

# Characteristics of shallow gas hydrate in Okhotsk Sea

LUAN XiWu<sup>1†</sup>, JIN YoungKeun<sup>2</sup>, Anatoly OBZHIROV<sup>3</sup>, YUE BaoJing<sup>1</sup>

<sup>1</sup> Key Lab of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China;

<sup>2</sup> Korea Polar Research Institute, KORDI, Incheon, 406-840, Korea;

<sup>3</sup> V.I. Il'ichev Pacific Oceanological Institute of the Far Eastern Branch of Russian Academy of Sciences, Vladivostok 690041, Russia

**Multidisciplinary field investigations were carried out in Okhotsk Sea by R/V Akademik M.A. Lavrentyev (LV) of the Russian Academy of Sciences (RAS) in May 2006, supported by funding agencies from Korea, Russia, Japan and China. Geophysical data including echo-sounder, bottom profile, side-scan-sonar, and gravity core sample were obtained aimed to understand the characteristics and formation mechanism of shallow gas hydrates. Based on the geophysical data, we found that the methane flare detected by echo-sounder was the evidence of free gas in the sediment, while the dome structure detected by side-scan sonar and bottom profile was the root of gas venting. Gas hydrate retrieved from core on top of the dome structure which was interbedded as thin lamination or lenses with thickness varying from a few millimeters to 3 cm. Gas hydrate content in hydrate-bearing intervals visually amounted to 5%–30% of the sediment volume. This paper argued that gases in the sediment core were not all from gas hydrate decomposition during the gravity core lifting process, free gases must existed in the gas hydrate stability zone, and tectonic structure like dome structure in this paper was free gas central, gas hydrate formed only when gases over-saturated in this gas central, away from these structures, gas hydrate could not form due to low gas concentration.**

Okhotsk Sea, shallow gas hydrates, free gas, dome structure

The Okhotsk Sea is the second large marginal sea along the West Pacific Ocean next to the South China Sea (Figure 1). Mountain ranges surrounded the Okhotsk Sea supply abundance sedimentary source forming wide continental shelves in the north and east. Sediment column on these shelves extending over 10 km were mainly Cenozoic in age<sup>[1–3]</sup>, in which the average concentration of total organic carbon was over 1.0%<sup>[4–6]</sup>. Tectonically, the Okhotsk Sea is a platelet that squeezed between four plates namely the Pacific Plate to the southeast, the North America Plate to the north, Amur Plate to the west, and the Eurasian Plate to the southwest<sup>[7]</sup>. Due to joint compression from surrounding plates, a series of mud volcano, mud diapir developed on the northeast Sakhalin Slope<sup>[8–11]</sup>. The favorable tectonic setting hosted promising gas source in the Sakhalin Slope that has become a main target area of gas hydrates exploration<sup>[12]</sup>.

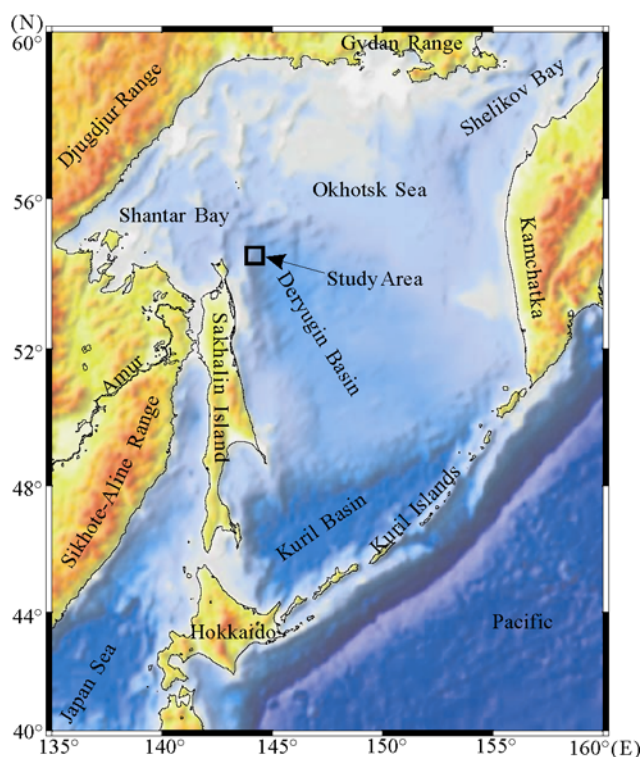
Since the 1990s, a series of geological and geophysical cruises were carried out in the Sakhalin Slope for understanding gas hydrates distribution and formation<sup>[13,14]</sup>. Among them, KOMEX<sup>[10,15]</sup> cruise and CHAOS<sup>[16]</sup> cruise were both successfully retrieved gas hydrates samples. The cruise on R/V “Akademik Lavrentyev” in May 2006 was the third one of the CHAOS project that coordinated and supported by Russian, Korean, Japan and Chinese governments<sup>[17]</sup>. Using the data from this cruise, the main feature of gas hydrate recovered is discussed in this paper.

Received October 10, 2007; accepted November 30, 2007

doi: 10.1007/s11430-008-0018-3

<sup>†</sup>Corresponding author (email: [xluan@ms.qdio.ac.cn](mailto:xluan@ms.qdio.ac.cn))

Supported by Korean MOMAF Program (Grant No. PM06020), Key Discipline Program of Chinese Academy of Sciences (Grant No. KZCX2-211-01), High Technology Research and Development Program of China (Grant No. 2006AA09Z234), and National Natural Science Foundation of China (Grant No. 40776032)



**Figure 1** Map of Okhotsk Sea and the study area.

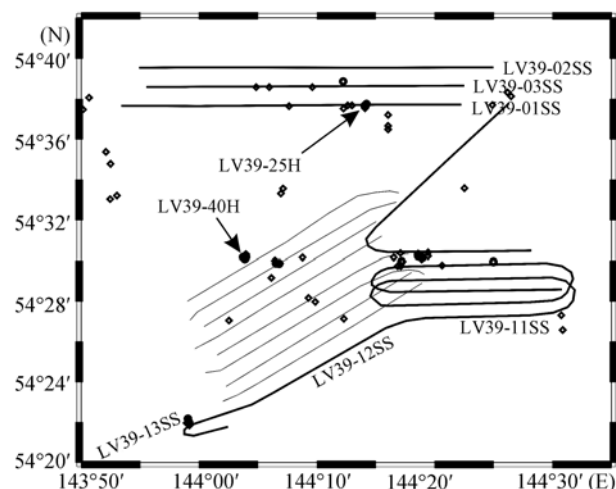
## 1 Methane flare

Hydroacoustic observations were carried out using a hydroacoustic complex created on the basis of several echo-sounders and multichannel digital registration system of hydroacoustic signals. The hydroacoustic complex provided a possibility of simultaneous registration of sonar echoes from four independent channels with frequencies of 12, 20, and 135 kHz. At the same time, echo signals were visualized on computer screen. Anomaly signals caused by internal waves, fish, zooplanktons can be easily distinguished due to its higher signal intensity. Signals from cold seepage methane bubbles can also be easily distinguished by its signal intensity and pattern. Usually, methane bubbles forms a flare shape anomaly on the echo signal screen.

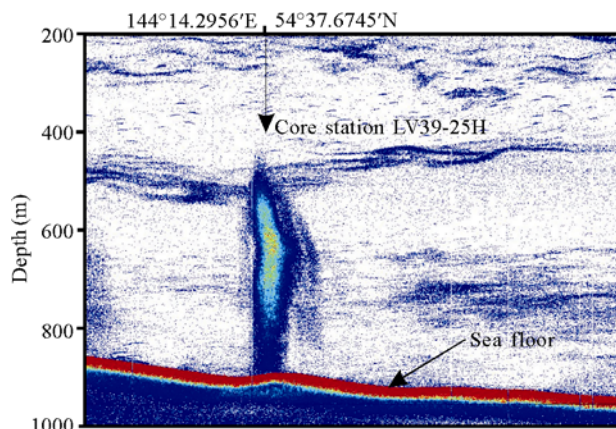
Thirty sites of methane flare were detected in the cruise (diamonds in Figure 2). Figure 3 gives a typical example of methane flare found on Line LV39-01SS, at 840 m deep. This methane flare was about 400 m in height, and 150 m in width with high signal intensity and a flare shape. Methane concentration of the water column was also measured. The measured results show that the methane concentration within the flare is much higher than that of the background water.

The other methane flares were almost the same. All of

them had high signal intensity and flare pattern. Due to difference in ship velocity, the width of the methane flare varied. Usually, the higher the ship velocity, the narrower the flare width, and vice versa. The height of the methane flare usually depends on the initial velocity of methane bubble.



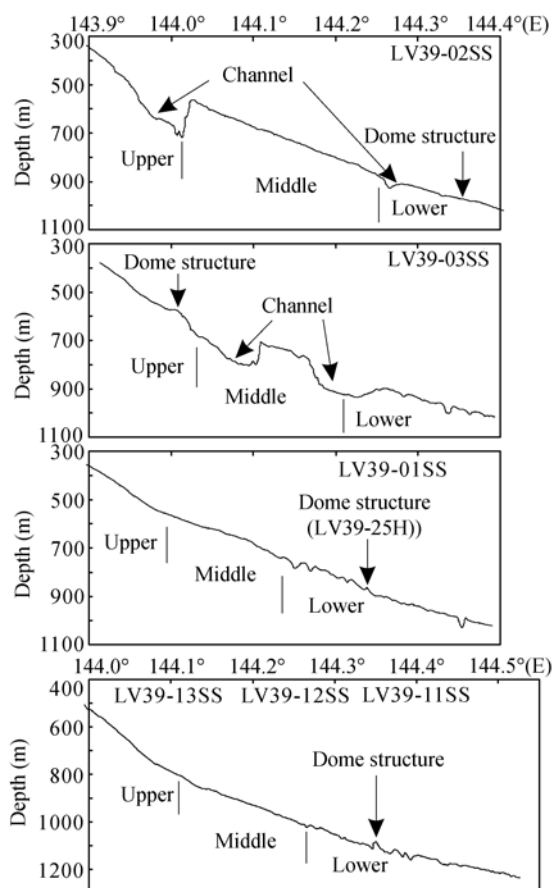
**Figure 2** The track lines, sites of methane flare (diamonds) and sites of gravity coring (black circles).



**Figure 3** Methane flare on the monitor screen.

## 2 The dome structure

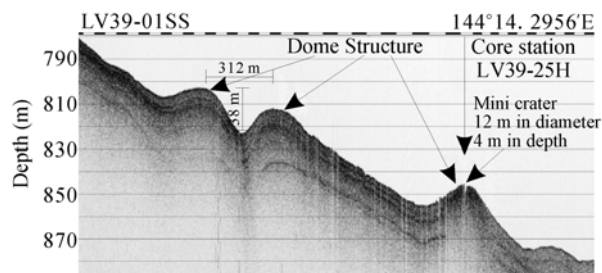
A deep water sonar system was used during the cruise, which composed of a 30 kHz side-scan sonar and a 8 kHz subbottom profiler. Both were towed and worked near to the sea bottom. A pressure sensor and a fish track underwater navigation system were also combined to indicate the working depth and the position. The objectives of the deep water sonar system survey were to search for the structures that related to discharge of fluids or gas on the seafloor and mapping the seafloor topography (Figure 4).



**Figure 4** Slope topography of the study area.

Dome structures were found by the sonar system alongslope (Figure 4). Figure 5 shows a dome structure on Line LV39-01SS about 600 m in diameters, and 40 m in height. As formed alongslope, the dome structure is often unsymmetry, having a slightly longer lower wing than that of the upper wing (Figure 5). A mini crater of

several meters in deep and about 10 m in diameter on top of dome structure is also shown on Figure 4, which was not found on other dome structures. Gravity coring in this cruise focused on these slope dome structures, of which two retrieved gas hydrate samples. It is believed that the mini crater on top of the dome structure indicates the outlet of the gas venting.

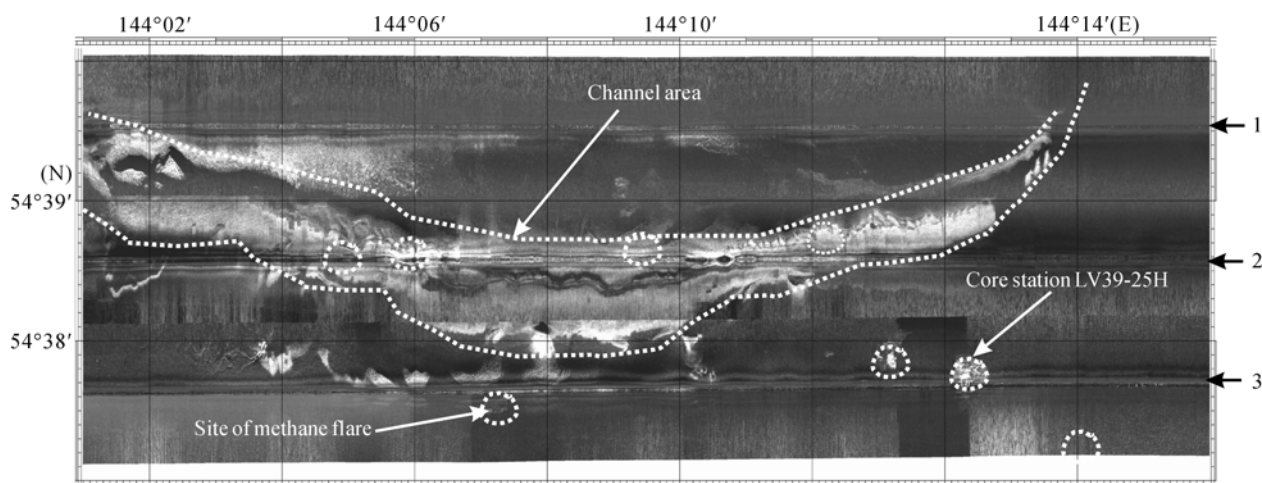


**Figure 5** Dome structure on the subbottom profile.

The side-scan sonar results show that the dome structures on slope did not join each other forming a pattern like sand ridge, but occurred in isolation. On side-scan image, those dome structures highlighted in bright dots in diameter of about 700 m. After the methane flares were located on the side-scan image, we found that almost all the methane flares matched the bright dots indicating the slope dome structures (Figure 6).

### 3 Characteristics of shallow gas hydrates

Gas hydrate samples were retrieved at Stations LV39-25H and LV39-40H (Figure 2). Station LV39-25H is on a lower slope dome structure in the north part of target area, in 880 m deep (Figure 4), and the Station LV39-40H is on a middle slope dome structure in the



**Figure 6** Bright dots on the side-scan image. 1, Sample LV39-02SS; 2, Sample LV39-03SS; 3, Sample LV39-01SS.



middle part of target area, in 670 m deep. Methane flares (Figure 3) and bright dots are all discovered on the two coring stations (Figure 6).

When gravity corer in Stations LV39-25H and LV39-40H was lifted to the sea surface, intensive gas bubbling was observed from the head of gravity corer. After the sediment core was transferred from deck to laboratory, noise of bubble cracking releasing from the sediment could still be heard and with very strong  $H_2S$  odor. The sediment is composed mainly of diatomic clayey silt, with fragments of bivalve shells, authigenic carbonate crusts and nodules, and some pebbles.

The gravity core at Station LV39-25H covered 270 cm of sedimentary section. Between 20 and 110 cm from the top appeared smooth and flat, below 110 cm, it became rough and showing a gas related structure. Gas hydrates occurred in the rough section, mainly between 150–210 cm, and 230–270 cm from the top. It took the form of melting ice, discontinuously and vertically embedded in the sediment, forming a pattern of rising vapour (Figure 7(a)). The gas hydrate was crystal flakes and white in color, about 1–2 cm in thickness, and 2–5 cm in width (Figure 7(b)). Close-up observation would see many tiny bubbles surrounding gas hydrate crystals, forming a “bubble skin” for the hydrate flake. The gas hydrate content in hydrate-bearing intervals was estimated 5% of sediment volume.

The gravity core in LV39-40H was 265 cm long. Gas hydrate occurred between 165 and 265 cm top down. Unlike rising-vapour distribution in Station LV39-25H, the gas hydrates were interbedded in thin horizontal lamination, or lenses from a few millimeters to 3 cm in thickness. Two neighboring hydrate layers were often

connected by a third inclined tilted band in thickness of a few millimeters to 3 cm. Gas hydrate content in hydrate-bearing intervals estimated visually 5%–30% of sediment volume (Figure 8).

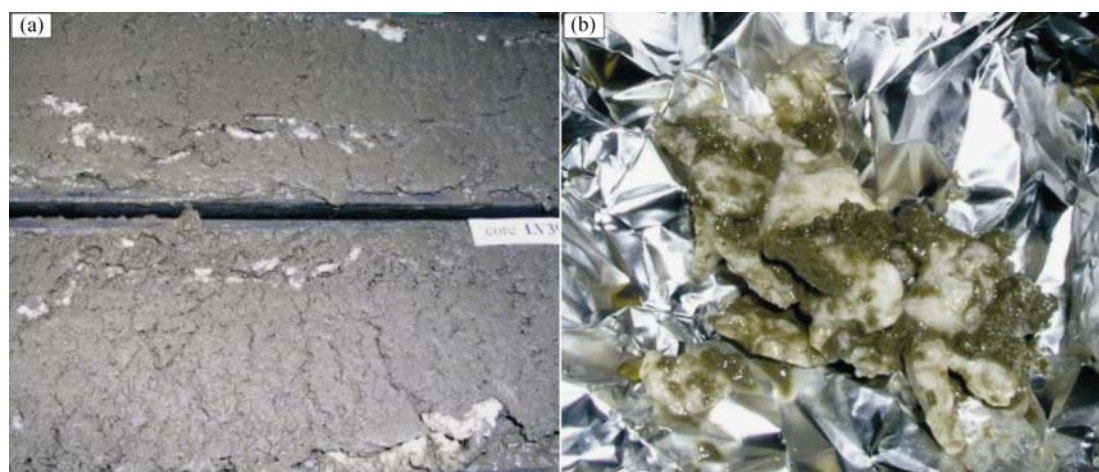
The temperature of sedimentary core was measured immediately when it was transferred to the laboratory in the vessel. The hydrate-bearing sediments were cooler than that of blank sediment. For example, the temperature of hydrate-bearing interval in core LV39-40H was about  $0.8^{\circ}C$ , while that of blank sediment was  $2.5$ – $4.0^{\circ}C$ , indicating endothermic reaction in hydrate decomposition.

## 4 Discussion

Gas bubbling observed when the gravity corer was lifted to the sea surface, Noise of bubbling releasing from the sediment in the laboratory all indicated the existence of gas content in the sediment.

Gas hydrates in both cores LV39-25H and LV39-40H did not decomposed completely and remained during the time of observation in the ship laboratory or even 30 min later (Figures 7 and 8). Therefore, the process of gas hydrate decomposition is slow.

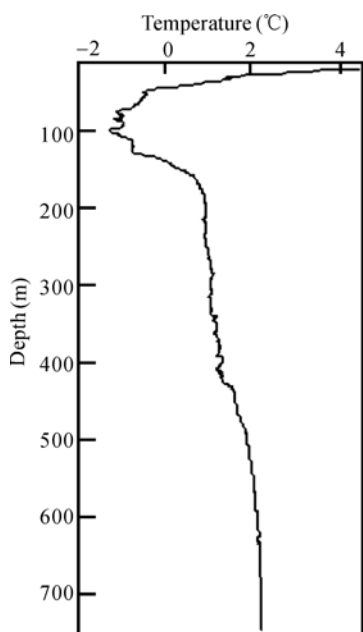
Figure 9 shows a typical temperature profile of the water column from CTD measurement in the study area. The bottom temperature of Sakhalin Slope area was  $1$ – $2^{\circ}C$  in May. The temperature decreased slightly when the CTD was lifted up from the bottom. There was usually a lower temperature cap between 80–120 m from the surface, at about  $0^{\circ}C$ , above which the temperature would increases quickly to  $5$ – $8^{\circ}C$  as the CTD reaches to the surface.



**Figure 7** Gas hydrate in Station LV39-25H.



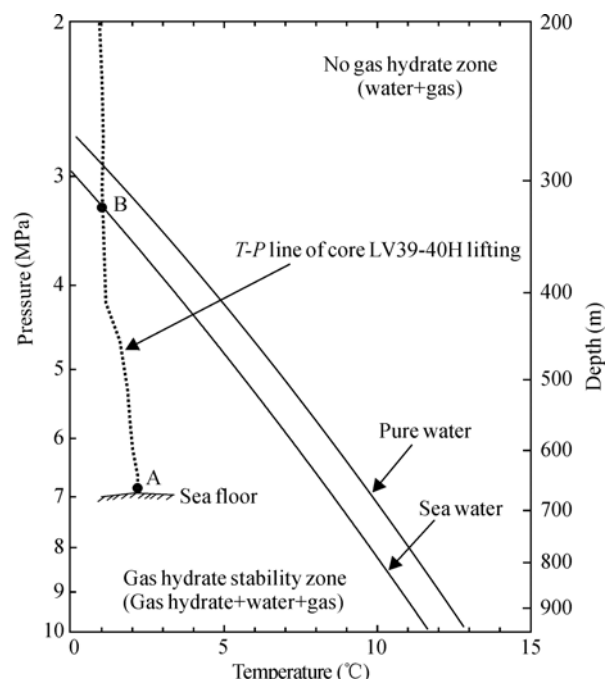
**Figure 8** Gas hydrate in Station LV39-40H.



**Figure 9** A typical temperature profile of the water column from CTD measurement in the study area.

Take the temperature/pressure of core station LV39-40H as example. The gas hydrate phase diagram (Figure 10) [18,19] tells that gas hydrate was in the gas hydrate stability zone as it was lifted from sea floor A until to B (see Figure 10), and it would remain undecomposed during this stage. However, when the core was lifted above B, the gas hydrate would begin to decompose due to higher temperature and lower pressure. It took only 5 minutes for the gravity corer from B (330 m, see Figure 10) to the sea surface in normal winch speed. Judging with our observation, the gas hydrate decomposition under the ship laboratory condition would not decompose out completely.

Therefore, it is believed that if gas hydrates have already formed in the sediment under the sea floor, it can be still seen in the gravity core on the ship. In fact, we



**Figure 10** Temperature and pressure changes during the corer lifting (based on refs. [18, 19]).

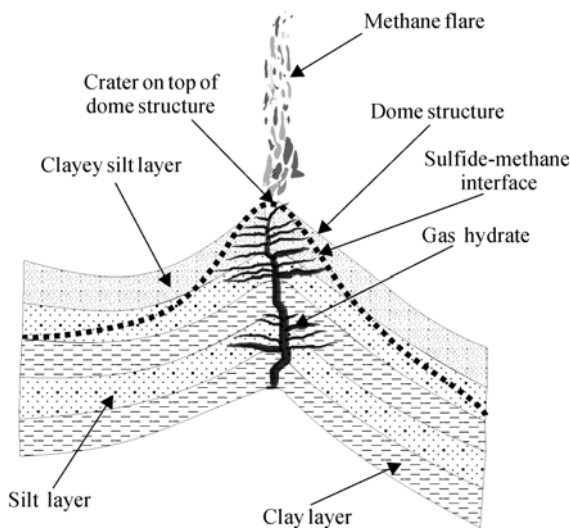
retrieved gas hydrate samples in only two gravity cores, in most of other ones, we evidenced gases other than gas hydrate. So we supposed that not all of the gases we saw on the sea surface and in the laboratory were from gas hydrate decomposition during being taken from the gas hydrate stability zone, free gases must have been originally in the sediment layer under the sea floor.

Laboratory examinations show that the main factors affecting gas hydrates formation are temperature, pressure, space and source of gas [20,21]. Near to the sea floor, spaces and water are enough in loose and shallow sediment for the formation of gas hydrate. In the study area, the water depth was over than 500 m, and the temperature near the sea floor was cold enough for the formation (Figure 10). So in the area of Sakhalin Slope, the availability of gases became the key factor in the gas hydrate formation.

Commonly, 1 unit volume of gas hydrate can trap as much as 164 unit volumes of methane gas [22]. In other words, for the formation of gas hydrate, the amount of gas must be large enough [21,23]. If there is no enough available gas, gas hydrate may not form even temperature and pressure conditions permit.

The methane flare detected with hydroacoustic complex in this cruise was the evidence of free gas in shallow sediment layer [24,25]. The dome structure may indicate mud volcano or mud diapir on the slope imaged by

side-scan sonar and bottom profiler was the root of gas venting<sup>[26–29]</sup>. The side-scan image shows that the size of dome structure was several hundreds meters in diameter (Figure 5), while the free gas outlet (the crater on Figure 5?) on top of the dome structure was several meters in diameter. Most the gravity cores were deployed on the dome structures, but only two of them retrieved gas hydrate. Therefore, free gases had filled indeed within the dome structures, and gas hydrate formed very limited within the central of dome structures where enough free gas was trapped. Figure 11 is an explanatory carton showing gas hydrate formation in shallow area base on our understanding. Tectonically formed structures on sea floor such as dome structures in this region are the free gas centers. The saturated gas was trapped in the center of these structures when they migrated from deep places to the shallow parts and formed gas hydrate under suitable temperature and pressure within the structure. Beyond the structures, due to fewer amount of free gas, gas hydrate could not formed. In shallow area, gas hydrate formation is controlled under the sulfide-methane interface<sup>[30,31]</sup>. Above this interface, micro-organism would consume most of the methane, so gas hydrate could not be formed. As there was no dynamic positioning system equipped on R/V “Akademik Lavr-



**Figure 11** Carton of shallow gas hydrate formation.

entiev”, it was hard to sample core precisely at the climax of a dome structure in size of only several hundreds meters in diameter in 1000 m depth. By chance, only cores of LV39-25H and LV39-40H were placed ideally to the center of dome structure, while others missed. The sulfide-methane interface became deeper away from the climax of dome structure, and would be more difficult to have gas hydrate sampled in this circumstance.

## 5 Conclusions

The methane flares detected by hydroacoustic complex in this cruise in Okhotsk Sea were the evidence of free gas in sediment layer. The dome structures on slope imaged by side-scan sonar and bottom profiler were the root of gas venting. The mini crater developed on top of the dome structure was the outlet of gas venting.

Gas bubbling observed when the gravity corer was lifted to the sea surface, Noise of bubbling releasing from the sediment in the laboratory all indicated the existence of gas content in the sediment.

Two of the gravity cores retrieved gas hydrate sample which was interbedded as thin lamination or lenses with thickness varying from a few millimeters to 3 cm. Gas hydrate content in hydrate-bearing intervals estimated visually 5%–30% of sediment volume.

Gas hydrates in cores of LV39-25H and LV39-40H did not decomposed completely and remained during the time of observation in the ship laboratory or even 30 min later. Therefore, the process of gas hydrate decomposition is slow.

Not all gases in the sediment cores were from gas hydrate decomposition during the gravity core lifting. Free gases may be exit in the gas hydrate stability zone. Tectonic structures like dome structures in this paper were the central places of free gases. Gas hydrate can form unless gases are over-saturated in these special structures under certain conditions of temperature and pressure. Away from the center of the dome structure, the gas concentration is low, and the gas hydrate might not be formed.

- 1 Kudelkin V V, Savitskiy V O, Karpey T I. Structure and evolution of the sediment cover of the near Sakhalin areas of the South-Okhotsk Basin. *Geol Pac Ocean*, 1986, 4: 3–13
- 2 Bikkenina S K, Anosov G I, Argentov V V. Crustal Structure of the Southern Okhotsk Sea According to Seismic Refraction Data (in Russian). Moscow: Science, 1987. 86

- 3 Bogdanov N A, Khain V E. The Tectonic Map of the Sea of Okhotsk Region, Scale 1: 2500000. Moscow: II RAS, 2000
- 4 Ternois Y, Kawamura K, Keigwin L. A biomarker approach for assessing marine and terrigenous inputs to the sediments of Sea of Okhotsk for the last 27000 years. *Geochim Cosmochim Acta*, 2001, 65(5): 791–802<sup>[DOI]</sup>

- 5 Seki O, Yoshikawa C, Nakatsuka T. Fluxes, source and transport of organic matter in the western Sea of Okhotsk: Stable carbon isotopic ratios of n-alkanes and total organic carbon. *Deep-Sea Res Part I. Oceanogr Res Pap*, 2006, 53: 253—270
- 6 Mazurenko L, Soloviev V, Matveeva T, et al. Methane venting on the continental margin off NE Sakhalin: Nature of gas, authigenic carbonates and gas hydrates. *Geophys Res Abstracts*, 2005, 7: 1607—1610
- 7 Bogdanov N A, Chekhovich V D. On collision between the West Kamchatka and Sea of Okhotsk Plate. *Geotectonics*, 2002, 36: 72—85
- 8 Savostin L A, Zonenshain L P, Baranov B V. Geology and plate tectonics of the Sea of Okhotsk. In: Hilde T W C, Uyeda S, eds. *Geodynamics of the Western Pacific-Indonesian Region*. Washington D C: American Geophysical Union, 1983. 189—222
- 9 Rozhdestvenskiy S S. Evolution of the Sakhalin folds system. *Tectonophysics*, 1986, 127: 331—339[DOI]
- 10 Ludmann T, Wong H K. Characteristics of gas hydrate occurrences associated with mud diapirism and gas escape structures in the northwestern Sea of Okhotsk. *Mar Geol*, 2003, 201: 269—286[DOI]
- 11 Shakirov R, Obzhairov A, Suess E. Mud volcanoes and gas vents in the Okhotsk Sea area. *Geo-Mar Lett*, 2004, 24: 140—149[DOI]
- 12 Luan X, Zhao K, Sun D, et al. Geological factors for the development of gas hydrates in Okhotsk Sea. *Mar Geol Quat Geol*, 2006, 23(6): 55—68
- 13 Ginsburg G D, Soloviev V A, Cranton R E. Gas hydrate from continental slope offshore from Sakhalin Island, Okhotsk Sea. *Geo-Marine Lett*, 1993, 13: 41—48
- 14 Obzhairov A I, Astakhov A S, Astakhov N V. Genesis and conditions for the formation of autogenetic carbonates in the Quaternary sediments layers in the gas-anomaly area of the Sakhalin-Derugin Basin, Sea of Okhotsk. *Oceanologia*, 2000, 40: 280—288
- 15 Biebow N, Ludmann T, Karp B. Cruise Reports: KOMEX V and VI GEOMAR Report. Kiel: GEOMAR, 2000. 88
- 16 Shoji H, Soloviev V, Matveeva T. Hydrate-Bearing Structures in the Sea of Okhotsk. *EOS*, 2005, 86: 13—24[DOI]
- 17 Jin Y K, Obzhairov A, Shoji H, et al. CHAOS III Project Cruise Report: RV Akademik M.A. Lavrentiev Cruise 39, May 24— June 18, 2006. Incheon: KORPRI, 2007. 132. ISSN978-89-990160
- 18 Englezos P, Bishnoi P R. Prediction of gas hydrate formation in aqueous solutions. *Am Inst Chem Eng*, 1988, 34: 1718—1721
- 19 Dickens G R, Quinby-Hunt M S. Methane hydrate stability in seawater. *Geophys Res Lett*, 1994, 21: 2115—2118[DOI]
- 20 Sloan J. *Clathrate Hydrates of Natural Gas*. New York: Marcel Dekker, 1998. 1—100
- 21 Waseda A. Organic carbon content, bacterial methanogenesis, and accumulation processes of gas hydrates in marine sediments. *Geochemica*, 1998, 32: 143—157
- 22 Davidson D W, El-Defrawy M K, Fuglem M O. Natural gas hydrates in northern Canada, in National Research Council of Canada. *Proceedings 3rd International Conference on Permafrost 1*, 1978. 938—943
- 23 Lu H. Preliminary experimental results of the stable *P-T* condition of methane hydrate in a nonfossil clay. *Geochemica*, 2002, 36: 21—30
- 24 Klaucke I, Sahling H, Weinrebe W, et al. Acoustic investigation of cold seeps offshore Georgia, eastern Black Sea. *Mar Geol*, 2006, 231(1-4): 51—67[DOI]
- 25 Sauter E J, Muyakshin S I, Charlou J L, et al. Methane discharge from a deep-sea submarine mud volcano into the upper water column by gas hydrate-coated methane bubbles. *Earth Planet Sci Lett*, 2006, 243(3-4): 354—365[DOI]
- 26 Limonov F, Weering T, Kenyon N H, et al. Seabed morphology and gas venting in the Black Sea mudvolcano area: Observations with the MAK-1 deep-tow sidescan sonar and bottom profiler. *Mar Geol*, 1997, 137(1-2): 121—136[DOI]
- 27 Kruglyakova R, Gubanov Y, Kruglyakov V, et al. Assessment of technogenic and natural hydrocarbon supply into the Black Sea and seabed sediments. *Cont Shelf Res*, 2002, 22(16): 2395—2407[DOI]
- 28 Somoza L, Díaz-del-Río V, León R, et al. Seabed morphology and hydrocarbon seepage in the Gulf of Cádiz mud volcano area: Acoustic imagery, multibeam and ultra-high resolution seismic data. *Mar Geol*, 2003, 195(1-4): 153—176[DOI]
- 29 Naudts L, Greinert J, Artemov Y, et al. Geological and morphological setting of 2778 methane seeps in the Dnepr paleo-delta, northwestern Black Sea. *Mar Geol*, 2006, 227(3-4): 177—199[DOI]
- 30 Treude T, Niggemann J, Kallmeyer J, et al. Anaerobic oxidation of methane and sulfate reduction along the Chilean continental margin. *Geochim Cosmochim Acta*, 2005, 69(11): 2767—2779[DOI]
- 31 Orcutt B N, Boetius A, Lugo S K, et al. Life at the edge of methane ice: microbial cycling of carbon and sulfur in Gulf of Mexico gas hydrates. *Chem Geol*, 2004, 205: 239—251[DOI]