

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

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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

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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

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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.

[2] Nagashima et al., J. Phys. Chem. B112 (2008), pp. 9876-9882.

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