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Isotopic composition of gas hydrates in subsurface sediments from offshore Sakhalin Island, Sea of Okhotsk

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Abstract Hydrate-bearing sediment cores were retrieved from recently discovered seepage sites located offshore Sakhalin Island in the Sea of Okhotsk. We obtained samples of natural gas hydrates and dissolved gas in pore water using a headspace gas method for determining their molecular and isotopic compositions. Molecular composition ratios $C_1/_{C2+}$ from all the seepage sites were in the range of 1,500–50,000, while $\delta^{13}C$ and δD values of methane ranged from −66.0 to −63.2‰ VPDB and −204.6 to −196.7‰ VSMOW, respectively. These results indicate that the methane was produced by microbial reduction of CO_2. $\delta^{13}C$ values of ethane and propane (i.e., −40.8 to −27.4‰ VPDB and −41.3 to −30.6‰ VPDB, respectively) showed that small amounts of thermogenic gas were mixed with microbial methane. We also analyzed the isotopic difference between hydrate-bound and dissolved gases, and discovered that the magnitude by which the δD hydrate gas was smaller than that of dissolved gas was in the range 4.3–16.6‰, while there were no differences in $\delta^{13}C$ values. Based on isotopic fractionation of guest gas during the formation of gas hydrate, we conclude that the current gas in the pore water is the source of the gas hydrate at the VNIIOkeangeologia and Giselle Flare sites, but not the source of the gas hydrate at the Hieroglyph and KOPRI sites.

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Introduction

Natural gas hydrates in the Sea of Okhotsk were first discovered in marine sediments near the seafloor located northwest of Paramushir Island in 1986 (Zonenshayn et al. 1987; Lein et al. 1989), and offshore to the northeast of Sakhalin Island in 1991 (Ginsburg et al. 1993; Cranston et al. 1994). In these fields, gas plumes vent from the seafloor. Geological, geophysical, and geochemical approaches have been attempted by many researchers as described by Ginsburg and Soloviev (1998), and references cited therein. A gas hydrate sample was retrieved from one of the gas seepage sites located offshore Sakhalin Island at a sub-bottom depth of 0.30–1.95 m (Ginsburg et al. 1993). The main component of that guest gas was microbial methane (C_1), produced by CO_2 reduction. For the Russian–German project KOMEX (Kurile-Okhotsk Sea Marine Experiment), seepage sites offshore Sakhalin Island were mapped by Biebow and Hütten (1999). One of the sites, where gas hydrate was discovered (Ginsburg et al. 1993), was named the Obzhirov Flare. On the KOMEX-2002 cruise (29th cruise onboard R/V *Akademik M.A. Lavrentyev*), gas hydrates were sampled again at the Obzhirov Flare, and it was found that gas hydrate was formed from an upward-migrating fluid, as interpreted from the perspective of pore water geochemistry (Matveeva et al. 2003). Other gas seepage sites were recently investigated as part of the CHAOS project (hydro-Carbon Hydrate Accumulations in the Okhotsk Sea). As a result of this project, three seepage sites (CHAOS, Hieroglyph, and Kitami) containing gas hydrate were discovered in 2003 (Matveeva et al. 2005; Shoji et al. 2005). Moreover, gas hydrate samples were retrieved from the Giselle Flare, where a gas flare is active in the upper part of the Sakhalin slope (Sahling et al. 2003; Obzhirov et al. 2004). Six new seepage sites (KOPRI, POI, VNIIOkeangeologia, Soloviev, KIT, and Dungeon) were discovered in 2005–2006 (Jin et al. 2006, 2007).

Molecular composition of hydrate-bound gas determines the crystallographic structures of gas hydrate. Takeya et al. (2006) and Kida (2007) reported that the crystallographic structures of the C_1-rich hydrate-bound gas obtained from the Kitami, Hieroglyph, and CHAOS seepages had the structure I (sI), using powder X-ray diffraction and ^{13}C NMR techniques, respectively. On the other hand, C_3 and iC_4 are known to be structure II (sII) hydrate formers, and are trapped only in large cages of sII (Sloan and Koh 2007). Although nC_4 cannot produce a simple gas hydrate of sI and sII, due to its large molecular size, sII hydrate can trap nC_4 into its large cages using C_1 as a “help gas” (Wu et al. 1976). The “help gas” supports the formation of the structure by filling in small cages. C_3 is excluded from the crystal lattice of sI, or it is first concentrated in sII during natural gas hydrate formation (Milkov et al. 2004).

The stable isotope ratio of hydrate-bound gases is useful not only to identify their gas sources, but also to assess the formation process of gas hydrates. Since isotopic fractionation of hydrocarbons occurs in the formation process of gas hydrates, isotopic differences between the hydrate-bound gas and dissolved gas in pore water provide information to assess if the current gas in pore water is the source of the hydrate-bound gas (Hachikubo et al. 2007, 2009a).

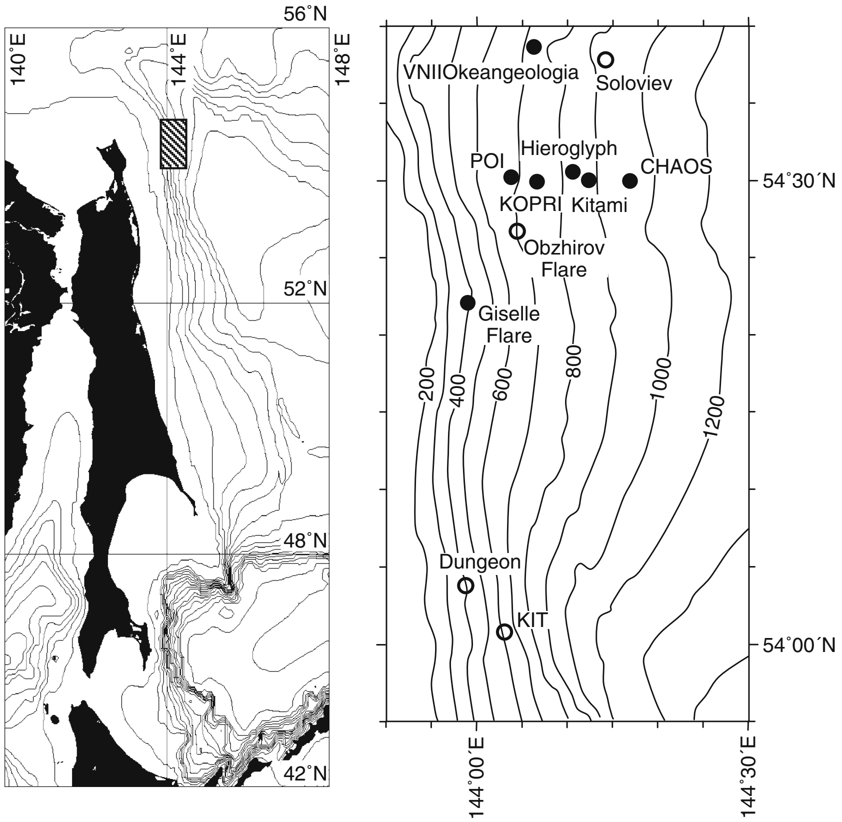
In this study, we used the molecular and isotopic compositions of the hydrate-bound and dissolved gases in pore water to trace gas sources, and the isotopic fractionation of the guest gas to determine the origin of the gas hydrate.

Materials and methods

Study areas

In the CHAOS project, eleven seepage sites were investigated offshore of northeast Sakhalin Island, Sea of Okhotsk (Fig. 1). The research was conducted during cruises

Fig. 1 Location map of seepage sites (structures) offshore northeast Sakhalin Island, Sea of Okhotsk. *Solid circles* Sampling sites of gas hydrates in this study, *open circles* data from other studies



onboard the R/V *Akademik M.A. Lavrentyev* (LV; Matveeva et al. 2005; Jin et al. 2006, 2007). Gas hydrate samples were obtained from seven sites: Kitami, Hieroglyph, and CHAOS sites in October 2003 (LV32 cruise, Leg II), KOPRI, VNIIOkeangeologia, and Giselle Flare sites in May–June 2005 (LV36 cruise), and the POI site in June 2006 (LV39 cruise), as shown in Table 1. Hydrate-bearing sediments were retrieved using a gravity or hydrostatic corer (5 or 9 m in length, 0.10 m inner diameter). Water depth of these sites ranged from 390 to 960 m (Table 1).

Sample analyses

Hydrate-bound gases were retrieved in the laboratory from gas hydrate samples stored at liquid nitrogen temperature. Gases of LV39-40H alone were collected on board using a plastic syringe, and injected into 5-mL sealed vials employing a butyl rubber septum. The dissolved gases in the pore water were analyzed by a headspace gas method described as follows: about 5 mL sediment and 10 mL $HgCl_2$ aqueous solution (5 wt%) were introduced into a 20-mL vial to make a headspace. Gas composition of hydrocarbons (from C_1 to C_4) and H_2S was measured using a gas chromatograph (GC-14B, Shimadzu Corp.) equipped with thermal conductivity and flame ionization detectors coupled with a packed column (Sunpak-S, Shimadzu Corp.). Carbon and hydrogen isotopes from C_1 to C_3 were measured using a CF-IRMS (DELTA plus XP, Thermo Finnigan), employing a Carboxen-1006 PLOT capillary column (30 m×0.32 mm I.D., Supelco). To avoid air contamination in low concentration samples of C_1, a Carboxen1010 PLOT capillary column (30 m×0.32 mm I. D., Supelco) also was used. A backflush system of GC coupled with CF-IRMS enabled us to resolve low concentrations of C_2 and C_3 (less than 0.1%) from C_1, and measure their isotopic composition. Isotopic compositions are defined in terms of δ values (in ‰) as follows:

$$\delta_{\mathrm{sample}} = \left(\frac{\mathrm{R_{sample}} - \mathrm{R_{standard}}}{\mathrm{R_{standard}}}\right) \times 1,000 \qquad (1)$$

where R denotes the ratio of $^{13}C/^{12}C$ or D/H, and δ values ($\delta^{13}C$ and δD) are reported with reference to VPDB and VSMOW standards, respectively. The analytical precision of $\delta^{13}C$ is 0.1‰, and that of δD is 0.6‰.

Results and discussion

Molecular and isotopic compositions of hydrocarbons in the gas hydrate samples are reported in Table 2, available online as electronic supplementary material. C_1 is the main component of the gas hydrate (more than 97.8%), and concentrations of C_2, C_3, iC_4, and nC_4 are in the range of 15–630 ppm (median: 36 ppm), 2–25 ppm (median: 3 ppm), 0–21 ppm (median: 0 ppm), and 0–6 ppm (median: 0 ppm), respectively. From the gas composition, the crystallographic structure was mainly sI. A very small amount of sII hydrate containing large hydrocarbons (C_3, iC_4, and nC_4) might have mixed with the sI hydrate, but it is likely that these heavy hydrocarbons were excluded from the sI crystal lattice and existed in the grain boundaries of the polycrystalline gas hydrate. In addition, H_2S was detected in the range of 0–2.2%. Raman spectroscopy confirmed that the hydrate samples of LV36-39H (KOPRI site), containing H_2S as a guest molecule, were found in both large and small cages of sI (Hachikubo et al. 2009b).

Figure 2 shows the relation between the isotopic ratios and gas composition of hydrate-bound gas sampled from the different sites in the Sea of Okhotsk. All the gas samples were located in a field of microbial gas (e.g., Whiticar et al. 1986; Schoell 1988), with a range in molecular composition of C_1/C_{2+} from 1,500 to 50,000, and $\delta^{13}C$ of the C_1 component ranging from −66.0 to −63.2‰, respectively (Fig. 2a). Additional information for interpreting the gas origin is provided by δD of C_1, as shown in Fig. 2b. According to this $\delta^{13}C$–δD diagram (Whiticar et al. 1986, 1999; Milkov 2005), data for C_1 hydrate-bound gas in the Sea of Okhotsk plot as having a microbial origin produced by CO_2 reduction. All the sites

Table 1 Position, water depth, and core length of hydrate-bearing cores at each site

Structure	Core name	Latitude	Longitude	Water depth (mbsf)	Core length (m)
Kitami	LV32-09GC	54.500°N	144.201°E	860	1.82
	LV32-11HC	54.500°N	144.213°E	855	2.5[a]
Hieroglyph	LV32-13GC	54.509°N	144.179°E	830	1.87
CHAOS	LV32-16GC	54.500°N	144.286°E	960	5.00
KOPRI	LV36-15H	54.498°N	144.113°E	721	1.65
	LV36-39H	54.498°N	144.111°E	720	1.20
VNIIOkeangeologia	LV36-59H	54.643°N	144.107°E	720	1.10
Giselle Flare	LV36-61H	54.367°N	143.984°E	390	0.68
POI	LV39-40H	54.503°N	144.065°E	670	2.60

[a] Estimated value, because the sediment portion was washed away from the corer during retrieval

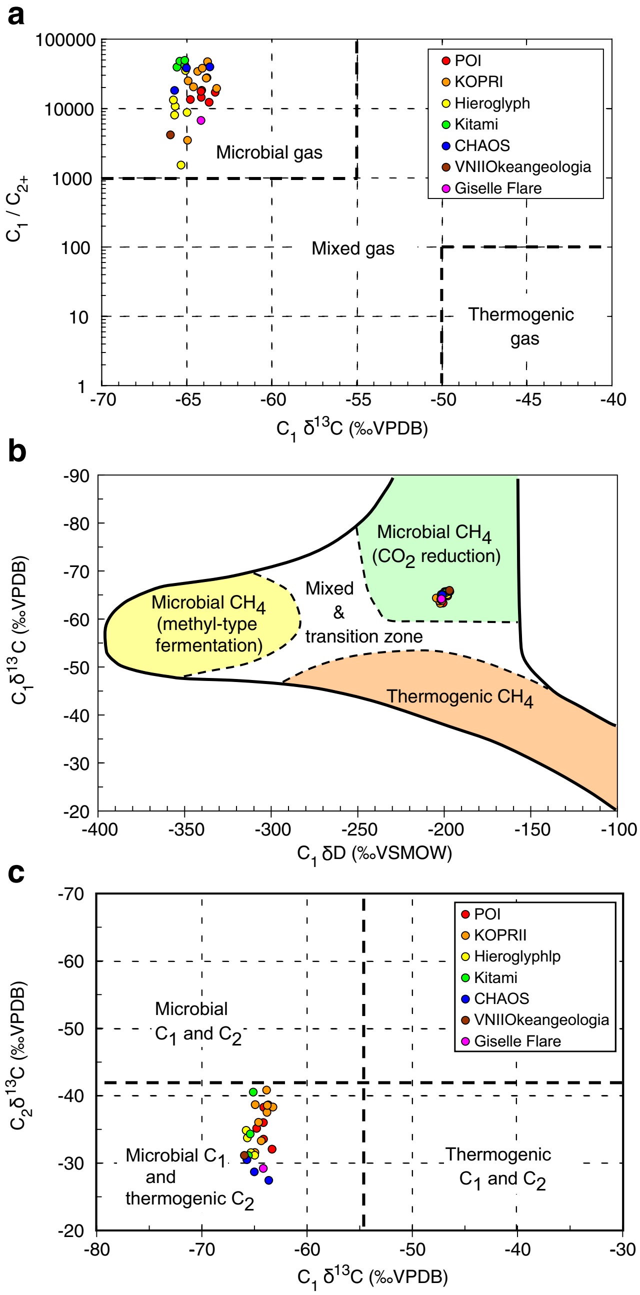


Fig. 2 Relationship between molecular and isotopic compositions. **a** C_1 $\delta^{13}C$ and the ratio C_1/C_{2+}. **b** $\delta^{13}C$ and δD of C_1. **c** $\delta^{13}C$ of C_1 and C_2. The gas origin fields are in accordance with Whiticar (1999), Taylor et al. (2000), and Milkov (2005)

have nearly the same C_1 isotopic composition, and C_1 δD is concentrated in the range of −204.6 to −196.7‰. Isotope data of hydrate-bound gas at the Obzhirov Flare site (Fig. 1) were reported as $\delta^{13}C$=−64.3‰ and δD=−207‰ (Ginsburg et al. 1993), and our isotope data agree well with this published information. The hydrate-bound C_1 at Blake Ridge located offshore of the southeastern United States (Lorenson and Collett 2000), the Black Sea (Blinova et al. 2003), the Congo-Angola Basin offshore of Gabon (Charlou et al. 2004), and Hydrate Ridge offshore of Oregon (Milkov et al. 2005) all are of microbial origin produced by CO_2 reduction, with $\delta^{13}C$ of the C_1 isotopes ranging from −69 to −64‰, while δD ranged from −199 to −186‰. Hence, there is a similarity of C_1 isotope values, not only among the hydrate-bearing sites located offshore of Sakhalin Island (about 100 km^2, see Fig. 1), but also throughout the world, even though they include a variety of gas migration pathways.

The relationship between $\delta^{13}C$ of C_1 and C_2 is shown in Fig. 2c. The boundaries between thermogenic and microbial origins are based on literature information (Taylor et al. 2000; Milkov 2005; Sassen and Curiale 2006). The distribution of $\delta^{13}C$ of C_2 is in the range of −40.8 to −27.4‰ (cf. Table 2 in electronic supplementary material), indicating a thermogenic origin of C_2. The distribution of $\delta^{13}C$ of C_3 is in the range of −41.3 to −30.6‰ (Table 2), and also is nearly the same as that of C_2. Matveeva et al. (2003) reported upward fluid infiltration with enhanced K^+, Mg^{2+}, and Cl^- concentrations at the Obzhirov Flare site. At the CHAOS and Kitami sites, depth profiles of pore-water δD suggest the existence of ascending fluid (Minami et al. 2009). Besides this, the geothermal gradient at the seafloor was up to seven times greater than that of the background value at the CHAOS site (Matveeva et al. 2005). Seismic profiles for the Hieroglyph, CHAOS, and Kitami sites show gas chimneys from the depths of the bottom simulating reflector (BSR), and an echogram shows active gas plumes from the seafloor (Shoji et al. 2009). Although the seismic images beneath the BSR were not clear at the above sites, in the southern area of the Dungeon and KIT sites (Fig. 1) gas chimneys initiate below the depth of the BSR (Baranov et al. 2008). Therefore, it is likely that ascending fluids from the deeper sediment layers provide small amounts of thermogenic gas containing hydrocarbons of higher $\delta^{13}C$ values, and form a mixed-gas hydrate with light microbial C_1.

Figure 3 shows the C_1 isotopic compositions of hydrate-bound gas and dissolved gas in pore water at the Hieroglyph (LV32-13GC), KOPRI (LV36-15H), VNIIOkeangeologia (LV36-59H), and Giselle Flare (LV36-61H) sites plotted against distance to the seafloor. It was found that C_1 $\delta^{13}C$ and/or δD of dissolved gas was depleted at 40 cm depth in the LV32-13GC, 120–140 cm depth in the LV36-15H, 70–83 cm depth in the LV36-59H, and 50–58 cm depth in the LV36-61H cores. These depths correspond to the layer in which H_2S is detected (cf. Table 3 available online as electronic supplementary material), with the exception of the LV32-13GC and LV36-59H cores where no data on gas composition are available. From the depth profile of sulfate and carbonate concretions, the sulfate–methane interface (SMI) is centered at about 40 cmbsf in the LV32-13GC core (Minami et al. 2009), which agrees with the depth of minimum C_1 $\delta^{13}C$ (Fig. 3a). These ^{13}C-depleted C_1 values are due to an ongoing biogeochemical process: anaerobic

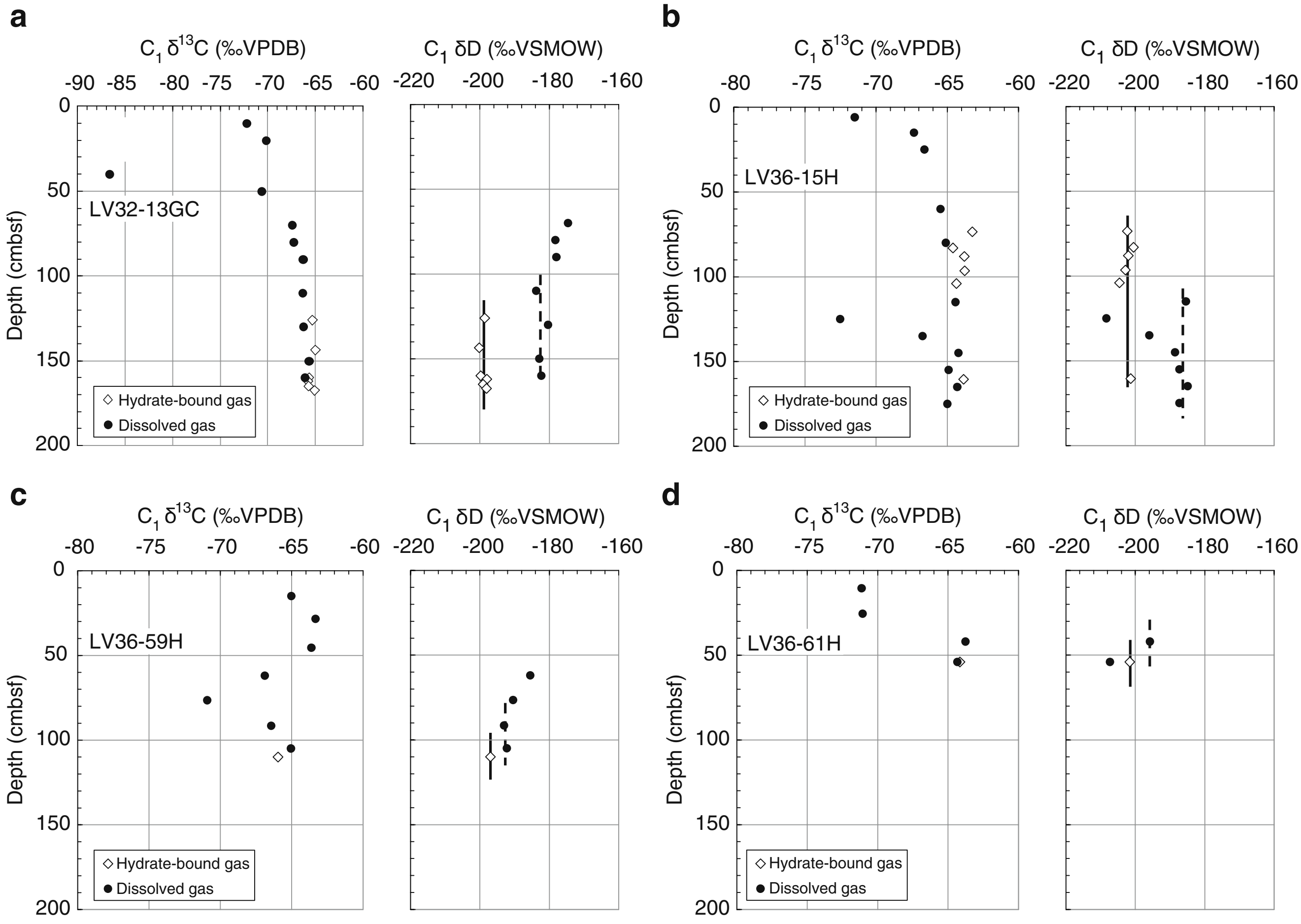


Fig. 3 Depth profiles of C_1 $\delta^{13}C$ and δD. **a** LV32-13GC, Hieroglyph, **b** LV36-15H, KOPRI, **c** LV3659H, VNIIOkeangeologia, and **d** LV36-61H, Giselle Flare. *Solid* and *dashed lines* indicate the hydrate-bound and dissolved C_1 in pore water, respectively

oxidation of methane (AOM) produces ^{13}C-depleted CO_2, and ^{13}C-depleted C_1 also is generated via CO_2 reduction (Borowski et al. 1997). Upward-migrating C_1 and downward-diffusing SO_4^{2-} are consumed at the depth of the SMI, and H_2S is still produced by sulfate reduction. Although we have no data for sulfate in the LV36-15H, LV36-59H, and LV36-61H cores, it seems reasonable to presume that the depth of the SMI corresponds to that of C_1 $\delta^{13}C$ and/or H_2S anomaly. The profiles of C_1 $\delta^{13}C$ seem to decrease upward, and are small in 0–20 cmbsf in the LV32-13GC, LV36-15H, and LV36-61H cores. We cannot interpret this trend, however, because of the small size of the C_1 pool above the depth of the SMI.

C_1 δD of hydrate-bound gas was approximately 4–17‰ less than that of dissolved gas in pore water, while C_1 $\delta^{13}C$ of the hydrate-bound gas was nearly the same as that of the dissolved gas in pore water located at the same depth (Fig. 3). During the formation of gas hydrates, isotopic fractionation of hydrocarbon gases occurs between the original gas and hydrate phases (Hachikubo et al. 2007). Hachikubo et al. (2007) produced synthetic C_1 hydrates in a pressure cell, and proved that δD of hydrate-bound C_1 becomes 4.8±0.4‰ less than that of the residual C_1 at 274.2 K, whereas $\delta^{13}C$ of hydrate-bound C_1 and residual C_1 remains almost constant. Based on these results, we conclude that hydrates in the LV36-59H (isotopic difference in δD: 4.3‰) and LV36-61H (5.8‰) cores are formed from the current gas dissolved in pore water.

On the other hand, the difference in δD between hydrate-bound and dissolved gases appears to be too large in cases within the LV32-13GC (16.6‰) and LV36-15H (16.1‰) cores to be explained by isotopic fractionation. Shoji et al. (2009) showed that almost no pull-up/disturbance of the BSR was observed at the Hieroglyph site by seismic imaging, suggesting low heat flux at this location. Conversely, these characteristics of the BSR around the gas chimney were interpreted as significant heat flows caused by ascending fluid at both the Kitami and CHAOS sites. Two gas plumes also were observed at the Hieroglyph site in the echogram (Shoji et al. 2009), suggesting active gas seepage. In addition, from the viewpoint of pore-water geochemistry, Minami et al. (2009) revealed that traces of ascending water from deeper in the sediment column are not found in core LV32-13GC (Hieroglyph site). Collectively, this evidence makes it clear that the ascending fluid is gas only at the Hieroglyph site. In the process of CO_2 reduction, the source of hydrogen in C_1 is water (Daniels et al. 1980; Valentine et al. 2004), as a simple linear relationship exists between C_1 δD and δD of the formation water (e.g., Whiticar et al. 1986). Assuming that the pore water still remains in the sediment layer where C_1 was formed by CO_2 reduction, we can explain the greater difference in C_1 δD in the LV32-13GC core as follows: light C_1 was first produced in the process of CO_2 reduction, and escaped upward. Heavy water remained (HDO is concentrated) in the sediment layer, and rather heavy C_1 in δD was then produced in the next stage. Gas hydrates in the upper layer formed from ascending light C_1, and δD of dissolved gas in pore water then increased by the ascending heavy C_1. Seismic data (Jin et al. 2006) at the KOPRI site show less disturbance of the BSR, and agree with the idea that the isotopic profiles of the LV36-15H core (KOPRI site) appear similar to those of the LV32-13GC core (Hieroglyph site). Therefore, it is reasonable to conclude that the current (present) gas in pore waters is not the source of gas hydrates in the LV32-13GC and LV36-15H cores.

Concluding remarks

We investigated molecular and isotopic compositions of hydrate-bound gas and dissolved gas in pore water, which were obtained using hydrate-bearing sediment cores located offshore Sakhalin Island in the Sea of Okhotsk. The main component of the hydrate-bound gas was microbial C_1 produced by CO_2 reduction at all seepage sites. Hydrate-bound gas sometimes contained H_2S levels on the order of a few percent, and also contained C_2 levels on the order of 10 or more ppm, and $C_{3–4}$ on the order of a few ppm. Because sI gas hydrates can encage only C_1, C_2, and H_2S, further investigation will be required to find sII gas hydrates and/or where and how the gas hydrate samples incorporated $C_{3–4}$. $\delta^{13}C$ of C_2 and C_3 indicated their thermogenic origin, and it seems likely that they are supplied by an ascending fluid from a deeper layer. The data of dissolved gas in pore water showed a layer of ^{13}C-depleted C_1 and/or H_2S rich in some sediment cores, which agrees with the depth of the sulfate–methane interface. The difference in C_1 δD between hydrate-bound gas and dissolved gas in pore water was analyzed, and it was concluded that the current gas in pore water is the source of gas hydrates at the VNIIOkeangeologia and Giselle Flare sites, but it is not the source at the Hieroglyph and KOPRI sites.

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