

Occurrence and origin of shallow gas hydrates

MATSUMOTO, Ryo^{1*}

¹Dept of Earth & Planet Sci Univ of Tokyo

It is almost 16 years since Leg 164 of the Ocean Drilling Project conducted the first gas hydrate drilling on the Blake Ridge, West Atlantic, and revealed that the anomalous reflector BSRs do not always indicate extensive distribution of gas hydrate but perhaps existence of free gas zones below the BSR. For the last decades, our understanding of marine gas hydrates has been remarkably deepened and developed. Direct observation of the seafloor by ROV, dense coring, high-resolution acoustic surveys have identified densely accumulated gas hydrate zones in shallow sediments and even on the seafloor. We have now two distinctive types of gas hydrate. One is deep-seated, pore-filling type accumulation, and the other is shallow massive accumulation. As for the industry efforts, National gas hydrate program MH21 is planning to conduct an offshore production test on the deep-seated type accumulation in Nankai Trough in 2012 and 2013. Gas hydrate exploration efforts are rapidly growing in nearby countries and districts, in which the projects seem to target not only the deep-seated type but also shallow and massive accumulation of gas hydrate. In the present paper, I would like to discuss and clarify the geologic, geochemical, and physical constraints to form shallow gas hydrates in Japan Sea with an intention to assess the resource potential of shallow gas hydrates, on the basis of our gas hydrate expedition since 2009.

Keywords: gas hydrate, gas chimney, hydrate mound

In situ measurement of the amount of free gas of deep sea sediments by Time Domain Reflectometry (TDR) method

OCHIAI, Hiroyuki^{1*}, MATSUMOTO, Ryo¹, HIROMATSU, Mineo¹, TOMARU, Hitoshi¹

¹Department of Earth and Planetary Science, University of Tokyo

In situ measurement of the amount of free gas of deep sea sediments by Time Domain Reflectometry (TDR) method

The amount of free gas in deep sea sediments is a critical factor for the stability of gas hydrate, however, it is not easy to obtain reliable free gas amount by conventional core sampling methods. In this study, we try to measure the in situ free gas amount of gas hydrate bearing Japan Sea sediments by introducing the Time Domain Reflectometry (TDR) method with an intention to estimate the behavior of methane in deep sea sediments. TDR method has been widely used to estimate the water content of soils in the field of agriculture science.

The TDR sensor is set at the bottom of piston corer and data-logger and battery are stored in a pressure vessel within the weight at the top of the system. The volume of gas has been estimated from observed change in the dielectric constant. The dielectric constant is different in each material, about water is 80 and the soil are 3-9, and air is 1. Moreover, ice is 4.2. The sediment core of a constant amount was taken from bottom of the sea by piston core samplings, and the dry density and the particle density of the soil are measured in a laboratory. Then the amount of solid phase ratios is estimated. Thus the liquid phase ratio can be estimated according to the value of the dielectric constant by the TDR method measured at the bottom of the sea. The volume of the gas can be requested from these measurements by the calculation.

The dielectric constant (ϵ) of the sediments was different according to the measurement point. The dielectric constant measure by the TDR method was applied to proofreading type $V_w = 3.71E06 \cdot \epsilon^3 - 3.60E-04 \cdot \epsilon^2 + 1.86E-02 \cdot \epsilon - 5.61E-02$ provided by the laboratory experiment, and liquid phase ratio ($m^3 m^{-3}$) was obtained. On the other hand the solid phase ratio ($m^3 m^{-3}$) of the sediments was directly obtained from the core samples. These results were brought together by each measurement point, and gas phase ratio ($m^3 m^{-3}$) was obtained from calculating formula. It is remarkable that the gas phase ratio of gas hydrate bearing sediments showed significant changed by approximately 5 % from sea bottom to sea surface during the experiment, suggesting dissociation of gas hydrate and degassing of dissolved methane due to depressurization during core recovery.

Keywords: TDR, measurement of free gas amount, Japan Sea, gas hydrate, method of marine survey

Thermal structure in the western Joetsu Basin, offshore Sado Island, Japan

GOTO, Shusaku^{1*}, MORITA, Sumito¹, TANAHASHI, Manabu¹, KANAMATSU, Toshiya², HACHIKUBO, Akihiro³, KATAOKA, Satsuki⁴, MACHIYAMA, Hideaki², KINOSHITA, Masataka², YAMANO, Makoto⁵, MATSUBAYASHI, Osamu¹, MATSUMOTO, Ryo⁶

¹GSJ, AIST, ²JAMSTEC, ³Kitami Institute of Technology, ⁴Hakodate National College of Technology, ⁵ERI, Univ. Tokyo, ⁶Earth and Planetary Sci., Univ. Tokyo

Stability of gas hydrate depends on pressure and temperature. Subsurface thermal structure thus provides key information to investigate formation of gas hydrate and distribution of gas hydrate stability zone. The western Joetsu Basin is one of areas where gas hydrate studies have been conducted intensively in the world (Matsumoto et al., 2009). In June 2010, MD 179/Japan Sea Gas Hydrates cruise using R/V Marion Dufresne was conducted in the western Joetsu Basin to investigate the mechanism of gas hydrate formation in the region. Measurements of heat flow were conducted during the cruise at seven sites along one of METI Sado-oki Nansei 2D seismic survey lines. The measured values of heat flow range from 84 to 90 mW/m², which is slightly lower than those measured around the Joetsu Knoll and Umitaka Spur by Machiyama et al. (2009). We inferred 2D thermal structure along the 2D seismic survey line to explain the heat flow values measured at the seafloor using the topography and geological structure interpreted from the seismic survey line and physical property data obtained during MD 179/Japan Sea Gas Hydrates cruise and from METI Sado Nansei Oki Well. In the calculation, we assumed that heat transport in the model is heat conduction only and that a constant basal heat flow is supplied at the base of the model. We sought the thermal structure model that best explains the measured heat flows, by giving various values of basal heat flow to the model. The best thermal structure model is of the basal heat flow of 88 mW/m². The calculation result suggests that in the modeled area, heat conduction dominates heat transport and that the basal heat flow in the area is about 88 mW/m².

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

References

Machiyama, H., M. Kinoshita, R. Takeuchi, R. Matsumoto, M. Yamano, H. Hamamoto, M. Hiromatsu, M. Satoh, J. Komatsubara (2009), Heat flow distribution around the Joetsu gas hydrate field, western Joetsu Basin, eastern margin of the Japan Sea, *Journal of Geography*, 118, 986-1007 (in Japanese with English abstract).

Matsumoto, R., Y. Okuda, A. Hiruta, H. Tomaru, E. Takeuchi, R. Sanno, M. Suzuki, K. Tsuchinaga, Y. Ishida, O. Ishizaki, R. Takeuchi, J. Komatsubara, A.F. Freire, H. Machiyama, C. Aoyama, M. Joshima, M. Hiromatsu, G. Snyder, H. Numanami, M. Satoh, Y. Matoba, H. Nakagawa, Y. Kakuwa, S. Ogihara, K. Yanagawa, M. Sunamura, T. Goto, H. Lu, T. Kobayashi (2009), Formation and collapse of gas hydrate deposits in high methane flux area of the Joetsu Basin, eastern margin of Japan Sea, *Journal of Geography*, 118, 43-71(in Japanese with English abstract).

Keywords: thermal structure, heat flow, western Joetsu Basin, gas hydrate, MH21

Marine surveys for gas-hydrate off Abashiri, the Sea of Okhotsk

YAMASHITA, Satoshi^{1*}, MATSUMOTO, Ryo², MINAMI, Hirotsugu¹, HACHIKUBO, Akihiro¹, HIROMATSU, Mineo², TOMARU, Hitoshi², OKUDA, Yoshihisa³, Hitoshi Shoji¹, TAKAHASHI, Nobuo¹

¹Kitami Institute of Technology, ²Earth and Planetary Sci., Univ. of Tokyo, ³AIST

When the resources project of gas-hydrate was stood in Japan at 1995, clear BSR has been also confirmed in the seismic data of the Kitami-Yamato Bank off Abashiri, the Sea of Okhotsk, and the possibility of existence of gas-hydrate has been pointed out (Sato et al, 1996; Sakai, 1996). Moreover, obvious BSR has been also confirmed in the seismic data (SBP and SCS) collected during GH01 cruise that carried out off Abashiri, the Sea of Okhotsk in 2001 conducted by Geological Survey of Japan, AIST (Noda et al, 2009). However, the sufficient survey is not carried out after GH01 cruise, and the actual condition is not clear.

Therefore, the cooperated survey for the gas-hydrate was performed with Kitami Institute of Technology which has the survey experience regarding the gas-hydrate in offshore Sakhalin Island, the Sea of Okhotsk and Univ. of Tokyo team which has that in the eastern margin of the Japan Sea. This survey is a pilot study to start the substantial survey after next year and the main purposes are below.

1) To retrieve the sea-bottom sediment of the length of 50 or more cm at least from the top of the gas chimney structure where decided from the SBP record published in the Web of AIST.

2) To check the presence of the trace of methane spring and/or gas-hydrate from the sediment properties.

3) To decide the SMI depth from the composition of pore water, and to evaluate the strength of methane flux.

4) To clarify the temperature profile of sea water, and to evaluate the stability of shallow gas-hydrate.

5) To clarify the composition and origin of dissolved gas in the pore water.

The surveys were carried out for three days in September, 2011, with the Abashiri Submarine Canyon area (water depth is about 900 m) that is in offshore about 30 km in the northeast from Abashiri. Used R/V is Taiki-maru (19 ton). To retrieve the sea-bottom sediment, a gravity core sampler (length is about 2 m) was used, and maximum retrieved core length was 1 m. To measure the strength of sediments immediately after recovery, the cone penetration test was performed on board. For sediment, pore water and gas analyses, subsampling was conducted for the cut core. The measurement of water temperature from the sea-surface to sea-bottom and the water sampling at regular interval were also conducted.

It was not possible to retrieve the gas-hydrate in this survey. On the other hand, it was confirmed that the methane is dissolving with high concentration in the pore water of sea-bottom sediments. The concentration was similar to that of the core sample retrieved from offshore Sakhalin Island, the Sea of Okhotsk, where the gas-hydrate was retrieved. Thus, it was suggested that there is the possibility of existence of gas-hydrate even from the temperature/pressure condition on the survey sea area.

Keywords: gas hydrate, marine survey, Sea of Okhotsk, sea-bottom sediment, pore water, dissolved gas

Crystallographic properties of gas hydrates off Sakhalin Island (Sea of Okhotsk) using Raman spectroscopy & calorimetry

HACHIKUBO, Akihiro^{1*}, Hirotohi Sakagami¹, MINAMI, Hirotsugu¹, YAMASHITA, Satoshi¹, TAKAHASHI, Nobuo¹, Hitoshi Shoji¹, Young K. Jin², Anatoly Obshirov³, Olga Vereshchagina³

¹Kitami Institute of Technology, ²Korea Polar Research Institute, ³Pacific Oceanological Institute, FEB RAS

Natural gas hydrates have been studied in the gas seep sites off Sakhalin Island, the Sea of Okhotsk. More than ten gas seep sites in the north area of the Lavrentyev seabed Fault (LVF) form gas hydrates in the sea-bottom sediments. In the framework of SSGH (Sakhalin Slope Gas Hydrate) project, hydrate-bearing sediments are also discovered in the south area of LVF, where more than 400 acoustic anomalies exist but the size of seepage structures are relatively small. We obtained samples of natural gas hydrate in the CHAOS project (2003-2006) and the SSGH project (2007-2011) and analyzed their crystallographic properties using a calorimeter and a Raman spectrometer. Their gas composition were mainly methane, suggested the cubic structure I of these crystals. The hydration number, cage occupancies of both large and small cages, and dissociation heat of the sample were almost same as those of pure methane hydrate. Raman spectra showed that hydrogen sulfide were encaged in both large and small cages. The peak ratio of large to small cages were about 2.4 and 3.5 for hydrogen sulfide and methane, respectively.

Keywords: gas hydrate, dissociation heat, cage occupancy, hydration number, Sea of Okhotsk

Sampling method and chemical analyses of gas hydrate waters retrieved from Kukuy K-9 mud volcano in Lake Baikal

MINAMI, Hirotsugu^{1*}, HACHIKUBO, Akihiro¹, Kazuya Tatsumi¹, Yusuke Soramoto¹, Yohei Kawagishi¹, Hirotohi Sakagami¹, Satoshi Yamashita¹, Nobuo Takahashi¹, Hitoshi Shoji¹, Marc De Batist², Lieven Naudts³, Oleg Khlystov⁴, Tatyana Pogodaeva⁴, Tamara Zemskaya⁴, Mikhail Grachev⁴

¹Kitami Institute of Technology, ²Renard Centre Mar. Geol., Univ. Ghent, ³MUMM, RBINS, Belgium, ⁴Limnological Institute, SB RAS, Russia

Lake Baikal, Russia, is one of the most attractive gas hydrate study areas, since the first gas hydrate (GH) in a freshwater lake was retrieved from the sub-bottom depths of 121 and 161 m and later from the subsurface of the lake floor. Many studies to determine the origin of the gases incorporated in and/or bound to GHs have been carried out on samples from this lake [see, e.g., Hachikubo et al [Hachikubo, 2010]]. On the other hand, chemical analyses of water samples from lake- and pore- waters have been carried out to clarify the geochemical characteristics of the GH-bearing sediment cores [see, e.g., Pogodaeva et al [Pogodaeva, 2007]]. The chemical analyses of such samples are important to identify the origin of water molecules contributing to the formation of GHs and to distinguish whether seepage structures and/or mud volcanoes observed at the lake floor are related to the discharge of gases with or without gas-saturated water.

In September of 2010, subsurface GHs were retrieved using steel gravity corers at Kukuy K-9 mud volcano in the central basin of Lake Baikal. GH water samples were obtained, on board, by the sequential and continuous dissociation of a piece of agglomerated/massive GH, in a closed vessel with inert gas, after its retrieval from the bottom of the lake floor, to acquire traces of the original gas hydrate-forming fluid in the GHs.

The purposes of this presentation are (i) to describe the sampling method used to obtain GH water samples without the use of lake or pore waters, (ii) to report the scientific results of the chemical (such as Cl-) and isotopic ($\delta^{18}\text{O}$ and $\delta^2\text{D}$) analyses of samples from lake- and pore- waters, and (iii) to find traces of the original water involved in the accumulation of subsurface GHs at Kukuy K-9 mud volcano in Lake Baikal.

Keywords: gas hydrate water, pore water, chemical analyses, ionic concentration, stable isotope ratio

High-resolution Seafloor Survey and Preliminary Geochemical Investigations in the Daini-Atsumi Knoll.

NAGAKUBO, Sadao^{1*}, NAKATSUKA, Yoshihiro², Fujio Yamamoto³, YAMAMOTO, Koji²

¹Japan Drilling Co. Ltd., ²Japan Oil, Gas and Metals National Corporation, ³Japan Agency for Marine-Earth Science and Technology

In 2012 JFY, the first offshore methane hydrate production test in the world will be conducted around the Daini-Atsumi Knoll in the eastern Nankai Trough.

Geohazard surveys are required to deepwater drillings in oil and natural gas industry, therefore, a high-resolution bathymetric and geological survey was conducted by the AUV 'Urashima' in the Daini-Atsumi Knoll in February, 2011.

The acquired data are as follows;

- (1) High-resolution bathymetric data by multi-narrow beam echo sounder
- (2) High-resolution back-scatter image by side scan sonar
- (3) High-resolution shallow sediment profile by sub-bottom profiler

Resultingly remarkable hazards are not identified around the production test area.

Nagakubo et al. (2009) constructed the bathymetric and seafloor amplitude maps of the Daini-Atsumi knoll by the seafloor reflection signals of the 3D seismic data acquired in the METI 3D seismic survey 'Tokai-oki to Kumano-Nada'. Furthermore a lot of geochemical data near on seafloor were acquired by the Research Consortium for Methane Hydrate Resources in Japan (MH21).

This presentation will show (1) Comparison of the AUV 'Urashima' and the 3D seismic data concerning the bathymetry and seafloor geological conditions, (2) Preliminary investigations concerning the geological and geochemical conditions of the Daini-Atsumi Knoll.

Reference

Nagakubo S., Kobayashi T., Saeki T., Shimoda N., Fujii T. and Noguchi S. (2009): The Relations between Methane Hydrate-bearing Formations and Seafloor Manifestations Accompanied by Methane Discharges in the Eastern Nankai Trough, *Journal of Geography*, 118(5), 835-853. (in Japanese with English abstract)

Keywords: AUV 'Urashima', methane hydrate, Daini-Atsumi Knoll, bathymetric survey

Biogeochemical processes in gas hydrate-bearing mud volcano sediments from the Kumano forearc basin, Japan

IJIRI, Akira^{1*}, TOKI, Tomohiro², YAMAGUCHI, Yasuhiko T.³, KAWAGUCCI, Shinsuke¹, HATTORI, Shohei⁴, MORONO, Yuki¹, Takeshi Terada⁶, YOSHIDA, Naohiro⁴, TSUNOGAI, Urumu⁷, NAKAMURA, Ko-ichi⁵, TAKAI, Ken¹, ASHI, Juichiro³, INAGAKI, Fumio¹

¹JAMSTEC, ²Ryukyu Univ., ³AORI, ⁴TITECH, ⁵Marine Works Japan, ⁶Hokkaido Univ., ⁷AIST

We investigated biogeochemical processes in mud-volcano subsurface sediments down to 20 meters from the summit, obtained from the Kumano forearc basin in the Nankai Trough during the CK09-01 D/V Chikyu training cruise in 2009.

The cored sediments contained several methane hydrates. The stable isotopic compositions of the pore fluid samples exhibit ¹⁸O-enrichment and D-depletion in proportion to the depletion of the chlorinity indicating that a mixing between seawater and the fresh water components derived from the dehydrate reaction of clay minerals at 60-160°C previously occurred in the deeply buried sedimentary layer. In contrast, hydrate water samples are strongly enriched in deuterium and slightly deviated from Cl-vs. oxygen isotopic composition trend indicating the pore fluid freshening is not governed by gas hydrate dissociation. High B (up to 13094 micoro-M) and Li (up to 188 micoro-M) concentrations in the pore fluid suggest the leaching from clay minerals at >150°C, and indicate that the fluid in the mud volcano was supplied from the accretionary prism (>4000 mbsf) beneath the forearc sediments probably through faults.

The carbon isotopic composition of dissolved inorganic carbon increased with the coring depth, reaching +40 per mil at 3 meters below the seafloor (mbsf). The highly ¹³C-enriched values are possibly due to strong microbial reduction of DIC to ¹²C-enriched products. The hydrogen isotopic composition of methane (ca. -180 permil) and magnitude of the carbon isotopic fractionation between DIC and methane (ca. 76 per mil) bellow 3 mbsf suggest the significant contribution of hydrogenotrophic methanogenesis as the source of methane. The carbon isotopic composition value of acetate was appeared to increase with the sediment depth (from -41 to -22 per mil), synchronous to the increase of carbon isotopic composition of DIC. The significant isotopic fractionation between DIC and acetate (ca. 54 per mil) indicates that the principal process producing acetate is homo-acetogenesis via the reductive acetyl-CoA pathway. Radioactive tracer experiments exhibited relatively high activities of homo-acetogenesis (14~34,900 pmol/cm³/day) compared to that of hydrogenotrophic methanogenesis (0.6~128 pmol/cm³/day). In ordinary marine sediments, homo-acetogenesis from H₂ and CO₂ is thermodynamically inhibited because H₂ concentrations are maintained at low levels less than several nM. However, the homo-acetogenesis was thermodynamically favorable in the cored sediments because of the high concentration of H₂ (>560nM). These results showed that homo-acetogenesis is dominant in the sediments around the summit of the mud volcano, while active hydrogenotrophic methanogenesis has been occurred in a deeper depth, and most portion of methane formed methane hydrates was supplied from the deep active methanogenic zone.

Keywords: Mud volcano, Methane hydrate, Deep origin fluid, homo-acetogenesis, methanogenesis, CO₂ reduction

Dissociation mechanism of methane clathrate hydrate in different size of pore spaces

TAKEYA, Satoshi^{1*}, Akihiro Hachikubo², Evgeny Chuvilin³, Vladimir Istomin⁴

¹National Institute of Advanced Industrial Science and Technology (AIST), ²Kitami Institute of Technology, ³Moscow State University, ⁴Gazprom VNIIGAZ LLC

Dissociation processes of methane hydrate synthesized with glass beads were investigated using powder X-ray diffraction technique. Although understanding of methane hydrate dissociation within natural settings, not so many studies were performed on methane hydrate dissociation within pore spaces from microscopic point of view. Recently, it was revealed that methane hydrate formed with hydrophilic glass beads less than a few microns in size show very high stability up to just below the melting point of ice, even though this temperature is well outside the zone of thermodynamic stability of the hydrate.[1] In contrast, methane hydrate formed with hydrophilic coarse glass beads (> 10 micron) dissociate quickly at 150-200 K; in this temperature range methane hydrate dissociates at the atmospheric pressure.

In this study, we performed observations of methane hydrate dissociation process using hydrophobic glass beads with sub-micron and several microns in size. In this case, kinetic high-stability of methane hydrate was not observed. Thus the experimental results obtained suggest that the dissociation rate of methane hydrate strongly depended on the surface property of glass beads used.

Reference

[1] Hachikubo et al., Phys. Chem. Chem. Phys., 13 (2011) 17449-17452.

Keywords: methane hydrate, dissociation, self-preservation, pore space

Observation of methane plumes with quantitative echo sounder

AOYAMA, Chiharu^{1*}

¹Japans Independent Institute

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

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

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

Keywords: Quantitative echo sounder, Methane Hydrate, Methane Plume

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

NUMANAMI, Hideki^{1*}, MATSUMOTO, Ryo², OCHIAI, Hiroyuki², HIROMATSU, Mineo², TOMARU, Hitoshi²

¹Tokyo Kasei Gakuin University, ²Department of Earth and Planetary Science, University of Tokyo

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

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

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

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

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

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

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

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

Detail of biomass in this area was also discussed.

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

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

YAMAMOTO, Naoya^{1*}, TANI, Atsushi¹, YANAGAWA, Katsunori², TOMARU, Hitoshi², Yasuyuki Muramatsu³, MATSUMOTO, Ryo²

¹Science, Osaka University, ²Science, University of Tokyo, ³Science, Gakushuin University

Natural gas hydrate is a clathrate compound. Gas molecules are encaged by hydrogen-bonded water molecules. Gas hydrate is found together with deep-sea sediments that contain natural radioisotopes like uranium-series, thorium-series, and ⁴⁰K. Natural radiation from those radioisotopes will break bonds of water and guest gas molecules, and form radical species. Although the radical species are unstable in the pressure and temperature of natural gas hydrate occurrence on the Earth, radical reactions may occur in the hydrates. The reaction products will be accumulated in gas hydrates (Tani et al., 2006). For example, ethane, methanol, and formaldehyde are mainly formed in gamma-irradiated methane hydrate (Ishikawa et al., 2007, Tani et al., 2011). Methanol and formaldehyde may be closely related to microbial activities in the seafloor sediments. Therefore, we are interested in depth profiles of these compounds in the deep-sea sediments.

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

Pore water was obtained by squeezing sediments recovered from Umitaka Spur and Joetsu Knoll, in Joetsu Basin. Each sample was taken into a glass vial (3-5 ml), sealed, and kept in a freezer. These procedures are performed on the ship. The vials were warmed at room temperature before the following analysis. Headspace gas in each vial was analyzed by gas chromatography-mass spectrometry (GC-MS). Because Henry's constant of formaldehyde is large (Sander, 1999), o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA) was used as a derivative reagent for aldehyde (Kobayashi et al., 1980).

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

This study was supported by MH21 Research Consortium Japan.

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

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

NAKAMURA, Yuya^{1*}, SUGAI, Toshihiko¹, ISHIHARA, Takeshi¹, Fernando FREIRE¹, MATSUMOTO, Ryo²

¹Environmental Studies, KFS, UT, ²Dept of Earth & Planet Sci, UT

Introduction

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

Study area

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

Calculation and the variation pattern of sedimentation rate

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

Relation between change of sedimentation rate and submarine geomorphological settings

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

Acknowledgements

This study has been financially supported by the cooperative research project of the MH21 Research Consortium Japan.

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

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

ISHIHAMA, Saeko^{1*}, OI, Takeshi², HASEGAWA, Shiro², MATSUMOTO, Ryo³

¹Kanagawa Prefectural Museum of Natural History, ²Kumamoto University, ³University of Tokyo

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

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

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

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

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

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

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

URABE, Tasuku^{1*}, KIGOSHI, Tomohiko¹, KUMON, Fujio¹

¹Department of science, Shinshu university

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

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

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

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

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

HACHIKUBO, Akihiro^{1*}, TOMARU, Hitoshi², HIROMATSU, Mineo², MATSUMOTO, Ryo², OKUDA, Yoshihisa³, MINAMI, Hirotsugu¹, YAMASHITA, Satoshi¹, Hitoshi Shoji¹, TAKAHASHI, Nobuo¹

¹Kitami Institute of Technology, ²University of Tokyo, ³National Institute of Advanced Industrial Science and Technology

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

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

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

TOMARU, Hitoshi^{1*}, MATSUMOTO, Ryo¹, HIROMATSU, Mineo¹, OKUDA, Yoshihisa², HACHIKUBO, Akihiro³, MINAMI, Hirotsugu³, YAMASHITA, Satoshi³, SHOJI, Hitoshi³, TAKAHASHI, Nobuo³

¹Earth and Planetary Science, University of Tokyo, ²National Institute of Advanced Industrial Science and Technology, ³New Energy Resources Research Center, Kitami Institute of Technology

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

Keywords: Sea of Okhotsk, Sediment, Sulfur isotope

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

MINAMI, Hirotsugu^{1*}, Satoshi Yamashita¹, Akihiro Hachikubo¹, Yusuke Soramoto¹, Yohei Kawagishi¹, Kinji Hyakutake¹, Hiroaki Hirata¹, Hirotohi Sakagami¹, Nobuo Takahashi¹, Hitoshi Shoji¹, Hitoshi Tomaru², Mineo Hiromatsu², Yasuhisa Okuda², Ryo Matsumoto²

¹Kitami Institute of Technology, ²University of Tokyo

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

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

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

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

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

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

NISHIO, Yoshiro^{1*}, IJIRI, Akira¹, TOKI, Tomohiro², MORONO, Yuki¹, INAGAKI, Fumio¹

¹JAMSTEC, ²Ryukyu Univ.

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

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

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

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

YAMAMOTO, Koji^{1*}

¹Japan Oil, Gas and Metals National Corporation

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

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

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

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

Keywords: methane hydrate, production technique, field test

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

TANI, Atsushi^{1*}, HIGUCHI, Takuya¹

¹Sci, Osaka Univ.

Clathrate hydrate is a crystal compound of water molecules encaging guest molecules. Natural gas hydrate, whose guest molecule is mainly methane, is found under deep sea and in permafrost region. Estimation of formation age in natural gas hydrate has been attempted using the ¹²⁹I method (e.g. Fehn et al., 2003), which is an indirect age determination method. In contrast, we have investigated to establish a direct age determination method from hydrate crystal itself. Since natural gas hydrate is formed in sediment and irradiated by natural radiation due to natural radioisotopes like ⁴⁰K, U-series and Th-series, chemical reaction via radicals may occur in natural samples. In methane hydrate, methyl radicals are induced by gamma-rays (Takeya et al., 2004). However, they are unstable at the temperature and pressure of natural gas hydrate occurrence, and dimerize to ethane (Ishikawa et al., 2007). In another reaction, methanol and formaldehyde are also formed in gamma-irradiated methane hydrate (Tani et al., 2011). If the radiation-induced compounds in hydrate accumulate after hydrate formation, the amount may be related to a formation age of natural gas hydrate. The formation efficiency of the compounds should be determined for estimation of the formation age. Therefore, we have measured dissociated water of gamma-irradiated methane and ethane hydrates to analyze alcohols and aldehydes in the hydrates quantitatively by gas chromatography-mass spectrometry (GC-MS).

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

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

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

MURAOKA, Michihiro^{1*}, Kazushige Nagashima¹

¹Meiji Univ

Objective

The methane hydrates found globally in oceanic sediments are of significant interest as a global climate change and as a potential energy resource. Sediment cores recovered from the ocean floor have been reported to have a variety patterns and sizes of hydrates, which were classified into four categories by Malone [1]: disseminated, nodular, layered, and massive. In order to reproduce the variety patterns, clarify the pattern formation mechanism of hydrates in the sediments, tetrahydrofuran (THF) clathrate hydrates were grown using a directional growth apparatus in oceanic sediment model. In addition, a method to measure those variety patterns is not established. It is important establishing the method to clarify the pattern formation mechanism. This study presents a simple image analysis technique to measure hydrates size scale.

Experimental Method

The oceanic sediment model is mixed glass beads of 2 μm (μm denotes micrometer) and 50 μm in diameter. The mixing ratio between 2 μm beads and 50 μm beads was unity. A model system consists of the mixed glass beads and a stoichiometric THF water solution (THF-17H₂O). The weight ratio of the solution and the glass beads was unity. A directional growth apparatus was used to grow the hydrates at a constant growth rate, V , under an applied temperature gradient. The effect of the growth rate was studied in the range of 0.04 $\mu\text{m/s}$ $\leq V \leq$ 20 $\mu\text{m/s}$.

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

Results and Discussions

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

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

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

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

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

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