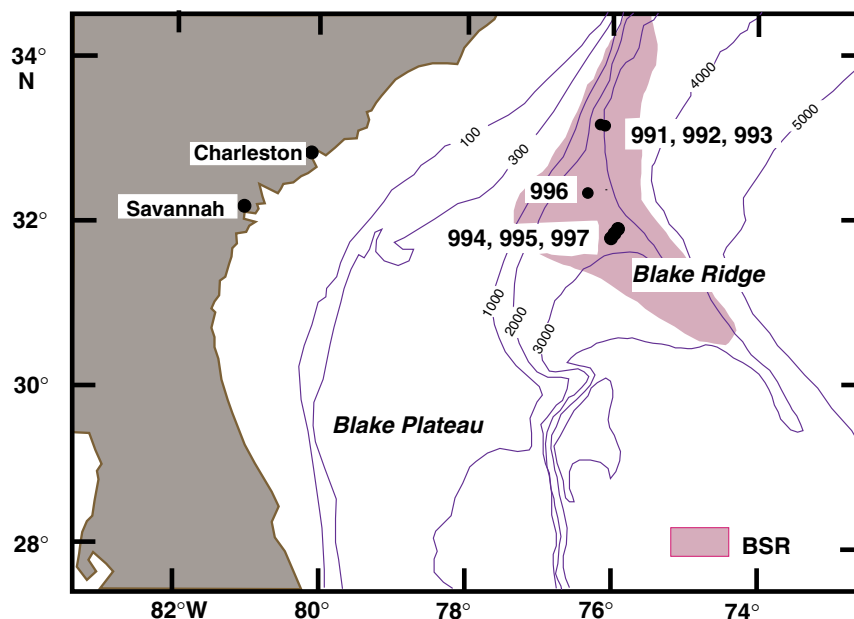


Figure 1. Map showing the locations of drilling sites on Leg 164. Shaded area represents the inferred distribution of BSR.

catwalk, solid gas hydrate were removed or cut from the sediment cores, transferred to Parr Pressure vessels, and stored in a freezer of -20°C . The pressure vessels were shipped to Tokyo by air cargo from Miami within 36 hr after the end of the cruise.

In this report, two samples from Site 994 and three samples from Site 997 were subjected to analysis and measurements. These samples were selected as the best preserved after more than two months storage in pressure vessels at $<-20^{\circ}\text{C}$.

Catwalk Observations

Gas hydrate samples provided for the present study were retrieved from nannofossil-rich clay at a sub-bottom depth of 260–330 m, about 200–120 m above the BSR.

Sample 164-994C-31X-7, 15–18 cm (259.90–260.30 mbsf)

Five large pieces of white, irregularly shaped nodules with soapy luster were observed to be embedded in nannofossil-rich clay in interval 164-994C-31X-7, 10–50 cm (259.90–260.30 mbsf). Samples were stored in two pressure vessels—1A and 2A. A broken appearance of hydrate samples and disturbance of the host sediments suggest that the recovered samples were part of the original subsurface gas hydrate layer that was broken into pieces during coring and recovery. The sediment cores in this section were slightly soupy, suggesting dissociation of gas hydrate during coring/recovery. Occurrence of massive gas hydrate from this horizon seems to correspond to the zone of anomalously high electric resistivity in interval 220–260 mbsf (Paull, Matsumoto, Wallace, et al., 1996).

Sample 164-997A-42X-3, 20–55 cm (330.20–330.55 mbsf)

A number of large pieces of massive gas hydrate were recovered from Section 164-997A-42X-3 at 330.03–331.17 mbsf. This section was anomalously cold, white-colored, and actively bubbling. After splitting the plastic core liner, an approximately 50-cm-long hydrate-bearing piece of sediment was revealed (Fig. 2). The top 30 cm of this section contained 10–15 angular fragments of white, fizzing hy-

drates, within 3–10 cm across, in drilling disturbed nannofossil-rich clay. The next interval appeared to consist of solid gas hydrate, ~ 6 cm in diameter and 30 cm in total length, which was broken into three pieces, 5, 7, and 15 cm in length (Fig. 3). Collected samples were stored in four pressure vessels—14, 16A, 16B, and 16C. Sample 16A was taken from the first 5-cm-long piece and 16B and 16C from the second 7-cm-long piece. The surfaces of these solid gas hydrate pieces were coated by a thin (<1 mm), transparent, shiny layer of freshwater ice. The interval contained rectangular fragments of gas hydrate in slightly soupy, disturbed clay. Well-logging conducted in Hole 997B, about 25 m northeast of Hole 997A, showed a resistivity anomaly at 360–365 mbsf, 30–35 m deeper than the thick, massive gas hydrate horizon (Paull, Matsumoto, Wallace, et al., 1996). This data suggests that the gas hydrates are not horizontal but slightly inclined with respect to the bedding plane.

X-Ray CT Imagery

Analyses of methane hydrate by the X-ray CT scanner is useful for recognizing occurrences of gas hydrate in sediments and its relationship to the surrounding host sediments without any disturbance to the gas hydrate samples.

Experimental Methods

A core plug sample, 1-in diameter, was cored from the large gas hydrate sample (Sample 164-997A-42X-3, 25–35 cm) by means of a desktop core driller and was subjected to X-ray CT imagery. The X-ray CT images were measured by the Toshiba X-ray CT scanner “X-force” of Technology Research Center of JNOC. Because the analyzing system was originally designed for medical use for human subjects, the system was slightly modified for observation of sediment/rock samples. Whereas the resolution of images is $350\ \mu\text{m}^2/\text{pixel}$ and 1 mm in thickness due to the low output voltage of 130 kV, 50 profiles were obtained within 3 min., which benefits the observation of gas hydrate.

The hydrate samples were first placed in an aluminum container, pressurized by helium and cooled down by dry ice, then placed in the

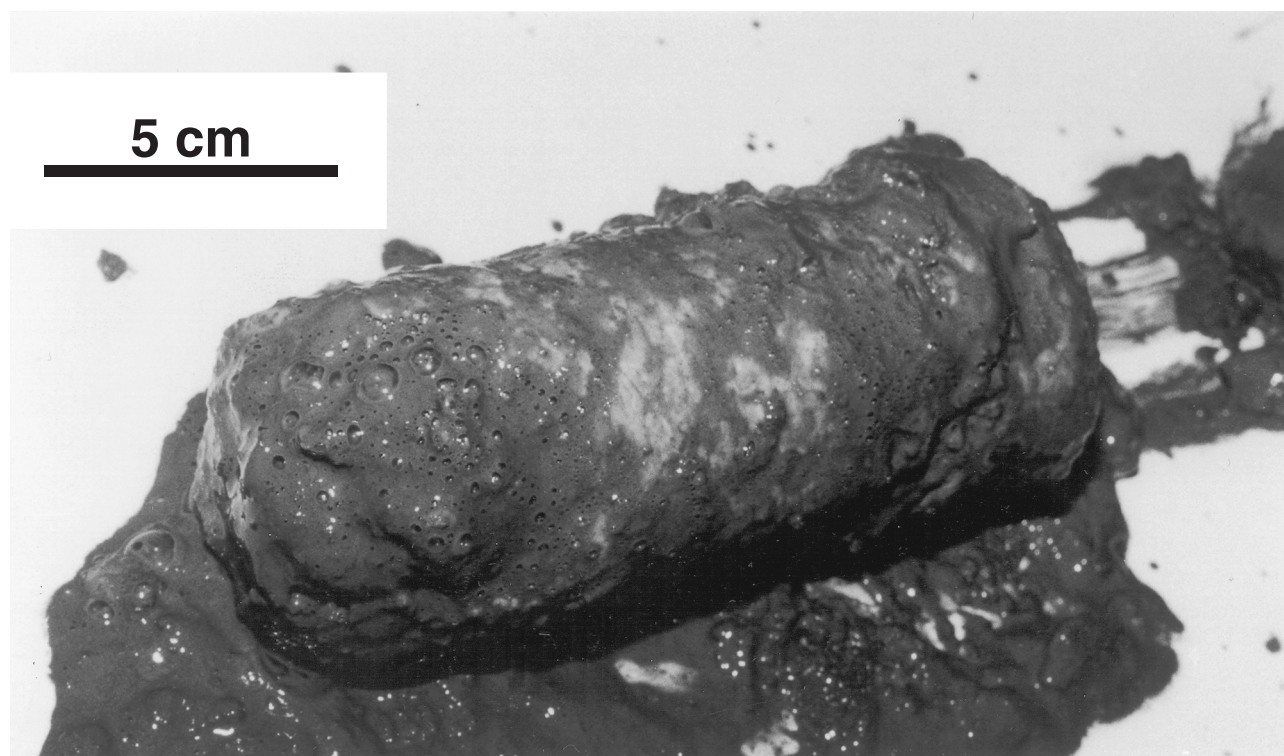
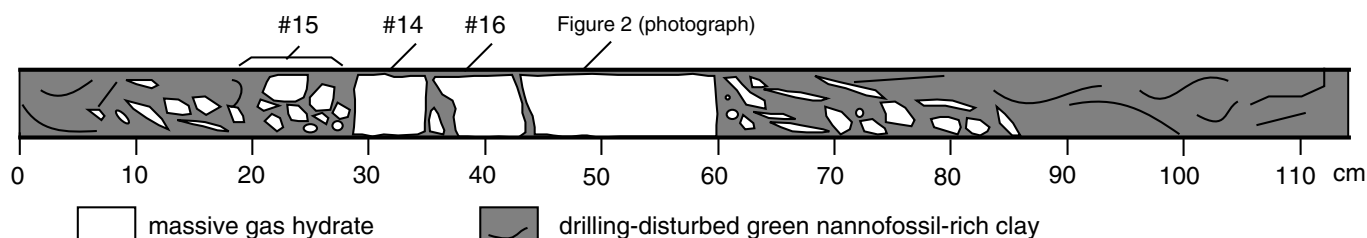


Figure 2. Photograph of a nearly pure, solid sample of gas hydrate (Sample 164-997A-42X-3, 5–14 cm; 331 mbsf).

Section 164-997A-42X-3, 0-114cm (329.9 - 331.4 mbsf)



X-ray CT equipment. Although we can observe hydrate in an aluminum vessel, CT images of gas hydrate samples were directly measured without an aluminum container to obtain stronger images. For comparison, freshwater ice and dry ice were also measured simultaneously.

Results and Implications

Figure 4 shows the X-ray CT imagery of methane hydrate-bearing sediments. Significant difference in CT values among methane hydrate, sediment, water ice, dry ice, and an acrylic tube are represented by color changes. Methane hydrates appear as blue and yellowish blue to light blue, although the CT values are not highly homogeneous and range from -100 to -250 , whereas water ice is shown as yellow (CT value = -65). Although the boundaries between sediments (red) and methane hydrates (light-blue) show yellow, they are not considered to designate water ice but the boundary effects. The histogram in Figure 5 depicts the distribution of CT values for meth-

ane hydrate, dry ice, and freshwater ice. Sediments are represented by red and yellow, whose CT values are around 1000. Dry ice is shown as pink (CT value = 400), and an acrylic tube is as orange (CT value = 140). Figure 4B is an enlarged picture of a portion of Figure 4A showing a nodular methane hydrate in sediments.

Shape, occurrence, and textural relation to surrounding host sediments of natural gas hydrate are easily recognized by the X-ray CT scanner. Figures 4B and 4C appear to indicate that hydrate forms nodules and veins in the host sediments. Measured CT values don't have units, and chiefly depend on the X-ray absorption coefficient of a substance. Because X-ray CT values eventually depend on the density of a substance, and the densities of liquid water ($d = 1.000$), freshwater ice ($d = 0.917$), and methane hydrate ($d = 0.91$) are nearly the same, it has been believed that methane hydrate would not be distinguished from freshwater and freshwater ice by X-ray CT imagery. However, the CT values of these substances are observed to be 0 (zero), -65 , -100 to -250 , respectively. As a result, natural methane hydrate can be clearly distinguished from freshwater ice and freshwater on CT images.

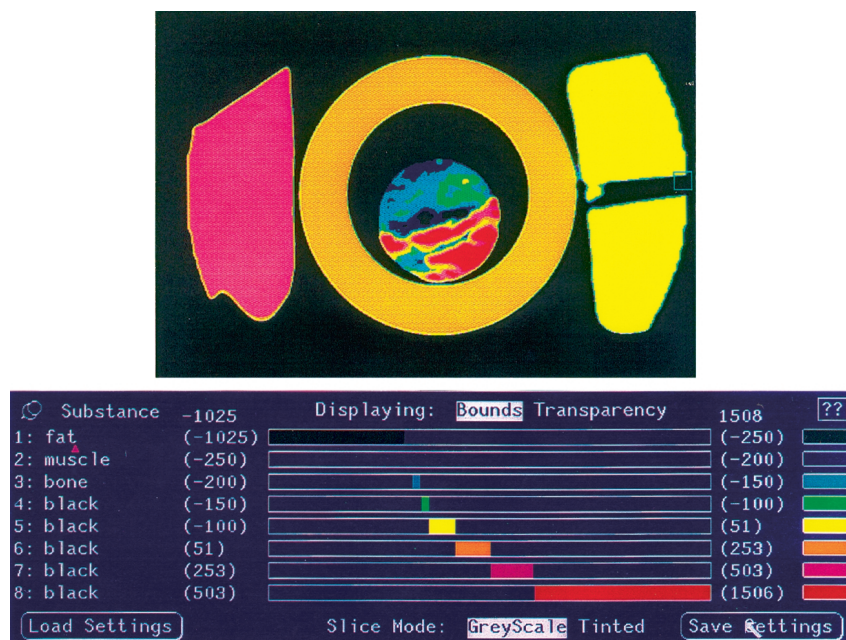
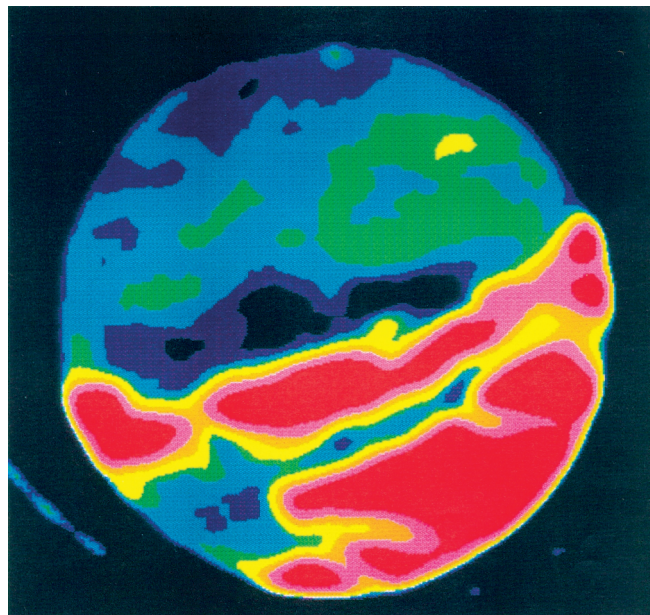
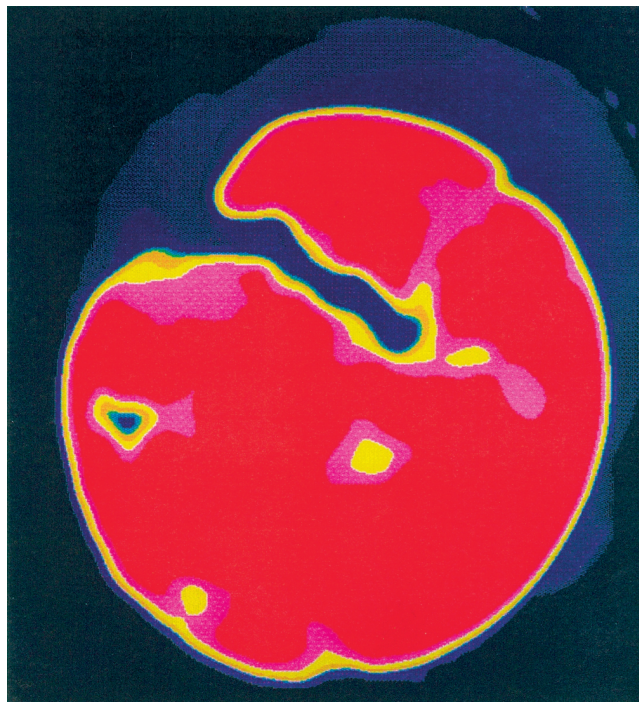
A**B****C**

Figure 4. X-ray CT imagery showing (A) definite differences in color among methane hydrates (dark blue, turquoise, green), minerals (red, yellow), water ice (yellow), dry ice (pink) and acrylic tube (orange); (B) nodular methane hydrates contained in sediments; and (C) vein hydrates (dark blue) penetrating sediments (red) that are coincident with flaky hydrate.

STRUCTURE AND HYDRATION NUMBER

The structure of natural gas hydrates and the molar ratio of water to gas are one of the more important parameters to estimate the amount of methane gas trapped in gas hydrate in marine sediment. Furthermore, the measurements of structure and composition of nat-

ural gas hydrates may also provide the knowledge of their formation conditions as have been documented by the measurements of synthetic methane hydrates (Uchida et al., unpubl. data).

The molar ratio of water to gas is usually examined by the dissociation test. However, the results obtained are largely scattered in each test and are not considered to be a "real" composition of gas hy-

X-ray CT

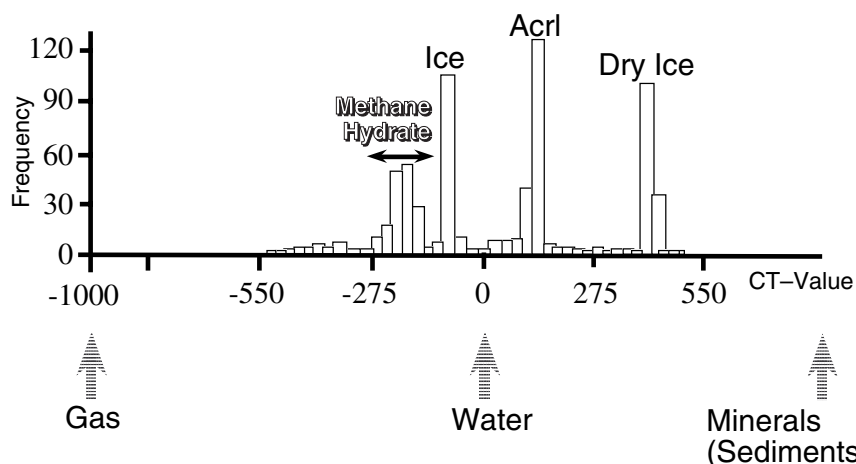


Figure 5. Histogram of CT values for the hydrate measured with freshwater ice and dry ice (Uchida et al., 1996; see Fig. 4A) showing clear discriminations between hydrates, water ice, and dry ice.

drates from the viewpoint of crystallography. Only a few technical notes have reported reliable values of the composition of natural samples, even by these kinds of tests. One of the excellent measurements for the composition of natural gas hydrates was conducted by the use of the calorimeter (Handa, 1988). However, because this technology requires that samples be damaged and destroyed, we employed a non-destructive technique to determine the structure and composition of the Blake Ridge gas hydrate.

NMR Spectrometry

Some nucleuses with magnetic moments of two directions, such as ^1H , ^{13}C , ^{29}Si , cause two different energy levels for those nucleuses in a strong magnetic field. By radiating radio waves whose energy levels are the same as those nucleuses, transitions between the two energy levels may occur when radio waves are absorbed to and released from those nucleuses. This phenomenon is called the nuclear magnetic resonance (NMR). The NMR spectrometry makes use of this phenomenon so as to observe relaxation of energy as a radio wave from the nucleuses. In such a radio wave its frequency becomes slightly changed in the electric environment around the nucleuses, which is known as the chemical shift. Solid NMR spectrometry has recently been well developed with the addition of cross polarization (CP) for improving sensitivity and magic angle spinning (MAS) for gaining high resolution. NMR spectrometry would provide information such as

1. Identification and quantitative evaluation of hydrocarbon in hydrate,
2. Identification of hydrate crystal types,
3. Occupation ratio of guest molecules in clathrate cages, and
4. Kinetic properties of guest molecules and host molecules.

Experimental Methods

A Bruker AMX-400 NMR spectrometer with a probe for solid samples was used for the measurements. A plug of hydrate sample was first crushed into silt-size grains, then placed in the zirconia rotor (I.D. = 8 mm, length = 10 mm) of the spectrometer and cooled down to -70°C by liquid nitrogen. The rotor was placed in the NMR probe and spun at 3000 rps with dried nitrogen gas atmosphere to maintain

low temperature and dry conditions. A thousand measurements were obtained cumulatively in 1 hr.

Results and Implications

The ^{13}C CP/MAS NMR spectra of hydrates are shown in Figure 6. The abscissa designates the chemical shifts, indicating relative differences in the characteristic frequency emitted by ^{13}C in slightly different molecular environments. Two peaks are clearly identified at -3 and -7 ppm. These two spectra designate methane molecules occupied in small and large cages of hydrate, respectively. Other hydrocarbon molecules were not detected.

It is concluded that the crystal type of the measured hydrate obtained from the Blake Ridge is Structure I, because ^{13}C NMR spectra indicate only the methane molecule occupations in small and large cages (Fig. 6A). Only one NMR measurement has ever been achieved on the natural gas hydrate sample collected from the Gulf of Mexico (Fig. 6B), which contains methane and propane and was identified to be Structure II (Davidson, Garg et al., 1986). The ^{13}C NMR spectra of synthetic gas hydrates of Structure II and Structure I enriched with ^{13}C methane and propane are shown in Figures 6C and 6D (Ripmeester and Ratcliffe, 1988). These experimental data help us identify gas hydrate from Leg 164 sediments as being Structure I.

X-Ray Diffraction Analysis

Experimental Methods

Specimens of a dimension of about 10 mm^3 were prepared from core samples in such a way that only gas hydrate and ice samples were included in each specimen. The specimen was sealed by Mylar film to avoid sublimation and placed on a polyethylene tube attached to a goniometer head as shown in Figure 7. Because the diffractometer was operated at room temperature, a specially designed apparatus with a cold air flow was used for cooling the specimen without disturbing the measurements. The temperature of the specimen was kept at about -50°C during the measurements. The surface of the specimen changed into ice, and this prevented the specimen from dissociating even at the atmospheric pressure. The X-ray intensity measurements were made using Molybdenum $\text{K}\alpha$ radiation. Diffraction peaks were automatically searched to locate 2θ angles between approximately 12° and 15° , a region in which no peaks were expected from ice crystals but only from gas hydrate. The diffracted X-ray was

NMR

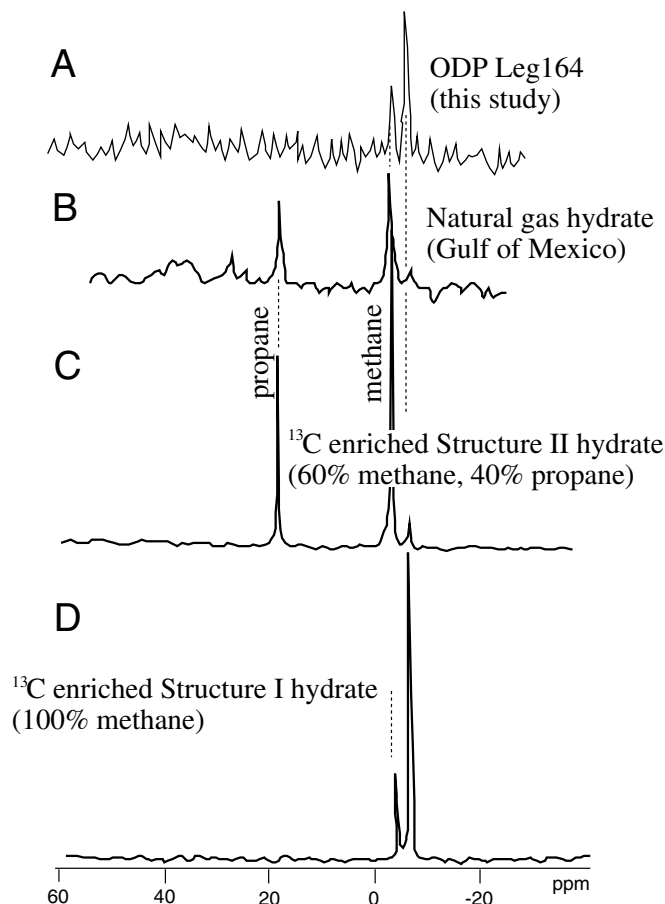


Figure 6. The ^{13}C CP/MAS NMR spectra for various hydrates (Uchida et al., 1997). **A.** Leg 164 methane hydrate (this study). **B.** Natural gas hydrate obtained from the Gulf of Mexico. **C.** Synthetic gas hydrate (Structure II) enriched with ^{13}C methane and propane. **D.** Synthetic methane hydrate (Structure I) enriched with ^{13}C methane. Parts B, C and D are derived from Ripmeester and Ratcliffe (1988).

accumulated for 120 s in 2θ steps of 0.02° , and the specimen was rotated 100° during each step to obtain the average diffraction of a mass sample.

Results and Implications

Figure 8 shows the intensity of the diffraction peaks of the natural gas hydrate specimen vs. 2θ angle. The crystal structure is cubic with a lattice constant

$$a = 11.95 \pm 0.15 \text{ \AA} \quad (1)$$

at about -50°C , averaged over several difficult to analyze specimens. The space group is uniquely determined as $\text{Pm}\bar{3}\text{n}$ from the systematic absence of the indices (h , k , and l).

The intensity of the diffraction peaks shown in Figure 8 was compared with that of the ethylene-oxide hydrate (Structure I) whose structure was carefully determined by McMullan and Jeffrey (1965) using a single crystal. The intensity of diffraction was calculated using their structure factors. The measured relative intensity ratio of the natural gas hydrate corresponds qualitatively to the calculated rela-

tive intensity ratio. This agreement indicates that the natural sample obtained included only Structure I hydrate.

Because the diffraction intensities of the specimen were measured by rotation, the resulting peaks should indicate the average value of the measured specimen. If the hydrates were fine powder and distributed homogeneously in the specimen, the resulting diffraction peaks were smooth. However, the diffraction peaks had some notched shapes, as shown in Figure 8. This means that there were some coarse particles of the hydrate in the specimen that were located inhomogeneously. This conclusion is supported by Laue photography of the same specimen, which shows the fact that the specimen includes many small, and some large hydrate crystals with random orientations.

Raman Spectroscopy

Experimental Methods

Preparation of the Raman spectroscopic specimen was almost the same as that used for X-ray diffraction measurements. The surface of the specimen was made flat by a knife edge to reduce signal losses by scattering. The specimen was placed in a cryostat that was specially designed for microscopic Raman spectroscopy. The temperature of the specimen was kept at about -50°C during measurement by controlling the sample-cell temperature with the flow speed of liquid nitrogen. The sample cell was equipped with a microscope Raman spectroscopy system. The magnification of the system was about 10^3 by using a $20\times$ long working distance objective lens (NIKON CF M Plan SLWD). The diameter of the incident laser beam on the specimen was about $1 \mu\text{m}$.

The Raman spectrometer SPEX RAMALOG-100 equipped with a 1-m, double-dispersed monochromator system was used for this study. The spectra were recorded with a photomultiplier tube detector system. The excitation source was an Ar-ion laser, emitting a 514.5 nm line and providing about 120 mW at the specimen (Fig. 9). A computer system (SPEX DM1B) provided control and data acquisition for the spectrometer system. Routine calibration of the monochromator was done by using the Raman scattering line of silicone plate, 520.0 cm^{-1} . The scattered radiation was collected at the 180° geometry with a slit at $300 \mu\text{m}$. Spectra were collected with a 5 cm^{-1} scanning step, and 3-s integration time steps were done with a measuring range from 100 to 4000 cm^{-1} . This wide-range measurement provides a measure of the content of guest molecules within the sensitivity of Raman scattering. Narrow-range measurements were performed from 2800 to 3000 cm^{-1} to investigate precisely the methane-molecule vibrations in the hydrate. Spectra were collected with a 0.5 cm^{-1} scanning step and a 5-s integration time/step.

Results and Implications

The wide-range measurements of the Raman spectra for natural gas hydrate and for coexisting ice in the same specimen showed that both spectra have several peaks that result from the vibration of H_2O molecules: the translational mode is observed at about 300 cm^{-1} and stretching vibrational modes are observed from 3000 to 3800 cm^{-1} . Comparison of the peak shapes indicates that vibrational conditions of the host molecules of the natural gas hydrate are almost the same as those of ice crystals. This is consistent with the fact that both crystals are constructed by the tetrahedral hydrogen-bonding network of water molecules.

On the other hand, no significant peaks were observed other than the clearly resolved double peaks observed at about 2900 cm^{-1} . These double peaks are the ν_1 symmetric band of methane. This result indicates that the specimen contains almost pure methane gas. The dissociated gas measurements of the natural gas hydrate by gas chromatography showed that more than 99% of the content is methane (Table 2). Figure 10 shows an example of the results obtained by the

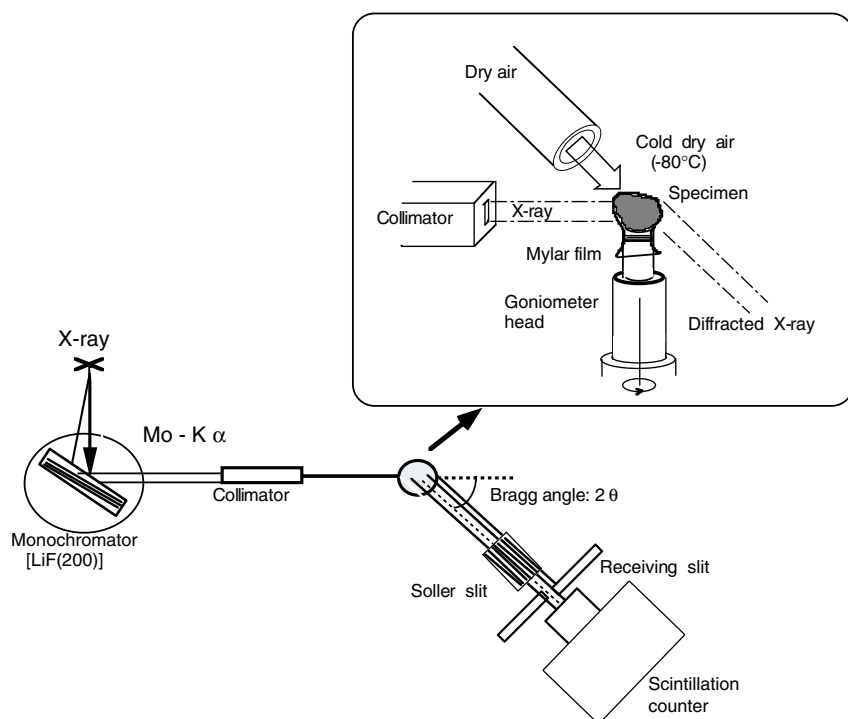


Figure 7. Schematic of the system for the X-ray diffraction measurement.

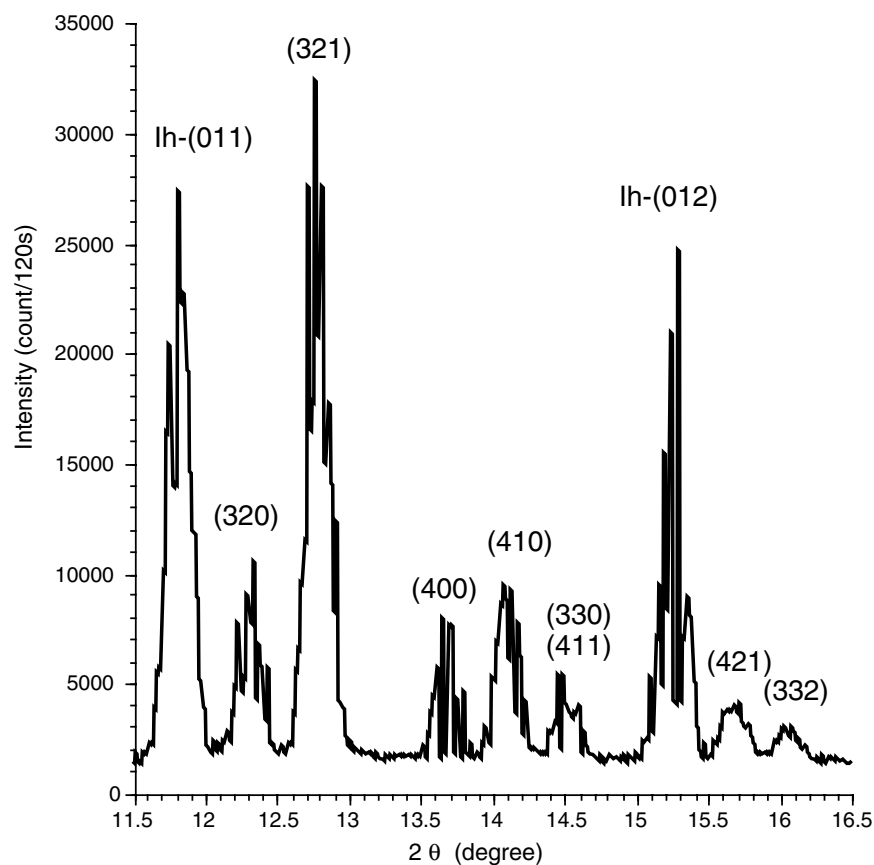


Figure 8. The relative intensity of the diffraction peaks of the natural gas hydrate specimen vs. 2θ angle. Numbers shown with brackets are the indices (h k l). Two of them attached with "Ih-" are the diffraction peaks from freshwater ice.

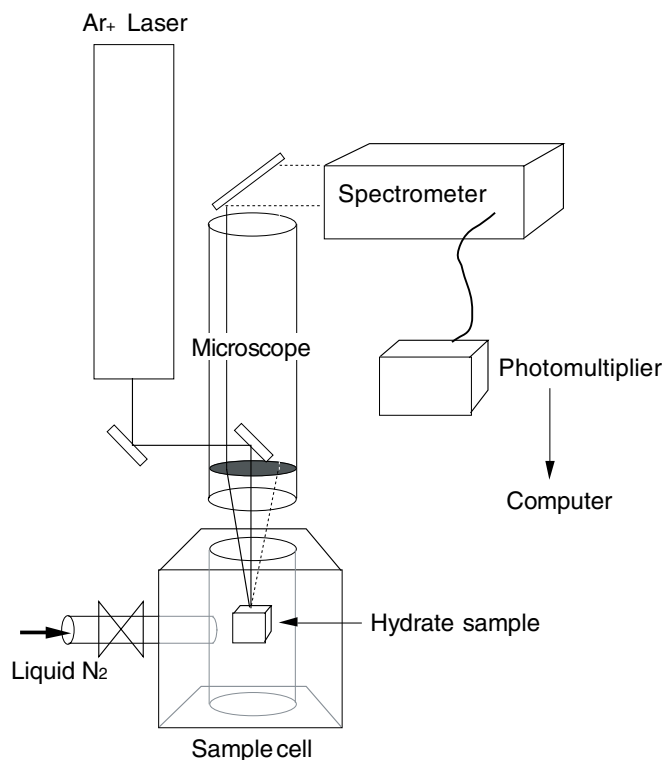


Figure 9. The schematic of the system for the Raman spectroscopic analysis.

narrow-range measurements. The spectrum of the natural gas hydrate is shown by a solid line and, for a comparison, that of the artificial methane hydrate is shown by a dotted line. The peak positions of the natural gas hydrate are 2904.1 cm^{-1} and 2915.1 cm^{-1} for the larger peak and the smaller one, respectively. Although the ν_1 stretching mode of methane vapor is the single peak at about 2917 cm^{-1} , this mode is known to be split into two peaks in the large and small cages of Structure I hydrate. This result quantitatively corresponds to that obtained on the artificial methane hydrates. Therefore, it is concluded that the natural gas hydrate samples are almost pure methane hydrates. This is consistent with the X-ray diffraction measurements.

To estimate the hydration number of the natural gas hydrate from Raman spectra, we applied a calculation method with a thermodynamic model, which was used for the evaluation of the hydration number of methane and propane hydrates from ^{13}C NMR measurements (Ripmeester and Ratcliffe, 1988). In the absence of guest-guest interaction and host-lattice distortions, the chemical potential of the water molecules in a Structure I hydrate, $\mu_w(h)$, is given by

$$\mu_w(h) - \mu_w(h^*) = RT[3 \ln(1 - \theta_L) - \ln(1 - \theta_S)] / 23, \quad (2)$$

where $\mu_w(h^*)$ is the chemical potential of water molecules in the lattice with empty cages; θ_L and θ_S are the large- and small-cage occupancy by a guest molecule, respectively; and R is the gas constant. When the hydrate is in equilibrium with ice, the left side of Equation 2 becomes

$$\mu_w(\text{ice}) - \mu_w(h^*) = -\Delta\mu_w^*, \quad (3)$$

where $\Delta\mu_w^*$ is the chemical potential of the empty lattice relative to ice. Davidson, Handa et al. (1986) reported that $\Delta\mu_w^*$ was $1297 \pm 110 \text{ J/mol}$ for a xenon-hydrate sample prepared under equilibrium conditions at 0°C . The integrated line intensities of Raman spectra allow the relative populations of two sites to be determined. After allowing for the fact that there are three times as many large cages

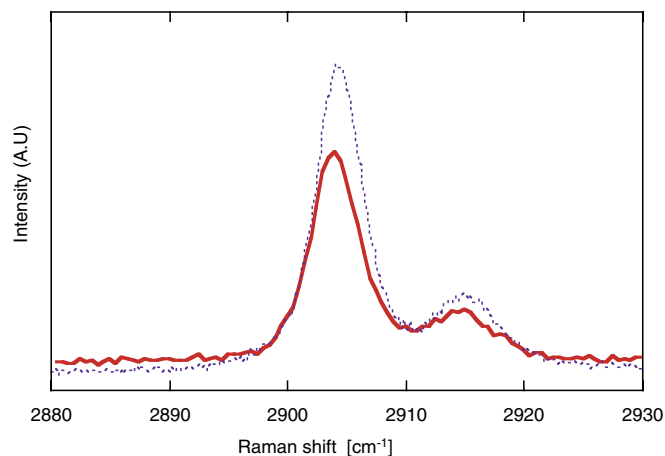


Figure 10. One of the Raman spectra obtained by the narrow-range measurements.

as small ones in type-I hydrate, the cage occupancy ratio $\theta_L/\theta_S = 1.25$. This, together with the above μ_w^* value, gives absolute occupancies $\theta_L = 0.97$ and $\theta_S = 0.78$. The hydration number n can then be obtained by the form $n = 23 / (3\theta_L + \theta_S)$, giving a value of 6.2. This value includes some errors resulting from the uncertainty in $\Delta\mu_w^*$ and the evaluation of peak intensities.

Hydration numbers of natural gas hydrates have been reported by Handa (1988), which were measured by using a calorimeter. He determined the hydration number of the sample obtained from the Middle America Trench slope sediment off Guatemala was 5.91, and the number obtained from the Green Canyon area of the northern Gulf of Mexico to be 8.2. The result obtained in the present study compares well with the former. The latter was discussed to be larger than expected, which may have resulted from the effect of the free water produced by the dissociation of gas hydrates (Handa, 1988). Other recent values for n of artificial methane hydrate, determined by using direct as well as indirect methods, range from 5.8 to 6.3 (Ripmeester and Ratcliffe, 1988). The present value is in good agreement with these results. Therefore, it is concluded that the composition of natural gas hydrate determined in the present study is almost similar to that of pure Structure I methane hydrate.

COMPOSITION OF WATER AND GAS OF GAS HYDRATE

The amount of gas hydrate present in marine sediments is one of the more important parameters when the importance of marine gas hydrate is examined as to the environmental impact and resource potential. Gas hydrate preferentially incorporates ^{18}O relative to ambient; therefore, the oxygen isotopic composition of water squeezed from sediment cores would provide information on the subsurface amount of gas hydrate waters (Hesse and Harrison, 1981; Ussler and Paull, 1995). Also, the isotopic fractionation between gas hydrate and water is crucial to study the effect of gas hydrate dissociation on the formation of authigenic carbonates (Matsumoto, 1989). The molecular and isotopic composition of gases in gas hydrate can provide information on the source and generation process of gases of the Blake Ridge hydrate.

Oxygen Isotopic Composition of Waters Contained in Gas Hydrate

Experimental Methods

Gas hydrate samples were placed in a Teflon-coated dissociation chamber and allowed to decompose at room temperature. Gas pres-

sure of the chamber steadily increased and reached a stable value in about 10 min.; then the hydrate gas was transferred to a small gas collection chamber for gas analysis. The volume of water left in the dissociation chamber was measured and stored in a glass ampoule for determination of the chemical composition and oxygen isotopic composition. Chloride and sulfate concentrations were measured to estimate the amount of pore-water contamination. The amount of interstitial water in the sample water was calculated from chloride and sulfate concentrations, assuming that the pristine gas hydrate-derived water was salt free. As shown in Table 1, the mole fractions of gas hydrate water were 0.88 to 0.99 in the analyzed samples.

The oxygen isotopic composition of gas hydrate-derived water was determined by the standard CO_2 equilibrium method (Epstein and Mayeda, 1953), as modified by Matsuhisa and Matsumoto (1986). A known amount (1.0–1.5 mL; 28–42 mmol of O_2) of sample water was transferred to a small flask, and the flask was evacuated after the water was frozen by liquid nitrogen. The flask was filled with 0.10 mmol of CO_2 and placed in a vibration water bath at 25.0°C for 15–20 hr to attain isotopic equilibration between water and CO_2 . After the completion of the isotopic exchange reaction, CO_2 gas was transferred to a cryogenic vacuum preparation line for refinement. Oxygen isotopic ratio $^{18}\text{O}/^{16}\text{O}$ of sample gas was determined by means of a Finnigan Delta E or Delta S mass spectrometer. The results were represented as oxygen isotopic composition $\delta^{18}\text{O}$ relative to standard mean ocean water (SMOW) using the per million notation. Precision (2 sigma) of the analysis was 0.01‰–0.05‰, whereas the reproducibility of the measurements was about 0.10‰, which was estimated from the repeated analysis of CO_2 samples prepared from the same sample water.

Chloride concentration of gas hydrate-derived waters was measured by a ICA-5000 ion-chromatograph. The standard deviation (2 sigma) of the measurements was within 2% of measured values.

Results and Implications

Results of $\delta^{18}\text{O}$ measurements of gas hydrate water are given in Table 1 along with gas and water volumes and chloride concentrations. The $\delta^{18}\text{O}$ values of water taken from gas hydrate samples were corrected for mixing effect of the interstitial water contamination.

Chloride concentrations of five water samples of gas hydrate were between 5 and 62 mM (Table 1); thus, the mole fraction of gas hydrate water in water samples is calculated to be 0.990–0.878. $\delta^{18}\text{O}$ values of water within gas hydrates are 2.67‰ for Section 164-994C-31X-7 and 2.82‰–3.51‰ (mean = 3.2‰) for Section 164-997A-42X-3. Site 997 gas hydrates are isotopically heavier than Site 994 gas hydrates by ~0.5‰. Moreover, the ~0.8‰ variation within a single, thick massive gas hydrate at Site 997 is significant; however, the reasons for these isotopic variations are uncertain.

The $\delta^{18}\text{O}$ of the interstitial water and gas hydrate at Sites 994 and 997 are given in Matsumoto et al. (Chap. 6, this volume). The difference in $\delta^{18}\text{O}$ values between gas hydrate and the ambient water ($\Delta\delta^{18}\text{O}_{\text{GH-IW}}$) is calculated to be 3.1‰ at Site 994 and 3.3‰–3.8‰ (mean = 3.6‰) at Site 997. Assuming that recovered massive gas hy-

drates were in isotopic equilibrium with ambient interstitial waters ($T = 12^\circ\text{--}16^\circ\text{C}$ and $P = 31\text{ MPa}$), the equilibrium isotopic fractionation factor ($\alpha_{\text{GH-IW}}$) is given as 1.0034 (Site 994) and 1.0037–1.0040 (Site 997). For comparison, oxygen isotopic fractionation of ice water is 1.0027–1.0035 (O'Neil, 1968; Craig and Hom, 1968; Jakli and Staschewski, 1977) and that of tetrahydrofuran (THF) hydrate–water association is 1.00268 ± 0.00003 at $0^\circ\text{--}4^\circ\text{C}$ (Davidson et al., 1983). The values estimated for Sites 994 and 997 are similar to these values.

Molecular and Isotope Compositions of Gases in Gas Hydrate

Molecular compositions of hydrocarbons and carbon isotope composition of methane is widely used for a genetic classification of hydrocarbon gases (Rosenfield and Silverman, 1959; Bernard, 1978; Schoell, 1980; Rice and Claypool, 1981). Schoell (1980) and Whiticar et al. (1986) have shown additionally that the hydrogen isotope composition of methane in combination with the carbon isotope composition characterizes different pathways of microbial methane formation. Here, we investigate the genetic characterization of hydrocarbons in gas hydrate samples by analyses of stable carbon and hydrogen isotope compositions in combination with molecular compositions of gases.

Experimental Methods

Dissociated gas samples were collected from six gas hydrate samples (Table 2). Two samples were taken from 259 mbsf at Site 994 and four samples from 330 mbsf at Site 997. The molecular compositions of hydrocarbon gases were determined on a Shimadzu GC-7A gas chromatograph. For isotope analyses, methane was separated from the other gas components by gas chromatography and subsequently combusted to CO_2 and H_2O over CuO at 850°C , using a vacuum preparation line (Schoell, 1980). The H_2O was then reduced to H_2 by reaction with zinc in flame-sealed glass tubes at 480°C (Vennemann and O'Neil, 1993). The stable carbon and hydrogen isotope compositions of methane were measured using a VG Isotech Sira Series II mass spectrometer. Isotope ratios are reported in the usual δ -notation relative to the Pee Dee belemnite (PDB) standard for carbon and SMOW standard for hydrogen. The reproducibility of isotope values is $\pm 0.15\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 3\text{‰}$ for δD .

Results and Implications

Hydrocarbon composition and $\delta^{13}\text{C}$ and δD values of methane are reported in Table 1. The $\delta^{13}\text{C}$ values of methane range between -70‰ and -65‰ (Table 2). The $\text{C}_1/(\text{C}_2 + \text{C}_3)$ ratios of all samples are higher than 5000. Those light carbon isotope values and methane-rich hydrocarbon compositions are similar to most gas hydrates recovered on the other DSDP and ODP cruises, indicating that the methane trapped in gas hydrate was mainly produced by microbial activity (Fig. 11). Microbial methane formation follows two principal pathways, CO_2 reduction and fermentation (Schoell, 1980; Jenden and

Table 1. Oxygen isotopic composition of the water of gas hydrates from Site 994 and 997.

No.	Hole, core, section	Depth (mbsf)	$\delta^{18}\text{O}$ of H_2O (‰ SMOW)	$[\text{Cl}^-]$ of H_2O (mM)	$[\text{Cl}^-]$ of pristine pore water (mM)	$\delta^{18}\text{O}$ of pristine pore water (per mil SMOW)	Mole fraction of gas hydrate water	$\delta^{18}\text{O}$ of gas hydrate water (‰ SMOW)
#2A	994C-31X-7	259.90	2.6	17	505	-0.4	0.966	2.7
#14	997A-42X-3	330.15	2.7	20	509	-0.5	0.961	2.8
#16A	997A-42X-3	330.25	3.3	5	509	-0.5	0.990	3.3
#16B	997A-42X-3	330.25	3.2	41	509	-0.5	0.919	3.5
#16C	997A-42X-3	330.30	2.7	62	509	-0.5	0.878	3.2

Note: Measured $\delta^{18}\text{O}$ values were corrected for contamination by the interstitial water (IW) using the chloride concentration and $\delta^{18}\text{O}$ of IW and observed Cl^- of sample waters.

Table 2. Molecular composition of hydrocarbons and the carbon and hydrogen isotope composition of methane in gas hydrate recovered on Leg 164, Blake Ridge.

Container No.	Hole, core, section	Depth (mbsf)	Hydrocarbon composition (relative vol%)								$\frac{C_1}{(C_2 + C_3)}$	$\delta^{13}C(\text{‰})$ C_1	$\delta D(\text{‰})$ C_1
			C_1	C_2	C_3	$i-C_4$	$n-C_4$	$i-C_5$	$n-C_5$	C_{6+}			
#1A	994C-31X-6	259	99.924	0.013	0.005	0.016	0.027	0.013	0.003	0.000	5.680	-69.7	ND
#2A	994C-31X-6	259	99.977	0.005	0.002	0.005	0.006	0.005	0.001	0.000	14.526	-67.4	-205
#14	997A-42X-3	330	99.981	0.019	0.000	0.000	0.000	0.000	0.000	0.000	5.163	-66.2	-201
#16A	997A-42X-3	330	99.956	0.014	0.006	0.009	0.008	0.007	0.000	0.000	5.082	-66.1	ND
#16B	997A-42X-3	330	99.978	0.007	0.004	0.004	0.004	0.001	0.001	0.000	9.121	-66.5	-206
#16C	997A-42X-3	330	99.993	0.007	0.000	0.000	0.000	0.000	0.000	0.000	15.088	-65.9	ND

Note: ND = not determined.

Kaplan, 1986; Martens et al., 1986; Whiticar et al., 1986; Burke et al., 1988). The fermentation processes are usually more important in recent freshwater sediments and swamps, whereas methane formed by CO_2 reduction is more common in marine sediments (Whiticar et al., 1986). The CO_2 reduction-derived methane and fermentation-derived methane can be differentiated by their deuterium concentration. The δD values of methane in the Blake Ridge gas hydrate range between -206‰ and -201‰ (Table 2), indicating methane was generated by microbial CO_2 reduction (Fig. 12).

THERMAL CONDUCTIVITY

Thermal conductivity of gas hydrate is one of the more important physical properties relevant to drilling, logging, and gas production from natural gas hydrate reserves, however, it is not easy to make direct measurement of thermal conductivity of gas hydrate due to its ephemeral nature at earth surface conditions.

Experimental Methods

A solid gas hydrate in Section 164-994C-31X-6 was used for measurement of thermal conductivity. The size of the sample was approximately $20\text{ mm} \times 10\text{ mm} \times 5\text{ mm}$. The sample was cut plane to fit the plate probe of a specially designed apparatus to measure thermal conductivity of small samples at elevated pressure. The measurement system is shown in Figure 13. This system has two types of probes for a hot-wire method, a plate probe and a needle probe. We used the plate probe because the sample was hard. The apparatus was cooled to -30°C , then the sample was inserted and pressurized at 12 MPa for 4 hr before measurement. We measured three times at the same temperature every 4 hr. The data were reported as the average of these three measurements.

Results and Implications

Results of the measurement are shown in Table 3 and Figure 14 along with the value reported by Sloan (1990). Thermal conductivity of the Blake Ridge gas hydrate ranges between 0.553 and 0.314 W/(m·K) for temperatures between -30° and 10°C . The conductivity values decrease with temperature from -30° to 0°C , then abruptly increase by 0.2 W/(m·K) at 0°C . This abrupt increase was probably caused by the release of liquid water, the higher thermal conductivity of water increased the thermal conductivity of the system.

EQUILIBRIUM DISSOCIATION EXPERIMENT

The pressure-temperature (P-T) stability conditions for the formation of methane hydrate have been determined on synthetic methane hydrate (e.g., Deaton and Frost, 1946; Yokoi et al., 1993); however, those of natural gas hydrate formed in marine sediments have not

been measured, because natural gas hydrate samples have not been available for such an experiment. Considering that the environment of formation of natural gas hydrate is quite different from that of laboratory experiments, the P-T conditions for the three-phase equilibrium of natural gas hydrate may not be the same as that determined on synthetic gas hydrate. Leg 164 scientists observed that the depth of the BSR was significantly shallower than that of the theoretically determined base of methane hydrate stability (Paull, Matsumoto, Wallace, et al., 1996). Therefore, it is crucial to determine equilibrium dissociation conditions of the Blake Ridge gas hydrate to investigate the discrepancy between the BSR and the base of gas hydrate stability (BGHS).

Experimental Methods

One gas hydrate sample (Sample 164-997A-42X-3, 25–35 cm) was observed to contain a gray part and black part. The former was expected to contain gas and hydrate, and the latter one seemed to be mainly the host sediment. It is crucial for this experiment to develop the method to detect a slight increase in pressure caused by the dissociation of natural gas hydrate. Because the equipment used for this experiment was originally designed for synthesis of a large gas hydrate, the volume of the vessel was too big (630 mL) to detect the dissociation of a small amount of gas hydrate. Therefore, the volume of the vessel was reduced to 160 mL by putting stainless steel blocks inside (Fig. 15). Consequently, the accuracy of temperature measurement was approximately $\pm 0.5\text{ K}$. The equilibrium conditions were obtained only by wrapping the gas hydrate sample in a vinyl bag.

A 6.5 g of the frozen sample that consists of mixture of both a black part and a grey part was placed in a thin vinyl bag, and the bag was tightly sealed after the air in the bag was evacuated. The sample was placed in a pressure vessel and the remaining volume of the chamber was filled with nitrogen and water.

The temperature of the vessel was increased from 268 to 275 K by circulating coolant and the pressure was increased up to 11 MPa. This condition is well within the methane hydrate stability. Equilibrium dissociation was initiated by careful pressure release by 0.05 MPa steps at a temperature of 274.5–275.0 K (Fig. 16). Gas hydrate did not dissociate upon step-wise pressure release while the pressure was maintained within the stability condition. However, when the pressure decreased down to 3.25 MPa at a temperature of 274.5–274.8 K, a slight pressure recovery was recognized in a few minutes. This pressure increase is explained to reflect partial dissociation of gas hydrate. The pressure finally attained constant value of 3.27 MPa in 15 min. These P-T values (3.27 MPa and 274.7K) are considered to be a close approximation of the three-phase equilibrium conditions of the Blake Ridge gas hydrate.

Results and Implications

As shown in Figure 17, the three-phase equilibrium condition of the Blake Ridge hydrate is almost the same as the equilibrium condi-

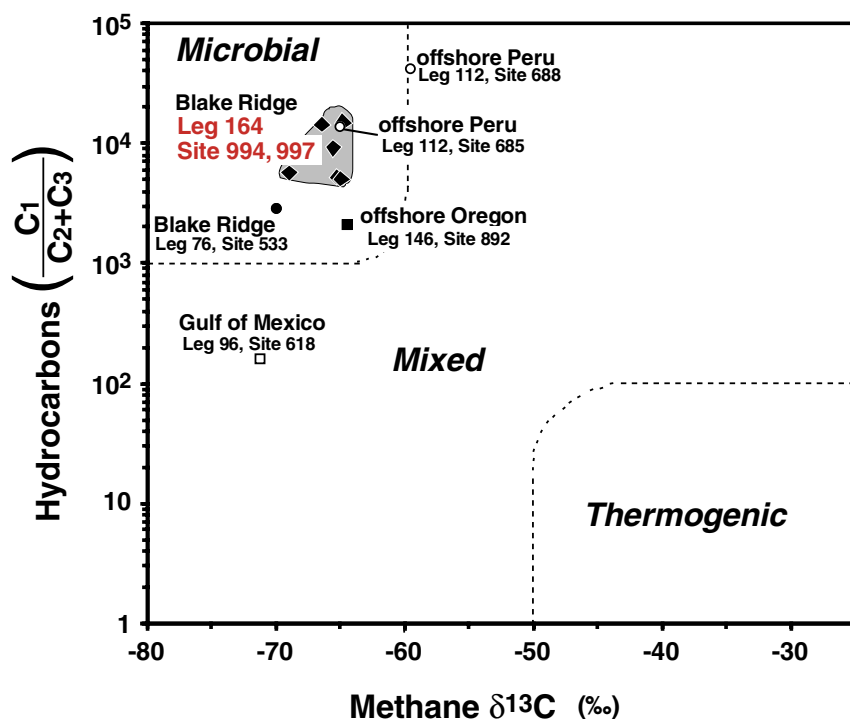


Figure 11. Interpretive plot of molecular ratios of hydrocarbons vs. carbon isotope compositions of methane in gas hydrate recovered from the Blake Ridge sediments on Leg 164 (diagram modified after Bernard, 1978). The other DSDP and ODP data are from Kvenvolden and Barnard (1983), Pflaum et al. (1986), Kvenvolden and Kastner (1990), and Hovland et al. (1995).

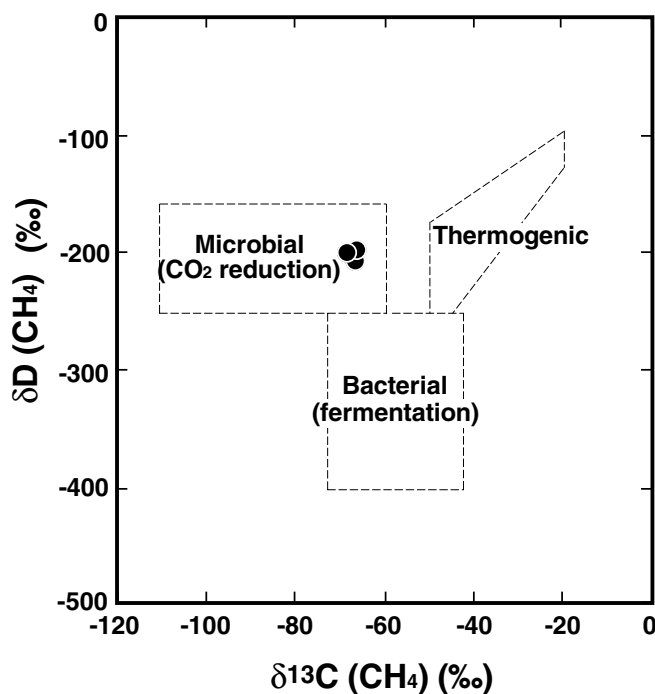


Figure 12. Interpretive plot of hydrogen and carbon isotope compositions of methane in gas hydrate recovered on Leg 164, Blake Ridge (diagram modified after Schoell, 1988).

tion of pure methane hydrate in pure water, with an error of about 0.5 K. As documented by the discrepancy between BSR and BGHS, the apparent phase boundary condition of methane hydrate in the Blake Ridge sediment is a few degrees lower than that of the pure methane hydrate in pure water or in seawater; however, the three-phase equilibrium condition as determined on recovered solid methane hydrate

samples does not greatly differ from the experimental data (e.g., Deaton and Frost, 1946).

SUMMARY AND CONCLUSIONS

1. Leg 164 scientists recovered a number of solid gas hydrates that were large enough to be visible to the naked eye from Sites 994 and 997 on the Blake Ridge and from Site 996 on the Blake Ridge Diapir. Blake Ridge samples are either nodular to thick massive whereas Carolina Rise samples mostly occurs as fracture-filling veins or as rectangular platy fragments.

2. Textural relations between gas hydrate and surrounding host sediment are clearly observed on an X-ray CT imagery in a resolution of 0.35 mm × 0.35 mm area and 1.0 mm in thickness. The CT value of gas hydrate is -65, whereas those of water and water ice are -100 and -250, respectively.

3. The NMR measurement has revealed that the Blake Ridge hydrate is Structure I methane hydrate in which both the small and large cages are filled by methane.

4. Low-temperature X-ray diffraction analysis has determined that Blake Ridge hydrate is Structure I; the crystal is cubic with a lattice constant of $a = 11.95 \pm 0.05 \text{ \AA}$ at -59°C , and the space group is Pm3n.

5. Raman spectroscopy indicates that the specimen is almost pure methane. Thermodynamic calculation based on observed Raman spectra gives the hydration number of 6.2.

6. Oxygen isotopic composition of the water of gas hydrate is 2.67‰–3.5‰ SMOW, which is 3.5‰–4.0‰ heavier than the ambient interstitial water.

7. Gases of the Blake Ridge gas hydrate are dominated by methane (99.9 vol%) with minor heavier hydrocarbon gases ($\text{C}_2\text{--C}_5 = 0.1 \text{ vol\%}$). The $\delta^{13}\text{C}$ (-66‰ to -70‰) and δD (-201‰ to -206‰) of methane strongly indicate that the methane trapped in gas hydrate was generated by bacterial CO_2 reduction.

8. Thermal conductivity of the specimens ranges between 0.3 and 0.5 W/(m·K), which is similar to that of synthetic methane hydrate.

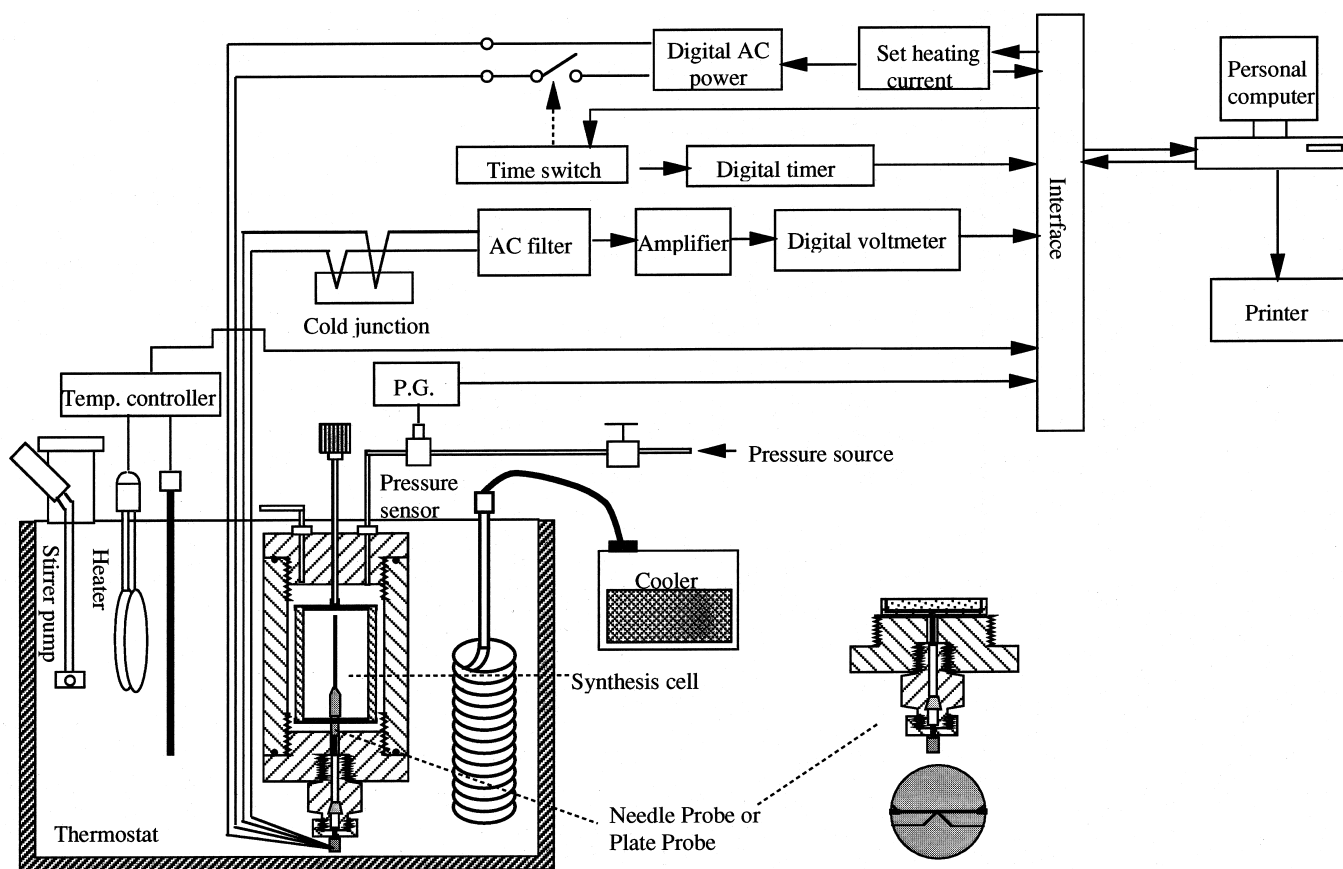


Figure 13. Schematic diagram of thermal conductivity measurement system for gas hydrate and freshwater ice.

Table 3. Results of measurements of thermal conductivity of gas hydrates of Blake Ridge.

Temperature (°C)	Thermal conductivity (W/[m-K])
-30	0.553
-20	0.500
-15	0.476
-10	0.386
-5	0.350
0	0.523
5	0.422
10	0.314

9. Equilibrium dissociation experiments indicate that the three-phase equilibrium condition of the Blake Ridge hydrate is 3.27 MPa at 274.7 K. This is nearly identical to that of a pure methane hydrate formed in pure water.

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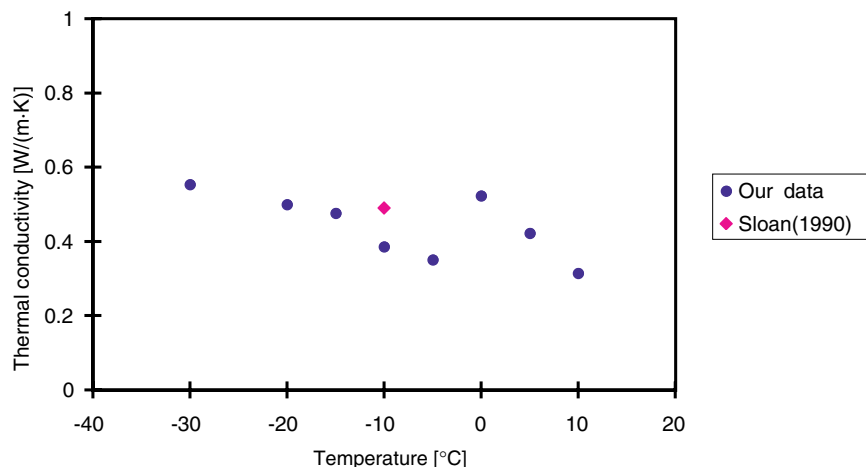


Figure 14. Relationship between thermal conductivity of gas hydrate and temperature.

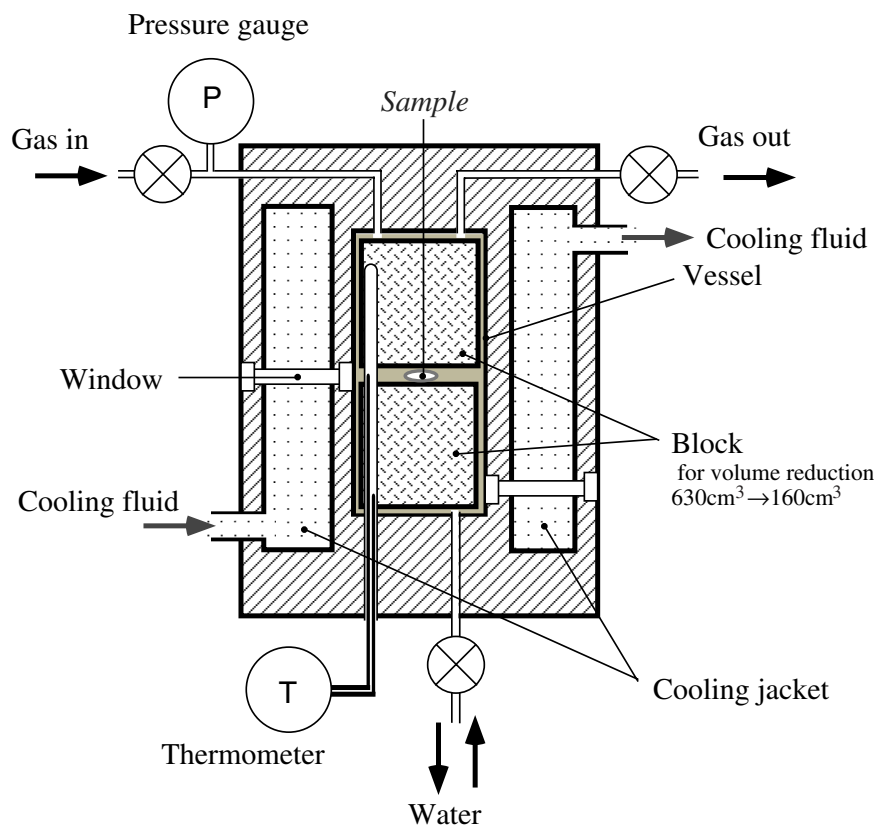


Figure 15. Schematic diagram of the experimental equipment to determine P-T condition of equilibrium dissociation of gas hydrate.

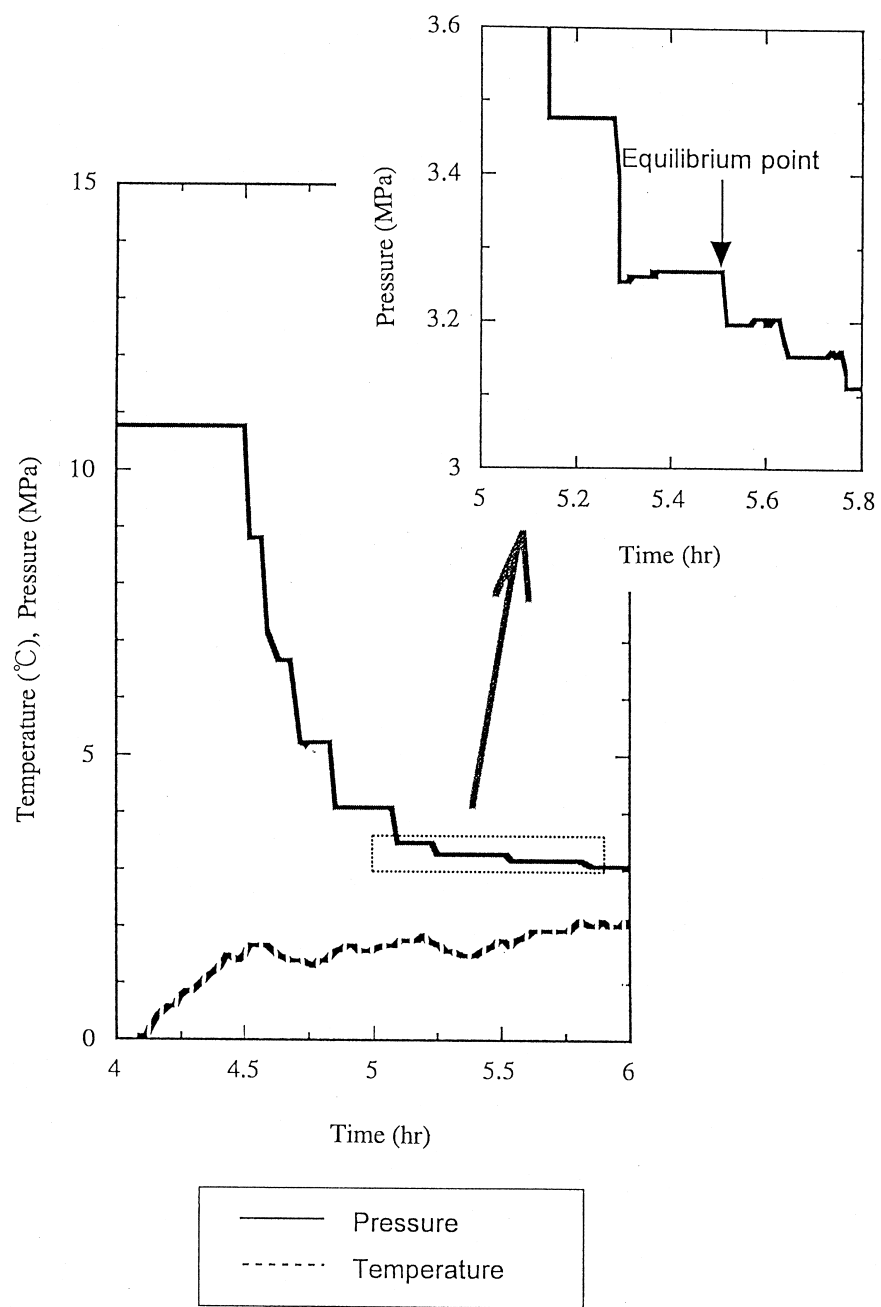


Figure 16. Pressure and temperature change during gas hydrate dissociation experiment.

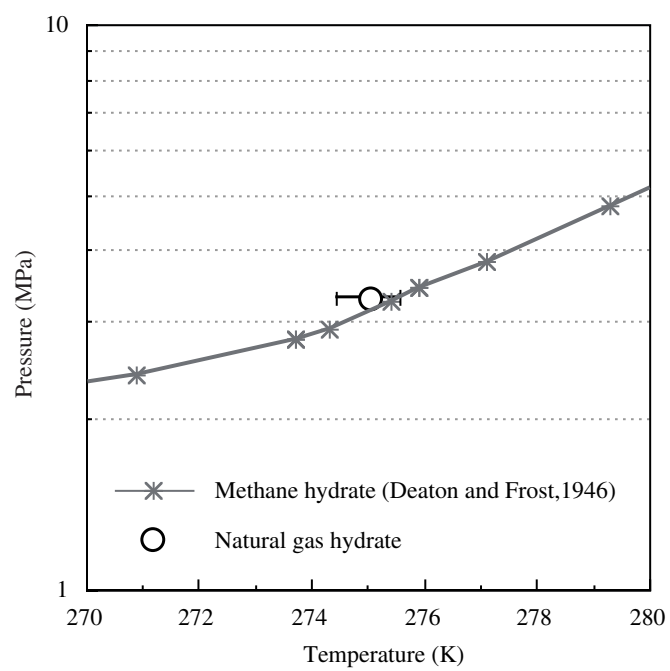


Figure 17. The P-T condition of equilibrium dissociation of the Blake Ridge gas hydrate plotted on the diagram of synthetic methane hydrate.