

Shallow gas hydrate exploration in Japan Sea: Past, Present and Future

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Japan Sea gas hydrate exploration has entered into a new phase since a number of shallow gas hydrate exposure and related phenomena were identified in wide area of in Japan Sea and offshore Abashiri of the Sea of Okhotsk in 2011 and 2012. Academic efforts to explore shallow gas hydrates have focused to delineate the occurrence and distribution in Joetsu Basin where the shallow gas hydrate has been first recovered in 2013. Intensive expeditions on and around the Joetsu knoll and Umitaka spur have demonstrated that shallow gas hydrates are closely associated with gas chimneys, shallow topographic high (hydrate mound), and occasional methane plumes. Gases of gas hydrates are predominated by thermogenic with very small amount of microbial methane. Recent gas hydrate expeditions has revealed that gas hydrates in the Sea of Okhotsk and in the eastern margin of Japan Sea off Akita and Yamagata occur within gas chimneys, though they are composed of the mixture of dominant microbial and minor thermogenic gases, and gas hydrate exposures are not always associated with methane plumes. Thus the gas chimneys and hydrate mounds have become the critical and reliable indicators of the presence of shallow gas hydrates. The criteria has found a number of gas hydrate exposures in western and southwestern part of the Joetsu basin, and is believed and expected to find new gas hydrate mounds not only within Joetsu basin but also off Akita-Yamaga area and off San-in areas.

Keywords: Shallow gas hydrates, Eastern margin of Japan Sea, Gas chimney, Hydrate mound

Environment changes of the Japan Sea viewed from the water and TOC contents of the cored sediments off Joetsu City

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We have measured water and total organic carbon contents of three sediment cores (MD179-2996, -3304, -3312) taken from the Joetsu area, the Japan Sea in a few-cm intervals. The water contents decrease in logarithmic ratio with increasing depth, but another cyclic change of short periodicity overlies on the general trend. This change of short term seems to imply increasing or decreasing of biological production of the Japan Sea.

The temporal changes of the total organic carbon (TOC) content from MD179-3304 and -3312 are very similar each other, and also resemble to the delta18O curve of NGRIP ice core in detail. As the TOC of homogeneous clayey sediments reflects biological productivity of the sea, some mechanisms controlled both the glaciation in Northern Atlantic region and biological productivity of the Japan Sea in the same timing. This is a problem to be solved in a near-feature.

It is found that the horizon of high TOC contents certainly corresponds with dark layer. This means that abundant organic matters in the surface water in a high productivity period sink down in a deeper water and causes anoxic condition in the bottom layer of the Japan Sea. High potential of organic matter in anoxic condition may be favorable for methane formation in the sediments of the Japan Sea.

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Keywords: total organic carbon, Japan Sea, water content, gas hydrate, environment change, climate change

Sedimentary environments and pore properties of subseafloor sediments in the eastern margin of Japan Sea

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Sedimentary environments and pore properties of subseafloor sediments in the eastern margin of Japan Sea

Keywords: hydrate, Japan Sea, pore

Source of pore water and distribution of shallow gas hydrates inferred from dissolved Li isotopes

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Pore waters collected from the Umitaka Spur area in the Japan Sea, off Joetsu (MD179 cruise, MH21 Research Consortium), where active gas seepage accompanying massive gas hydrate formation near the seafloor have been observed particularly on the summit. Rapid decreases of sulfate concentration with alkalinity increases result from anaerobic methane oxidation in the shallow sediments both on the spur and basin sites, indicating methane flux is high over the research area. Contrary, pore water freshening and Li input due to clay mineral dehydration are dominant on the spur. Li isotopic analyses result that the dissolved Li in pore waters were released from clay minerals at >1100 mbsf over the area. Shallow biogeochemical processes significantly change pore water geochemistry, however, the focused delivery of deep-sourced materials like Li and thermogenic methane is a key to deposit massive gas hydrates near the seafloor.

Keywords: lithium isotope, pore water, gas hydrate

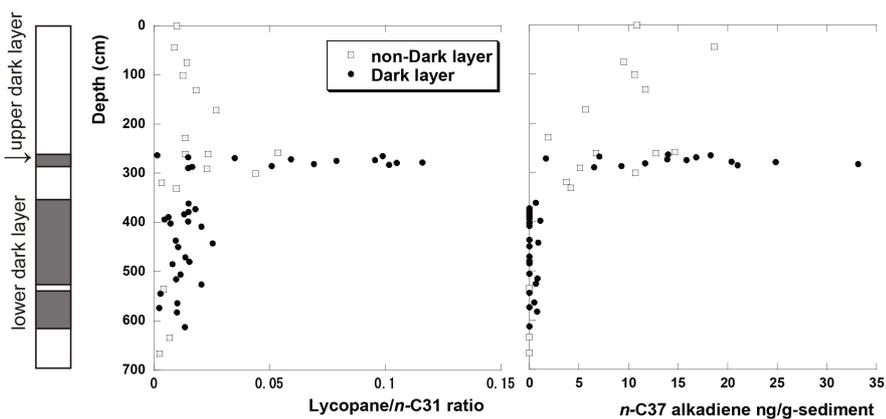
Unusual distribution of lycopane in the surface sediment from Japan Sea collected by the MD179 Cruise

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The piston core samples of MD179-3312 from Japan Sea were geochemically analyzed. These samples were collected approximately 700 cm from the surface, and contain darkly colored layers. The lower dark layer, which was deposited in a strong anoxic bottom water environment, did not show a high lycopane/n-C31 ratio. In contrast, the upper dark layer, which was deposited in a weak anoxic bottom environment, had a high lycopane/n-C31 ratio. Although the lycopane/n-C31 ratio was not useful proxy to assess palaeoanoxicity, it did indicate surface productivity of some phytoplankton in the sediment in Japan Sea. The depth profile of n-C37 alkadiene was similar to the depth profile of the lycopane/n-C31 ratio. This study was supported by MH21, Research Consortium for Methane Hydrate Resources in Japan.

Keywords: anoxic bottom water, dark layer, lycopane, Japan Sea



Estimate of interval velocity of sediment between the seafloor and BSR in Joetsu Basin, eastern margin of the Japan Sea

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Joetsu Basin is one of the areas where gas hydrate studies have been conducted intensively in the world. Previous studies conducted in Joetsu Basin (Matsumoto et al., 2009; Saeki et al., 2009) indicated that seismic velocity of sediment above bottom-simulating reflectors (BSRs) is lower than sound velocity of seawater (ca. 1500 m/s). These studies suggested that such low velocity of sediment could be explained by an existence of gas in the sediment. To investigate an existence of gas in sediment above BSRs in Joetsu Basin, we estimated interval velocity of sediment above BSRs from heat flow and BSR depth data in this basin.

We measured heat flows at seven stations in Joetsu Basin in June 2010 during the MD179 Japan Sea Gas Hydrates cruise. The measured heat flows ranged from 84 to 90 mW/m². Because of discrete heat flow data, we calculated a 2D-steady state thermal structure model along a 2D seismic profile from the heat flow data and the borehole physical properties data in the basin, and then calculated heat flow distribution at the seafloor of the model. The heat flow calculated from the thermal structure model well explains the heat flows measured at the seafloor. We also calculated heat flows from BSR depths (hereafter called "BSR-derived heat flows"). The estimated BSR-derived heat flows are significantly lower than heat flows at the seafloor predicted from the thermal structure model. We estimated interval velocity of sediment above BSRs by matching BSR-derived heat flows to heat flows at the seafloor predicted from the thermal structure. The estimated interval velocity ranged from 1100 to 1600 m/s. Sediment interval velocity that is lower than sound velocity of seawater could be explained by an existence of gas in the sediment, supporting the results of Matsumoto et al. (2009) and Saeki et al. (2009). The survival of gas above BSR is explained by water depletion as a consequence of formation of gas hydrate and strong capillary forces of the muddy sediment under an environment of high-methane flux, as speculated by Clennell et al. (1999).

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

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Keywords: thermal structure, heat flow, BSR, interval velocity, Joetsu Basin

The phase transformation of methane caused by pressure change during its rising from seepage

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Recent studies found that, in the Sea of Japan, methane hydrate exists in crystal form on the surface of the seabed or in the shallow layer of about 100m from the seabed. To study the methane hydrate that exists at depth in the sediment, the Bottom Simulating Reflector (BSR) can be used as an indicator. On the other hand, methane hydrate near the sediment surface (surface-type) is scattered in crystal form, and thus the BSR cannot be used as an indicator.

The surface-type methane hydrate often exists with methane plumes. The methane plumes are the visualized image of the acoustic differences of the physical properties among solid phase, gas phase, and liquid phase that emerge when the methane hydrate or bubbles gush from the seabed. By sending ultrasonic waves from the transducer of a fish detector or sonar in the water and measuring the echo of the scattered ultrasonic waves that come back after they hit the methane hydrate or bubbles, we can see the visualized image of the methane plumes on the screen of the fish detector or sonar.

When piston coring is conducted at the root of the methane plumes, the collection of surface-type methane samples can be carried out efficiently. Furthermore, it is possible to guide an unmanned submersible to the gushing point or sampling site of the methane hydrate based on the location of the methane plumes. Thus, the methane plume is a good indicator for exploring the surface-type methane hydrate.

Quantification of the methane plumes is extremely important for the global environment as part of the carbon cycle. The authors have already conducted the rising experiments of methane hydrate in the nearby ocean area using a fish detector and computed the rising speed. The authors also measured and analyzed the bubble echo of the rising methane hydrate and estimated the quantity of the rising methane hydrate per bubble unit in the area. At that time, the gas phase of the methane hydrate bubble was computed for gas and solid substance, separately. The results of the above study were provisional. Thus, we enhanced the precision for this study.

For this study, in order to quantify the methane plumes, we observed the image of methane plumes using a submersible vessel (hyper dolphin, property of Japan Agency of Marine-Earth Science and Technology (JAMSTEC)) as well as collected the methane bubble using a funnel.

The observation was carried out at Umitaka Kaikyaku in the Sea of Japan. In this area, the authors had been observing the methane plumes every year since 2004, and every year, the authors could observe the methane plumes in the same ocean area in a similar way. Thus, it was chosen as the observation site.

The experiment in the ocean revealed the followings. The methane hydrate particles that are gushing out from seabed are solid substances just above the seabed. In the studied ocean area, the volume of methane hydrate bubbles is gushing out every second per unit area.

Keywords: methane plume, methane hydrate, volume of seepage, phase

Discovery of *Calyptogena ochotica* (Scarlato, 1981) from Abashiri Bay, Eastern Hokkaido (Bivalvia: Vesicomidae)

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Calyptogena ochotica (Scarlato, 1981), which had been described from the Sea of Okhotsk, 192-1643 m depth was discovered from Abashiri Bay, 744-2217 m depth. Although all specimens collected by Tansei-Marui and Umitaka-Marui are dead valves, occurrence of this species suggests the presence of chemoautosynthetic environment nearby.

Keywords: *Calyptogena*, Cold seep, Chemosynthetic community, Sea of Okhotsk

Distribution of the structure II gas hydrate in Lake Baikal

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Gas hydrates are crystalline clathrate compounds composed of water and gas molecules that are stable at low temperatures and high partial pressures of each gas component. Natural gas hydrates exist in sublacustrine sediments of Lake Baikal, Russia. In the framework of MHP (Multi-phase Gas Hydrate Project, 2009-2012), more than 15 new places where gas hydrates exist in the sub-bottom sediments were discovered. Gas hydrate crystals were retrieved onboard and stored in liquid nitrogen. We also measured molecular and isotopic compositions of hydrate-bound gas and dissolved gas in pore water. Kida et al. (2006) first reported coexistence of the structure I and II gas hydrates at the Kukuy K-2 mud volcano (MV) in the central Baikal basin. Granular sII hydrates appeared above the massive sI hydrates, and sometimes connected with each other by vein-like sI hydrates. sII hydrate layers contained about 14% of ethane; on the contrary, sI hydrate layers contained several % of ethane. In the MHP cruises, existence of sII hydrate was suggested by the high ethane concentration at the Kukuy K-10 MV in 2010. Granular sII hydrates were also discovered at the Kukuy K-4 MV in 2011 and the Kukuy K-3 MV in 2012. They exist not only in the Kukuy Canyon area (central Baikal basin), but also in the PosolBank area (southern Baikal basin). Concentration of ethane in sII hydrates ranged 13-15% in the total hydrocarbon gases, whereas that of propane was relatively small (several hundred ppms). Neopentane (2,2-dimethylpropane) was concentrated in the guest gas of sII hydrates. The concentration of neopentane was about 1% of the total hydrocarbon gases at the Kukuy-Pockmark, located between K-2 and K-3 MVs. These heavier hydrocarbons are the signal of thermogenic origin; however, some questions regarding selective enclathration (scarce propane, and enrichment of ethane and neopentane) remain unresolved. Concentration of hydrate-bound ethane widely ranged from several hundred ppms to 15%, and mixed-gas of microbial and thermogenic gases is dominant in Lake Baikal.

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Keywords: gas hydrate, crystallographic structure, Lake Baikal, ethane, methane

Analysis of lipid biomarkers of methane hydrate bearing sediments from the eastern Nankai Trough by two dimensional GC

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In order to investigate the microbial activities related to methane generation, we performed analyses of lipid biomarkers in the sediments from three wells (Alpha-1, Beta-1 and AT-1) in the eastern Nankai Trough by using the comprehensive two-dimensional gas chromatography (GC x GC). Previous geochemical studies have shown that the biogenic methane forms methane hydrate (MH) in the eastern Nankai Trough. Methanogens (methanogenic archaea) produce methane, which forms a vast quantity of methane hydrate in continental margin accretionary sediments. However, it is unclear at which depths methane was produced in the sediments. To address this issue, we attempted to identify and quantify the biomarkers of methanogens in the sediment cores by GC x GC equipped with qMS and FID.

The core samples at Alpha-1 and Beta-1 were collected from the eastern Nankai Trough by JOIDES Resolution during the multi-well drilling campaign "Tokai-oki to Kumano-nada" in 2004. Those at AT-1 was collected from Dai-ni Atsumi Knoll in the eastern Nankai Trough during site survey by the scientific drilling vessel CHIKYU in 2011. The lipids were extracted with methanol/dichloromethane, and the extract was saponified with 0.5 M KOH/methanol. The neutral fraction was converted to trimethylsilyl esters (TMS) by heating with BSTFA. The TMS-derivatives were analyzed using a ZOEX KT2006 comprehensive GC x GC equipped with qMS and FID. The content of total organic carbon and its isotopic ratio were determined by the flow-injection method using a Thermo DELTA V mass spectrometer connected with a Flash EA.

The neutral lipids fractions of the all core samples mainly consisted of n-alkanes, acyclic isoprenoids, n-alcohols, sterols and hopanols. Hopanols such as 17,21-homohopanol, 17,21-bishomohopanol, trishomohopane-32,33-diol and anhydrobacteriohopanetetrol were detected in all sediment samples, which might reflect the activity of in situ bacteria. The concentrations of hopanols in clay layers were significantly higher than those in sand layers. The TOC values were also higher in the clay layers. 2,6,10,15,19-Pentamethylcosane (PMI), which is considered to be the biomarker for methanogens and methanotrophic archaea, was detected in all samples from the three sites. Most of the delta ¹³C values of PMI were higher than -50 permil, suggesting that methanogens are the likely source organisms. In the sediments from Alpha-1 and Beta-1, PMI concentrations were relatively high at the MH bearing zone and below the MH bearing zone, suggesting higher abundance of methanogen biomass. In the sediments from AT-1, the concentrations were relatively high at 42mbsf and 216 mbsf. Interestingly, the methane production rates through the carbonate reduction pathway measured by ¹⁴C-tracer experiments were also high at these depths, exceeding 10 pmol/cm³/d. Furthermore, hydrogenotrophic methanogens were also abundant at the same depths, as revealed by molecular analysis using deep rRNA gene sequencing. We therefore consider that PMI detected by GC x GC in this study is reliable as the indicator of methanogen biomass.

This study was carried out as a part of the research undertaken by the Research Consortium for Methane Hydrate Resources in Japan (MH21).

Distribution of hydrocarbons in sediment in Nankai accretionary prism off Kumano: IODP Expedition 338 preliminary result

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During IODP Expedition 338, D/V *Chikyu* drilled deep-sea sediment in Nankai accretionary prism off Kumano from October 1 2012 to 12 January 2013. In the first half, mud gas monitoring and sampling of cuttings were conducted between 875.5 and 2,005.5 m below the seafloor (mbsf) at Site C0002 in southern Kumano Basin. In latter half, coring was carried out at Site C0002 (200-505, 902-940 and 1,100.5-1,120 mbsf) in Kumano Basin, and Sites C0021 (0-294 mbsf) and C0022 (0-420 mbsf) on a slope of the accretionary prism. We, geochemical group, collected headspace gas and void gas samples and interstitial water samples.

In this expedition, gas hydrates could not be recovered, but low-temperature anomalies were observed by IR-camera and low- Cl^- anomalies were detected in analytical results of interstitial water between 200 and 400 mbsf in Site C0002. In this interval, high resistivity anomalies had been observed in LWD data during IODP Expedition 314 in 2007, which was interpreted as the presence of gas hydrates (Expedition 314 Scientists, 2009). These facts suggest gas hydrates distribute between 200 and 400 mbsf in Site C0002. Based on hydrocarbon ratios ($\text{C}_1/(\text{C}_2+\text{C}_3)$) and carbon isotope ratios of methane ($\text{d}^{13}\text{C}(\text{CH}_4)$), the origin of methane in formation gas of gas hydrates would be of microbial.

Data of $\text{C}_1/(\text{C}_2+\text{C}_3)$ and $\text{d}^{13}\text{C}(\text{CH}_4)$ in this expedition continuously filled the gap of these data in IODP Expedition 315. Mud gas monitoring data were consistent with headspace gas data in cross over intervals between coring and mud gas monitoring, suggesting mud gas monitoring data could be reliable in deeper part of the cross over intervals. Based on the mud gas monitoring data, around half of methane would be derived from thermal decomposition of organic matter around 2,000 mbsf. Taking account of thermal gradient of 43 degree C per 1 km acquired during IODP Expedition 315, temperature around 2,000 mbsf is estimated to be more than 80 degree C, and it is reasonable that thermal decomposition of organic matter occurs around 2,000 mbsf.

At Site C0022, where bottom simulating reflections (BSRs) had not been observed, sediment in cores showed no evidence of gas hydrates in this expedition. However, a lot of gas pockets were observed in sediment in cores, and extraordinary degassing broke core liners, suggesting sediment contained a large amount of gas, though such gases was not enough to form gas hydrates *in-situ* conditions of pressure and temperature. Based on $\text{C}_1/(\text{C}_2+\text{C}_3)$ and $\text{d}^{13}\text{C}(\text{CH}_4)$, the origin of the methane in headspace gases would be of microbial. A peak of methane in a fracture zone around 100 mbsf was observed, but isotopic composition of the methane showed no anomaly. It suggests the peak of methane were accumulated from ambient sediment not deeper sediment.

Keywords: Nankai Trough, accretionary prism, hydrocarbons, IODP, Expedition 338

Qualitative interpretation of CO₂/CH₄ Gas Exchange Field Trial in Alaska

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”Depressurization method” is now considered as the central method for producing methane from methane hydrate under ocean bottom and permafrost. It has, however, not known whether the depressurization method alone is able to ensure cost-effectiveness in development. CO₂/CH₄ gas exchange, where a methane molecule is exchanged in situ with a CO₂ molecule within a methane hydrate structure and is released for production, is a candidate to complement the depressurization method in commercial production.

The first-ever field trial of a methane hydrate production by gas exchange was executed in the North Slope of Alaska. JOGMEC participated with ConocoPhillips and the U.S. Department of Energy in carrying out this project. The objectives of this trial were to evaluate the viability of CO₂/CH₄ gas exchange as a production technique and to understand the implications of the process at a field scale. Ignik Sikumi #1 was drilled vertically to a depth of 791.6 m. A mixture of CO₂ (23%) and N₂ (77%) was injected through the perforated section of 10 m thickness. The downhole pressure was lowered during production at initially above and then below the dissociation pressure of native methane hydrate. (Schoderbek *et al.*, 2012)

The planned volume of mixture gas was successfully injected into the formation without any loss of injectivity. An increased temperature at the sand face measured by fiber-optic DTS during injection implies exothermic CO₂ hydrate formation. Methane produced above the hydrate stability pressure at first of production phase. This indicates produced methane generated not by depressurization, but by gas exchange.

Schoderbek, David, Kenneth Lloyd Martin, James Howard, Suntichai Silpngarmert, and Keith Hester, 2012, North Slope Hydrate Fieldtrial: CO₂/CH₄ exchange. OTC-23725.

Keywords: methane hydrate, gas exchange, carbon dioxide, permafrost, Alaska

Estimation of decrease in global methane hydrate inventory associated with global warming

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Large amounts of methane hydrate are trapped in the sediments along the continental margins, owing their stability to low temperature and high pressure conditions. Increase in temperature due to global warming could destabilize methane hydrate and cause a release of methane into the water column. Released Methane (and/or carbon dioxide from methane oxidation) would affect climate and global biogeochemical cycle. However, the amount of released methane due to decomposition of methane hydrate is poorly constrained.

In this study, we calculated the global changes in gas hydrate stability zone (GHSZ) volume and methane hydrate inventory associated with potential future climate change. A series of potential future climate change experiments are under taken using the Model for Interdisciplinary Research on Climate (MIROC), an atmosphere-ocean coupled general circulation model (AOGCM), with resulting seafloor temperature changes applied to a simple methane hydrate inventory model based on Pinero et al (2012).

Our model predicts GHSZ volume along the continental margins has decreased by 30(14) % under the condition of 4(2) \times CO₂. The methane hydrate inventory is decreased from present 550 Pg of C to 200(380) Pg of C under the condition of 4(2) \times CO₂.

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Keywords: methane hydrate, global warming

Age models in two piston cores (MD179-3312 and 3304) off Joetsu in the southwestern part of the Japan Sea: based on the

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We constructed the age models of MD179-3312 and MD179-3304 off Joetsu, in the southwestern part of the Japan Sea based on AMS ¹⁴C determinations, tephra identifications, MIS events (as control points) and correlations of TL layers (as sub-control points). Bases of 11 TL layers (TL-1, TL-2, TL-3, TL-12, TL-14, TL-18, TL-19, TL-20, TL-21, TL-22 and TL-23) could be recognized the same horizons by the correlations with microfossil dates. The estimated sedimentation rates of core 3312 in average were about 0.24 m/kyr lower than those of core 3304, 0.32 m/kyr.

Keywords: Japan Sea, biostratigraphy, age model, late Quaternary, gas hydrates, TL layers

Depth distribution of trace elements in pore water collected from Japan Sea sediments associated with methane hydrate

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Methane hydrate occurs in the deep ocean floor, and also in the permafrost layers of Siberia and Alaska. In Japan, relevant gas hydrate studies have been carried out in Nankai Trough since the 1990s and in the Japan Sea since 2004.

This study focuses on the trace element concentrations, with a special reference to iodine, in pore water samples collected from Japan Sea sediments. The long-lived iodine isotope, ¹²⁹I, which is produced by the spallation of atmospheric and by spontaneous fission, was also measured in order to provide an estimation of the age of iodine.

Marine sediment samples were collected from methane hydrate areas of Umitaka Spur and Joetsu Knoll, Japan Sea, during the cruise with R/V Marion Dufresne (MD179; MH21 Research Consortium) in 2010. The depths of the sediment cores obtained with a giant piston corer reached maximum depths of about 40 mbsf, which is much deeper than previous piston core samples (down to 8 mbsf) recovered by R/V Umitaka-maru on previous cruises in the region. Pore waters were extracted from the sediment soon after recovery. The concentrations of iodine, bromine and some trace metals (such as Mn, Sr, Ba) were later determined by ICP-MS. Samples having a high iodine concentration were selected for ¹²⁹I analysis. For this, iodine from samples was extracted by solvent extraction and precipitated as AgI. ¹²⁹I/¹²⁷I ratios were determined by accelerator mass spectrometry (AMS) at MALT, the University of Tokyo.

Our results show that iodine concentrations in pore water increase constantly with depth in almost all cases. In particular, samples on the Umitaka Spur showed a markedly high increase of iodine concentrations, i.e. the concentration at 35 mbsf was 0.4 mM, which is about 800 times higher than the average iodine concentration in the ocean. Bromine concentration in pore water also increased with the depth, but not as much (only about 1.7 times seawater). On the other hand, profiles show a decreasing trend with depth in pore water chlorine concentrations. This may be explained by the dilution effect with non-saline water produced by the dissociation of methane hydrate.

Analytical results for ¹²⁹I/¹²⁷I ratio in pore waters deeper than 3 mbsf ranged from 0.20 - 0.35 x 10⁻¹². These values were much lower than the background value of ¹²⁹I/¹²⁷I ratio of 1.5 x 10⁻¹² in the ocean in the pre-atomic age. Considering the ¹²⁹I systematics, iodine age for the samples was estimated to be 30-45 Ma. This age is almost the same or older than the age when the Japan Sea was formed. The results of lower ¹²⁹I/¹²⁷I ratios and increasing iodine concentration in pore water with depth suggest that iodine did not originate from shallow marine sediments. The iodine must be derived from deeper layers, such as old sediments rich in organic matter and iodine which were deposited in the sediments at the opening of Japan Sea. Alternatively, since the iodine ratios indicate minimum ages, it may be possible that iodine was released from sediment layers which were formed before the formation of Japan Sea.

This study was supported by MH21 Research Consortium Japan.

Keywords: iodine, methane hydrate, Japan Sea, radioisotope ratio

3D observation of shallow gas hydrates in eastern margin of the Sea of Japan by X-CT

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Gas hydrate has clathrate structure of a gas molecule in a water cage, and is found naturally in deep-sea and permafrost sediments. Natural gas hydrates were recovered in eastern margin of the Sea of Japan through scientific expeditions since 2005 (Matsumoto et al., 2011) and their characterization was investigated (Lu et al., 2011). On-board observation of the hydrate samples indicated that occurrence of the gas hydrates in silt sediments was classified into roughly three groups; flake-like, laminated, and massive types. Sometimes, many hydrate pieces appeared in one depth, which gave us questions how they occurred in sediment and whether they connected each other, or not. Therefore, we here study 3D observation of shallow gas hydrates in eastern margin of the Sea of Japan by X-CT. The samples recovered during MD179 expedition were used in this study. Histograms of gray scales in slice images of all the samples show that we can distinguish between sediment and gas hydrate/water. Flake-like, laminated, and massive gas hydrates are observed. In one sample, platy gas hydrates are broken and sediment seems to intrude into platy gas hydrates. This implies that dynamic activity occurs after gas hydrate formation.

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Keywords: gas hydrate, X-ray CT, 3D observation

Chemical analysis of LV59 sediment pore waters retrieved off Sakhalin Island, Russia

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The Sakhalin Slope Gas Hydrate Project (SSGH) is an international collaborative effort by scientists from Japan, Korea, and Russia to investigate natural gas hydrates (GHs) that have accumulated on the continental slope off Sakhalin Island, Okhotsk Sea. In 2012, the field operation of the SSGH-12 project was conducted as the LV59 cruise of the R/V Akademik M.A. Lavrentyev. GH-bearing and -free sediment cores were retrieved using steel hydro- and gravity corers.

The pore water was sampled on board using squeezers designed and constructed at the Kitami Institute of Technology (KIT). A 10-cm depth interval of the sediment core was drawn into the squeezer, and pore water was then directly collected into a polyethylene syringe connected to the discharge tube of the squeezer. The other end of the syringe was connected to a membrane filter cartridge containing a 0.2-um filter. Seawater samples were obtained from the top of the corer. All water sample was filtrated through a 0.2-um filter and then taken into a polypropylene bottle.

The concentrations of anions in the pore waters were measured at KIT. Sulfate concentrations decreased linearly with depth to the sulfate methane interface (SMI). The linearity of these profiles suggested that sulfate depletion is largely driven by an upward flux of methane, rather than by the flux of organic matter from above, and the anaerobic oxidation of methane (AOM) at the SMI. The linear sulfate profiles are formed in a steady state based on sulfate and methane co-consumption at the SMI and the balance of sulfate and methane fluxes. The SMI of the GH-bearing LV59-27HC core was 0.5 m below the seafloor (m bsf). Since the depth of the SMI depends on the intensity of the upward methane flux, we can conclude that intensive methane flux was observed at the GH-bearing core.

Keywords: gas hydrate, pore water, chemical analysis, Sakhalin Island, Russia

Natural gas hydrates retrieved at the Terpeniya Ridge and the Tatar Trough, off the Sakhalin Island

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We report molecular and isotopic compositions of hydrate-bound hydrocarbons in the new seepage sites of offshore Sakhalin Island, the Sea of Okhotsk. Sakhalin Slope Gas Hydrate (SSGH) project was started from 2007 and we retrieved sediment cores off northeastern Sakhalin Island in 2009-2011. We also sampled some cores at the Terpeniya Ridge, southeastern Sakhalin Island in these cruises; however, we could not retrieve hydrate-bound cores at the area. Because gas plumes ascend and the dissolved methane in pore water was very rich, existence of gas hydrate crystals in the shallow sediment layers were expected. In August 2012, we visited the Terpeniya Ridge again and the Tatar Trough (southwestern Sakhalin Island) and got hydrate-bound sediment cores from both fields in the cruise of SSGH12. We sampled gas hydrate crystals and stored into liquid nitrogen tank. We also obtained the samples of hydrate-bound gas and dissolved gas in pore water on board, and we measured molecular and stable isotope compositions of them in our laboratory. Empirical classification of the methane stable isotopes; delta ¹³C and delta D according to Whiticar *et al.* (1986) indicated that the gases obtained at the Terpeniya Ridge are microbial origin via carbonate reduction, whereas some cores at the Tatar Trough showed typical thermogenic origin (methane delta ¹³C = -47 permil). Because ethane delta ¹³C of the all gas samples suggested their thermogenic origin, microbial methane is mixed with the small amount of thermogenic gas at the Terpeniya Ridge. Results of Raman spectroscopic analysis revealed that the hydrate crystals of both Terpeniya Ridge and Tatar Trough belonged to the structure I, and the hydration number was 6.0 in the both fields. Small amount of hydrogen sulfide was also enclathrated with methane.

Whiticar MJ, Faber E, Schoell M (1986) Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate fermentation - Isotope evidence. *Geochim Cosmochim Acta* **50**: 693-709

Keywords: gas hydrate, stable isotope, Terpeniya Ridge, Tatar Trough, Sea of Okhotsk, Raman