

Japan Geoscience Union Meeting 2011

(May 22-27 2011 at Makuhari, Chiba, Japan)

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MIS027-01

Room:201A

Time:May 22 14:15-14:30

Ultra high resolution bathymetric map of gas hydrate mounds of shallow gas hydrate areas in Joetsu Basin , Eastern margin

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Mega pockmarks and mounds, both of which are 300m to 500m in diameter and 30m to 40 m deep or high, characterize the Umitaka Spur and Joetsu Knoll of the Joetsu Basin. A number of pockmarks and mounds develop in NNE to SSW direction parallel to the general trend of mobile belt along the eastern margin of Japan Sea, suggesting that the topography has been strongly controlled by regional tectonics. Seismic profiles have revealed well-developed chaotic to transparent zones (gas chimneys) in the area of pockmarks and mounds, from which a number of active methane plumes stand up to 700m above sea floor. Ultra-high resolution bathymetric data and reflection images were acquired by Multi Beam Echo Sounder (MBES) and Side Scan Sonar (SSS) of the AUV URASHIMA during the YK10-08 cruise of R/V YOKOSUKA (JAMSTEC), July 2010. Bathymetric image data of MBES by AUV URASHIMA is about eight to ten times high resolution compare with mother ship board MBES Systems. As a result, Ultra-high resolution bathymetric data provide us give a chance to discuss tens of centimeters scale images. Based on mosaic images of MBES and SSS, we could identify several types of the hydrate mounds over gas chimney zones. Some are represented as a smooth and low bulge without strong reflections of background level, but the others show rough and uneven topography, featured by a few meter scale depressions, crevasses and minor ridges with strong reflector images, indicating the development of hard ground. Such strong reflectors are due to carbonate crusts and concretions and gas hydrate exposures as observed by ROV. Micro-topographic features are likely to represent a growth stage of hydrate mounds, and perhaps the accumulation of shallow gas hydrates. MBES and SSS onboard AUV are powerful tools to identify gas hydrate accumulation and evolution of shallow gas hydrate system.

Keywords: gashydrate, JapanSea, Topography, URASHIMA

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MIS027-02

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High-resolution gas-chimney structures over a marine gas hydrate field off Joetsu, eastern margin of Japan Sea.

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Active marine gas hydrate systems and related phenomena on and near seafloor are identified off Joetsu, southern part of the eastern margin of Japan Sea (Matsumoto et al., 2005, 2009). In this area, large pockmarks and mounds, 200 to 500 m in diameter and 20m to 40 deep or high, have been observed on a two ridges, Umitaka Spur and Joetsu Knoll, at water depth of 900-1000m, associated with fault systems. High resolution 2-D single channel seismic surveys were conducted for the last six years to obtain high resolution and high density seismic records on this area. Based on these seismic data, 'Gas chimney structures' that indicate fluid migration from deeper zone up to seafloor are recognized below pockmarks, mounds, and seafloor methane seepage and shallow natural gas hydrate locations, in both Umitaka Spur and Joetsu Knoll. BSRs are recognized at 0.2-0.25 sec TWT below seafloor in both Umitaka Spur and Joetsu Knoll. Umitaka Spur and Joetsu Knoll are characterized by asymmetric structure related to the thrust faults at the western margin of the Spur and the southeast margin of the Knoll. The Joetsu Knoll is considered to be younger than the Umitaka Spur as revealed by transect seismic survey lines through the two ridges. Ultra-high resolution sub-bottom profiling data, multi-beam bathymetric data, and Side Scan Sonar (SSS) image obtained with AUV 'URASHIMA' seem to indicate that 'Gas chimney structures' continued up to the mounds.

Keywords: methane hydrate, gas-chimney, BSR, pockmark, mound, Japan Sea

MIS027-03

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Shallow accumulation of gas hydrates and evolution of gas hydrate mounds, Joetsu Basin, Eastern Margin of Japan Sea

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During the R/V Marion Dufresne expedition in June 2010, a robust box corer CASQ deployed on hydrate mounds has recovered 2 to 10 m long strongly disturbed soupy sediments with abundant massive and platy gas hydrates and carbonate nodules. This confirmed that the mounds are made up of the massive accumulation of mixed gas hydrate and carbonate nodules. Giant piston corer CALYPSO could not penetrate through the mixed hydrate-carbonate zones, and was often bent or broken during the deployment, however the corer was powerful to penetrate down the sediments as deep as 40 mbsf off mound area of low methane flux. The standard sequence is represented by (I) 5-10 m thick bioturbated unit, (II) 30-35 m thick unit composed of inter-bedded dark gray thinly laminated beds, bioturbated beds and occasional debris flow deposits, and (III) 5 m thick massive units. Unit boundaries I/II and II/III have been dated by C-14 and tephra chronology as approximately 20 ka and 100 ka, respectively. Dark gray laminated beds are likely to have deposited in stagnant bottom waters during the low sea-level of LGM and stadial episodes. AUV-Urashima and Tuna-Sand surveys have revealed ultra-high resolution bathymetry, topographic features, and subsurface structures over the Joetsu gas hydrate field in August 2010. MBES (multi beam echo sounder, 400kHz) identified two types of hydrate mounds. One is a conical shaped low hills with gentle smooth surface, while the other is characterized by high relief topography with strong backscatter, crater-like depression and outer rim. SBP (sub-bottom profiler, 1-6 kHz chirp) has demonstrated high-resolution sedimentary sequences down to 30-50 mbsf, which are well consistent with the lithologic units I, II, and III of the CALYPSO cores. SBP of hydrate mounds is represented by column-shaped acoustic transparent zones, representing gas charged sediments. The columns are either capped by high amplitude reflectors at around the boundary II/III, I/II or extrude on the seafloor to form hydrate mounds. Hard caps atop the acoustic columns are probably composed of mixed gas hydrate and carbonates. In conclusion, thermogenic gases migrate through gas chimneys to accumulate gas hydrate above the base of gas hydrate stability (BGHS) at 120 mbsf, whereas the formation of hydrate is limited by the amount of free waters in sediments. The excess methane continues to move up through the dry sediments into the shallow, water-saturated sediments, where the methane forms gas hydrate at around II/III and I/II. On the other hand methane and seawater-derived sulfate react to increase alkalinity and precipitate carbonates through AOM. The ceiling of the columns is considered as a front of the mineralization of gas hydrate and carbonates, and the buildups finally grow up to the seafloor. The exposed gas hydrate-carbonate buildups eventually collapse and decay through rift-up and dissolution to the seafloor. The present study has been partially supported by the national methane hydrate program MH21.

Keywords: gas hydrate, Eastern margin of Japan Sea, R/V Marion Dufresne, AUV Urashima

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MIS027-04

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Environment changes since the Last Glacial time deduced from MD10-3312 core off Joetsu, Japan Sea

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Sediment core, MD10-3312 is collected from a small ridge at 1026 m depth off Joetsu, Japan Sea during MD179 cruise, and is as long as 31.14 m, which is composed mostly of silty clay with some marker tephra beds. Based on the relationship between the depth and age of the identified marker tephra beds, the sedimentation rate is 0.25 mm/year and the age of core bottom is calculated as old as 125 ka. Water content of every 1 cm has been measured completely, and TOC and TN have been analyzed for every 2 cm, attending back to 76 ka now.

The TOC amount varies from 0.6 % to 2 %, showing quasi-periodic fluctuations. The TOC profile is very similar to the delta 18O profile of ice core from Greenland. General trend of TOC content is almost same as LR04 curve of marine delta 18O isotope, and small peaks on the TOC profile also well correspond to the GIS 1 to 20 peaks since 76 ka. This fact means that the temperature in the North Atlantic region affected the biological productivity of Japan Sea probably via air temperature controlled by circum-Arctic circulation of atmosphere. This is an excellent record of climate change in a middle latitude area of Far East Asia.

Dark-colored units which alternate with light-colored bioturbated units characterize the sediment of Japan Sea. Two types of dark units were identified. One type is of low TOC contents in MIS 2, the coldest period, and another one is of high TOC contents found in MIS 3 to 5.

MD179/Japan Sea gas hydrate cruise of R/V Marion Dufresne was performed under the financial supports from MH21 project.

Keywords: Environment change, Japan Sea, MD10-3312 core, total organic carbon, MH21, gas hydrate

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MIS027-05

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Geochemical Investigation of long core collected by MD179 Cruise

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The two long piston cores were collected from Japan Sea during the MD179 Cruise, at June of 2010. Biomarker analysis, quantitative and isotope analysis of total sulfur and elemental sulfur were investigated in these two cores.

(1) An analytical method for the determination of elemental sulfur using gas chromatography ? mass spectrometry (GC-MS) was developed. (2) The quick method for sulfur isotope analysis was developed for not only sediment samples but also interstitial water. (3) The conventional analysis was carried out to determine the sedimentary environment of Japan Sea.

Keywords: black shale, biomarker, sulfur isotope, elemental sulfur

MIS027-06

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Soil properties of sea-bottom sediments in the Eastern Margin of Japan Sea

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Gas hydrates are attracting attention as a next-generation energy source. On the other hands, Methane gas contained in the natural gas hydrates has approximately 20 times the greenhouse effect of CO₂. There are concerns that dissociation of methane gas from the gas hydrates distributed in submarine surface layers (shallow type gas hydrates) by rising ocean temperatures or by vaporization at recovery of the hydrates for energy may contribute to global warming, which in turn may raise the sea level and causing climatic instability. In addition, many gas-hydrate-bearing areas are distributed near the boundaries of tectonic plates, as shown in the figure. Gas hydrates in the surface layer of seafloor may dissociate when seismic activities cause seafloor landslides that in turn cause gas hydrate-bearing layers to fail. There have been concerns over the environmental effects of shallow type gas hydrates, but surveys for shallow type hydrates have been few.

In this study, we clarify the similarities and differences in physical and mechanical properties of sediments with and without gas hydrates by conducting various physical and mechanical tests on gas hydrate-bearing sediments recovered from Eastern Margin of Japan Sea. Changes in mechanical properties associated with the disturbance of the sediment sample recovered from the gas hydrate-bearing ground will be clarified.

Test results showed that the strength of sediments contained with gas hydrates were lower than those of standard sea-bottom sediments. It would seem that this is because the effect of the disturbance of sedimentary layers by gas and water upwelling from underground and the pressure release during the sampling. Accordingly, it is considered that the gas hydrate-bearing ground is unstable compared with other ground.

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

Keywords: Sea-bottom sediment, mechanical properties, gas hydrate

MIS027-07

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Estimate gas mass in sea floor with gas hydrate by Time Domain Reflectometry(TDR) method

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As for the carbon dioxide generated from the natural gas, 20-30% of the carbon dioxide generated from coal and the oil that burns to obtain the same calorie is also few, and the carbon dioxide reduction is expected. The gas hydrate is an ice solid material that consists of the natural gas (methane) and the water molecule. It is paid attention as new natural gas resources in recent years. In many cases, it is thought that the deposit consists of the deposit particle and interstitial water. However, the methane flux from the depth that by the way of the gas chimney and the fracture is large, and there is a possibility including a free gas in the deposit that accumulates the gas hydrate in the superficial deposit though the marine sediment. As for Matsumoto and others (2009), it thought the cause to be free gas distribution that existed in the deposit by finding P wave propagation speed of 100m under bottom of the sea to be an abnormally small (1.0-1.3km/sec) from depth of the time of gas hydrate BSR and the heat flow of the sea area. The existence of a free gas in the deposit leads to understanding the mechanism of the gas hydrate accumulation in the superficial deposit. However, it is difficult to estimate the amount of the gas only from the velocity anomaly accurately because it is thought that there is no linear relationship between the speed and the amount of the gas, and the speed decreases remarkably by very small amount gas. Then, it was tried to apply TDR (Time Domain Reflectometry) method, which is used by measuring the water content of the farmland, to estimate the amount of the gas in the present study. In the experiment, the estimate of the amount of the gas in the bottom of the sea deposit is done by using the Time Domain Reflectometry (TDR) method. The TDR method presumes the dielectric constant of the soil by using the wave velocity of the electromagnetic radiation, and obtains the soil water content(=liquid phase rate) there. The dielectric constant is different in each material, about water is 80 and the soil are 3-9 and air is 1, and ice is 4.2. The sediment core of a constant amount is taken from bottom of the sea, the dry density and the particle density of the soil are measured in a laboratory. Then the amount of solid phase rate is estimated. 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 TDR probe is used 2 stainless rods of 300mm long, 10mm across, and 100 mm apart. The measurement of the dielectric constant by the TDR method attenuates in the probe terminal reflection strength of the electromagnetic radiation, and becomes impossible to measure in measuring the solution that the electrical conductivity is very high like seawater it. For this case, the measurement of the dielectric constant by the TDR method becomes impossible. Then, the rod was covered with the heat-shrinkable tubing and the electromagnetic radiation was prevented being attenuated in the TDR probe by film in the present study as shown by Moret-Fernandez (2007). As a result, it succeeded in the suppression of the attenuation of reflection strength of the electromagnetic radiation, and the measurement of the relative permittivity in seawater became possible.

Keywords: Time Domain Reflectometry, dielectric constant, gas phase rate, bulk density, particle density

MIS027-08

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Molecular and isotopic compositions of gas hydrate-bound hydrocarbons retrieved from off Joetsu, Japan Sea

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Gas hydrates are crystalline clathrate compounds composed of water and gas molecules that are stable at low temperature, high partial pressure of each gas component, and high gas concentration. Recently, natural gas hydrates were obtained at the Umitaka Spur and the Joetsu Knoll on the eastern margin of the Japan Sea (Matsumoto *et al.*, 2009; Hiruta *et al.*, 2009). We investigated the molecular and stable isotope compositions of hydrate-bound gas and dissolved gas in pore water in sediments of these areas. The purpose of this study is to clarify the gas origin and to understand the migration system of the shallow gas hydrate accumulation in this area. Hydrate-bearing sediment cores were retrieved during the cruise onboard *R/V Marion Dufresne* in June 2010. The Calypso piston coring system enabled us to take long sediment cores (up to 40m). Hydrate-bound hydrocarbons are primarily thermogenic at the Umitaka spur (C_1 $\delta^{13}C$: -36 permil-VPDB, C_1 δD : -165 permil-VSMOW), on the contrary, those at the Joetsu knoll (about 30m depth from the sea floor) partly contain microbial methane because ^{13}C and deuterium are both depleted (C_1 $\delta^{13}C$: -55 permil-VPDB, C_1 δD : -194 permil-VSMOW) and close to the field of microbial methane via CO_2 reduction. Depth profiles of methane in sediment showed the minimum depth in $\delta^{13}C$, corresponded to the SMI depth where hydrogen sulfide was concentrated. Methane concentration in sediment increased drastically beneath the depth of SMI. $\delta^{13}C$ of methane increased slightly along with depth, whereas δD of methane decreased. Thermogenic ethane and propane are detected both in hydrate-bound gas and dissolved gas in pore water. Heavy propane ($\delta^{13}C$: +5 permil-VPDB) indicated its microbial oxidation. The molecular composition of thermogenic ethane in hydrocarbons was relatively high at the gas hydrate sites, whereas microbial ethane is dominant in the peripheral area. High concentration of neopentane (2,2-dimethylpropane) was detected in the dissolved gas around the depths of gas hydrate at the both sites of Umitaka Spur and Joetsu Knoll. Since neopentane cannot be engaged to the crystallographic structure I of gas hydrate, it might be discharged from the hydrate crystal at the formation process and remained in the sediment.

This study was supported by the MH21 Research Consortium for Methane Hydrate Resources in Japan.

Hiruta, A., G.T. Snyder, H. Tomaru, R. Matsumoto (2009) Geochemical constraints for the formation and dissociation of gas hydrate in an area of high methane flux, eastern margin of the Japan Sea. *Earth Planet. Sci. Lett.*, **279**, 326-339, doi:10.1016/j.epsl.2009.01.015.

Matsumoto, R., and 28 others (2009) Formation and collapse of gas hydrate deposits in high methane flux area of the Joetsu Basin, eastern margin of Japan Sea. *J. Geogr.*, **118**(1), 43-71.

Keywords: gas hydrate, stable isotope, Japan Sea

MIS027-09

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Changes in concentrations of ions in pore waters of LV47 and LV50 subsurface sediment cores from offshore Sakhalin

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The Sakhalin Slope Gas Hydrate Project is an international collaboration effort among scientists from Japan, Korea and Russia to investigate on natural gas hydrates accumulated on a continental slope offshore Sakhalin Island. From July to August of 2009 and June of 2010, field operations of SSGH-09 and SSGH-10 projects were conducted as the 47th and 50th cruises of R/V Akademik 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 by using a squeezer designed and constructed at Kitami Institute of Technology. The ionic compositions (chloride, sulfate, hydrogen carbonate, calcium etc.) in sediment pore- and seawater samples were compared to figure out the geochemical characteristics of the cores.

The concentration-depth profiles of sulfate in pore water samples have inverse correlations with those of methane in the pore water. The anaerobic bacterial oxidation of methane is responsible for the phenomena. The depths of sulfate-methane interface (SMI) 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 SMI is not observed for the reference LV47-33HC core.

Twenty cores showed the linear depth-profiles of the concentrations of sulfate in the pore waters until SMI whereas ten cores showed the concave up profiles for LV47 and LV50 cores. The possible increase of the methane flux might be thought to form the concave up profiles. The further investigations/discussions will be presented.

Keywords: gas hydrate, pore water, chemical analysis, ions, Sea of Okhotsk

MIS027-10

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Pore water geochemistry associated with biogeochemical processes in shallow sediments in the Japan Sea

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Pore waters were collected from the shallow sediments along the eastern margin of the Japan Sea during the intensive piston coring expedition by R/V Marion Dufresne in 2010 (MD179 Japan Sea Gas Hydrates). Samples were collected from the high methane potential area off Joetsu, Niigata (Umitaka Spur and Joetsu Knoll region) where shallow-deep gas hydrate system has been developed, from the central Toyama Trough, west of Sado Island, from the ridge flank, southwest of the Henashi-zaki Peninsula, near the Tsugaru Strait, and from the west of Okushiri Island. Concentrations of alkalinity, H₂S, major anions and cations, and delta¹³C_{DIC} values were preliminary analyzed in order to assess the biogeochemical processes associated with shallow diagenesis of organic matter, i.e. solid organic matter in sediment and methane dissolved in pore water. Concentrations of dissolved sulfate, an important oxidant for organic matter oxidation near the seafloor, decrease linearly to ~0 mM in the upper 2 to 10 m below seafloor (mbsf) at all sites, indicating upward methane flux is generally high in the entire research area including the sites away from gas venting/gas hydrate occurrences. Alkalinity is an indicative of products from organic matter oxidation, increasing rapidly downward to the SMI. H₂S is also produced during organic matter oxidation, increasing up to 5 mM near the SMI. Concentrations of Ca and Mg simultaneously decrease with depth due to carbonate precipitation that is encouraged by alkalinity increase. delta¹³C_{DIC} values show negative peaks of 0 to -20 per-mil around the SMI, ¹³C-depleted methane from deep sediments is responsible mainly for organic matter oxidation at the SMI.

There are two modes of organic matter oxidation (sulfate reduction) between the seafloor and SMI; ordinary oxidation of sedimentary organic matter and anaerobic oxidation of methane. Because 1 mole sulfate reduction results in 2 moles alkalinity increase in the former state and results in 1 mole increase in the latter state, gradient of sulfate reduction vs. alkalinity increase that is compensated with Ca and Mg changes can point to the mode of organic matter oxidation. Our results indicate that the ordinary oxidation of sedimentary organic matter is dominant just below the seafloor (DeltaSO₄<~10 mM), and the anaerobic oxidation of methane thereafter. Degradation of organic matter in the shallow sediments is a result of combined biogeochemical processes and plays an important role in shallow carbon cycle system in marine environments.

This research is supported by MH21 Research Consortium JAPAN.

Keywords: pore water, gas hydrate, Japan Sea

MIS027-11

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Thermodynamic control on anaerobic oxidation of methane below the sulfate-methane interface

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The methane flux from marine environment accounts for only 2% of the global methane flux, because most of methane in anoxic marine environment is microbiologically consumed by anaerobic oxidation of methane (AOM). In the AOM, sulfate is used as a terminal oxidant in the following net reaction: $\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$. Molecular biological and biogeochemical studies demonstrated that microbial consortium of anaerobic methanotrophic archaea (ANME) and sulfate reducing bacteria (SRB) is the major candidate for AOM reaction. The metabolic process of AOM is speculated to be an intermediate shuttling between ANME and SRB, which account for a transfer of reducing equivalent or organic carbon compound directly derived from methane. AOM was considered to be restricted to the sulfate-penetrated sediment due to the close coupling between methane oxidation and sulfate reduction. However the previous study showed that single phylogenetic group of anaerobic methanotrophs, ANME-1, was dominant in the sediments underlying the sulfate-methane interface (SMI). In this study, we focused on the ANME-1-mediating process of the interaction between sulfate reduction and methane oxidation, and the environmental control in marine sediment off Joetsu, Japan. Control factor and putative AOM reaction mechanism of ANME-1 occurring below the SMI were discussed from the perspective of thermodynamic and kinetic constraints. ANME-1-dominated sediment was rich in methane and alkalinity but was poor in sulfate and hydrogen sulfide, suggesting that net AOM reaction was thermodynamically and kinetically favorable. However, absence of consortium-like structure composed of ANME and syntrophic bacterial partner suggested the AOM proceeded independently of direct association with sulfate reduction. Considering the concentration of molecular hydrogen in the porewater, methanogenesis can be thermodynamically more favorable than sulfate-independent methane oxidation. ANME-1 might act as methanogen in deep sediment below the SMI.

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Keywords: archaeal methanotroph (ANME), anaerobic oxidation of methane (AOM), gas hydrate, Japan Sea

MIS027-12

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Analysis of volatile organic compounds in the dissociated water of gas hydrate recovered from Joetsu Basin

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Radiation-induced radicals and further radical reactions in gas hydrate were investigated by electron spin resonance (ESR) and gas chromatography-mass spectrometry (GC-MS). Although methyl radical is the most stable radical in methane hydrate, it cannot survive in the pressure and temperature condition of natural gas hydrate occurrence. Recently our studies revealed that methanol and formaldehyde were formed in methane hydrate by gamma-ray irradiation (Tani et al., 2008; Tani et al., 2010). Therefore, we conjecture that these compounds might be also formed by natural radiation and have been accumulated in natural gas hydrate after formation of gas hydrate. To test this hypothesis, we analysed volatile organic compounds (VOCs) in the dissociated water of natural gas hydrates.

Investigation of gas hydrate was carried out at Umitaka Spur and Joetsu Knoll, in Joetsu Basin, eastern margin of the Sea of Japan during MD179 cruise in 2010. Gas hydrate samples were recovered from 4 sites and kept at 77 K in liquid nitrogen. We selected one massive gas hydrate sample for this study to avoid contamination of pore water. After the sample broken, several pieces of gas hydrate were picked up and dissociated in a glass vial. The headspace gas from the dissociated water was analyzed by GC-MS. Both methanol and ethanol were detected. The successful detection of methanol from natural gas hydrate might be a positive signal for the determination of the age of hydrate formation.

This research is supported by MH21 Research Consortium JAPAN.

Keywords: gas hydrate, Joetsu Basin, volatile organic compounds, methanol, natural radiation, formation age

MIS027-13

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Analysis of volatile organic compounds in the pore water from Joetsu Basin, eastern margin of the Sea of Japan

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Natural gas hydrate is a clathrate compound. Gas molecules are engaged by hydrogen-bonded water molecules. Gas hydrate is found together with deep-sea sediments that contain natural radioisotopes like uranium-series, thorium-series, and ⁴⁰K. Natural radiation from those radioisotopes will break bonds of water and guest gas molecules, and form radical species. Although the radical species are unstable in the pressure and temperature of natural gas hydrate occurrence on the Earth, radical reactions may occur in the hydrate. Our recent studies reported that methanol and formaldehyde were mainly formed in gamma-irradiated methane hydrate (Tani et al., 2008; Tani et al., 2010). The amount of these compounds will become one of the indicators for the formation age of natural gas hydrate, because they may be accumulated in gas hydrate. For age estimation, it is necessary to determine the amount of them captured from pore water when natural gas hydrate is formed. However, abundance of methanol and formaldehyde in pore water of seafloor sediments is veiled. In this study, we have investigated light volatile organic compounds such as methanol and formaldehyde in pore water of the sediments obtained during MD179 cruise in 2010.

Pore water was obtained by squeezing sediments recovered from Umitaka Spur and Joetsu Knoll, in Joetsu Basin. Each sample was taken into a glass vial (3-5 ml), sealed, and kept in a freezer. These procedures are performed on the ship. The vials were warmed at room temperature before the following analysis. Headspace gas in each vial was analyzed by gas chromatography-mass spectrometry (GC-MS). Especially for formaldehyde analysis, *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA) was used as a derivative reagent for aldehyde (Kobayashi et al., 1980).

In preliminary results, the concentration in pore water was 1-2 micro M (methanol) and 0.5-1 micro M (formaldehyde) beneath the seafloor, and 10-20 micro M (methanol) and 1-2 micro M (formaldehyde) around 30 m below the seafloor. It means that (1) both methanol and formaldehyde increases in depth and (2) the amount of the increase is about 10 times for methanol, which is 5 times larger than for formaldehyde. These results indicate that the amount of these compounds initially captured into hydrate may depend on the depth. For more detailed discussion, distribution coefficients for them into gas hydrate are necessary and will be investigated in future.

This study was supported by MH21 Research Consortium Japan.

Keywords: pore water, gas hydrate, Joetsu Basin, GC-MS, volatile organic compounds

MIS027-14

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Radiation-induced radical reactions at different temperatures in CO₂ hydrate

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CO₂ hydrate is one of clathrate hydrates, which is composed of water molecules encaging CO₂ molecules, and stable at atmospheric pressure below 220 K. It has been suggested that CO₂ hydrate exists in Okinawa Trough (Konno et al., 2006) and Martian surface (Max and Stephen, 2001). Natural CO₂ hydrate will have been constantly irradiated by natural radiation from sediments, and radicals will have been induced by the radiation and reacted in CO₂ hydrate.

In the case of CH₄ hydrate, methyl radicals are mainly formed by gamma-rays at 77 K (Takeya et al., 2004). Since they are not stable over 200 K, no radicals remain and radical reactions occur in CH₄ hydrate. Methanol, formaldehyde, and ethane are main products in these reactions (Ishikawa et al., 2007; Tani et al., 2010). In the case of CO₂ hydrate, HOCO radicals were observed after gamma-ray irradiation at 77 K and decayed over 130 K. Analysis of the dissociated water by ion chromatography showed that a little amount of formic acid was formed (Tani et al., 2008). These results suggest that main radical reaction may change if gas hydrate is irradiated at different temperatures because radiation-induced radicals become stable below a certain temperature.

In this study, we investigated the compounds formed by radical reactions in CO₂ hydrate after gamma-irradiation at 77, 195, and 273 K. The thermal stabilities of the induced-radicals have been investigated by electron spin resonance (ESR). The dissociated water of irradiated CO₂ hydrate has been measured by ion chromatography. HOCO radicals and H atom are observed at 120 K in irradiated CO₂ hydrate. HOCO radicals disappeared within 20 min at 195 K, though 80% of HOCO radicals remained after 6 hours at 120 K. H atoms were not observed at 130 K. As well as formic acid, oxalic acid has been newly observed in the dissociation water. The amounts of formic acid and oxalic acid were changed by temperature history of radical. Especially, the amount of oxalic acid increased with temperature. They may be partially caused by the decay processes of the radicals in CO₂ hydrate.

Keywords: CO₂ hydrate, Radicals, Carboxylic acid, Radiation, Electron spin resonance (ESR), Ion chromatography

MIS027-15

Room:201A

Time:May 22 18:00-18:15

Pattern formation of methane hydrates in oceanic sediments

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Objective

The methane hydrates found globally in oceanic sediments are of significant interest as a global climate change and as a potential energy resource. Sediment cores recovered from the ocean floor have been reported to have a variety patterns and sizes of hydrates, which were classified into four categories by Malone [1]: disseminated, nodular, layered, and massive. In order to reproduce the variety patterns, clarify the pattern formation mechanism of hydrates in the sediments, tetrahydrofuran (THF) clathrate hydrates were grown using a directional growth apparatus in oceanic sediment model.

Experimental Method

The oceanic sediment model is mixed glass beads of 2 μm (μm denotes micrometer) and 50 μm in diameter. The mixing ratio between 2 μm beads and 50 μm beads, $W_2:W_{50}$, was variable. A model system consists of the mixed glass beads and a stoichiometric THF water solution (THF-17H₂O). The weight ratio of the solution and the glass beads was fixed unity. A directional growth apparatus was used to grow the hydrates at a constant growth rate, V , under an applied temperature gradient. That is, a growth rate, V , and a mixing ratio, $W_2:W_{50}$, were variable.

Results and Discussions

Various patterns such as layered, nodular, massive and disseminated pore space type hydrates were reproduced. Our previous work showed that the hydrates formed a layered type in the 2 μm glass beads [2]. However, mixing small amount of 50 μm beads in the present study, the layered type changed to massive type, nodular type. Finally, disseminated type formed in the 50 μm glass beads only. In the mixed glass beads of $W_2:W_{50} = 5:5$, the layered type changed to massive type, nodular type when V increased from low growth rate. Finally, disseminated type formed at high growth rate. Additionally, needle type formed in the mixed glass beads of $W_2:W_{50} = 3:7$, at $V = 8\mu\text{m/s}$. Thus, all patterns classified by Malone are reproduced, and the hydrates patterns classified into diagram about experimental conditions. Pattern formation of various patterns of hydrates formed in soil model was qualitatively explained by our model based on mechanism as frost heave during ice growth in soil.

[1] R.D. Malone, Gas Hydrate Topical Report, DOE/METC/SP-218, U.S. Department of Energy, April 1985.

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Keywords: Methane hydrates, Tetrahydrofuran, Pattern formation, Frost heave

MIS027-P01

Room:Convention Hall

Time:May 22 10:30-13:00

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 ¹³C 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 ¹³C 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 ¹³C 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).

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Keywords: gas hydrate, stable isotope, Sea of Okhotsk

MIS027-P02

Room:Convention Hall

Time:May 22 10:30-13:00

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 Akademik 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 by using a squeezer designed and constructed at KIT (Kitami Institute of Technology, Japan). The stable isotopic compositions ($\delta^{18}\text{O}$ and δ^{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 $\delta^{18}\text{O}$ and δ^{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

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MIS027-P03

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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 *Neoglobobulimina* *incompta* and disappear of *Pullenia* *apertura* in the uppermost part of the core.

Keywords: Japan Sea, benthic foraminifera, gas-hydrate, suboxic species

MIS027-P04

Room:Convention Hall

Time:May 22 10:30-13:00

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 Dufresne*.

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/m³ and 0 to 1656.41g/m³, 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 0.1m² of the bottom surface. Numerical density and biomass were under 1 individuals/0.1m² and under 0.5g/0.1m² in Core No. 3307, 15 individuals/0.1 m² and 33.49g/0.1 m² in Core No. 3318 and 5.1 individuals/0.1 m² and 0.21g/0.1 m² in Core No. 3324. According to Tsujimoto et al. (2006), bivalves and the polychaetes were collected, macrobenthos of 18-64 individuals/0.1 m² (average was 33.8 individuals/0.1 m²) in the Toyama Bay abyssal floor (393-631m in depth). Also, biomass was 0.41-1.86g/0.1 m² (average was 1.05 g/0.1 m²). 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 caused 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

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Keywords: gas hydrate, benthos, distribution, chemosynthetic benthic community

MIS027-P05

Room:Convention Hall

Time:May 22 10:30-13:00

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/m^2 with a temperature reversal profile was measured in 2007. After two years (in 2009), high heat flow value 970 mW/m^2 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/m^2 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 $250\text{-}520 \text{ mW/m}^2$ 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

MIS027-P06

Room:Convention Hall

Time:May 22 10:30-13:00

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

MIS027-P07

Room:Convention Hall

Time:May 22 10:30-13:00

Biomarkers analyses of methane hydrate bearing sediments from the eastern Nankai Trough by two dimensional GC

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¹JOGMEC

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-Pentamethylcosane (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).

MIS027-P08

Room:Convention Hall

Time:May 22 10:30-13:00

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

MIS027-P09

Room:Convention Hall

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Investigation of formation efficiency of volatile organic carbons by gamma-rays in methane hydrate

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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 ¹²⁹I 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 ⁴⁰K, 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

MIS027-P10

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Study of Phase Boundary Change with Cage Occupancy by Molecular Dynamics Simulations

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It has been suggested that carbon dioxide (CO₂) has the potential to replace methane (CH₄) from natural gas hydrates, which is one of the promising methods to recover CH₄ from hydrates and in the meanwhile sequester CO₂ underground. It is important for this method to get the three-phase coexistence lines (solid hydrate, liquid water, and liquid or vapor CH₄/CO₂) of CH₄/CO₂ hydrates. In this work, we estimated the phase boundaries of CH₄ hydrate and CO₂ hydrate by molecular dynamics simulations, and discussed the phase behavior of gas hydrates.

In CH₄-hydrate case, the estimated phase boundary is in very good agreement with the experimental data. In CO₂-hydrate case, the experimental data are between the estimated phase boundaries using the full occupancy CO₂-hydrate and the partial occupancy CO₂-hydrate. The estimated melting temperature of the full occupancy hydrates is higher than that of the partial occupancy hydrates in both CH₄-hydrate and CO₂hydrate 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, CO₂ hydrate, molecular dynamics, phase boundary, cage occupancy, gas hydrate