

## Occurrence and origin of shallow gas hydrates

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It is almost 16 years since Leg 164 of the Ocean Drilling Project conducted the first gas hydrate drilling on the Blake Ridge, West Atlantic, and revealed that the anomalous reflector BSRs do not always indicate extensive distribution of gas hydrate but perhaps existence of free gas zones below the BSR. For the last decades, our understanding of marine gas hydrates has been remarkably deepened and developed. Direct observation of the seafloor by ROV, dense coring, high-resolution acoustic surveys have identified densely accumulated gas hydrate zones in shallow sediments and even on the seafloor. We have now two distinctive types of gas hydrate. One is deep-seated, pore-filling type accumulation, and the other is shallow massive accumulation. As for the industry efforts, National gas hydrate program MH21 is planning to conduct an offshore production test on the deep-seated type accumulation in Nankai Trough in 2012 and 2013. Gas hydrate exploration efforts are rapidly growing in nearby countries and districts, in which the projects seem to target not only the deep-seated type but also shallow and massive accumulation of gas hydrate. In the present paper, I would like to discuss and clarify the geologic, geochemical, and physical constraints to form shallow gas hydrates in Japan Sea with an intention to assess the resource potential of shallow gas hydrates, on the basis of our gas hydrate expedition since 2009.

Keywords: gas hydrate, gas chimney, hydrate mound

## In situ measurement of the amount of free gas of deep sea sediments by Time Domain Reflectometry (TDR) method

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In situ measurement of the amount of free gas of deep sea sediments by Time Domain Reflectometry (TDR) method

The amount of free gas in deep sea sediments is a critical factor for the stability of gas hydrate, however, it is not easy to obtain reliable free gas amount by conventional core sampling methods. In this study, we try to measure the in situ free gas amount of gas hydrate bearing Japan Sea sediments by introducing the Time Domain Reflectometry (TDR) method with an intention to estimate the behavior of methane in deep sea sediments. TDR method has been widely used to estimate the water content of soils in the field of agriculture science.

The TDR sensor is set at the bottom of piston corer and data-logger and battery are stored in a pressure vessel within the weight at the top of the system. The volume of gas has been estimated from observed change in the dielectric constant. The dielectric constant is different in each material, about water is 80 and the soil are 3-9, and air is 1. Moreover, ice is 4.2. The sediment core of a constant amount was taken from bottom of the sea by piston core samplings, and the dry density and the particle density of the soil are measured in a laboratory. Then the amount of solid phase ratios is estimated. Thus the liquid phase rate can be estimated according to the value of the dielectric constant by the TDR method measured at the bottom of the sea. The volume of the gas can be requested from these measurements by the calculation.

The dielectric constant ( $\epsilon$ ) of the sediments was different according to the measurement point. The dielectric constant measure by the TDR method was applied to proofreading type  $V_w = 3.71E06 \cdot \epsilon^3 - 3.60E-04 \cdot \epsilon^2 + 1.86E-02 \cdot \epsilon - 5.61E-02$  provided by the laboratory experiment, and liquid phase ratio ( $m^3 m^{-3}$ ) was obtained. On the other hand the solid phase ratio ( $m^3 m^{-3}$ ) of the sediments was directly obtained from the core samples. These results were brought together by each measurement point, and gas phase ratio ( $m^3 m^{-3}$ ) was obtained from calculating formula. It is remarkable that the gas phase ratio of gas hydrate bearing sediments showed significant changed by approximately 5 % from sea bottom to sea surface during the experiment, suggesting dissociation of gas hydrate and degassing of dissolved methane due to depressurization during core recovery.

Keywords: TDR, measurement of free gas amount, Japan Sea, gas hydrate, method of marine survey

## Thermal structure in the western Joetsu Basin, offshore Sado Island, Japan

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Stability of gas hydrate depends on pressure and temperature. Subsurface thermal structure thus provides key information to investigate formation of gas hydrate and distribution of gas hydrate stability zone. The western Joetsu Basin is one of areas where gas hydrate studies have been conducted intensively in the world (Matsumoto et al., 2009). In June 2010, MD 179/Japan Sea Gas Hydrates cruise using R/V Marion Dufresne was conducted in the western Joetsu Basin to investigate the mechanism of gas hydrate formation in the region. Measurements of heat flow were conducted during the cruise at seven sites along one of METI Sado-oki Nansei 2D seismic survey lines. The measured values of heat flow range from 84 to 90 mW/m<sup>2</sup>, which is slightly lower than those measured around the Joetsu Knoll and Umitaka Spur by Machiyama et al. (2009). We inferred 2D thermal structure along the 2D seismic survey line to explain the heat flow values measured at the seafloor using the topography and geological structure interpreted from the seismic survey line and physical property data obtained during MD 179/Japan Sea Gas Hydrates cruise and from METI Sado Nansei Oki Well. In the calculation, we assumed that heat transport in the model is heat conduction only and that a constant basal heat flow is supplied at the base of the model. We sought the thermal structure model that best explains the measured heat flows, by giving various values of basal heat flow to the model. The best thermal structure model is of the basal heat flow of 88 mW/m<sup>2</sup>. The calculation result suggests that in the modeled area, heat conduction dominates heat transport and that the basal heat flow in the area is about 88 mW/m<sup>2</sup>.

This study is supported by MH21, Research Consortium for Methane Hydrate Resources in Japan.

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Keywords: thermal structure, heat flow, western Joetsu Basin, gas hydrate, MH21

## Marine surveys for gas-hydrate off Abashiri, the Sea of Okhotsk

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When the resources project of gas-hydrate was stood in Japan at 1995, clear BSR has been also confirmed in the seismic data of the Kitami-Yamato Bank off Abashiri, the Sea of Okhotsk, and the possibility of existence of gas-hydrate has been pointed out (Sato et al, 1996; Sakai, 1996). Moreover, obvious BSR has been also confirmed in the seismic data (SBP and SCS) collected during GH01 cruise that carried out off Abashiri, the Sea of Okhotsk in 2001 conducted by Geological Survey of Japan, AIST (Noda et al, 2009). However, the sufficient survey is not carried out after GH01 cruise, and the actual condition is not clear.

Therefore, the cooperated survey for the gas-hydrate was performed with Kitami Institute of Technology which has the survey experience regarding the gas-hydrate in offshore Sakhalin Island, the Sea of Okhotsk and Univ. of Tokyo team which has that in the eastern margin of the Japan Sea. This survey is a pilot study to start the substantial survey after next year and the main purposes are below.

1) To retrieve the sea-bottom sediment of the length of 50 or more cm at least from the top of the gas chimney structure where decided from the SBP record published in the Web of AIST.

2) To check the presence of the trace of methane spring and/or gas-hydrate from the sediment properties.

3) To decide the SMI depth from the composition of pore water, and to evaluate the strength of methane flux.

4) To clarify the temperature profile of sea water, and to evaluate the stability of shallow gas-hydrate.

5) To clarify the composition and origin of dissolved gas in the pore water.

The surveys were carried out for three days in September, 2011, with the Abashiri Submarine Canyon area (water depth is about 900 m) that is in offshore about 30 km in the northeast from Abashiri. Used R/V is Taiki-maru (19 ton). To retrieve the sea-bottom sediment, a gravity core sampler (length is about 2 m) was used, and maximum retrieved core length was 1 m. To measure the strength of sediments immediately after recovery, the cone penetration test was performed on board. For sediment, pore water and gas analyses, subsampling was conducted for the cut core. The measurement of water temperature from the sea-surface to sea-bottom and the water sampling at regular interval were also conducted.

It was not possible to retrieve the gas-hydrate in this survey. On the other hand, it was confirmed that the methane is dissolving with high concentration in the pore water of sea-bottom sediments. The concentration was similar to that of the core sample retrieved from offshore Sakhalin Island, the Sea of Okhotsk, where the gas-hydrate was retrieved. Thus, it was suggested that there is the possibility of existence of gas-hydrate even from the temperature/pressure condition on the survey sea area.

Keywords: gas hydrate, marine survey, Sea of Okhotsk, sea-bottom sediment, pore water, dissolved gas

## Crystallographic properties of gas hydrates off Sakhalin Island (Sea of Okhotsk) using Raman spectroscopy & calorimetry

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Natural gas hydrates have been studied in the gas seep sites off Sakhalin Island, the Sea of Okhotsk. More than ten gas seep sites in the north area of the Lavrentyev seabed Fault (LVF) form gas hydrates in the sea-bottom sediments. In the framework of SSGH (Sakhalin Slope Gas Hydrate) project, hydrate-bearing sediments are also discovered in the south area of LVF, where more than 400 acoustic anomalies exist but the size of seepage structures are relatively small. We obtained samples of natural gas hydrate in the CHAOS project (2003-2006) and the SSGH project (2007-2011) and analyzed their crystallographic properties using a calorimeter and a Raman spectrometer. Their gas composition were mainly methane, suggested the cubic structure I of these crystals. The hydration number, cage occupancies of both large and small cages, and dissociation heat of the sample were almost same as those of pure methane hydrate. Raman spectra showed that hydrogen sulfide were encaged in both large and small cages. The peak ratio of large to small cages were about 2.4 and 3.5 for hydrogen sulfide and methane, respectively.

Keywords: gas hydrate, dissociation heat, cage occupancy, hydration number, Sea of Okhotsk

## Sampling method and chemical analyses of gas hydrate waters retrieved from Kukuy K-9 mud volcano in Lake Baikal

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Lake Baikal, Russia, is one of the most attractive gas hydrate study areas, since the first gas hydrate (GH) in a freshwater lake was retrieved from the sub-bottom depths of 121 and 161 m and later from the subsurface of the lake floor. Many studies to determine the origin of the gases incorporated in and/or bound to GHs have been carried out on samples from this lake [see, e.g., Hachikubo et al [Hachikubo, 2010]]. On the other hand, chemical analyses of water samples from lake- and pore- waters have been carried out to clarify the geochemical characteristics of the GH-bearing sediment cores [see, e.g., Pogodaeva et al [Pogodaeva, 2007]]. The chemical analyses of such samples are important to identify the origin of water molecules contributing to the formation of GHs and to distinguish whether seepage structures and/or mud volcanoes observed at the lake floor are related to the discharge of gases with or without gas-saturated water.

In September of 2010, subsurface GHs were retrieved using steel gravity corers at Kukuy K-9 mud volcano in the central basin of Lake Baikal. GH water samples were obtained, on board, by the sequential and continuous dissociation of a piece of agglomerated/massive GH, in a closed vessel with inert gas, after its retrieval from the bottom of the lake floor, to acquire traces of the original gas hydrate-forming fluid in the GHs.

The purposes of this presentation are (i) to describe the sampling method used to obtain GH water samples without the use of lake or pore waters, (ii) to report the scientific results of the chemical (such as Cl-) and isotopic ( $\delta^{18}\text{O}$  and  $\delta^2\text{D}$ ) analyses of samples from lake- and pore- waters, and (iii) to find traces of the original water involved in the accumulation of subsurface GHs at Kukuy K-9 mud volcano in Lake Baikal.

Keywords: gas hydrate water, pore water, chemical analyses, ionic concentration, stable isotope ratio

## High-resolution Seafloor Survey and Preliminary Geochemical Investigations in the Daini-Atsumi Knoll.

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In 2012 JFY, the first offshore methane hydrate production test in the world will be conducted around the Daini-Atsumi Knoll in the eastern Nankai Trough.

Geohazard surveys are required to deepwater drillings in oil and natural gas industry, therefore, a high-resolution bathymetric and geological survey was conducted by the AUV 'Urashima' in the Daini-Atsumi Knoll in February, 2011.

The acquired data are as follows;

- (1) High-resolution bathymetric data by multi-narrow beam echo sounder
- (2) High-resolution back-scatter image by side scan sonar
- (3) High-resolution shallow sediment profile by sub-bottom profiler

Resultingly remarkable hazards are not identified around the production test area.

Nagakubo et al. (2009) constructed the bathymetric and seafloor amplitude maps of the Daini-Atsumi knoll by the seafloor reflection signals of the 3D seismic data acquired in the METI 3D seismic survey 'Tokai-oki to Kumano-Nada'. Furthermore a lot of geochemical data near on seafloor were acquired by the Research Consortium for Methane Hydrate Resources in Japan (MH21).

This presentation will show (1) Comparison of the AUV 'Urashima' and the 3D seismic data concerning the bathymetry and seafloor geological conditions, (2) Preliminary investigations concerning the geological and geochemical conditions of the Daini-Atsumi Knoll.

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Keywords: AUV 'Urashima', methane hydrate, Daini-Atsumi Knoll, bathymetric survey



## Biogeochemical processes in gas hydrate-bearing mud volcano sediments from the Kumano forearc basin, Japan

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We investigated biogeochemical processes in mud-volcano subsurface sediments down to 20 meters from the summit, obtained from the Kumano forearc basin in the Nankai Trough during the CK09-01 D/V Chikyu training cruise in 2009.

The cored sediments contained several methane hydrates. The stable isotopic compositions of the pore fluid samples exhibit <sup>18</sup>O-enrichment and D-depletion in proportion to the depletion of the chlorinity indicating that a mixing between seawater and the fresh water components derived from the dehydrate reaction of clay minerals at 60-160°C previously occurred in the deeply buried sedimentary layer. In contrast, hydrate water samples are strongly enriched in deuterium and slightly deviated from Cl-vs. oxygen isotopic composition trend indicating the pore fluid freshening is not governed by gas hydrate dissociation. High B (up to 13094 micoro-M) and Li (up to 188 micoro-M) concentrations in the pore fluid suggest the leaching from clay minerals at >150°C, and indicate that the fluid in the mud volcano was supplied from the accretionary prism (>4000 mbsf) beneath the forearc sediments probably through faults.

The carbon isotopic composition of dissolved inorganic carbon increased with the coring depth, reaching +40 per mil at 3 meters below the seafloor (mbsf). The highly <sup>13</sup>C-enriched values are possibly due to strong microbial reduction of DIC to <sup>12</sup>C-enriched products. The hydrogen isotopic composition of methane (ca. -180 permil) and magnitude of the carbon isotopic fractionation between DIC and methane (ca. 76 per mil) bellow 3 mbsf suggest the significant contribution of hydrogenotrophic methanogenesis as the source of methane. The carbon isotopic composition value of acetate was appeared to increase with the sediment depth (from -41 to -22 per mil), synchronous to the increase of carbon isotopic composition of DIC. The significant isotopic fractionation between DIC and acetate (ca. 54 per mil) indicates that the principal process producing acetate is homo-acetogenesis via the reductive acetyl-CoA pathway. Radioactive tracer experiments exhibited relatively high activities of homo-acetogenesis (14~34,900 pmol/cm<sup>3</sup>/day) compared to that of hydrogenotrophic methanogenesis (0.6~128 pmol/cm<sup>3</sup>/day). In ordinary marine sediments, homo-acetogenesis from H<sub>2</sub> and CO<sub>2</sub> is thermodynamically inhibited because H<sub>2</sub> concentrations are maintained at low levels less than several nM. However, the homo-acetogenesis was thermodynamically favorable in the cored sediments because of the high concentration of H<sub>2</sub> (>560nM). These results showed that homo-acetogenesis is dominant in the sediments around the summit of the mud volcano, while active hydrogenotrophic methanogenesis has been occurred in a deeper depth, and most portion of methane formed methane hydrates was supplied from the deep active methanogenic zone.

Keywords: Mud volcano, Methane hydrate, Deep origin fluid, homo-acetogenesis, methanogenesis, CO<sub>2</sub> reduction



## Dissociation mechanism of methane clathrate hydrate in different size of pore spaces

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Dissociation processes of methane hydrate synthesized with glass beads were investigated using powder X-ray diffraction technique. Although understanding of methane hydrate dissociation within natural settings, not so many studies were performed on methane hydrate dissociation within pore spaces from microscopic point of view. Recently, it was revealed that methane hydrate formed with hydrophilic glass beads less than a few microns in size show very high stability up to just below the melting point of ice, even though this temperature is well outside the zone of thermodynamic stability of the hydrate.[1] In contrast, methane hydrate formed with hydrophilic coarse glass beads (> 10 micron) dissociate quickly at 150-200 K; in this temperature range methane hydrate dissociates at the atmospheric pressure.

In this study, we performed observations of methane hydrate dissociation process using hydrophobic glass beads with sub-micron and several microns in size. In this case, kinetic high-stability of methane hydrate was not observed. Thus the experimental results obtained suggest that the dissociation rate of methane hydrate strongly depended on the surface property of glass beads used.

### Reference

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Keywords: methane hydrate, dissociation, self-preservation, pore space