Analysis of benthic community food web at gas hydrate deposits using stable isotope analysis

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To better understand the ecology of benthic community at gas hydrate deposits, the stable isotopic signatures of carbon, nitrogen and sulfur (δ¹³C, δ¹⁵N and δ³⁴S) of the surface sediment and benthic fauna collected at Joetsu Basin and Mogami Trough were evaluated. We analyzed their food web and speculated the carbon and sulfur cycles in the benthic water at hydrate deposits.

Sampling of benthic fauna at seeps using a slurp gun and a strainer was conducted during September 2013 and October 2014 at seep and reference sites. We obtained surface sediment sample using MBARI ROV coring system at depths of 0-2.5 and 2.5-5 cm below seafloor. Macrofaunal sample was dissected on board and frozen. Meiobenthos were removed by sieving of sediment samples and frozen. In laboratory, faunal sample was powdered after freeze drying. We measured stable isotope signatures of carbon and nitrogen using IRMS (Flash 2000/Delta V IRMS, Thermo Scientific Inc.) after removal of inorganic carbon using HCl solution and neutralization by NaOH. Similarly, stable isotope signature of sulfur was measured using free dried faunal sample. We collected the precipitates of zinc and barium in pore water extracted from the sediment sample and seawater by filtration for sulfur isotope composition of sulfate and sulfide.

Our result shows that no distinct difference between the isotopic signatures of red snow crab, one species of eelpout, Bothrocara hollandi, northern shrimp and amphipods collected both at seep site and reference site. It suggests that their food habitat depends mainly on photochemically-produced organic carbon and sulfur from seawater sulfate even in an individual inhabiting around methane seep.

While, biplots of δ¹⁵N versus δ¹³C and δ³⁴S versus δ¹³C suggest that some benthic animals such as solemyid clam and frenulata tube worm depend on carbon and sulfur derived from chemosynthetic bacteria.

This study was conducted as a part of the shallow methane hydrate exploration project of METI.

Keywords: methane hydrate, benthic fauna, food web, Stable isotope signatures
Detailed Topographic survey on basin areas of the Japan Sea and around Hokkaido

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Regional bathymetric and backscatter data were obtained by a multibeam echo sounder (MBES) and a sub-bottom profiler (SBP) in 10 promising basin areas of the Japan Sea and around Hokkaido, for estimation of shallow methane hydrate resources. Survey was conducted on basin areas between West of the Oki Island and the Okushiri Basin of Japan Sea, and in the Hidaka Trough, off Tokachi and off Abashiri area around Hokkaido, using EM302 and TOPAS PS18 of Kongsberg, during the 7K13(43 days), 7K14(62 days) and 7K15(75 days) Cruises of R/V Kaiyo-maru No.7 (Matsumoto et al., 2014, Matsumoto and Satoh, 2015). Topographic shade maps are produced from obtained bathymetric data, and many topographic features concerning sedimentary processes, such as cliffs, slide sheets, submarine channels, are recognized in the survey areas.

Many sets of submarine slide sheet and adjacent cliff are observed in West of the Oki Islands and the Oki Trough areas, and no major submarine channels are found in these areas. In the southwest part of Oki Trough, almost of all trough floor are occupied by a large number of slide sheets. Although several number of slides are found, large submarine channels, flat basin floor are observed, and many topographic highs formed by tectonic inversion (Okamura et al., 1996a, b) are distributed in the Toyama Trough and the Mogami Trough area. Many sets of cliffs and slide sheets are found in the slopes of western and northeastern margin of the Hidaka Torough, and with no major submarine canyons. Two remarkable submarine channels are observed and topographic highs are extended from south to north between two channels off Abashiri area in the Okhotsk Sea.

This study was conducted as a part of the shallow methane hydrate exploration project of METI.

References:

Keywords: marine topographic map, submarine slide, submarine channel
Sedimentary Environment and Early Diagenesis of Thin Sandy Sediment Layers below Sea Floor in the Eastern Margin of Japan Sea

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Sediments in most of the sites along the eastern margin of Japan Sea are mainly composed of muddy fine clastics, and can be often found accompanied by a small amount of very fine to medium grained sandy intercalations, which are usually observed as thin layers and laminations in muddy layers. Fine-grained sediment samples below the seafloor were retrieved by the MD179 in 2010, the HR14 in 2014 and the PS15 in 2015 at the Umitaka Spur, Joetsu Channel, Toyama Trough, Japan Basin, Nishi Tsugaru and Okushiri Ridge areas. It is important to clarify the relationship between burial depths and absolute porosities of the argillaceous sediments in relation to early diagenesis. They consist of silt- to clay-grained particles, and they sometimes contain very fine- to medium-grained thin sandy layers. Average porosities of these fine-grained sediments are 50% in all study areas, which quickly reduce from 60% to less than 50% within 10 meters and gradually decrease to the depth. However, mean pore sizes in the Nishi Tsugaru are around 1000 nm while 100 nm in the other areas, which tend to decrease with depth. It is suggested that repacking of the muddy particles gradually advances by mechanical compaction, which may crucially influence permeability.

This research is a part of the METI project entitled “FY2015 promoting research and development on methane hydrate.”
Characteristics of sedimentation rates around hydrate seep area in the eastern part of Japan Sea

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**Background**

It is difficult to estimate the sedimentation age in methane hydrate area of eastern parts of the Japan Sea due to unable to find TL (thin laminated) layers, suitable for correlation with Japan sea stratigraphy, from core sediments. Oi et al. (2015MS) anticipated that sediment expands by hydrate growth caused to remarkable differences of sediment age with a reference core and a hydrate bearing core.

**Purpose**

One purpose is to clear the Chronostratigraphy based on radiocarbon dating and age from diatom fossils of several meter drilled cores in hydrate bearing area, Umitaka Spur and Oki Trough during the cruise from August to October 2015. The other purpose is to compare the sedimentation rate changes with approximately 60 m long core from Mogami Trough off Tobishima West (Oi et al., 2015MS).

**Method**

For radiocarbon dating, we used shells, woods and foraminiferal picked from undisturbed mud sediments. δ¹³C correction and calibration (Reimer et al. 2013; Bronk Ramsey 2009) were dated by the 3MV AMS at the Institute of Accelerator Analysis Ltd. as the basis samples (HOxII) after serial oxidation and reduction reactions. For Analysis of diatom fossils, we made untreated spraying slides using mud samples of core sediments or included massive hydrate. Certifications of Diatom zones followed two standard stratigraphic classifications applied in North Pacific wide area (Yanagisawa and Akiba, 1989) and the upper Quaternary in Japan Sea (Akiba et al., 2014).

**Discussions**

30 radiocarbon dates of 2015 samples indicate that upper parts of sedimentation rates off Joetsu were 2 to 3 times as fast as those of Oki Trough and Mogami Trough during the last 50 kyr. These difference might have relevance to the distance from Japan Island. Furthermore, we found the basic boundary (300ka) by the distinct of diatom fossils, Proboscia curvostris, from 20-25mbsf of Oki Trough cores and about 88mbsf of Umitaka Spur. These dates and previous data of Mogami Trough (about 42mbsf) also describe both remarkable slow depositions in Oki Trough and fast depositions in Umitaka Spur. In this presentation, we discuss stratigraphy of other cores including methane hydrate.

**Reference**


**Keywords:** methane hydrate, sediment age, microfossils
Benthic foraminifera at cold seeps on the Hidaka Trough, northwestern Pacific were studied to investigate the effects of methane on the geochemistry and faunal characteristics of benthic foraminifera assemblages and to discuss potential applications of foraminifera for reconstruction of methane release in the past and present. Sediment cores for this research were collected from eight chimney sites and one reference site with gravity corer in July 2015. Calcareous forms dominate benthic assemblages, accounting for 90 percent or more of the benthic populations for most samples. Results from Rose Bengal staining method indicate that certain species inhabit seep sites in the study area. Rutherfordoides cornuta, which is related to high methane gas content of the sediments and reported as methanophilic taxa from methane seepages at Sagami Bay (Akimoto et al., 1994; Kitazato, 1996), found alive (cytoplasm containing specimens) within surface sediments at four chimney sites in our study area including cores at the center of chimney. Other calcareous foraminiferal assemblages associated with chimney sites were typically infaunal species including Brizalina pacifica, Bolivina spissa, Chilostomellina fimbriata, Globobulimina auriculata, Nonionella globosa, Nonionella stella, Stainforthia fusiformis, and Uvigerina akitaensis, which can inhabit below water-interface and are also abundant in organic-rich oxygen-depleted environments. Geochemical analyses of living (stained) benthic foraminifera in our research sites doesn't show highly negative δ¹³C values comparable to those fossil (unstained) benthic foraminifera that are reported from seep sites such as the Gulf of Mexico (Sen Gupta and Aharon, 1994) or Monterey Bay (Martin et al., 1999); however differences in δ¹³C values for living benthic foraminifera of a given species were observed within a single core or between cores at chimney sites, which are unusual. For instance chimney site cores contain live specimens of B. spissa with δ¹³C values ranging from -0.43‰ to -1.07‰, -0.71‰ to -1.97‰, and -0.37‰ to -0.94‰, respectively. In contrast, at reference core the δ¹³C composition of B. spissa varies little and remains approximately constant around -0.70‰ over the length of the core. Variable carbon isotope values are also evident in other species such as U. akitaensis. These results suggest that δ¹³C values of foraminifera tests are influenced by methane seepage and different pore-water chemistry. Therefore, variations in isotopic composition can suggest temporal variations in seep activities and the differences in carbon isotope values will be expect to increase with the activity of the seeps. A good comprehending on ecology and stable isotope composition of modern benthic foraminifera at cold seeps may help identify paleo-seeps and will enhance our knowledge of climatic and oceanographic changes. This study was conducted as a part of the shallow methane hydrate exploration project of METI.

Keywords: Benthic foraminifera, Cold seeps, Hidaka Trough, Methanophilic taxa, Northwestern Pacific, Stable isotopes
Isotopic composition and U-Th age of methane derived authigenic carbonates

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Shallow gas hydrates often occur in close association with carbonate concretions. The precipitation of carbonates is considered as the results of sulfate reduction-methane oxidation (AOM) at SMT at around 2 to 5 mbsf in high methane flux fields. Methane derived authigenic carbonates (MDAC) of shallow gas hydrate fields in Japan Sea range in size from a few mm to a few meters. They are mostly composed of high mangesian calcite (HMC) and/or aragonite (AR). Oxygen isotopic signatures seem to indicate that HMC were formed in waters slightly depleted in O-18 while AR were from slightly enriched in O-18, or alternatively, HMC from higher temperature and AR from lower temperature. Frequency and amount of MDAC should reflect the intensity of AOM, that is, the intensity of methane fluxes. Therefore, the secular variation of methane flux in the past can be referred from the age distribution of MDAC. Ages of the precipitation of MDAC were determined by means of the U-Th isotope disequilibrium method. Previous studies (Watanabe and Nakai, 2006; San-no, 2008MS; Suzuki, 2010MS) have revealed that the age of the MDAC collected from surface sediments (< 4 mbsf) tends to concentrate around 20ky, and discussed the relation with glacio-eustasy. MDAC of this study ranges from the sea floor to about 80 mbsf, covering the entire depth range of shallow gas hydrate. Precise age determination of the MDAC should reveal the time constraint and conditions of the formation of shallow gas hydrate of Japan Sea. This study was conducted as a part of the shallow methane hydrate exploration project of METI. We express our thanks for allowing us to present this work.


Keywords: MDAC methane derived authigenic carbonates, shallow gas hydrates, U-Th isotopic disequilibrium
Isotopic compositions of Carbon, Oxygen, and Strontium in authigenic carbonates from Umitaka Spur, off-Joetsu, southeast of Japan Sea

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We present isotopic compositions of Carbon (δ¹³C), Oxygen (δ¹⁸O), and Strontium (⁸⁷Sr/⁸⁶Sr) in authigenic carbonates from Umitaka Spur, off-Joetsu, southeast of Japan Sea. The carbon isotopic values in authigenic carbonate from Umitaka Spur are higher than those of Joetsu Knoll and west off-Tobishima Island. This range corresponds to the δ¹³C values of thermogenic methane (Bernard et al., 1978). Range of the δ¹⁸O values of authigenic carbonates from Umitaka Spur is mostly equal to those of Joetsu Knoll and west off-Tobishima Island. The ⁸⁷Sr/⁸⁶Sr ratios in authigenic carbonates from shallow depth of Umitaka Spur is equal to those of modern surface seawater in off-Joetsu. The Sr-isotopic ratios in authigenic carbonate from deeper depth are lower ratios. This Sr-isotopic trend can be correlated to the global Sr-isotopic trend in seawater from late Pleistocene to present. It indicates that Sr-isotopic ratio of authigenic carbonate reflects the Sr-isotopic ratio of seawater at the time of deposition. The Sr-isotopic ratios in pore water are parallel lower than those of authigenic carbonate. It indicates that pore water includes light Sr by diagenetic procedure.

Acknowledgments: This study was conducted as a part of the shallow methane hydrate exploration project of METI. Isotopic measurement of Strontium was performed in Kochi Core Center, by visiting scientist program of JAMSTEC.

Keywords: authigenic carbonates, shallow gas hydrate, Japan Sea
Geochemistry of pore water, dissolved gas, and sediment from offshore Hidaka area, Hokkaido

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Precise acoustic investigations resulted in the wide distribution of gas chimney structures accompanying high backscatter anomalies, which indicates strong methane migration from deep sediments to the seafloor and the potential formation of gas hydrate/carbonate near the seafloor in the offshore area of Hidaka, Hokkaido. We have deployed gravity corer and collected sediments to analyze compositions of sediment, pore water, and dissolved gas for characterizing geochemical system related to the high methane environments near the seafloor.

Concentrations of sulfate dissolved in pore waters just on the gas chimney show rapid decrease with depth. Concentration of methane and the depth of sulfate-methane interface, indicative of methane flux, locates at 74 to 420 cmbsf, equivalent to the shallow gas hydrate area in the eastern margin of the Japan Sea. Carbonates are observed only at the western slope region where the moderate methane flux is estimated. Geochemical environments are different among the locations reflecting subseafloor structures.

This study was conducted as a part of the shallow methane hydrate exploration project of METI.
Geochemistry of dissolved gas around gas chimney structures in the Mogami Trough, Japan

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In the Mogami Trough, eastern margin of the Japan Sea, active gas venting has not been observed on the seafloor, however, distribution of mounds and pockmarks on the gas chimney structure (vertical acoustic blanking zone of shallow sediment) indicates the strong flux of gas-rich fluid from deep sediments and formation of gas hydrates near the seafloor. Concentrations and isotopic compositions of headspace gases collected inside and outside the well-developed gas chimneys were analyzed in order to characterize geochemical structure across the gas chimney and surrounding sediments. Distributions of methane (C₁) and ethane (C₂) concentrations and C₁/C₂ ratios show gradual increase toward the center of gas chimney particularly in shallow sections, reflecting higher biogenic methane production in the higher gas migration zone within the chimney. The stable carbon isotopic compositions of methane are also high in the center of the chimney due to higher contribution of thermogenic gas derived from deep section. The higher concentration and upward flux of gas are observed in the mound area rather than pockmark area, reflecting that the activity of gas chimney may control the distribution of gas hydrate responsible for shallow topographic anomalies.
Shallow gas hydrates have been often found on the gas chimney structures in the eastern margin of the Japan Sea. Although the strong gas flux through the gas chimney is a key for the massive accumulation of gas hydrates near the seafloor, geochemical nature inside/across the gas chimney has not been discussed well. We have collected pore waters from shallow sediment inside/outside the gas chimney in the Mogami Trough and analyzed major ion concentrations to understand the special change of pore water geochemistry reflecting the activity of gas chimney. We found significant relation between the distance from the center of gas chimney and the gradient of alkalinity/depth of sulfate-methane interface, indicative of methane flux; they decrease similarly in response to the distance, particularly outside the chimney. Although the activity of gas chimney indicated by the chimney size and methane flux varies in the same area of the Mogami Trough, gas hydrates potentially accumulate near the center of gas chimneys.

Keywords: Gas Hydrate, Gas chimney
The characteristic seafloor topography associated with gas hydrates in shallow sediments was reported in the seafloor of the SE margin of Tsushima Basin and Oki Trough, Japan. Interstitial water and seawater collected from these areas during the UT14 cruise were analyzed for characterizing the fluid geochemistry responsible for methane migration toward the seafloor and formation of hydrates. In the eastern margin of Tsushima Basin, high concentrations of sulfate and alkalinity in interstitial water reflect very shallow SMI depths (~1.7mbsf), strong methane fluxes, and methane generation due to the decomposition of organic matters in shallow sediments. The low concentrations of silicate dissolved in seawater indicate that the buried old organic matters are responsible for the formation and distribution of gas hydrates near the seafloor.
Time-series analysis of pore water from shallow gas hydrate area on the Umitaka Spur, Japan Sea

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Active gas venting (seepage) from the seafloor and outcropping of massive gas hydrate have been observed on the Umitaka Spur in the eastern margin of the Japan Sea. Submersible observation revealed that the strength and location of gas venting had changed within a few days, geochemical environment near gas venting including gas hydrate might have also changed within a short period compared to geological time scale. We have deployed a long-term osmotic fluid sampler (OsmoSampler) near the gas venting site on the Umitaka Spur from September 2013 to March 2014 (160 days, NT13-E02 and NT14-E03 cruises) and collected pore waters continuously to examine the potential changes of pore water geochemistry and the impacts on the near-surface environments.

Concentrations of dissolved ions change shortly, for 3-5 days, through the entire sampling period, which are controlled by the input of saline water from gas hydrate formation and of fresh water from gas hydrate dissociation. Gas venting was observed 10 m away from OsmoSampler, however, concentrations of methane dissolved in pore water were low during the first 20 days and occasional high methane concentrations were observed only from the 20th to 40th day. Rapid gas hydrate formation caused by high gas flux might plug the path delivering gas-rich fluids to the seafloor, contrary, the reduced gas flux (venting) caused the dissociation of gas hydrate. After the 70th day on, methane concentration was constant at low level, <1 mM, indicating that the location of gas venting had been moved due to the gas hydrate plugging. Significant concentrations of ethane during that period also indicate the gas hydrate plugging and subsequent change of major gas source from biogenic-rich to thermogenic-rich. Geochemistry of pore water has changed dynamically and shortly in response to the change of gas venting activity.

This study was conducted as a part of the shallow methane hydrate exploration project of METI.

Keywords: Time-series analysis, pore water, Shallow gas hydrate, gas venting
Distribution of methane in seawater from shallow gas hydrate areas in the Japan Sea

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We have analyzed the concentrations of methane dissolved in the bottom seawaters collected from shallow gas hydrate occurrences including active gas venting and the associated distribution of carbonates/bacterial mats during the NT15-E03 expedition in the Japan Sea. Methane concentrations are close to the normal bottom water level over the mud seafloor, however, they increase typically near the gas venting, carbonate, and bacterial mat sites; gas venting had only been active during the formation of carbonates and bacterial mats. Contrary, the number of benthos does not correlate with the concentration of dissolved methane, it probably reflects the location and seafloor condition, not the present concentration of methane. The concentration of methane rapidly decreases with shallowing depth due to the oxidation and diffusion of methane ejected from the seafloor in water column, reaching normal seawater level at the intermediate depth. Environmental impacts of the gas venting, possibly gas explosion on the seafloor, are very limited near the seafloor. This study was conducted as a part of the shallow methane hydrate exploration project of METI.
Characteristics of natural gas hydrate retrieved off Abashiri, the Sea of Okhotsk

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In the area of southwestern margin of the Sea of Okhotsk, an existence of natural gas hydrate has been expected using seismic data. Yamamoto et al. (2002) suggested existence of natural gas hydrate off Shiretoko, the Sea of Okhotsk, by a long piston coring. Recovery of sediment core for gas hydrate started in the cruise of TK11 in 2011 in the framework of joint research between Kitami Institute of Technology and University of Tokyo, and obtained gas-rich sediment cores off Abashiri. Gas hydrate crystals were first retrieved in the cruise of UT12 (T/S Umitaka-Maru) in 2012. New hydrate-bearing sites were also discovered in the cruise of NT13-20 (R/V Natsushima in 2013. We planned operations using T/S Oshoro-Maru, and obtained sediment cores and gas hydrates at this area in the cruise of OS249 (2012), OS263 (2013), and C020 (2015). Gas hydrate crystals were obtained and stored in liquid nitrogen for Raman spectroscopic analysis and calorimetry. Samples of hydrate-bound gas were obtained onboard and stored in 5-mL vials, and sediment gas were also obtained using a headspace gas method. We measured molecular and stable isotope compositions of these samples. We summarized the results as follows:
1) Gas hydrates belong to the cubic structure I, containing methane (more than 99%) and hydrogen sulfide (less than 1%). C1/C2+ ranges from 5,500 to 5,800.
2) Hydration number is estimated as 6.03±0.04, agrees well with 6.04±0.03 for synthetic methane hydrate (Sum et al., 1997).
3) Dissociation heat from hydrate to gas and water is estimated as 55.1±0.3 [kJ/mol], agrees well with 54.19±0.28 [kJ/mol] for synthetic methane hydrate (Handa, 1986).
4) Hydrate-bound gas is of microbial origin according to C1/C2+ and stable isotopes of hydrocarbons, however, delta 13C of ethane seems relatively large.
5) Gas hydrate in the NT13-20 PC06 core contains trace amount of ethane (several ppm), whereas that in the NT13-20 PC02 core contains about 100 ppm of ethane.
6) SMI (sulfate-methane interface) depth of the sediment cores are less than 1 m, indicating high methane flux off Abashiri.

We appreciate the support of the crew onboard R/V Natsushima during the NT13-20 cruise, and T/S Oshoro-Maru during the cruises of OS249, OS263, and C020. This study was supported by the Grant-in-Aid for Scientific Research (B) 25289142 and 26303021 of the Japan Society for the Promotion of Science (JSPS).


Keywords: hydrate, the Sea of Okhotsk, stable isotope
Isotopic fractionation of ethane at the formation of sII gas hydrate composed of methane and ethane

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Methane and ethane mixed-gas hydrate of the cubic structure II exists at the central and southern Baikal Basin. We found "double structure gas hydrate" composed of the structure I and II in a same sediment core. The structure II gas hydrate contained 13-15% of ethane, on the contrary, the structure I has only several % of ethane. Subramanian et al. (2000a; 2000b) reported that a structure II forms in appropriate gas composition of methane and ethane. Hachikubo et al. (2009) showed that delta D of hydrate-bound ethane in the structure II is smaller than that in the structure I, whereas delta 13C of methane and ethane, and delta D of methane are the same between the structure I and II. It has been unknown how the structure II concentrates light ethane in delta D (hydrogen isotope).

In this study, synthetic mixed-gas (methane and ethane) hydrates were formed and checked isotopic fractionation between phases of hydrate and residual gas. We made a hydrate sample from methane and ethane mixed-gas (85% C1; 15% C2) in a pressure chamber (volume: 120 mL). Before the retrieval of gas hydrate sample, residual gas was also sampled. We measured isotopic compositions (13C and D) of methane and ethane using CF-IRMS. Crystallographic structure of gas hydrate was determined using a Raman spectrometer.
The Raman spectra of C-C stretching mode of ethane in hydrate phase indicated that the sample belonged to structure II. Delta D of hydrate-bound ethane was several permil smaller than that of residual ethane, similar to the behavior of methane delta D in the structure I. Although the mechanism of ethane fractionation at the formation process of the structure II is not fully understood, the results agree with the observation at the Kukuy K-2 mud volcano reported by Hachikubo et al. (2009).

Subramanian et al. (2000b) Structural transitions in methane + ethane gas hydrates - part I: upper transition point and applications.
Chem Eng Sci 55: 5763-5771. doi:10.1016/S0009-2509(00)00162-7

Keywords: gas hydrate, stable isotope, ethane, Lake Baikal
Effect of water depth on hydration number of natural gas hydrate in Lake Baikal

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Natural gas hydrates exist under the deep sea/lake or permafrost are considered to be a potential natural gas resource. Hydration number "n" of methane hydrate (CH₄ₙH₂O) decides the amount of methane in an unit volume/weight of crystal. In the case of ideal full-occupation of hydrate cages, the value of hydration number is 5.75 (Sloan and Koh, 2008). However, researchers have reported that the hydration number is around 6, because small amount of empty cages decrease the free energy and stabilize the crystal. Natural gas hydrates have been retrieved from lake-bottom sediment at Lake Baikal, where the water depths ranged from 450m to 1400m, and their main gas component is methane. Hydration number may change under various pressure condition, but it has not been examined yet. In this study, we report the pressure effect on hydration number of synthetic methane hydrate and natural gas hydrate of Lake Baikal.

Methane hydrate was synthesized under the pressure range between 3 MPa to 20 MPa. Natural hydrate samples were retrieved at the southern Baikal basin (Malenky, Bolshoy, Peschanka P-2, and Goloustnoye G-1) and central Baikal basin (Kukuy K-1, K-2, K-8, K-9, K-10, and Novosibirsk). Raman spectroscopic measurements were made to assess the hydration numbers of samples. Raman spectra were obtained at 123 K in the range 2,800-3,000 cm⁻¹ for the C-H stretching peaks of methane, and fitted using a Voigt function to obtain the integrated intensities of the two peaks corresponding to methane encaged in large and small cages of the cubic structure I. The cage occupancies and the hydration numbers were estimated from these peak intensities using a statistical thermodynamic model (Sum et al., 1997). Hydration number of synthetic methane hydrate decreased with pressure, from 6.05 (2.7 MPa) to 5.97 (20.9 MPa), and those of natural gas hydrate also decreased slightly with water depth.

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Keywords: hydrate, hydration number, Lake Baikal, Raman spectroscopic analysis
Volume proportion of gas hydrate evaluated from oxygen isotope of water in locus sub-samples

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Gas hydrate distributed offshore around the Japanese Island is actively studied for evaluating its resource. However, the evaluation is not always easy because gas hydrate rapidly decomposes in a low-pressure onboard condition. We contrive a new method using oxygen isotope ratio of locus sub-samples of muddy sediment and hydrate. Together with the isotope ratio of the bulk pore-water, we can calculate volume proportion of gas hydrate.

This study was conducted as a part of the shallow methane hydrate exploration project of METI. During the expedition with the research vessel Poseidon in August-October 2015, we analyzed mixed sediment of hydrate and mud from 26 core sections drilled from Oki trough and Joetsu Basin. From each core section, we quickly encapsulated locus sub-samples of mud and hydrate (3-5 sub-samples for each) in 4.5-ml vials. Air in the vial was later substituted in laboratory by He for the mud sub-sample, by He-CO₂ for the hydrate and bulk pore-water sub-samples. After leaving more than 2 days in a constant temperature (at 23 degrees), me measured the isotopic ratio by Finnigan DeltaPlus with GasBench II (2SD = 0.15‰).

Mud sub-samples generally recorded larger deviation in oxygen isotopic ratio than hydrate sub-samples. This is because of difficulty in avoiding contamination of hydrate-molten water. After excluding the contaminated sub-samples, we found that oxygen isotopic ratio was always higher in hydrate than in mud, likely reflecting isotopic fractionation during hydrate formation. Difference between the hydrate value and the mud value was site-specific ranging from 1 to 4 permil, and tended to decrease with increasing the volume proportion of hydrate. The oxygen isotope ratios of water in locus sub-samples successfully provided the hydrate volume proportion from 28 core sections, which appear consistent with images observed onboard.

Keywords: Oxygen isotope, Gas hydrate
Isolation of methanogenic archaea and distribution of methanogenic and methanotrophic archaea in subseafloor sediment

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Shallow gas hydrates are estimated to be buried around Japan, especially in Japan Sea. The methane trapped in those hydrates are produced by biogenic (microbial) or thermogenic system. But the relationship between shallow gas hydrates and the methanogens are yet to be confirmed. So this study focuses on isolation and diversity of methanogenic and methanotrophic archaea.

Sediment samples were collected from the subseafloor (with or without specific structure) by the MBARI push corer, during an environment assessment cruise. Samples were collected from the top, middle, bottom of the recovered sediments of each push core. The samples were stored in different temperature for the microbiological cultivation experiment and microbiological diversity analysis, respectively.

For the methanogenic archaea isolation, cultivation was carried out by enrichment culture using methanogen medium. The cultures were cultivated by 15°C and 30°C, respectively. We successfully isolated several methanogenic archaea from the surface sediment. The result of the 16S rRNA gene sequence analysis showed the isolated strains identified as one of the order of the methanogen, Methanomicrobiales.

For the methanogenic and methanotrophic archaea diversity analysis, DNA was extracted from the sediment samples, using ISOIL kit. The methane related functional gene, the mcrA gene of methanogenic and methanotrophic archaea was choosen as the target gene. The genes were amplified by PCR method. The PCR products were purified by FastGene Gel/PCR Extraction Kit. The purified products were analyzed by clone library method. The result of the clone library analysis indicated that specific structure of the surface of the subseafloor have specific methanogenic and methanotrophic archaea structure.

This study was conducted as a part of the shallow methane hydrate exploration project of METI.

Keywords: shallow gas hydrate, methanogenic archaea, methanotrophic archaea
Pyrosequencing of planktonic and benthic biota above the sediment-water interface in methane hydrate-bearing areas in the eastern margin of the Japan Sea

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In this study, we have conducted pyrosequencing analysis of eukaryotic community structures from the water columns and the sediment-water interfaces at sites associated with and without methane seeping and bacterial mats in the area associated with the shallow methane hydrate deposits in the Joetsu Basin, Japan Sea. Dominant 18S rRNA gene sequences from shallow water columns at water depths of ~50 m and ~200 m were related to marine dinoflagellates of the genera Gyrodinium, copepods of the genera Centropages, radiolarians of the subclass Acantharia. From bottom seawater at water depths of ~1000 m, the community structures were distinct at the sites associated with methane seeping and bacterial mats from that at the reference site. The former structures were abundantly composed of the genera Nanomia and Pantachogon of Cnidaria phylum. Although marine dragon nematodes of the family Chromadorea were dominantly detected from shallow sediments at the site associated with methane seeping and bacterial mats, the overall community structures from shallow sediments were similar at all investigated sites.

This study was conducted as a part of the shallow methane hydrate exploration project of METI.

Keywords: methane hydrate, 18S rRNA, Pyrosequencing, Eukaryotic communities, DNA
Investigation microbial community for gas-hydrate site off-Sakhalin Island

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Gas hydrates (GH) are widely spread in the sediments under the subsea floor and form at high pressure and low temperature. GH oriented gas were grouped to thermogenic and microbial gas according to composition carbohydrate gas and isotopic molecular weight of methane. The role of microbial communities in the GH sites have been already investigated by several research groups. Isotopic composition of gas hydrate is often use to determine gas derivation such as thermogenic or microbial gases. However, combination study both isotopic gas analysis and microbial diversity have not been performed at all. Recently we successfully obtained mix gas-derived GH core sediment in the western Sakhalin slope off Sakhalin Island by exploration using ultrasonic wave sonar and gravity coring, in SSGH 15 project by using Russian research vessel Akademik M. A. Lavrentyev. We will demonstrate that results of investigating molecular and isotropic composition of the sediment gas, sulfate and sodium compositions, and microbial composition of a GH-bearing sediment core obtained in SSGH15.

Molecular composition ratio $C_1/C_2+C_3$ below SMI were in the range between 116 and 225, while $d^{13}C$ and $dD$ values of methane were in the range of -48.9 and -45.7 permil, and of -165 and -149 permil, respectively. These results indicated that the gas compose of large amount of thermogenic gas and small amount of microbial gas.

Forty two individual clones have successfully analyzed, until we submit this article. Three Aciduliprofundum related clones, and three Methanobrevibacter related clones were detected. These sequences were clustered into oceanic methanogen in the phylum Euriarcheota. This result implied that these archaeon generate microbial methane in the core, and may correspond to decrease isotopic $^{13}C$ ratio of methane and increase the $C_1/C_2+C_3$ ratio. Slight amount of sequence in Crenarchaeota, which may be involved anaerobic methane oxidation (annamox). Interestingly, heterotrophic bacteria in cluster of Dehalococcoidetes-related Chroloflexi, of Candidatus artibacteria (named as division JS1/OP9), and of Planctomycetes were frequently widespread in the core. The phylum Chloroflexi is a lineage for which the class ‘Dehalococcoidetes’ was proposed to accommodate the tetrachloroethane respiring coccus Deharococcides (1). These bacteria may contribute to decomposition of difficultly degradable organic matters accumulated on deep sea floor. Planctomycetes have been often detected, and widespread in methane-seep (2), but the functional characters have been unknown. Recently, candidatus artibacteria have been revealed to play significant role as symbiotic scavenger in artificial methanogenic bioreactor, by using single cell genome analysis (3). According to the study, artibacteria may support methanogen and chloroflexi through the by-product generation such as acetate, butyrate, and $H_2$. These results implied that thermogenic and microbial mixed-derived gas composition may be formed by symbiotic metabolism of those species, but not simply generated from inorganic gases such as CO$_2$ and $H_2$ by methanogen.

