Characteristics of hydrate-bound hydrocarbons retrieved from southern Lavrentyev seabed fault, the Sea of Okhotsk

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We report molecular and isotopic compositions of hydrate-bound hydrocarbons in the new seepage sites of offshore Sakhalin Island, the Sea of Okhotsk. More than ten gas seep sites have been discovered since 1990s in the north area of Lavrentyev Fault and hydrate-bearing sediments were recovered (Ginsburg et al., 1993; Hachikubo et al., 2010). These sites often accompany with gas plumes from the sea floor and gas hydrates exist in a shallow sediment layer. Recently, Sakhalin Slope Gas Hydrate (SSGH) project was started from 2007 and we retrieved sediment cores from the southern area of Lavrentyev Fault during the SSGH09 and SSGH10 cruises in 2009-2010. We obtained the samples of hydrate-bound gas and dissolved gas in pore water on board, and we measured molecular and stable isotope compositions of them. Empirical classification of the methane stable isotopes; delta $^{13}$C and delta D according to Whiticar et al. (1986) and Schoell (1988) indicated their microbial origin via carbonate reduction. Profiles of methane concentration in the pore water suggested a shallow SMI (sulfate-methane interface). SMI depth was estimated as 30-50cm from the sea floor in the case of hydrate-bearing cores, and around 2m from the sea floor in the case of gas-rich cores. Molecular compositions of hydrate-bound gas were almost the same in both northern and southern areas of Lavrentyev Fault. Stable isotope compositions of hydrate-bound gas were concentrated in the range of -204.6 permil to -196.7 permil for delta D and -66.0 permil to -63.2 permil for delta $^{13}$C in the north area (Hachikubo et al., 2010). On the other hand, both isotopes were more depleted in the south area about 6 permil in $^{13}$C and 7 permil in deuterium, respectively, suggested much more active microbial processes in the shallow sediment. Isotopic difference in delta D between hydrate-bound and dissolved gases was about 5 permil at several sites, indicating that the gas hydrates formed from the current gas in pore water (Hachikubo et al., 2009).


Keywords: gas hydrate, stable isotope, Sea of Okhotsk
Isotopic analyses of pore waters of LV47 and LV50 gas hydrate-bearing sediment cores from offshore Sakhalin Island

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From July to August of 2009 and June of 2010, field operations of SSGH-09 (Sakhalin Slope Gas Hydrate Project, 2009) and SSGH-10 projects were conducted as the 47th and 50th cruises of R/V Akademic M.A. Lavrentyev.

Gas hydrate-bearing and -free sediment cores were retrieved using steel gravity- and hydro- corers. The sediment pore water was obtained onboard using a squeezer designed and constructed at KIT (Kitami Institute of Technology, Japan). The stable isotopic compositions (delta 18O and delta D) of these water samples, ionic compositions in sediment pore water, gas hydrate water (dissociated gas hydrate water) and seawater samples and water content distribution in the sediment cores and lithologies of the cores were compared to figure out the geochemical characteristics of the cores.

The depths of SMI (sulfate-methane interface) are 0.4-0.8 mbsf for the gas hydrate-bearing LV47-24HC, LV50-29HC, LV50-31HC and LV50-33HC cores and 0.5-4.0 mbsf for the other gas hydrate-free (by visual observation) cores.

The relationship between the delta 18O and delta D values of the pore water of the gas hydrate-bearing LV50-29HC core, the gas hydrate water from the LV50-29HC core and seawater from the corer of the LV50-29HC was investigated and a linear relation among them was found. These results suggest that the source of the water is the same and that it might be the pore water primarily originated from seawater.

Some sediment cores have shown traces of gas hydrate formation or dissociation, i.e., changes in concentrations of dissolved ions and/or in stable isotopic compositions of hydrogen and oxygen. The further investigations/discussions will be presented.

Keywords: methane hydrate, pore water, hydrate water, stable isotope ratio
Foraminiferal assemblages from the Joetsu region in the Japan Sea

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A giant piston core, MD10-3312 of 31.115m long), obtained from the Site F (WD: 1026m) on a unnamed spur off Joetsu, southeastern margin of the Japan Sea during MD179 cruise of R/V Marion Defresne. It is characterized by alternation of light and dark layers, without influence of gas-hydrate, and thus has potential of a biostratigraphic standard in the Joetsu region. The followings are preliminary results by foraminiferal analysis:

1. Faunal composition on the benthic foraminifera is quite different between the dark and light layers, each other.
2. The suboxic species-group are highly abundant even in the light layers.
3. The time of establishment of the modern condition in the Japan Sea will be indicated by dominant occurrence of Neogloboquadrina incompta and disappear of Pullenia apertura in the uppermost part of the core.

Keywords: Japan Sea, benthic foraminifera, gas-hydrate, suboxic species
Quantitative and qualitative analysis of distribution of macrobenthos around Joetsu Gas Hydrate Field.

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Distribution of macrobenthos was investigated in the Joetsu Gas Hydrate Field, the Japan Sea, in June 2010. Benthic organisms and bottom sediments were collected using a CASQ corer by the R/V Marion Dufresne and also using a slurp gun and a Kumade sampler (like scoop) by the ROV Hyper-Dolphin. The core sample collected in two points (Core No. 3297 in 894 m deep, Core No. 3307 in 930m deep) in the Umitaka Spur, 2 points (Core No. 3318 in 1000m deep, Core No. 3324 in 1179m deep) in the Joetsu Knoll, and 1 point (Core No. 3328 in 3444m deep) in the Okushiri Ridge was used for the analysis. The columnar core of 15cm X 13cm in width was divided from the bottom surface to 5cm, 5-10cm, 10-20cm, 20-30cm, 30-50cm, and 50-100cm, and cryopreserved onboard of the R/V Marion Dufresen.

Living macrobenthos such as porifera, bivalvia, polychaete, pogonophora and amphipoda were collected by a CASQ corer. Numerical density and biomass of each section was 0 to 2051.28 individuals/m$^3$ and 0 to 1656.41g/m$^3$, respectively. The core where living specimens appeared was one station (Core No. 3307) in the Umitaka Spur and 2 stations (Core No. 3318 and 3324) in the Joetsu Knoll. A lot of living specimens were distributed from 0 to 10 cm, but were few in a deep section. Among five cores analyzed in the present study, the gas-hydrate was included only in Core No. 3318. There were neither other cores nor great differences though solemyid bivalvia in which chemosynthetic bacteria were lived together appeared in this core. About the appearance of shells that related to the methane seep, the diversity of shells were high, and living specimens or shell fragments of chemosynthetic bivalvia and gastropoda such as Solemyidae, Thyasiridae and Provannidae was collected by each section in Core No. 3318. It was thought that the methane had been comparatively supplied for a long term in this station. Moreover, it was thought that the existence of the gas-hydrate influenced the amount of distribution of macrobenthos because there were a lot of biomasses in Core No. 3318. It is general to do the biomass investigation of macrobenthos by using a Smith-Macintyre grab sampler and a box corer. Then, the biomass of the section from the bottom surface to 10cm where a Smith-Macintyre grab sampler was able to be collected was converted into the biomass per 0.1m$^2$ of the bottom surface. Numerical density and biomass were under 1 individuals/0.1m$^2$ and under 0.5g/0.1m$^2$ in Core No. 3307, 15 individuals/0.1 m$^2$ and 33.49g/0.1 m$^2$ in Core No. 3318 and 5.1 individuals/0.1 m$^2$ and 0.21g/0.1 m$^2$ in Core No. 3324. According to Tsujimoto et al. (2006), bivalves and the polychaetes were collected, macrobenthos of 18-64 individuals/0.1 m$^2$ (average was 33.8 individuals/0.1 m$^2$) in the Toyama Bay abyssal floor (393-631m in depth). Also, biomass was 0.41-1.86g/0.1 m$^2$ (average was 1.05 g/0.1 m$^2$). When the biomass was compared with Core No. 3318 where the gas-hydrate existed, it was high with 8-82 times. But, the number of individuals was little with 20-86%. As for this, it was suggested that it be causes that the gas-hydrate’s existing the comparatively large size benthos (bivalves) that mainly depended on chemosyntheses was distributed at the bottom, and polychaetes and non-chemosyntheses bivalves that occupied the majority of the biomass in other sea areas were few. And, result of the ROV Hyper-Dolphin survey is also discussed.

Reference

Keywords: gas hydrate, benthos, distribution, chemosynthetic benthic community
High-density heat flow measurements and their temporal variation in the Joetsu Gas Hydrate Field, Japan Sea

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Joetsu Gas Hydrate Field, located in the western Joetsu Basin in the eastern margin of the Japan Sea is one of the best fields for gas hydrate studies. There are many methane plumes and active methane seeps associated with massive gas hydrates on and around several gas hydrate mounds on the Umitaka Spur and Joetsu Knoll. Evolution of gas hydrate mounds depends on the development of gas chimneys, and is closely related with the formation and collapse of surface-type gas hydrate accumulation (Matsumoto et al., 2009).

The result of heat flow measurement through nine research cruises in 2004–2008 is summarized in Machiyama et al. (2009). They observed not only extremely high heat flow anomalies but also non-linear temperature profile such as concave/convex profiles and negative geothermal gradients on the mounds. The distribution of high heat flow anomalies and non-linear temperature profiles is important to understand a hydrological regime in the high methane flux area of the Joetsu Gas Hydrate Field. To clarify a detailed fluid activity and temporal variation in the high methane flux area, high-density heat flow measurement using SAHF (Stand-Alone Heat Flow meter) was conducted at the methane seep site on the Umitaka Spur and at the crater site on the Joetsu Knoll in the ROV surveys of R/V Natsushima NT10-10 Leg 2 Cruise.

1) Heat flow around bacterial mats on the Umitaka Spur

We conducted precise observations around bacterial mats, where very high heat flow 4 W/m² with a temperature reversal profile was measured in 2007. After two years (in 2009), high heat flow value 970 mW/m² with a similar temperature reversal profile was observed at the same point, though subsurface temperature went down. Eight months later (in 2010), approximately 350 mW/m² of heat flow was measured and no temperature reversal profile was observed at the same bacterial mat. Fluid activity, therefore, shows a steep decline and a temperature reversal profile disappeared in the last two years and eight months. This result suggests that fluid pathway has temporal dependence. Thus, it seems very possible that heat flow at the bacterial mat declined due to the change of fluid pathway, such as clogging of conduits.

2) Heat flow around the crater site on the Joetsu Knoll

Heat flow measurements were conducted in and around a crater-like depression, which was probably formed by self-collapse and floating up of gas hydrate block under the condition of high methane flux (Matsumoto et al., 2009). Seafloor in the crater is covered by about 30 cm-thick muddy sediments in the last two years and eight months. Methane gas bubbles discharging from seafloor are found, when SAHF was penetrated into the seafloor by 20-30 cm. Approximately 250-520 mW/m² of heat flow were observed around the crater, and maximum heat flow value in the crater is similar to that measured in 2007. Thus, methane seep activity seems to be still high. A kinked temperature reversal profile is observed in the crater, though there are no methane seep phenomena, such as bacterial mats. The cause of this temperature reversal is still under consideration.

Keywords: gas hydrate, heat flow, methane seep, Japan Sea, Joetsu Knoll, Umitaka Spur
Heat flow measurements in western Joetsu Basin, offshore Sado Island, Japan

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Heat flow is calculated by the product of the gradient of vertical temperature profile in the earth material and thermal conductivity of the material and is used to infer subsurface thermal structure and regime of fluid migration. Stability zone of methane hydrate depends on pressure and temperature. Furthermore, it is guessed that fluid flow in sediment acts as an important role for the formation and dissociation of methane hydrate. Thus, heat flow provides information on spatial distribution of stability zone of methane hydrate and formation and dissociation of methane hydrate.

The western Joetsu Basin, southwest of Sado Island, Japan, is one of target areas where methane hydrate studies have been conducted intensively (Matsumoto et al., 2009). Machiyama et al. (2009) measured heat flows on and around the Joetsu Knoll and spur (called ‘Umitaka Spur’) on its eastern side. They obtained heat flow values of about 98 mW/m² around the Joetsu Knoll and Umitaka Spur. On the other hand, heat flows of 150 mW/m² or more were measured at active seep sites on the summit areas of the Joetsu Knoll and Umitaka Spur, strongly suggesting upward fluid migration at these sites.

During MD 179/Japan Sea Gas Hydrates cruise using R/V Marion Dufresne, which was conducted to investigate the mechanism of formation of methane hydrate in the eastern margin of the Sea of Japan, we measured heat flows at seven positions on and around the Joetsu Knoll and Umitaka Spur to infer subsurface thermal structure and regime of fluid migration in the western Joetsu Basin. The measured geothermal gradients range from 88 to 97 mK/m. Because thermal conductivity of sediment measured from recovered sediment core samples show an increase with depth, we calculated heat flow by applying ‘Bullard plot’ (Bullard, 1939), which calculates heat flow by taking the changes in thermal conductivity with depth into account. The calculated heat flow values are similar to those around the Joetsu Knoll and Umitaka Spur recently measured by Machiyama et al. (2009). Using the heat flow data obtained in this study and previous studies, we will calculate thermal structure in the western Joetsu Basin and will investigate subsurface fluid migration and formation of methane hydrate in the area.

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

Keywords: heat flow, western Joetsu Basin, methane hydrate, MH21
In order to clarify the microbial activities related to methane generation in the eastern Nankai Trough, we performed analyses of biomarkers in the sediment samples obtained from the METI Exploratory Test Wells Tokai-oki to Kumano-nada by using the comprehensive two-dimensional gas chromatography (GC x GC). Previous geochemical studies have shown that the biogenic methane forms methane hydrate (MH) in the eastern Nankai Trough. Methanogenic archaea produces methane which forms a vast quantity of gas hydrate in continental margin accretionary sediments. In this study, we attempted to identify and quantify the biomarker in the sediment cores by GC x GC equipped with qMS and FID.

The sediment samples were collected from Tokai-oki, Daini-Atsumi knoll and Kumano-nada with METI exploratory test wells Tokai-oki to Kumano-nada in 2004. The lipids were extracted by methanol/dichloromethane, and then extract was saponified with 0.5 mol KOH/methanol. The neutral fraction was converted to trimethylsilyl esters (TMS) by BSTFA. The TMS-derivatives were analyzed using a ZOEX KT2006 comprehensive GC x GC equipped with qMS and FID. The carbon content and carbon isotopic ratio of organic matter were determined by the flow-injection method using a Thermo DELTA V mass spectrometer connected with a Flash EA.

The neutral lipids fractions of the core samples from Tokai-oki mainly consist of n-alkanes, acyclic isoprenoids, n-alcohols, sterols and hopanols. 2,6,10,15,19-Pentamethylicosane (PMI), which is the biomarker related to methanogenic archaea, were detected in all samples from Tokai-oki. PMI concentrations increase below Sulfate-Methane Interface (SMI) and below MH bearing zone in the sediment from Tokai-oki.

The neutral lipids compositions in MH bearing zone were comparatively similar between at Tokai-oki and Daini-Atsumi knoll, those at Kumano-nada was different from those at others. It was suggested that the activities of methanogens and the compositions of microbial assembly are different in the Kumano-nada well. Several hopanols, which indicated bacterial activity, such as 17,21-bishomohopanol, 17,21-homohopanol and anhydrobacteriohopanetetrol were detected in all sediment samples.

This study was carried out as a part of the research undertaken by the Research Consortium for Methane Hydrate Researches in Japan (MH21).
Methodological investigation of light volatile organic compounds in water

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Recent our studies revealed that methanol and formaldehyde were mainly formed in methane hydrate by gamma-ray irradiation (Tani et al., 2008; Tani et al., 2010). Although these compounds may also be formed in natural gas hydrate, their concentrations should be very low because a dose rate of natural radiation from deep-sea sediment is not so high. Therefore, we have the methodological curiosity to detect very low concentration of methanol and formaldehyde in water. We tested two methods: (a) a direct injection method by proton-transfer-reaction mass spectrometry (PTR-MS) (Jurschik et al., 2009) and (b) a headspace method by gas chromatography-mass spectrometry (GC-MS). For methanol, the method (b) has a better detection limit than the method (a). For formaldehyde, quantitative detection is difficult in the method (a) due to similar proton affinities of water and formaldehyde (Hansel et al., 1997). In addition, a good derivative is available for an analysis of aldehyde in water (Kobayashi et al., 1980). In this study, we focused on the method (b) and tested it in different experimental conditions (e.g. oven temperature in GC-MS, heating temperature and time in headspace, reproducibility, influence of multiple sampling, etc.) to develop the method of quantitative evaluation of low-concentration methanol and formaldehyde in water.

Keywords: volatile organic compounds, GC-MS, methanol, formaldehyde, gas hydrate
Clathrate hydrate is a crystal compound of water molecules encaging guest molecules. Natural gas hydrate, whose guest molecule is mainly methane, is found under deep sea and in permafrost region. Estimation of formation age in natural gas hydrate has been attempted using the $^{129}$I method (e.g. Fehn et al., 2003), which is an indirect age determination method. In contrast, we have investigated to establish a direct age determination method from hydrate crystal itself. Since natural gas hydrate is formed in sediment and irradiated by natural radiation due to natural radioisotopes like $^{40}$K, U-series and Th-series, chemical reaction via radicals may occur in natural samples. In methane hydrate, methyl radicals are induced by gamma-rays (Takeya et al., 2004). However, they are unstable at the temperature and pressure of natural gas hydrate occurrence, and dimerize to ethane (Ishikawa et al., 2007). In another reaction, methanol is also formed after gamma-ray irradiation to methane hydrate (Tani et al., 2008). If the amount of radiation-formed compounds in hydrate increases after hydrate formation, it may suggest a formation age of natural gas hydrate. The formation efficiency of radiation-induced compounds is necessary for estimation of the formation age. Therefore, we have investigated the dissociated water of gamma-irradiated methane hydrate and analyzed quantitatively radiation-formed compounds in methane hydrate by gas chromatography-mass spectrometry (GC-MS).

Methane hydrate was synthesized and irradiated by gamma-rays of about 6 kGy at 273 K under high pressure to avoid dissociation of the hydrate. Headspace gas of the dissociated water was analyzed by GC-MS. Methanol and formaldehyde were formed and the other small peaks were observed. The amounts of methanol and formaldehyde by gamma-rays in methane hydrate were almost the same. We will discuss the formation efficiencies of those compounds in the presentation.

Keywords: clathrate hydrate, methane, gamma rays, GC-MS, radical, volatile organic compounds
Study of Phase Boundary Change with Cage Occupancy by Molecular Dynamics Simulations

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It has been suggested that carbon dioxide (CO\textsubscript{2}) has the potential to replace methane (CH\textsubscript{4}) from natural gas hydrates, which is one of the promising methods to recover CH\textsubscript{4} from hydrates and in the meanwhile sequester CO\textsubscript{2} underground. It is important for this method to get the three-phase coexistence lines (solid hydrate, liquid water, and liquid or vapor CH\textsubscript{4}/CO\textsubscript{2}) of CH\textsubscript{4}/CO\textsubscript{2} hydrates. In this work, we estimated the phase boundaries of CH\textsubscript{4} hydrate and CO\textsubscript{2} hydrate by molecular dynamics simulations, and discussed the phase behavior of gas hydrates.

In CH\textsubscript{4}-hydrate case, the estimated phase boundary is in very good agreement with the experimental data. In CO\textsubscript{2}-hydrate case, the experimental data are between the estimated phase boundaries using the full occupancy CO\textsubscript{2}-hydrate and the partial occupancy CO\textsubscript{2}-hydrate. The estimated melting temperature of the full occupancy hydrates is higher than that of the partial occupancy hydrates in both CH\textsubscript{4}-hydrate and CO\textsubscript{2}-hydrate cases, and the gas hydrate stability zone expands. This result implies that the cage occupancy of gas hydrates influences the stability of gas hydrates.

Keywords: methane hydrate, CO\textsubscript{2} hydrate, molecular dynamics, phase boundary, cage occupancy, gas hydrate