

Types and distribution of gas chimneys: host structure of shallow gas hydrates

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Gas chimney is defined as a subsurface columnar structure of a few 100 m to a few km in longest diameter, characterized by well-developed acoustic blanking down to more than a km. Gas chimney is a major host structure of shallow gas hydrates in Japan Sea, often capped by hard ground as recognized by strong back-scatter image of a side scan sonar, indicating surface exposure of massive gas hydrate, carbonate concretions and bacterial mats and related chemosynthetic communities. Intensive acoustic surveys such as MBES and SBP confirmed 971 gas chimneys over 30,000 km² areas during the reconnaissance survey in 2013-2014.

Based on the occurrence and distribution pattern of gas chimneys, three morphological types have been identified in survey areas. Type A: Single, cylinder shaped chimney with about 200 to 400 m in diameter, randomly scattered on basin floors. Type A is common on the basin floor of the Oki trough, which is characterized by thick organic rich sediments. Gases are predominated by microbial methane. Type B: Composite, irregularly shaped blanking zone with horizontal area of about 500 m x 3,000 m, often occur in transition from slope to basin floors. Type C: Single to composite, cylinder shaped chimney with about 400 to 600 m in diameter, occurs on the crest zone of ridges and spurs along the faults. Type B has been identified by high-resolution AUV surveys on the slope area of the Oki trough, and is suspected to occur in the Tsushima basin and off Hidaka. Hydrate gases have not been collected and analyzed yet. Type C is characteristic in the Toyama (off Joetsu) and Mogami trough, which developed along the mobile belt of the eastern margin of Japan Sea. Inversion tectonics at around 5 to 2 Ma caused folding and reverse faulting to provide conduits for upward migration of deep seated thermogenic gases. Hydrate gases are either thermogenic or variable mixture of thermogenic and microbial. Distribution of the types and size of gas hydrate-bearing gas chimney structures provide fundamental constrains for the resource assessment of shallow gas hydrates.

Keywords: shallow gas hydrates, gas chimney, Oki trough

FY2014 AUV survey in shallow methane hydrate fields in Japan Sea

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As a part of national project of shallow methane hydrate exploration, high-resolution acoustic survey (SK14 cruise) using an autonomous underwater vehicle (AUV) was performed in offshore areas of Oki, Joetsu, and Mogami Trough from May 10th through June 3rd in 2014. The survey was carried out basically in the same manner as that of SK13 cruise. We used AUV 'Deep1' and the mother vessel 'Shinkai-maru (329 t)' (both are from Fukada Salvage & Marine Works Co., Ltd.). The Deep1 is installed three acoustic observation equipment, a multi-beam echo sounder (MBES), a sub-bottom profiler (SBP) and a side-scan sonar (SSS), and its battery can make the vehicle perform over 20 hours dives. An ultra-short base line (USBL) system was taken for navigation. For the surveys, we applied normal mode taking line interval of 150 m and precise mode taking that of 10m. The vehicle keeps altitude above the seafloor at 50 m for the normal mode and 25 m for the precise mode. The targets of the survey were chosen from some topographical anomaly points, called mounds and pockmarks, which had been identified by the previously performed wide area surveys (7K13 and 7K14 cruises). The AUV were able to clarify detailed topography and shallow geologic structures in the mounds, pockmarks and the surroundings and grasped characteristic features and the variations of acoustic blanks, high reflection layers, seafloor high reflections and so on.

Keywords: Methane hydrate, AUV, multi-beam echo sounder, SBP, sub-bottom profile, side-scan sonar

Investigation of seafloor methane hydrates by marine controlled source electromagnetic method in offshore Joetsu areas

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We have conducted an investigation of seafloor methane hydrates by towing-type marine controlled source electromagnetic method in offshore Joetsu areas. The MCSEM system, owned by Scripps Institution of Oceanography, is composed of one transmitter and four receivers installed with 100m space, which are connected with a cable. The system was towed at the height of about 50m from the seafloor. The transmitter transmitted electrical current with the particular wave form containing various frequency components. The combinations of the transmitter and four receivers at each frequency have the information on sub-seafloor resistivity structure at different depths. The maximum depth of investigation was about 100m. The investigation was carried out for about three weeks, from the middle of August to the beginning of September, 2014. We used the survey ship, Shinnichmaru operated by Fukada Salvage & Marine Works construction Co., Ltd., and the operation of MCSEM system was mainly conducted by Ocean Floor Geophysics Inc. (OFG) Corporation.

The plane views and sections of apparent resistivity values show some resistive anomalies consistent with those of the sub-bottom profiling results. Moreover, three-dimensional inversion of MCSEM data was applied to illustrate more detailed sub-seafloor resistivity structure, and we compared the resultant structure with some features of submarine topography.

Keywords: seafloor methane hydrates, marine controlled source electromagnetic method, offshore Joetsu areas

Exploration results of shallow gas hydrate by 2014 Logging While Drilling in Off-Joetsu and Mogami Trough, Japan Sea

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Research cruise GR14 of Greatship Ragini with Geoquip Marine GMTR 120 for LWD (Logging While Drilling) survey was conducted by Meiji University, in Off-Joetsu and Mogami Trough areas on the eastern margin of Japan Sea, during June 20th to July 17th, in 2014. The objective of the cruise is to explore the "gas chimney structure", which have been inferred from the acoustic blanking on the high resolution seismic profiles and from which methane gas hydrate have been sampled in the shallow subbottom (mainly down to about 10m by the gravity coring), from the seafloor to the base of gas hydrate stability zone (BGHSZ), whose depths are 50 to 120 m bsf in the survey area.

LWD tools to hire for the survey consists of Schlumberger geoVISION (resistivity imaging and gamma ray), TeleScope (telemetry) , sonicVISION (acoustic), and proVISION (CMR: Combinable Magnetic Resonance). The LWD survey was planned to explore down to 150 m bsf to penetrate BGHSZ. 10 sites were drilled in gas chimney structures and one site was drilled as the reference nearby a gas chimney structure. While 9 wells were drilled down to 150 m bsf as planned, drilling at two wells were stopped because of the stiffness of the formation and gas emission from the seafloor at 80 m and 100 m below seafloor, respectively.

LWD data quality was very fine, excepting very shallow depth intervals from the seafloor to 10 - 20 m bsf in most of wells. Methane gas hydrate concentrated intervals were identified from the high resistivity, high acoustic velocity, low natural gamma ray intensity and low CMR porosity. LWD data of most of the drilled gas chimney structures show the intense anomaly to suggest high concentration of methane gas anomaly in the shallow intervals from the seafloor to several tens of meters and deeper intervals over the BGHSZ. These two intervals are continuous in some sites. Only the deeper interval was observed in the reference site. Most of anomalous intervals are shown by the series of spikes on acoustic logs and broader resistivity peaks.

This research is a part of METI's project entitled "FY2014 Promoting research and development on methane hydrate."

Report on the drilling results of gas chimneys by R/V Hakurei (HR14) in the eastern margin of the Japan Sea

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Several gas chimney structures, which develop on the topographic highs in the off Joetsu and the off Akita - Yamagata areas in the eastern margin of the Japan Sea, were drilled and a lot of sediment, gas and water samples were collected by R/V Hakurei belonging to JOGMEC from 21st of June to 10th of July 2014. This cruise is named HR14. The drilling depths of the Joetsu knoll in the off Joetsu and Tobishima West in the off Akita - Yamagata areas is as deep as 122 m and 111.5 m, respectively, and the drilled cores penetrated through the expected base of gas hydrate stability zone (BGHSZ). By this, we could know the constituents and structure of the gas chimney structures from the surface to the BGHSZ.

Two neighboring sites are selected to drill on a small mound of Tobishima West by the results of the SBP in order to characterize the gas chimney structure; the one shows a clear stratified structure (RC1408) and the other shows a sonic blanking zone that is called a gas chimney structure (RC1407). The drilling results show the stratified part bears no methane hydrate as deep as around 48 m and consists of alternated thinly laminated and bioturbated layers that is the typical sediments of the Japan Sea. On the other hand, the gas chimney structure is found to be composed of silty clay with methane hydrate and carbonate nodules.

The occurrence and the vertical distribution of methane hydrate in the gas chimney structure show characteristic features. The surface methane hydrate obtained was subdivided into massive, granular, platy and veined types by the occurrence in the cores. Massive and granular types are common in the shallower horizons, while the platy and veined types develop well in the much deeper horizons. Methane hydrate was abundant in the shallower horizons than 40 m to 60 m in two long cores. Gas is also found as well as solid methane hydrate within both methane hydrate and mud.

A model of the subsurface distribution of the shallow gas hydrate and gas in the gas chimney structure is proposed by the drilling results. The proposed model of the gas chimney structure of the shallow gas hydrate, although, has a weak point that it is based only on the three different drilling sites and the lateral changes in the occurrence and amount of methane hydrate within each gas chimney structure is not clarified yet.

Observed vertical distribution of the types of methane hydrate denies a concept that a constant and continuous supply of gas in a stable stability zone of methane hydrate as long as a few hundreds of thousands of years. Instead a catastrophic methane event that occurred in recent years such as the last glacial maximum should have caused the distribution pattern of the types of methane hydrate observed.

We express sincere gratitude to all the persons in JOGMEC who engaged to operate R/V "Hakurei". This research is a part of METI's project entitled "FY2014 Promoting research and development of methane hydrate".

Keywords: shallow methane hydrate, Japan Sea, gas chimney, drilling

Changes of pore water geochemistry constrained by gas hydrate formation/dissociation in the Japan Sea

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Gas hydrate is composed of water and gas, mostly methane in natural environment, its formation and dissociation must change the geochemical signature of pore water in sediment in response to the amount, rate, and sedimentary environment of the gas hydrate. The eastern margin of the Japan Sea is one of the places where very active methane accumulation through the gas chimney structure sustains the formation of dense and thick gas hydrates near the seafloor. We have collected large number of sediment cores on and around the gas chimneys and have measured the geochemistry of pore waters to examine the existence and potential of gas hydrate, material transfer via fluid, and relationship with biological activities and mineral precipitations. The profiles, however, have not reached well down to or below the massive accumulation zone of gas hydrates, the entire model of pore water changes has not been discussed well. We report the analytical results of pore waters collected successfully from the sediments within/deeper than the gas hydrate stability during the HR14 expedition and show that the pore water geochemistry has been modified strongly by the formation/dissociation of gas hydrate through the gas chimney structures compared to that outside the chimney.

The sulfate concentration of pore water at the site outside the gas chimney progressively decreases with depth, reaching 0 mM at 10 mbsf (sulfate-methane interface; SMI), and is stable at very low level. The chloride concentration is close to the seawater level throughout the sediment. The high concentration anomaly only of sulfate occurs exceptionally at 42 mbsf where the sediment core looked "wet/loose", reflecting contamination of seawater during coring. The significant concentration of sulfate below the SMI is therefore useful for the correction of contamination with seawater/drilling mud. Contrary, the sulfate concentrations at two sites within the gas chimney are strongly variable below the SMI through the gas hydrate stability, indicating the contamination of seawater/drilling mud by the coring of tight gas hydrate layers or the intrusion of these fluids into the loosen sediment due to gas hydrate dissociation or gas expansion. After the correction of contamination with seawater/drilling mud, pore waters collected from gas hydrate-free sediment layers between dense massive/granular/platy gas hydrate accumulation zones are strongly enriched in chloride compared to the seawater value of 560 mM, reaching up to ~1200 mM at 15 to 25 mbsf, and the in-situ chloride concentration (Cl-baseline) shifts to ~600 mM to the bottom of gas hydrate stability at both sites. This is because the rate of gas hydrate formation and chloride exclusion from the crystal exceeds the diffusion of pore water. The most rapid and active formation of gas hydrate occurs as shallow as 15 to 25 mbsf in the research area, the formation of dense gas hydrates at these depths responsible for the topographic change like mound overlying gas chimney. The high Cl-baseline below this interval indicates active gas hydrate formation as well, the in-situ pore water geochemistry is essentially characterized by the rapid formation and distribution of massive gas hydrates within the gas chimney.

The concentrations of chloride from gas hydrate-bearing sediment and sometimes from normal sediment decrease by ~200 mM from the Cl-baseline value. The former results from the dissociation of gas hydrate during the core recovery, and the latter indicates that the invisibly small gas hydrates existed in the sediments and dissociated. The chloride concentration also decrease to ~400 mM below the gas hydrate stability, indicating the dissociation of all of the gas hydrates in sediments after the burial and subsequent diffusion of gas hydrate-derived fresh water into sediments.

This research is a part of METI's project entitled "FY2014 Promoting research and development on methane hydrate".

Keywords: Shallow gas hydrate, pore water, Japan Sea

The biomarker composition of petroleum-like substance isolated from methane hydrate in RC 1403 core

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A substance like petroleum was isolated from the thick methane hydrate layer located at the RC 1403 core depth of 27m. Similar petroleum-like substance was included in the rounded gravel bed above the methane hydrate layer.

After the isolation and separation of a biomarker, GC/MS analysis was performed. The nature of the substance like petroleum, origin, history of the heat and microorganism decomposition was argued. The hydrocarbon fraction and ketone/ester fraction were used for this study.

A hydrocarbon fraction is characterized by the existence of hump in the low carbon number area, and two kinds of bicyclic sesquiterpanes and small amount of C₂₅ tetracyclic terpane. On the other hand, n-alkane nor acyclic isoprenoids such as pristane and phytane were not detected in the chromatogram of hydrocarbon fraction. The feature of hydrocarbon fraction resembled to the very heavy biodegraded oil.

Ketone/ester fraction was characterized by hopanic and hopenic ketone.

In a particular, the angiosperm marker such as upanoid ketone, ursanoid ketone was detected. The existence of angiosperm marker indicates that the source of substance like petroleum was affected by terrestrial higher plant.

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Keywords: Japan Sea, Methane hydrate, biomarker

Profiles of methanol in pore water of deep-sea sediments in eastern margin of Japan Sea and around Oki islands

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Methane hydrate, a clathrate compound of methane in water cages, is recognized as an unconventional natural gas and has been studied for natural gas resource in future. For better understanding of shallow methane hydrate, it is of great interest to elucidate the microbial environment related to generation and consumption of methane. In geochemical approaches, the depth profiles of methane as well as CO₂, sulfate ion, and so on have been investigated. Although the other C1 compounds like methanol and formaldehyde may be closely related to microbial activity, a few studies have revealed profiles of methanol and formaldehyde in deep-sea environment. Yamamoto et al. (2011) reported that methanol concentration in deep-sea sediments of the off-Joetsu area, eastern margin of Japan Sea was lower than detection limit in shallow region and increased gradually with depth deeper than ~10 mbsf. The profile of formaldehyde had a similar trend to the methanol profile. The deepest sample was recovered from ~40 mbsf at that time. Therefore, we are keen to explore deeper region for further understating of depth profiles of methanol and formaldehyde. We had an opportunity to have deeper samples in HR14 cruise (June-July, 2014). The pore water samples were obtained by squeezing deep-sea marine sediments and measured by headspace GC/MS. The concentrations of methanol are below the detection limit in shallow region and increase from a certain depth. The tendency of the profiles is good agreements with the previous results by Yamamoto et al. (2011). The concentration at much deeper region does not monotonically increase, so that methanol would be not only diffused from deeper region but also affected by microbial activity. In addition, pore water samples around Oki islands were obtained in UT14 cruise (July, 2014) and analyzed by the same procedures to investigate methanol and formaldehyde profiles in different sampling locations. Methanol concentrations are below detection limit in most core samples. Nevertheless, high concentrations of methanol in pore water in shallow region were observed in PC1415. This may indicate that methanol distribution is not homogeneous even inside the mound of shallow gas hydrate. This study was supported by 2014 development and promotion program of methane hydrate.

Keywords: pore water, deep-sea sediment, water-soluble volatile organic compounds

Cross section observation of shallow gas hydrates by Raman imaging

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Natural gas hydrate, an inclusion compound of natural gas in water cages, is found in deep-sea sediments and permafrost region. In eastern margin of Japan Sea, shallow gas hydrates have been found and recovered by piston coring (Matsumoto et al., 2011; Lu et al., 2011). X-CT observation of the shallow gas hydrates revealed that icy materials divided into two regions (darker and lighter regions) by CT-values (Tani et al., 2013). Since CT-values of ice and natural gas hydrate are close each other due to similar X-ray linear attenuation coefficients, it is difficult to specify which region is gas hydrate only by CT images. In this study, cross section of the shallow gas hydrate was observed by Raman imaging to understand the differences of the darker and lighter regions in CT-values. The sample recovered from the eastern margin of Japan Sea in UT13 cruise was measured by X-CT first and then broken into two pieces. The cross section was measured by Raman imaging. The results indicate that pieces of natural gas hydrate with a few mm in diameter are scattered in the sample. Comparison between Raman images and CT images reveals that the lighter region of icy materials in CT images is natural gas hydrate and the darker region is ice. This study was supported by 2014 development and promotion program of methane hydrate.

Keywords: shallow gas hydrates, imaging, Raman, X-CT, dissociation

Analysis of benthic community food web at gas hydrate deposits of Joestu Basin

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The ocean floor ecosystem depends largely on photosynthetically-derived organic matter and the degraded products. Also, we can find some ecosystems supported by chemosynthetically-derived carbon in deep seafloor. Chemosynthetic organisms use inorganic material, such as sulfur and methane as source of energy. In some methane seeps, benthic chemosynthetic communities are dominated by macrobenthos, such as gastropod, bivalve, crustacean and pogonophoran. It is known that many red snow crabs often congregate around cold seep in the Sea of Japan and that *Provanna* known as a chemosynthetic gastropod species in hydrothermal vent and cold seep also inhabits. However, their relationship between their ecology and chemical energy derived methane seep remains unknown.

To better understand the ecology of benthic community at gas hydrate deposits of Joetsu Basin, we analyzed their food web using the stable isotopic ratios of carbon and nitrogen ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) for the surface sediment and benthic fauna, such as red snow crab, eelpout, whelk and polychaete. Carbon and nitrogen signature reflects carbon source and trophic level, respectively.

Sampling of benthic fauna at seeps using a slurp gun and a strainer was conducted during 24-30 September 2013 at Umitaka Spur and Torigakubi Spur. We obtained surface sediment sample using MBARI ROV coring system at depths of 0-2.5 and 2.5-5 cm below seafloor. Sampling at reference site was conducted at Joetsu Knoll on 23 September 2013. Macrofaunal sample was dissected on board and frozen at $-20\text{ }^{\circ}\text{C}$. Meiobenthos were removed by sieving of sediment samples and frozen. In laboratory, faunal sample was powdered after freeze drying. We removed carbonate from the sample by HCl steam treatment. Sample was refilled after neutralization by NaOH steam and drying. We measured stable isotope signature using IRMS (Flash 2000, Thermo Scientific Inc.). Similarly, sediment sample was removed carbonate by HCl solution, dried on a hotplate and measured.

Our result shows that no distinct difference between the isotopic signature of red snow crab and one species of eelpout, *Bothrocara hollandi* collected both at seep site and reference site. Other macro carnivores such as a squid and some individuals of whelk also have similar isotope signature. Biplot of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values suggests that the red snow crab mainly eat small crustaceans including amphipods and shrimps although we know the crab eats squids and cannibalizes by ROV observation at sea floor. Our results indicate that food habitat of red snow crab depends on photochemically-produced organic matter even in an individual inhabiting around methane seep. That means the red snow crab is a component of phototrophic ecosystem.

In this investigation, isotopic signature of *Provanna* collected at Joetsu Basin shows similar value with that of polychaete. We collected another species of eelpout, *Petroschmidia toyamensis*, which have isotopic value showing they eat *Provanna* and polychaete differently from *B. hollandi* as a component of photosynthesis ecosystem. Our direct observation of gut supports the predator-prey relationship between the former eelpout and *Provanna*. Small $\delta^{13}\text{C}$ of *Provanna*, polychaete and *P. toyamensis* indicates that they depend on methane-derived carbon microorganism produced. That suggests that they are components of chemosynthetic ecosystem at Joetsu Basin.

Meanwhile, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of a whelk, *Buccinum tenuissimum* varied at site in spite of same species. We considered that the food habit of the whelk was affected by site-specific factors rather than the maturity.

Our research showed that we could analyze the benthic food web at seep site more precisely rather than direct observation and elucidate the dependence of benthic community on methane-derived carbon using stable isotope analysis of widespread species.

This work was conducted as a part of METI's methane hydrate exploration project.

Keywords: methane hydrate, benthic fauna, food web, stable isotope analysis

Distribution of atmospheric gas concentration in eastern margin of Japan Sea: A preliminary report from the 7K14 cruises

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Hydrate of natural gas is widely distributed in marine sediments in the eastern margin of Japan Sea. The natural deposits of gas hydrates are estimated to hold higher reserves than known conventional gas reservoirs. An active seepage of gas from the seafloor has previously been reported from gas hydrate fields worldwide. Atmospheric methane (CH₄), major component of seep gases, is an important short-lived climate pollutant. Our objective was to measure the distribution of atmospheric CH₄ concentration over the sea surface of gas hydrate areas along the eastern margin of Japan Sea.

We used the R/V Kaiyo-Maru No.7 (Kaiyo Engineering Co., Ltd., Japan) for the survey in the Oki Trough and offshore Akita-Yamagata (Mogami Trough) from mid April to early June 2014. Continuous measurement of atmospheric CH₄ was performed on the ship using a wave-length-scanned cavity ring-down spectrometer (WS-CRDS) (model G2201-i, Picarro Inc., USA). Air sample was collected from an air intake at the top deck of the ship using an air pump placed in the observation room. To our experience, the ship sailed at approximately 6 knot. Location data were obtained from the nautical GPS.

Observed CH₄ concentration over the sea surface was not uniform in Mogami Trough, while mostly uniform throughout the Oki Trough. In addition, there was a tendency that CH₄ concentration in Mogami Trough was higher than that in Oki Trough.

This research was a part of METI's project entitled "FY2014 Promoting research and development on methane hydrate".

Keywords: shallow gas hydrates, methane gas, distribution of gas concentration

Geochemistry of continuous pore water intake by Osmotic Fluid Sampler

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On the Umitaka Spur of the Japan Sea, methane venting on the seafloor has been observed by ROV Hyper Dolphin, its strength and location change in short period. These changes effect on chemical and ecological environment of pore water and shallow sediments, continuous observation of these fluctuations are key to understand the dynamics of gas hydrate system near the seafloor. We have applied an osmotic fluid sampling system (OsmoSampler) from September 2013 to October 2014 to collect pore waters near the seafloor continuously and show the variations of gas and fluid geochemistry associated with the activity of gas venting. Although the concentration of sulfate is lower than that of seawater, it fluctuates for days accompanying small variation of methane concentration. The concentrations of chloride and other major ions also fluctuate near the seawater value. These changes of gas and fluid geochemistry may reflect the change of methane flux and following formation/dissociation of gas hydrates.

This research is a part of METI's project entitled *FY2014 Promoting research and development on methane hydrate*.

Keywords: Gas Hydrate, Methane Flux, SMI

3D Seismic Velocity Structures Associated with BSRs and Gas Hydrate Accumulations on Joetsu Knoll in the Japan Sea

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Characteristics of BSRs

In the eastern margin of Japan Sea, gas hydrates in shallow sediments are characterized by blanking or gas chimney associated to mounds and pockmarks on the seabed. SadoW 3D seismic survey was conducted by METI offshore Niigata in 2008. 3D seismic data on Joetsu Knoll shows aligned BSR bumps on the ridge characterized by structural and velocity pull-ups associated to seabed morphology initiated mainly by large-scale methane seepage.

In this area, multiple BSRs are commonly observed. BSR map was illustrated for the shallowest. For BSR identification, we prepared the curves of seabed depth vs. thickness of BGHS below seabed as a function of geothermal gradients with seabed temperatures. Estimated BGHS is governed by several unknown factors. BSR shows acoustic impedance change and corresponds to BGHZ or top of free gas. Free gas exists if mass fraction of upward flux of gas exceeds its solubility in liquid. Once fraction is less than its solubility, separation of BGHZ and BGHS occurs.

On the ridge of Joetsu Knoll, aligned BSR bumps are conspicuous and have upward correspondence to mounds and adjacent pockmarks on the seabed, some of which appear to be related to subvertical faults interpreted as venting passes, which show blanking. Pull-up effects of higher velocity above them exaggerate relief of bumps. Along 2D sliced lines, acoustic velocity is estimated by continuous velocity analysis. Zone of higher velocity more than approx. 1700m/s spreads above BSR, which sandwiches relatively lower velocity zone. Below BSR bumps, two types of spreading of lower velocity zones is prominent, i.e., downward and horizontal on strong reflectors.

Blanking has multifold background; intense gas hydrates formation, free gas venting passes and other seismic wave attenuation/scattering phenomena. Important point is that apparent amplitude features are dependent on the frequency bands of respective surveys. It has not been commonly mentioned that amplitude behaviors alone could not rule out others as possible origins. Velocity information is important to reason probable origins. Lower velocities just above BSR show velocity smearing related to resolution limit of the current velocity analysis. Note short scale complex subsurface structure deteriorates the accuracy of velocity estimate in conventional velocity analysis. This shortcoming shall be overcome by more advanced approaches for fine and accurate mapping. Velocity evaluations by FWI as an example are taken for some velocity model inversion.

Seismic line along LWD locations

GR14 LWD survey was conducted in 2014 by METI. On L18.Line 6 of METI SK13 AUV/SBP survey, a 2D sliced seismic line is taken along the line of GR14 sites D1-1 and D10-1 from 3D seismic data and velocity structure map is generated. At site D1-1 for LWD1410, seismic blanking is prominent above and below BSR. Just below BSR, lower velocity compartment is striking and prominent blanking zone above BSR shows higher velocity. At site D10-1 for LWD1409, above and below BSR there are no prominent seismic blanking zones. Just above BSR, laterally spreading higher velocity is prominent.

Synthetic seismograms are computed by invariant imbedding method and compared with seismic data. Its frequency band of synthetics with Ricker wavelet source is adjusted to that of seismic data and amplitude of seismic data is adjusted to synthetic seismogram. Synthetic seismograms of LWD sonic show relatively higher amplitudes in later phases are partly caused by assumed density models and/or possible attenuation mechanism for seismic data. LWD resistivity converted to TWT indicates that estimated BGHZ does not correspond to BSR, which suggests higher LWD sonic velocities and/or probable frequency effects under the assumption of no separation of BGHZ and BSR in these locations and no specific site locality.

We would like to thank the permission of METI/JOGMEC for the usage of SadoW3D data in the current study and publication.

Keywords: Gas Hydrate, Blanking, Gas Chimney, FWI, Joetsu Knoll, SadoW 3D Seismic Survey

Characteristics of natural gas hydrate retrieved at northern central Baikal basin

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Lake Baikal (Russia) is the solitary example of hydrate-bearing area in the environment of fresh water. Gas hydrate samples in sandy turbidites were first obtained at the southern Baikal basin in the Baikal Drilling Project in 1997. Multi-phase Gas Hydrate Project (MHP, 2009-2014), the international collaboration between Japan, Russia, and Belgium, has revealed distribution of gas hydrate in sub-bottom sediment at the southern and central Baikal basins. In the last cruise (MHP-14) we obtained gas hydrate crystals from four new places (Kukuy K-5, Khoboy, Akadem Ridge, and Barguzin) at the central Baikal basin. We report the characteristics of hydrate-bound gases at these sites.

Samples of hydrate-bound gas were obtained onboard and stored in 5-mL vials. We measured molecular and stable isotope compositions of the samples. According to the $C_1/C_2 - C_1\delta^{13}C$ diagram (Bernard *et al.*, 1976), the $\delta^{13}C$ - δD diagram for C_1 (Whiticar, 1999), and the $C_1\delta^{13}C - C_2\delta^{13}C$ diagram (Milkov, 2005), the gas characteristics show the following information:

1) Hydrocarbons at the Khoboy, Akadem Ridge, and Barguzin are microbial origin, and those of Kukuy K-5 is in the field of mixed-gas between microbial and thermogenic gases.

2) In the "Bernard diagram", hydrate-bound hydrocarbons of Kukuy K-5 locate on the mixing line of microbial gas at the Kukuy K-9 and thermogenic gas at the Kukuy K-4, those are the end members at the Kukuy Canyon area.

3) $C_2 \delta^{13}C$ of the hydrate-bound gas at the the Khoboy, Akadem Ridge, and Barguzin are low (less than -50 ‰), indicating microbial C_2 . Microbial C_2 in the hydrate-bound gas has been observed at the Krasnyi Yar and Peschanka P-2 at the southern Baikal basin, and the Ukhan and Unshuy at the central Baikal basin.

4) The site Barguzin locates only 7 km distance from the site Gorevoy Utes, where oil-stained gas hydrate with thermogenic gas was retrieved.

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Keywords: gas hydrate, crystallographic structure, Lake Baikal

Micropore effect on dissociation process of methane hydrate and fractionation of stable isotopes

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Gas hydrates are clathrate compounds that the guest-gas molecules are trapped in host-cages composed of water molecules, and are stable at low temperatures and high pressure conditions. Natural gas hydrate exists in the sea bottom sediments off Sakhalin Island (Sea of Okhotsk), those comprised of diatom with many small pores. Sediment particles may affect to formation and dissociation processes of gas hydrate because their small pores change equilibrium pressure of gas hydrate. Isotopic fractionation of guest gas between gas and hydrate phases has been reported (Hachikubo *et al.*, 2007), however, little is known about the effect of micropore on the fractionation of stable isotopes. We conducted calorimetric measurements of methane hydrates (MH) formed with silica-gel pores to investigate thermal properties of MH in the small pores, and measured isotopic difference in methane molecules between MH and residual gas at their formation process.

The silica-gel sample (pore diameter: 15 nm) was dried at 423 K for 24 hours and then adsorbed water in a chamber for three days. Methane hydrates were formed with the adsorbed water in silica-gel pores under high pressure of methane (10 MPa) at 273.2 K. Silica-gel samples with methane hydrate were stored in liquid nitrogen and the residual gas was also sampled. Thermographs of the hydrate sample were obtained by a calorimeter. Stable isotopes (carbon and hydrogen) of hydrate-bound and residual methane were measured by an IRMS.

The thermograph revealed that a broad peak around 173 K and other peaks ranged from 193 K to 203 K corresponded to dissociation of pore and bulk hydrates, respectively. Because the dissociation of hydrate formed ice and plugged the pores, a large endothermic peak appeared in the range from 223 K to 273 K and the internal pressure increased due to dissociation of confined hydrate.

δD of hydrate-bound methane was 6.2-7.2 ‰ lower than that of residual methane in the formation processes, agreed fairly with the result of Hachikubo *et al.* (2007). While there was no difference in the case of $\delta^{13}C$ (Hachikubo *et al.*, 2007), our results showed that $\delta^{13}C$ of hydrate-bound methane was several ‰ higher than that of residual methane, suggesting effect of micropores.

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Keywords: gas hydrate, micropore, diatom, stable isotope, isotopic fractionation, calorimetry

Importance of physical property evaluation for methane hydrate R&D and pressure coring-analysis operation

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In the cases of either natural phenomenon or an artificial operation for resource development, a gas hydrate dissociation process can be regarded as transportation of heat and fluid masses in porous media. Because the convection term is dominant, the heat transport is highly affected by the fluid flow. The reasons why those basic physical problems are complicated are intrinsic complexity of geological formations, alternation of the physical parameters due to hydrate dissociation, and mechanical behaviors of soft sediments that can transform the properties dynamically. Therefore the focus of studies on the energy production technique from gas hydrate deposits is to understand the hydraulic, thermal, and mechanical properties and processes.

In the study program of the MH21 research consortium, evaluation of such physical properties, their distribution in geological formations, and dynamic behavior of them have been investigated through seismic surveys, drilling operations including geophysical logging, sampling and in-situ testing, laboratory experiments, numerical simulation, and so on. As one of those efforts, pressure core sampling in which the in-situ condition is kept, and measurement of the properties of the retrieved sample are especially important.

In June and July of 2012, the MH21 consortium has conducted core sampling operation in Daini Atsumi Knoll of the eastern Nankai Trough using a pressure coring device and D/V Chikyu (JAMSTEC). In the operation, about 35m samples were recovered by the device, and majority of them were fully or partially pressure-preserved.

After the on-board analyses, some of those retrieved samples were delivered to onshore laboratory testings under more controlled conditions. The main purpose of the study is to measure hydraulic and mechanical properties. Also relationship of the properties and geological features are important, and analyses on them could drive important knowledge about the sedimentation conditions of them.

A part of the study was conducted under Japan-US collaboration. The results are publicized in a special issue of Journal of Marine and Petroleum Geology. In this presentation, objectives, core sampling operation, and analysis flow are presented.

Keywords: methane hydrate, pressure core, hydraulic, mechanics, physical properties

Crystallographic features of natural gas hydrates recovered by pressure coring in the eastern Nankai Trough area

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Natural gas hydrates are crystalline clathrate compounds that natural gas components are incorporated into cage-like frameworks consist of hydrogen-bonded water molecules. Natural gas hydrates are stable under high pressure and low temperature conditions such as deep marine environments. Crystallographic structures of gas hydrates are related to amount of trapped gas or thermodynamically stable condition for natural gas hydrates, which are important to characterize natural gas hydrate reservoirs.

In this study, the crystallographic properties of the natural gas hydrates recovered by pressure coring in the eastern Nankai Trough area were characterized by the spectroscopic analyses. The hydrate-bearing sediments were recovered from the eastern Nankai Trough area during the 2012 JOGMEC/JAPEX Pressure coring operation, aboard the DV Chikyu.

The primary hydrocarbon component is microbial methane for gases released from the hydrate-bearing sediments. The released gas contained trace amounts of ethane and heavier hydrocarbons. NMR and Raman spectroscopic analyses reveal that the crystallographic structure is structure I and the hydration number is 6.1.

This work was supported by funding from the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium) planned by METI.

Keywords: gas hydrate, methane hydrate, hydrocarbons, pressure-coring, crystal structure

Pressure Core Analysis on Permeability of Methane-Hydrate-Bearing Sediments

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Permeability is the most important factor affecting the gas productivity of hydrate-bearing sediments. In this study, effective water permeability of hydrate-bearing sandy sediments was measured by core-flooding test. The core samples were recovered under pressure from a methane hydrate reservoir located at the Daini-Atsumi knoll in the Eastern Nankai Trough off the shore of Japan. The cores were shaped cylindrically with liquid nitrogen spray after rapid pressure release and inserted into a core holder to maintain the hydrate phase stable P-T conditions and to apply a near in situ effective stress. The results showed that the effective water permeability in hydrate-bearing sandy sediments was in the range of 1-100 md. After depressurization-induced hydrate dissociation, absolute permeability of host sediments was analyzed. Absolute permeability of sandy host sediments was estimated to be up to 1.5 d. The results indicate that the hydrate-bearing sandy sediments at this location have promising permeability conditions for achieving depressurization-induced gas production. In addition, the change of absolute permeability caused by depressurization-induced gas production was analyzed. It was found that absolute permeability was reduced by the high effective stress and fresh water originating from hydrate dissociation most likely due to the sediment compaction and the clay swelling. Although depressurization is a promising method for the gas production at this location, the results indicate that reservoir formation damage should be considered during long-term gas production.

This study was financially supported by the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium) to carry out Japan's Methane Hydrate R&D Program conducted by the Ministry of Economy, Trade and Industry (METI).

Keywords: pressure coring, Nankai Trough, turbidite, flooding test, effective permeability, absolute permeability

Geomechanical Properties of Methane Hydrate-Bearing Sediments from Pressure Coring at the Eastern Nankai Trough

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Geomechanical properties are essential parameter for methane gas extraction from methane hydrate to achieve safe and secure production. In this study, natural methane gas hydrate-bearing sediments were subjected to triaxial tests using transparent acrylic cell to investigate the strength and stiffness of sediments from deep seabed in the Eastern Nankai Trough. The samples were recovered using pressure coring which is a progressive technology to maintain the pore fluid pressure from in-situ to the laboratory. Triaxial compression test of hydrate-bearing sediments at in-situ pressure conditions were successfully done without any hydrate dissociation. The digital photographs were taken during the tests and the local deformation of sediments was quantified in each 0.1% of axial strain level by image processing technique. From the results, hydrate-bearing sediments showed brittle failure with shear banding as evidenced by the stress-strain softening response. In contrast, hydrate-free sediments showed ductile failure mode. The shear strength increases with hydrate saturation. This result is consistent with the results of synthetic hydrate-bearing sediments. Local strain which was calculated from local deformation showed that there is the distribution in stiffness in each centimeter due to distribution of hydrate saturation. This study successfully demonstrates the use of pressure core samples to investigate geomechanical and geotechnical properties of intact hydrate-bearing sediments at in-situ pressures.

This study was financially supported by the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium) to carry out Japan's Methane Hydrate R&D Program conducted by the Ministry of Economy, Trade and Industry (METI).

Keywords: pressure core, triaxial test, strength, stiffness, image processing, shear band

Thermal constants of methane hydrate-bearing sediment and surrounding mud core samples recovered from Nankai Trough well

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This study presents measurements of the thermal constants of natural methane-hydrate-bearing sediments samples recovered from the Tokai-oki test wells (Nankai-Trough, Japan) in 2004. To investigate the influence of sediment composition on the thermal properties, the thermal constants of natural hydrate-bearing sediments were measured at 5 °C and 10MPa over a porosity range of $0.41 \leq \psi \leq 0.47$. In this porosity range, the thermal conductivity of natural hydrate-bearing sediments decreased slightly with increasing porosity. The specific heat of the hydrate-bearing sediments was almost constant and independent of porosity. The thermal diffusivity of hydrate-bearing sediment decreased with increasing porosity.

We also used simple models to calculate the thermal conductivity and thermal diffusivity. The results of the distribution model are relatively consistent with the measurement results. In addition, the measurement results are consistent with the thermal diffusivity, which is estimated by dividing the thermal conductivity obtained from the distribution model by the specific heat obtained from the arithmetic mean.

The thermal conductivity of silt soil in the mud layer sample was estimated by the distribution model, the result of which was much lower than that of the sand soil in hydrate-bearing sediment. This suggests that small grains influence the thermal conductivities.

Acknowledgments. This work was financially supported by MH21 Research Consortium for Methane Hydrate Resources in Japan on the National Methane Hydrate Exploitation Program planned by the Ministry of Economy, Trade and Industry.

Keywords: methane hydrate, thermal conductivity, thermal diffusivity, specific heat, gas hydrate-bearing sediment, hot-disk transient method

Development of pressurized subsampling system for structural imaging of pressured methane hydrate bearing sediments

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Gas clathrate hydrates (gas hydrates, GHs) are ice- like crystalline compounds consisting of gas and water molecules, in which the gas molecules are stored in a framework of water. GHs exist in oceanic and permafrost sediments; because they are a primary means of storing methane (CH₄), natural GHs are of interest as a potential new energy resource. On March 12, 2013, the first off-shore gas production test from the sandy GH layer in the eastern NT area; CH₄ gas productions were produced from the offshore hydrate layer. Here, porosity of GH bearing sediment is a key of gas production efficient from natural gas-hydrate reservoir. Developable natural GHs by conventional gas/oil production apparatus almost exist in unconsolidated sedimental layer. Because sand matrix in GH sediments could have been changed by freezing water in pores in the case of quenched sample, porosity discussed using quenched GH bearing sediment may be over estimated comparing with nature of sediments at in situ condition. Therefore, we developed in situ sub-sampling system for pressured natural GH sediments due to in situ porosity estimation. In this study, we demonstrated sub-sampling from an artificial GH sediment and confirmed sub-sampling results through micro-imaging.

This work was supported by funding from the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium) planned by the Ministry of Economy, Trade and Industry (METI), Japan.

Keywords: Pressurized core, Methane hydrate, X-ray CT

Characterization of grain-size distribution and mineral composition of hydrate-bearing sediments in the Nankai Trough

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Gas hydrate-bearing sediments taken by a hybrid pressure coring system (Hybrid PCS corer) were recovered from the eastern Nankai Trough region at the AT-1 well during the 2012 JOGEMC/JAPEX Pressure coring operation using D/V Chikyu. The recovered sediments are mainly composed of the unconsolidated sand and mud alternation layers, which can be interpreted as turbidite and hemi-pelagic mud, respectively. Gas hydrates accumulated in unconsolidated sands as a pore-filling morphology. The purpose of our study is to prepare the standard samples, which represent the sedimentary features such as grain size and mineral composition in the eastern Nankai Trough sediments. For preparing the standard sample appears to be important for laboratory experimental studies such as physical properties from the engineering point of view.

Using the gas hydrate-bearing sediments, the sedimentary features such as gain size and mineral composition were analyzed systematically. Based on this grain size distribution data, we categorized typical three kinds of standards samples: silty sand, sandy silt, and clayey silt, respectively. As a result of mineral composition analysis of sediment measured by X-ray diffraction (XRD), the bulk mineral compositions are characterized by 10 compositions, i.e., the quartz, hornblende, feldspars (orthoclase, Plagioclase), pyrite, smectite, kaolinite, calcium carbonate, chlorite, and mica. These mineral compositions are strongly correlated with grain size features such as median or means sizes. According to the above results, we prepared typical three kinds of standard samples, and measured pore-size distribution and permeability features using the nuclear magnetic resonance (NMR) method. In the presentation, we will compare with those physical features between standard samples and natural sediments from the eastern Nankai Trough.

This work was financially supported by the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium) of the National Methane Hydrate Exploitation Program planned by the Ministry of Economy Trade and Industry (METI).

Keywords: Nankai Trough, gas hydrate sediments, grain size, mineral composition, sediment core, standard sample

CMR log analysis of the First Offshore Production Test at Daini-Atsumi knoll in the eastern Nankai Trough

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As preparatory drilling operations for the first offshore methane hydrate(MH) production test, monitoring wells (AT1-MC and AT1-MT1) and the upper part of production well (AT1-P) were drilled in FY2011. To confirm methane hydrate bearing circumstances, logging while drilling (LWD) and wireline logging (WL) were performed in AT1-MC. The production test was started on March 12, 2013. After a large amount of sand was produced on March 18, the production test was closed. During well-abandonment operations in August 2013, two LWD wells (AT1-LWD1 and AT1-LWD2) were drilled around the AT1-P, and open-hole WL were performed at the two wells.

The objectives of this study are to understand the characteristics of MH reservoirs and to confirm dissociation behavior of MH in the offshore production test field by analyzing logging data acquired in the wells that of AT1-MC, LWD1 and LWD2, especially CMR(Combinable Magnetic Resonance ; principle is same as Nuclear Magnetic Resonance) logging data. In AT1-MC, we acquired CMR data before the Test. In AT1-LWD1 and LWD2, we acquired CMR data after the Test.

CMR can measure T2 relaxation time, which indicates the amount of proton. But it can not measure rigid proton like in the ice, also included in MHs. This feature is usable to estimate MH dissociation behavior. Because, if the MH dissociate, water volume increase in the sediment. It may cause the change of T2 distribution that T2 relaxation time shifts to the longer time and the peak of T2 distribution increases. In addition, T2 distribution includes pore size information that short T2 relaxation time correspond to smaller pore and long relaxation time correspond to larger pore. Therefore, we might be able to discuss dissociation behavior.

In this study, we compared log plot of AT1-MC, LWD1 and LWD2. We can confirm some T2 distribution shift to the longer relaxation time in MH-bearing sandy layer in the AT1-LWD1, LWD2. Then, to observe the details, we separate the relaxation time to 8 bins. As a result of comparison of T2-mean(T2 logarithmic mean) in the each bin, T2-mean shift particularly observed in short relaxation time interval. The T2-mean of short relaxation time about AT1-LWD1 and LWD2 is longer than AT1-MC. It probably indicates dissociation of MH.

This study is a part of the program of the Research Consortium for Methane Hydrate Resource in Japan (MH21 Research Consortium).

Keywords: Methane Hydrate, NMR

Density structure of the pore-filling-type methane-hydrate reservoir at the Daini-Atsumi Knoll, Central Japan

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The permeability of methane hydrate sediments is controlled by the lithology of the sediments and the saturation of methane hydrate in pore spaces. Thus, estimates of porosity in the reservoir are important. However, sediments in gas hydrate reservoirs are soft; thus, disturbances during drilling easily degrade the quality of data, despite the sediment-reinforcing effects of gas-hydrate crystals. Hence, methods for correcting the measured properties of sediments are quite important. We obtain the density (porosity) structure of sediments within and above the methane hydrate reservoir. Due to uncertainties in the density logs, we corrected the logs using borehole caliper data, which is sometimes negatively correlated with density. The corrected density data agreed well with results inferred from analysis of sediments recovered in pressure cores. On these samples, we conducted mercury injection porosimetry on frozen depressurized samples from 2004 and 2012 and also determined density from the onboard multisensor core logger (MSCL) data on conventional cores, especially in methane hydrate concentrated zone (MHCZ). Our results allow us to divide the sediments above the gas hydrate stability zone (GHSZ) on Daini-Atsumi Knoll into four zones. The zone boundaries correspond to facies boundaries. This implies that the sedimentary facies strongly influenced not only the lithology, but also physical properties such as density (porosity).

Keywords: Gas hydrate, Logging-while-drilling (LWD), Density log, Borehole enlargement, Sedimentary facies

Resources assessment of methane hydrates in offshore surround Japan

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Japan Oil, Gas and Metals National Corporation (hereinafter, JOGMEC), as a member of research group for resources assessment of Research Consortium for Methane Hydrate Resources in Japan (MH21), is conducting resources assessment of methane hydrates (hereinafter, MHs) in offshore surround Japan.

The seismic interpretation of migrated profiles of two/three dimensions-seismic surveys acquired by geophysical vessel Shigen that JOGMEC owns, are carried out. MHs are being extracted to search the Bottom Simulating Reflector (herein after, BSR) and assumed sand intervals, which is characterized high-amplitude reflected waves. In addition, based on the knowledge of the MHs are correlated to high-velocity, the comparison between extracted MHs and the high velocity anomalies in the velocity-analysis-profiles run in two-dimensions-seismic-survey lines, or the three-dimensions-seismic-survey area carrying out high-density-velocity analysis. This introduced example is an example of seismic interpretation in the data of three dimensions-seismic-survey area, which have not drilled.

The characteristic in this area shows fold structure, which undulates severalfold. In addition, the gaps of the reflected waves can interpret faults, which does not show the large displacement, are seen. Clear velocity contrast to assume BSR and the high-velocity anomaly above BSR are confirmed in the high-density-velocity-analysis profiles.

Multiple reflector of assumed sand facies is estimated by the results of seismic interpretation in the migrated profiles of three dimensions seismic survey, and each flow shows different sedimentation environment and geological age. In addition, heterogeneity of lithology (different grain size and sand/ mud ratio) is suggested by the variety of amplitude and velocity distribution in the high-density-velocity-analysis profile. In the high-density-velocity-analysis profile, characteristic high velocity anomalies in the sand facies above BSR are visible, but these are estimated MHs because those anomalies are shown in the sand facies above BSR.

As above, even the area has not been drilled, the existence of MHs can be estimated from seismic interpretation of the migrated profile of the seismic survey, and the velocity distribution of the high-density-velocity-analysis profile. And it is expected that these results become useful information for the plan of the future drilling programme. This introduction is the example of the three dimensions seismic survey area; hence, it is a useful information for a programme of three-dimensions-seismic-survey plan by performing similar interpretation in two-dimensions-seismic-survey lines.

Keywords: Methane hydrate, 3-D seismic reflection survey, High density velocity analysis

In-situ stress analysis using the anelastic strain recovery (ASR) method at the first off-shore gas production test site

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To evaluate in-situ stresses by applying the anelastic strain recovery (ASR) method to drilling cores, four cores retrieved from different depths between 265?313 meters below seafloor in a well at the first offshore gas production test site in the eastern Nankai Trough, Japan were utilized to measure anelastic strains onboard the drilling ship. The onsite ASR measurements suggest this depth range in the study area is a normal faulting stress regime dominated by gravitation. In subsequent laboratory experiments, the cores were returned to their in-situ stress states via the K0 consolidation procedure, then elastic and anelastic strains were measured during and after the unloading process to verify the onboard measurements and quantify in-situ stresses. These laboratory calibration experiments verified that the ASR measurements following the stress release could provide reasonable estimates for the artificially applied preload stress.

Keywords: In-situ stress, Anelastic strain recovery method, Unconsolidated formation, K0 consolidation

Grain size analysis of sands by an optical microscopy/digital image method

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Grain size is a fundamental property of earth materials. However, no two of the many techniques yield a consistent measurement of this property; thus, elucidating the relationships among different methods is valuable for understanding what constitutes grain size. This study compares the grain size distributions analyzed by optical microscopy/digital image (Morphologi G3 instrument (Malvern Ltd; the UK)) and those analyzed by laser diffraction. In most of the investigated samples, the size distributions obtained by both methods were very similar. However, a shift toward a coarser grain-size distribution was observed in the optical microscopy analysis of finer sand samples, and the frequency distribution was broadened. The fractions of sand and silt size fractions were also consistent between the two methods, but optical microscopy indicated a smaller clay size fraction than the laser diffraction method. The median particle size (30 – 200 μm) was similar in both methods. The standard deviation was lower in the optical microscopy method than that in the laser diffraction method. We conclude that optical microscopy is a useful technique for determining the grain size distribution. Additionally, we investigated the particle shape and particle size in the experimental fault formed by ring-shearing test. This study is financially supported by METI and Research Consortium for Methane Hydrate Resources in Japan (the MH21 Research Consortium).

Keywords: grain size analysis, digital image method, laser diffraction method, sand, ring-shear test

Gravels Associated with a Massive Gas Hydrate Obtained from HR14 RC1403-7

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Some subseafloor core samples were obtained in the scientific cruise HR14 performed by the JOGMEC-Hakurei in the eastern margin of Japan Sea. Sediments in most of the sites are mainly composed of muddy fine clastics, and can be often found accompanied by a small amount of very fine to medium grained sandy layers, which are usually observed as thin laminations in muddy layers. The gravel layer was observed thicker than 20 cm associated with the massive methane hydrate layer longer than 130 cm in the RC1403 (Sec. 7). Over than 1,100 gravels were obtained, of which major size, minor size, aspect ratio, roundness, sphericity, lithology and color were investigated. These are generally pebble (average 8.29mm). They are composed only of very well-rounded, greyish white to dark grey calcareous mudstone. According to the probability plot of their grain-size distribution, it consists of one segment showing the normal distribution, which may indicate gravel transportations by a high energy flow.

This research is a part of the METI project entitled "FY2014 promoting research and development on methane hydrate."

Keywords: gas hydrate, Japan Sea, gravel

Pore Characteristics and Early Diagenesis of Muddy Sediments below the Sea Floor in the Eastern Margin of Japan Sea

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

They usually contain much opal-A, quartz, feldspar, illite and smectite that do not change definitely with depth. By optical and microscopic observations, diatom tests, foraminifers and framboidal pyrites are commonly observed, and, in particular, the shapes of diatom are usually various, dominantly fragmental and infrequently preserved. It is remarked that physical diagenesis proceeds first due to mechanical compaction, whereas chemical diagenesis advances very slowly in early diagenesis.

This study was performed as a part of the MH21 Research Consortium on methane hydrate in Japan and the METI project entitled "FY2014 promoting research and development on methane hydrate."

Keywords: Japan Sea, gas hydrate, muddy sediment, diagenesis, burial diagenesis

Oxygen and carbon isotope records of foraminifera and depositional age from HR14-RC1408 core, Mogami Trough

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The eustatic sea level changes in the Late Quaternary have strongly affected the hydrography and environment of Japan Sea because of its geographical condition. Stable isotopes of foraminifera have played important roles in previous paleoceanographic studies of the Japan Sea. (Oba *et al.*, 1991; Ishihama *et al.*, 2014). For example 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.

We analyzed oxygen and carbon isotope of both planktonic and benthic foraminifera with 1 core from Mogami Trough (HR14-RC1408: water depth approximately 830 m, core length 48m). Planktonic and benthic foraminifera from the >150 micrometer fraction were hand-picked, reacted with phosphoric acid at 90 degrees C and analyzed by a GV IsoPrime mass spectrometer at the Center for Advanced Marine Core Research (CMCR), Kochi University. HR14-RC1408 core can be correlated Marine Isotope Stage (MIS) 1 to 9 from $d^{18}O$ of planktonic foraminifera. Negative excursions in $d^{18}O$ of planktonic foraminifera and the existence of *Globigerinoides ruber*, *Neogloboquadrina incompta* (dextral) and *Globigerina bulloides* (thin-walled form) in MIS 1, 5e, and 9 suggest the influx of Tsushima Warm Current. The large negative excursions in $d^{18}O$ of planktonic foraminifera implying freshwater input are recognized during the glacial maximum periods in MIS 2 and 6.

This research is a part of METI's project entitled "FY2014 Promoting research and development on methane hydrate". Isotopic analyses were performed under the cooperative research program of Center for Advanced Marine Core Research (CMCR), Kochi University (Accept No. 14A010, 14B008).

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

Late Quaternary occurrences of methane-related species, *Rutherfordoides cornuta*, in the eastern margin of the Japan Sea

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Introduction

Each Benthic foraminiferal species can be adapted to the various environmental changes of the bottom water and the marine sediments. In the Japan Sea, there are characteristic evidences, that the agglutinated assemblages, differenced from the open ocean, exist in the Japan Sea Proper Water and the drastic changes between suboxic and oxic fossil assemblages correspond to the Quaternary paleoenvironment. On the other hands, unique foraminiferal species might live on some methane seep area around Japan Island because the unique colony of the bacteria and macro-benthos form around methane seep. *Rutherfordoides cornuta*, related to high methane gas content of the sediments in the Sagami Bay (Akimoto et al., 1996), lives on plural area from the northwest Pacific but not from the Japan Sea (Matoba and Nakagawa, 2009). Nakagawa et al. (2009) found the distributions of *Rutherfordoides rotundata* (closely related *R. cornuta*) from the last glacial maximum (LGM; 27-17ka) at the Umitaka Spur, the eastern margin of the Japan Sea. These distributions, corresponded to the negative peak signal of benthic foraminiferal carbon isotope (Takeuchi et al., 2007), indicate to dissociations of methane hydrate and active methane seeps by the lowest sea level.

Purpose

We study benthic foraminiferal assemblages and discover the occurrence of *R. cornuta* (not *R. rotundata*) from the late Quaternary sediment around methane seep area in the eastern margin the Japan Sea (off Joetsu, Oki Trough and Mogami Trough). In this presentation, we will introduce a relationship with the particular geological analysis and the hydrate dissociation at each study area.

Sample and age control

Study samples are collected from three sediment cores recovered on the Umitaka Spur (MD179-3304), a west part of the Oki Trough, and a north part of the Mogami Trough. Each sedimentation age is calculated by the ages of ¹⁴C, tephra, stable isotope events, and bottoms of TL layer.

Results

Obvious occurrences of *R. cornuta* are found from three all core sediments, and these sedimentation ages range to 25-28ka, early LGM. At the thick dark layer (TL-2 layer) above these occurrences, rare benthic foraminiferal number indicates an anoxic bottom condition where most benthic foraminifera couldn't live (Oba et al., 1991), nonetheless, *R. cornuta* and *R. rotundata* lived continuously until LGM. And, these occurrences might show the methane seep environments from 28 ka to LGM (Nakagawa et al., 2009). Therefore, active methane seep events might occur by hydrate dissociations at the Umitaka Spur, west Oki Trough and north Mogami Trough at the same time during the LGM.

In addition, we will discuss the relationship with benthic foraminiferal results and methane seep events during the MIS6 and MIS8, lowstand periods. samples.

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Keywords: fall of sea level, benthic foraminifera, methane hydrate, last glacial maximum, methane seep, *Rutherfordoides*

Paleoenvironmental change elucidated from the total organic carbon concentration and stable isotope from Mogami trough

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The temporal changes in total organic carbon (TOC) concentration for cored sediment off Joetsu city, Japan Sea is very similar to the millennial scale climate change at the northern hemisphere (Urabe et al., 2014). Then, we analyzed the TOC, total nitrogen (TN) concentration and these stable isotope ratio $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values with high temporal resolution for new core RC1408 from Mogami trough, Japan Sea. TOC concentration and $\delta^{13}\text{C}$ value for RC1408 is high during Holocene, and low in Last glacial maxima (LGM).

The high TOC concentration during middle to late Holocene suggests high biological productivity in the sea surface. The contribution of marine organic matter to TOC was increasing with sea level rising, suggesting the decreasing trend of C/N ratio and increasing trend of $\delta^{13}\text{C}$ value during 6.0~9.8 ka, and then becoming current oceanological condition at 6.0 ca. In the last deglaciation, the rapid increasing TOC concentration and $\delta^{13}\text{C}$ value suggest increasing marine biological productivity. In the last glacial maxima, the marine biological productivity was very low and the contribution of terrestrial organic matter increased but the inflow was very little, according to the lowest TOC concentration and $\delta^{13}\text{C}$ value. This study is a part of a development methane hydrate project, Ministry of Economy, Trade and Industry.

Keywords: Paleoenvironmental change, Quaternary, Japan sea, organic carbon, stable isotope

Sediment transportation changes based on spatiotemporal variations of Ni and Cr in the Hida range and off-Joetsu area.

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Submarine sediments in the eastern margin of Japan Sea are presumed to contain materials originated from Japan islands substantially. It is important to clarify transportation and sedimentation processes of the land source materials for understanding formation of methane hydrate component layers. Because Ni and Cr in the submarine sediments in the eastern margin of Japan Sea are considered to be supplied by the Hime river basin (Imai et al., 2010), we can reconstruct the history of sediment transportation from the Hime river basin by the temporal change of Ni and Cr in the sediments. River fed sediments are supposed to deposit on not only submarine canyons but also submarine ridges. This study revealed the temporal changes of Ni and Cr since the last interglacial in three boring cores on submarine ridges. We analyzed MD179-3296 (approximately 45 km distant from Hime river mouth) and 3312 (61 km) cores (approximately depth is 1,000m) close to continental shelf in off-Joetsu area. RC1408 (284km) core drilled in off-Akita-Yamagata area was also examined for a comparison with the MD179 cores. And this study investigated spatial changes of sediment transportation between Hida range and Japan Sea by revealing spatial distribution of Ni and Cr in riverbed sediments of the main river among Hokuriku area and beach sediment of Joetsu area.

The samples were dried and powdered, and then pressed as tablets. Ni and Cr contents were measured by Wavelength Dispersive X-ray Spectrometry (Rigaku Primus II). Age models of 3296 and 3312 cores have been well-established by tephrochronology, radiometric dating, and oxygen isotope ratio of foraminifer (Nakamura et al., 2013; Takizawa et al., 2014, etc). Grain size of river bed sediments of Hime and Oumi river we analyzed by Laser diffraction particle size analyzer (Shimadzu SALD 3000S).

According to spatial distribution of Ni and Cr in geochemical map (Imai et al., 2010), clastic materials from Hime river appear to suspend and be transported by ocean current with gradually sinking within 20~30km from Hime river mouth, and farther than 20~30km, clastic materials appear to flow down by sediment gravity flow. Grain size analysis of river bed sediments of Hime and Oumi river indicates that Ni and Cr are included mainly in coarse grain, and suggests that Ni and Cr are mineral state. Ni and Cr show high concentration near the ultramafic rock, and it is suggested that origin of Ni and Cr is especially restricted in specific parts of Hime and Oumi rivers. Hime and Oumi rivers are steep and have extremely narrow continental shelf around their river mouths, and their source is the northern part of Hida range.

Concentration of Ni and Cr in 3296 and 3312 cores are very similar to each other, and tend to be high (low) during interglacial (glacial) age. However, peaks of Ni and Cr concentration in 3296 core are higher than the other cores. Ni and Cr content rate of RC1408 core is half or one third of 3296 core. Temporal changes of Ni and Cr shows close relation with temperature or rainfall of the Japan Alps estimated from total organic carbon proxy of sediments at the bottom of some lakes (Kumon et al., 2009). Considering topographical steep condition of Hime river, main factor to change concentration of Ni and Cr appear to be changing supply of the serpentine because of changing rainfall influenced by summer monsoon.

This research was a part of METI's project entitled "FY2014 Promoting research and development on methane hydrate".

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Keywords: MD179 marine core, glacial-interglacial cycle, element analysis, Hime river, sediment transportation, summer monsoon

Dissolved gas in pore water at the hydrate-bound field off Sakhalin Island

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We summarize characteristics of dissolved gas in pore water in sub-bottom sediments off Sakhalin Island, where gas hydrates were retrieved. Gas hydrates have been discovered at the northeastern, southeastern and southwestern Sakhalin Island in the cruises of LV31 (2003), LV32 (2003), LV36 (2005), and LV39 (2006) in the framework of hydro-Carbon Hydrate Accumulations in Okhotsk Sea (CHAOS) project, and those of LV47 (2009), LV50 (2010), LV56 (2011), LV59 (2012), LV62 (2013), and LV67 (2014) in the framework of Sakhalin Slope Gas Hydrate (SSGH) project. We retrieved sediment cores (184 cores in total) including gas hydrates (29 cores) in these cruises (R/V Akademik M. A. Lavrentyev).

The dissolved gases in the pore water were extracted according to a headspace gas method. Basically, 10 mL of sediment and 10 mL of saturated aqueous solution of NaCl with a small amount of benzalkonium chloride (preservative) were introduced into a 25 mL vial to create a 5 mL headspace. The headspaces were flushed with nitrogen or helium as an inert gas. The vials were then shaken thoroughly and stored overturned. Molecular and stable isotope compositions of these samples were measured in our laboratory (Kitami Institute of Technology).

The depths of sulfate-methane interface (SMI) distributed mainly 1-3 mbsf, and those of hydrate-bound core were shallower (30 cm to 1 m). The dissolved gases in pore water below the SMI depth were primarily methane (more than approximately 99% of the total hydrate-bound gas), although ethane, propane, CO₂, and hydrogen sulfide were also detected. The molecular and isotopic compositions of dissolved gas in the pore water indicated that the sediment cores including gas hydrates contain ¹³C-rich methane and relatively high concentrations of ¹³C-rich ethane compared to other gas-rich sediment cores. The gas-rich sediment cores without gas hydrates are characterized by high C₁/(C₂+C₃) ratios and ¹³C-depleted methane and ethane. We suggested the idea that small amount of thermogenic gas controlled occurrence of gas hydrate in the subsurface sediment off Sakhalin Island.

Keywords: gas hydrate, pore water, stable isotope, Sea of Okhotsk, Sakhalin Island

Formation of sII gas hydrate during dissociation of sI mixed-gas hydrate composed of methane and ethane

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Double structure gas hydrate, composed of the cubic structure I and II, has been discovered in a same sediment core retrieved from the Kukuy K-2 mud volcano at Lake Baikal (e.g., Kida *et al.*, 2006). The structure II gas hydrate contained 13-15% of ethane, on the contrary, the structure I has only several % of ethane. It has been reported that a structure II gas hydrate appears in appropriate gas composition of methane and ethane (Subramanian *et al.*, 2000a; 2000b). Some models tried to explain how the double structure formed (Hachikubo *et al.*, 2009; Manakov *et al.*, 2013), however, which structure first formed has been still unknown.

Synthetic mixed-gas (methane and ethane) gas hydrates were formed and their dissociation process was investigated by using a calorimeter (Hachikubo *et al.*, 2008). In most cases, two peaks of heat flow appeared and the dissociation process was divided into two parts. This can be understood in the following explanation that (1) the sample contained both crystal structures (I and II), and/or (2) ethane-rich gas hydrate formed simultaneously from dissociated gas and showed the second peak of heat flow. However, Raman spectra of these samples showed that the crystallographic structure of the samples was originally unique in most cases. In this study we tried to check the latter process, namely a secondary formation of ethane-rich gas hydrate.

We made a methane and ethane mixed-gas hydrate (3.62% C₂) in a pressure chamber (volume: 20mL), and stored in liquid nitrogen. A part of the sample was put into a calorimeter (Setaram BT2.15) and dissociated under the temperature gradient of 0.15 K min⁻¹. We observed double peaks in the thermograph, indicating that a new gas hydrate formed from the dissociation gas of the original hydrate, concentrated ethane, and then dissociated. In the next experiment, we put the rest of the sample into the calorimeter, heated in the same condition, and recovered the sample at the end of the first peak of dissociation. The Raman spectra of the sample revealed that a structure II ethane-concentrated gas hydrate formed secondarily in the sample. The composition of ethane was 23.4%, corresponded to the field of structure II (Subramanian *et al.*, 2000a; 2000b). Stable isotopes ($\delta^{13}\text{C}$ and δD) of methane and ethane were also measured, and confirmed the existence of several ‰ difference in ethane δD between the first and second peaks, corresponded to the field data of the double structure observed at the Kukuy K-2 mud volcano (Hachikubo *et al.*, 2009).

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Keywords: gas hydrate, methane, ethane, Lake Baikal