

Observation of methane plumes with quantitative echo sounder

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Quantitative echo sounder for fishery is a powerful tool to identify methane plumes from deep ocean floors, and has been commonly used for gas hydrate study worldwide. However, the precise position of gas venting has not easily obtained so far. This paper propose the method to exactly locate the venting sites.

The acoustic data of methane hydrate bubbles was obtained with quantitative echo sounder by staying in the methane hydrate upwelling area for a long period of time, and analyzed with the single fish detection function. As a result, the methane hydrate seeping spot was precisely located.

The circular graph on the display of the quantitative echo sounder represents the single target position. The center of this circle denotes the sound axis, that is, the center of the vibration plane of the transducer. The size of the circle represents the illumination range of pulse wave. In the case of EK60 (SIMRAD), the diameter of the circle is about 100 m at a depth of 1,000 m. If a seep point is found at the lower left of the circle, its location can be calculated accurately from the direction and distance from the center, because the location of the center, that is, the transducer, is already known with the GPS on the ship. In addition, by decreasing the threshold of the quantitative echo sounder, it is possible to detect the methane plumes with low backscatter intensity and the strong scattering bodies below the seabed. Consequently, it was found that the use of quantitative echo sounder is effective for the assessment for methane hydrate search.

Keywords: Quantitative echo sounder, Methane Hydrate, Methane Plume

Preliminary account of chemosynthetic benthic communities associated with gas hydrate at the eastern margin of Japan Sea

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Distribution of macrobenthos was investigated in the eastern margin of Japan Sea.

The NSS (Navigable Sampling System) surveys have discovered the benthic community. The NSS was used to observed remotely and record the video images in real time. And benthic organisms and bottom sediments were collected using the Ocean-type grab sampler.

Three areas, the Torigakubi spur and the Umitaka spur off Joetsu, west off the Sado Island and off the Akita Prefecture, were investigated.

Torigakubi spur (740-790 m in depth): Benthos was collected twice by the glove sampler in this area. The chemosynthesis bivalves were not collected. However, a lot of polychaetes that appeared from methane seep's bottom in the investigation by hyper dolphin of NT10-10 that had been done in 2010 were collected in this investigation. Moreover, the brittle stars not collected in the Umitaka spur by current investigations were collected.

Umitaka spur (896-919 m in depth): It investigated by using NSS and the glove sampler in this region. Carbonate crusts, abundant red snow crabs and bacterial mats were observed. Strong gas bubbling when the piston corer dropped and hit the bottom.

West off the Sado Island: The area where the under bottom structure like a white mound was seen with the sub bottom profiler was surveyed. The bottom (1119m in depth) near a white mound structure was mud. Red snow crabs and zoarcid fishes were sparsely distributed at the bottom. The area where the reflection like a black dot at the bottom was seen with the side scanning sonar was surveyed. The gravel of a large amount of rhyolite was collected by the glove sampler. But, the benthos was few. In these survey areas, the red snow crab was not in a high density.

Off the Akita Prefecture (533-552 m in depth): The bottom condition was mad with carbonate rocks, bacterial mats well developed, and a white mass like a gas hydrate was seen. As the benthos, brittle stars were observed at high frequency, and zoarcid fishes, buccinid gastropods and prawns were distributed. And provanid gastropod that was distributed only from chemosynthetic benthos community was collected by the glove sampler. Moreover, neither the red snow crab nor the snow crab was observed, and the benthic fauna was different from the gas hydrate region off Joetsu.

In this investigation, the benthic fauna of the gas hydrate region where depth was different. These differences of benthic fauna was suggested the relation to depth.

Detail of biomass in this area was also discussed.

Keywords: chemosynthetic benthic community, gas hydrate, benthos, Japan Sea, methane hydrate

Depth profile of formaldehyde concentration in pore water from eastern margin of the Sea of Japan

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Natural gas hydrate is a clathrate compound. Gas molecules are encaged 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 hydrates. The reaction products will be accumulated in gas hydrates (Tani et al., 2006). For example, ethane, methanol, and formaldehyde are mainly formed in gamma-irradiated methane hydrate (Ishikawa et al., 2007, Tani et al., 2011). Methanol and formaldehyde may be closely related to microbial activities in the seafloor sediments. Therefore, we are interested in depth profiles of these compounds in the deep-sea sediments.

We investigated methanol concentration in pore water of the deep-sea sediments obtained during MD179 cruise in 2010. The methanol concentration in pore water beneath the seafloor was less than 2 microM, which is the detection limit. The concentration increased with depth, and reached to 10-20 microM around 30 m below the seafloor (Yamamoto et al., 2011). In this study, we have investigated the depth profiles of formaldehyde concentration in pore water of the same sediments.

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). Because Henry's constant of formaldehyde is large (Sander, 1999), o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA) was used as a derivative reagent for aldehyde (Kobayashi et al., 1980).

The results show that formaldehyde concentration in pore water is 0.3-0.8 microM beneath the seafloor, increased with depth, and 1-2 microM around 30 m below the seafloor. Formaldehyde concentration is well correlated with methanol one. These results indicate that formaldehyde and methanol in pore water may have similar production, consumption, and diffusion processes.

This study was supported by MH21 Research Consortium Japan.

Keywords: pore water, gas hydrate, Joetsu Basin, formaldehyde

The Changes of Sedimentation Rates Based on Tephrochronology in the Late Pleistocene Sediments off Joetsu, Japan

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Introduction

The sedimentation rate of the muddy sediment distributed over a submarine surface part is calculated using time markers contained in a core sample, such as tephra, the value of the ^{14}C and a horizon of crowd change of a microfossil, in many cases. For example, Suganuma et al. (2006) computed sedimentation rate from the eruption age value of tephra using the core of the northwestern Pacific Ocean. On the other hand, in Katayama and Itaki (2007), spatial distribution of sedimentation rates was estimated in the large area in the eastern Japan Sea off Akita, using depths of reflectors on 3.5 kHz sub-bottom profiler (SBP) records and estimated ages of the reflectors. Clarifying spatial distribution and its changes of sedimentation rate enable us to know change of the mass transfer system by environmental change. In this research, sedimentation rates were calculated from the eruption age value of tephra for 7 core samples with calm depositional environment extracted in the Joetsu basin circumference region.

Study area

The Joetsu basin located in the east of the Toyama trough is composed of various kind of geomorphology such as Umitaka spur, Joetsu knoll, submarine canyon. There is methane hydrate in the top part of Umitaka spur and Joetsu knoll (Matsumoto et al., 2011). The core samples extracted at such various geographical feature places consists of muddy sediments, such as sediments carried by the river, Kosa and a living thing. Since methane hydrate was inserted into the sediment as for the core extracted by methane hydrate area, most sedimentation structures do not remain and it was not able to identify a tephra layer. The cores extracted at the lower part of a slope or a submarine canyon contains the slump sediments and the landslide sediments, tephra in these cores were referred to lack or rework. In this research, 7 cores with calm depositional environment are used.

Calculation and the variation pattern of sedimentation rate

The sedimentation rate between tephra was calculated from the eruption age of the adjacent two tephra. For all 7 cores, the sedimentation rate between tephra layers was found and the variation pattern was clarified. The variation pattern of sedimentation rate was divided into four groups as compared with the oxygen isotopic curve. For the group 1, its sedimentation rate increased from MIS3 to MIS2 and decreased at MIS1. The group 2, unlike the group 1, has a high sedimentation rate at MIS1. For the group 3, its sedimentation rate decreased from MIS3 to MIS2 and increased at MIS1. For the group 4, its sedimentation rate increased from MIS2 to MIS1.

Relation between change of sedimentation rate and submarine geomorphological settings

By comparing sedimentation rate between cores, the flux of the sediment was discussed. The group 1 is the cores extracted by the physiographic rise. Sediment supply from land increased the low sea level periods and decreased the high sea level periods. Therefore, sedimentation rate of the group 1 changes depending on the quantity of sediment from land. It is thought that the group 2 has sediment supply from land and a continental shelf slope since it is located in the lower part of a continental shelf slope. The group 3 is the core extracted in the physiographically low place. In MIS1, since sedimentation rate is high, it is thought that sediment supply from the surrounding slopes. Since the group 4 was the cores extracted by the submarine canyon, it is thought that sedimentation rate increased by sediment supply from the continental slope at MIS2 and by sediment supply from land at MIS1. Moreover, change of the sedimentation rate which suggests that the methane hydrate decomposed at MIS2 was not recognized.

Acknowledgements

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Keywords: Sedimentation Rate, tephra, Off Joetsu, chronology, Late Pleistocene, SEM-EDS

Paleoceanographic change in the eastern margin of Japan Sea, based on oxygen and carbon isotope during the last 130 kyr

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The eustatic sea level changes in the Late Quaternary has strongly affected the hydrography and environment of Japan Sea because of its geographical condition. During the Last Glacial Maximum (LGM), freshwater input to the Japan Sea has been assumed to cause the large negative excursion in $d^{18}O$ of planktonic foraminifera. The severe anoxic conditions eliminated most benthic fauna due to a well-stratified water column and limited vertical circulation (Oba et al., 1991). However, some recent studies have cleared the existence of benthic foraminifera also during LGM, particularly around methane seep area.

In June 2010, R/V Marion Dufresne sailed the eastern margin of Japan Sea (MD179 Japan Sea Hydrates cruise) and recovered sediment cores. We analyzed oxygen and carbon isotope of both planktonic and benthic foraminifera with selected 2 cores from off Joetsu (MD179-3312, water depth 1,026 m; MD179-3304, water depth 896 m). Both cores are more than 30 m length, and considered to record continuous paleoceanographic change without large sedimentary gap.

Both cores can be correlated Marine Isotope Stage (MIS) 1 to 5 from $d^{18}O$ of planktonic foraminifera. One core (MD179-3312) shows the peak of MIS 5e with the existence of *Globigerinoides ruber*, *Neogloboquadrina dutertrei* and *Neogloboquadrina incompta* (dextral), so its bottom is considered to reach MIS 5e to 6. $d^{13}C$ of planktonic foraminifera varied roughly in synchrony with $d^{18}O$ of planktonic foraminifera.

We can recognize a number of benthic foraminifera during LGM from MD179-3304 core, which locate relatively near active methane seep area. During LGM, $d^{18}O$ of benthic foraminifera shows negative excursion in parallel with planktonic foraminifera. This fact shows fresh water input or/and some environmental change affected not only surface water but also deep water column. Negative trend in $d^{13}C$ of benthic foraminifera may show a possibility of relationship to methane seepage or gas hydrate dissolution event during LGM.

This study has been financially supported by the cooperative research project of the MH21 Research Consortium Japan, and isotopic analysis was performed under the cooperative research program of Center for Advanced Marine Core Research (CMCR), Kochi University (Accept No. 11A011, 11B011).

Keywords: Japan Sea, planktonic foraminifera, benthic foraminifera, oxygen isotope, carbon isotope, gas hydrates

Plaeoclimatology and palaeoceanography of Japan Sea based on the organic carbon contents of MD10-3304 core for the past

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The organic carbon (TOC) and the nitrogen (TN) contents were measured at 3 cm interval for a long sediment core (MD10-3304) taken from a site of 896 m depth of Umitaka ridge in Japan Sea off Joetsu City. The bottom of the 33 m-long core is estimated as old as 103 ka, and data interval is 50 to 100 years on average. TOC was separated into the marine organic carbon (MAOC) and the terrigenous organic carbon based on difference of C/N ratio.

The temporal changes of TOC and MAOC content well correspond both to the marine oxygen isotope curve (LR-04) and to the oxygen isotope curve from Greenland ice sheet (NGRIP). Glacial-interglacial cycle on orbital scale, Heinrich event and furthermore stadial-interstadial cycle called Dansgaard-Oeschger(D-O) cycle are well identified on the TOC and MAOC profiles. This fact suggests a strong teleconnection between the Northern Atlantic and Far East Asia.

The relationship of TOC and MAOC contents with dark layer (TL) in Japan Sea is classified into the four modes, which might be caused in response to temperature and sea level changes. For example, the combination of very low TOC and MAOC content and thick TL layers (TL 2, 3), Mode 1, was observed in the Last glacial maximum (MIS 2), resulting from very cold climate and persistent anaerobic bottom-water conditions forced by lower sea level and density stratification. Mode 3, which is characterized by many thin TL layers of high TOC and MAOC content are observable in MIS 3, 4, 5a, 5b, and 5d. TL layers of this mode were caused by enhanced biological productivity due to warm climate, resulting in anaerobic condition of the bottom water due to oxygen consuming for decomposition of abundant organic matter. The temporal change of TROC content well corresponds to annual precipitation reconstructed by the best-modern-analogues method applied to the pollen data from Lake Nojiri in the north of Nagano Prefecture.

Keywords: Plaeoclimate change, Total organic carbon, Japan Sea, Teleconnection, TL layer, Air temperature variation

Molecular and isotopic signatures of dissolved gas in sub-bottom sediments retrieved off Abashiri, the Sea of Okhotsk

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We measured molecular and isotopic compositions of dissolved gas in sub-bottom sediments retrieved off Abashiri, the Sea of Okhotsk, where sub-bottom profiler revealed the existence of gas chimneys ascending from the deep sediment layer. In the cruise of TK11 (September 2011), we obtained sea-bottom sediment cores by using a gravity corer (1.5m length) and sampled (1) dissolved gas in pore water, (2) dissolved inorganic carbon (DIC), and (3) dissolved gas in the sea-bottom water. Methane concentration in the four sediment cores increased rapidly at around 40-70cmbsf, that indicates shallow SMI (sulfate-methane interface) and high methane flux. Compared to the gas data obtained off Sakhalin Island, these high concentration of methane and shallow SMI imply that gas hydrate layers could exist below 1mbsf. Because the length of the corer was only 1.5m, the length of core recovery was less than 1m and we could not get gas hydrate samples. At the SMI depths, $\delta^{13}\text{C}$ profiles of methane showed their minimum value (less than -85 permil VPDB), suggested ongoing biogeochemical process: anaerobic oxidation of methane (AOM) produces ^{13}C -depleted CO_2 , and ^{13}C -depleted methane also is generated via CO_2 reduction (Borowski et al., 1997). In this process, hydrogen sulfide (H_2S) is still produced by sulfate reduction at the depth of SMI, however, we could not detect H_2S in the headspace samples due to the simplified process of sampling procedure. $\delta^{13}\text{C}$ and dD of dissolved methane ranged from -87 to -75 permil VPDB and from -210 to -203 permil VSMOW, respectively. Molecular ratio of hydrocarbons (methane/ethane) below the SMI depth ranged 5000-40000. Therefore, we conclude that these gases are microbial origin produced by CO_2 reduction. In the upper SMI layer, the concentration of methane was depleted and its $\delta^{13}\text{C}$ increased because methane oxidation was dominant. The profiles of DIC $\delta^{13}\text{C}$ agrees with that of methane $\delta^{13}\text{C}$ and showed minimum $\delta^{13}\text{C}$ at the SMI depth.

Keywords: gas hydrate, stable isotope, Sea of Okhotsk, off Abashiiri

Sulfur concentration and isotopic composition in gas-charged marine sediments from the Sea of Okhotsk, off Abashiri

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Gassy sediments have been recovered from the continental slope, approximately 1000m in the Sea of Okhotsk, off Abashiri, Hokkaido, in which gas chimney like structures are identified on the sub-bottom profilers. Geochemical analyses of gas and pore water collected from this area result sulfate-methane interface locating at <1mbsf, indicating very high methane flux and high potential of gas hydrate accumulation near the seafloor. Because oxidation of organic matter in sediments and ascending methane (anaerobic oxidation of methane; AOM), with dissolved sulfate produces hydrogen sulfide in pore water, pyrite can precipitate just below the seafloor. The isotopic composition of sulfur from pyrite, thus, reflects processes of shallow diagenesis associated with sulfate reduction. Variations of sulfur concentration and isotopic composition are useful to characterize geochemical environment in sediments constrained by methane flux. Environmental impact of shallow gas and AOM are discussed in relation with pyrite precipitation.

Keywords: Sea of Okhotsk, Sediment, Sulfur isotope

Chemical and isotopic analyses of sediment pore waters collected off Abashiri, Hokkaido, Japan

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In September 2011, field operations of the TK-11 cruise were conducted in a collaborative effort by scientists from Kitami Institute of Technology and the University of Tokyo to investigate natural gas hydrates (GHs) that have been suggested by a bottom-simulating reflector off Abashiri, Hokkaido.

In the present study, chemical and isotopic analyses of the sediment pore waters were carried out to determine geochemical features relevant to possible GH occurrence in the studied area. The concentrations of sulfate ions in the pore waters were measured to investigate the depth profile down to the depth of the sulfate methane interface (SMI), since the SMI depth is reported to depend on the upwelling methane.

Five sediment cores up to 1 m in length were recovered (TK-11 GC1101 to GC1105). A 5-cm depth interval of the internal portion of the sediment core was drawn into titanium hydraulic Manheim squeezers, and pore waters were collected in plastic syringes attached to the squeezers. The outer part of the sediment, which was in contact with the PVC liner tube, was left in the liner to avoid contamination. In addition to coring, sampling of seawater was conducted from the water column at the coring site using a Van Dorn sampler and from inside the liner tube just over the sediment cores. All water samples were filtrated through a 0.2-um filter and then stored in 50-mL plastic bottles and refrigerated until analyses. The concentrations of anions such as sulfate ions were determined by an ion chromatograph. A flame atomic absorption spectrometer or inductively coupled plasma optical emission spectrometer was used to determine the concentration of metals such as sodium, potassium, etc. Stable isotope ratios of oxygen and hydrogen of the water samples were analyzed by an isotope ratio mass spectrometer.

The fact that the sulfate concentrations decreased linearly with depth from seawater value to under the detection limit (UDL) is consistent with the anaerobic oxidation of methane by a bacterial consortium that uses sulfate as an oxidant in the process of oxidation. In other words, we can estimate that the depth where the sulfate is UDL is the SMI depth. The finding that the SMI depth of all cores is less than 1 m below the seafloor (including extrapolated SMI of TK-11 GC1105) suggests an intense methane flux from below in the studied area. The fact that no ionic anomaly of chloride and sodium ions and no isotopic anomaly of hydrogen and oxygen was observed in the pore waters suggests that GH was not contained in the cores.

Keywords: sediment pore water, ion concentration, stable isotope ratio, Abashiri

Origin of lithium in pore fluid of Kumano mud volcano, Nankai accretionary prism

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Deep-rooted fluids in the accretionary prism play an important role in the occurrence of earthquakes near trench. The fluid samples from forearc mud diapirs help us to delineate possible fluid origins and/or sediment-water interactions at depth within the accretionary prisms. It is, however, difficult to research deep-seated fluids from pore water samples using traditional hydrogen and oxygen isotopic compositions owing to contamination from seawater. Lithium (Li) is relatively unsusceptible to contamination from seawater because the Li content of deep-rooted fluid is significantly higher than that of seawater. In addition, Li has two stable isotopes, ⁷Li and ⁶Li, with respective relative abundances of 92.5% and 7.5%, and ⁷Li/⁶Li ratios may provide further insight into the origin of deep-rooted fluids. We therefore analyzed ⁷Li/⁶Li ratios of pore fluids in mud volcano in the Kumano forearc basin to investigate the fluid regime in Nankai accretionary prism. In this study, we analyzed two different drilled mud cores at site C0004 and site C0005 that were recovered from center and margin of the Kumano #5 mud volcano, respectively. These samples were recovered using D/V CHIKYU that was equipped with a riser drilling system.

The results show that delta ⁷Li values of analyzed Kumano mud volcano fluid vary from +5.5 to +10.6 per-mil (delta ⁷Li = $[\frac{[\text{Li-7}]/[\text{Li-6}]_{\text{sample}}}{[\text{Li-7}]/[\text{Li-6}]_{\text{L-SVEC standard}}} - 1] \times 1000$). Judging from the delta ⁷Li values were correlated with the Rb/Li ratios, we argued that the lowest delta ⁷Li value, +5.5 per-mil, as that of a deep-derived end-member fluid. It has already reported that the delta ⁷Li value of decollement fluid in Nankai subduction zone is +10 per-mil (You et al., 1995. *Geology* 23, 37-40). Because the Cl/Li ratios are significantly lower than seawater value, the Li isotopic difference between Kumano mud volcano fluids and Nankai decollement fluids are not due to seawater contamination. Thus, our Li isotopic data revealed that the Li in Kumano mud volcano fluids are originated from deeper (higher temperature) than those in the Nankai decollement fluids. Based on the Li isotopic data, we further estimated the fluid-sediment reaction temperature is 300°C. From the geothermal gradient in this are, we inferred that the Li in the Kumano mud volcano fluids is originated from 10 km depth.

Keywords: lithium isotope, mud volcano, Nankai, accretionary prism, deep-rooted fluid, gas hydrate

The science program for the first offshore production test of methane hydrates

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As a part of the study program of the Research Consortium of Methane Hydrate Resources in Japan (MH21), and to develop a production technique, the world's first gas production test from gas hydrate bearing marine sediments will be conducted in early 2013 in the Daini Atsumi (Atsumi No.2) Knoll area off Atsumi peninsula, the Pacific coast of Japan. In the area, past seismic surveys and a drilling campaign revealed existence of a gas hydrate concentrated zone (a turbidite sediment in which gas hydrates fill pore spaces of sandy layers with high saturation) has been discovered in a 50-70m-thick interval around 300m below seafloor at a location of 1000m water depth.

During the production test, the depressurization technique will be applied in which pore pressure is drawn down by formation water production through a wellbore to dissociate the gas hydrates for several weeks. Two and three-dimensional seismic surveys and geophysical logging and coring during the METI Tokai-oki to Kumano-nada drilling campaign have been conducted. For the 2013 production test, one production well and monitoring holes are drilled in early 2012, and intensive logging is planned in one of the monitoring holes. Also another hole dedicated for coring will be drilled to take pressure cores to conserve gas hydrates in samples. In the location, a geotechnical survey had been done with core sampling from shallower sediments than gas hydrate concentrated zone and a cone penetration test in February 2011. Those data and samples are used to develop reservoir characterization models.

One of the monitoring holes is kept open by steel casing to allow cased-hole geophysical logging before and after the production test to detect alternation of petro-physical parameters including gas hydrate saturation. All of the monitoring holes have temperature sensors to detect temperature drop due to gas hydrate dissociation. Extended-term temperature monitoring until half year later than the end of the production test will be done in some of them for the monitoring of temperature recovery. A geophone array in an ocean bottom cable (OBC) will be deployed for a multi-component and time-lapse seismic survey on the seafloor.

During the flow test, water and gas production rates, downhole temperature and pressure will be monitored. Geochemical data will be taken from samples. Comparison between actual well response and computed value from the established reservoir model will correct and improve our knowledge about reservoir characters and forecast of long-term productivity of the well.

Keywords: methane hydrate, production technique, field test

Study on formation efficiency of alcohols and aldehydes in gamma-irradiated methane and ethane hydrates

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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 and formaldehyde are also formed in gamma-irradiated methane hydrate (Tani et al., 2011). If the radiation-induced compounds in hydrate accumulate after hydrate formation, the amount may be related to a formation age of natural gas hydrate. The formation efficiency of the compounds should be determined for estimation of the formation age. Therefore, we have measured dissociated water of gamma-irradiated methane and ethane hydrates to analyze alcohols and aldehydes in the hydrates quantitatively by gas chromatography-mass spectrometry (GC-MS).

Methane and ethane hydrates were synthesized and irradiated by gamma-rays at 273 K under high pressure to avoid dissociation of the hydrates. Headspace gas of the dissociated water was analyzed by GC-MS. The formation efficiency of aldehydes is higher than that of alcohols. In addition, the formation efficiency of the compounds in ethane hydrate is higher than that in methane hydrate. These may be caused by the formation mechanism of the alcohols and aldehydes. We will discuss the possibility of dating natural gas hydrate based on these results.

Keywords: methane hydrate, ethane hydrate, radiation, GC-MS, alcohol, aldehyde

Pattern formation of tetrahydrofuran hydrate and an image-analysis technique to measure hydrates size scale

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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. In addition, a method to measure those variety patterns is not established. It is important establishing the method to clarify the pattern formation mechanism. This study presents a simple image analysis technique to measure hydrates size scale.

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 was unity. 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 unity. A directional growth apparatus was used to grow the hydrates at a constant growth rate, V , under an applied temperature gradient. The effect of the growth rate was studied in the range of 0.04 $\mu\text{m/s}$ $\leq V \leq$ 20 $\mu\text{m/s}$.

The digital pictures of hydrates convert to 256 gray-scale pictures. Processing of the 256 gray-scale pictures produced binary (black and white) images, where white pixels represent the pure hydrate and black pixels represent glass beads rich region. Those pictures were processed on a Windows computer, using public domain Image J program. Area of hydrate and grain number was measured using Analyze Particle function of Image J. And White pixels and Black pixels were counted. To calculate hydrate diameter and distance of each hydrate from those data, hydrate patterns were simplified to 2D square lattice and shapes of hydrate were simplified to disk. The detail of this method will be stated in poster session.

Results and Discussions

The large size hydrates were formed at the growth rate $V = 0.04\mu\text{m/s} \sim 1.0\mu\text{m/s}$. These patterns were regarded as massive type hydrate because the hydrates were much larger than nodular hydrates and contain about 5 % glass beads (This is one of criterion of massive pattern by Malone). When the growth rate was increased, the sizes of hydrates were decreased. Thus, the massive patterns changed to nodular patterns at $V = 1.0\mu\text{m/s} \sim 5.0\mu\text{m/s}$. When the growth rate was much increased, pure hydrates region was not formed at $V = 10\mu\text{m/s} \sim 20\mu\text{m/s}$. Consequently, as growth rate was increased, sizes of hydrates were decreased and the massive patterns changed to nodular patterns. Finally, disseminated type formed at high growth rate.

The relationship between area of hydrate and growth rate V was measured by the method as previously explained applied to massive, nodular and disseminated patterns. When growth rate was increased, the area of hydrate was decreased. And the area of hydrate was discontinuously decreased at $V = 1.0\mu\text{m/s}$. Thus, the value of area was discontinuously decreased at the point of massive pattern changed to nodular pattern. The distance of each hydrate and grain number was similarly measured.

Massive, nodular and disseminated patterns were reproduced. And those hydrate diameter was measured by hydrate patterns were simplified to 2D square lattice and shapes of hydrate were simplified to disk. This method is automatically, and enable to measure hydrate size scales in short time.

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

[2] Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, <http://imagej.nih.gov/ij/>, 1997-2011.

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