MOLECULAR AND ISOTOPIC CHARACTERISTICS OF HYDROCARBONS IN SEDIMENTS AND GAS HYDRATE AT EASTERN MARGIN OF JAPAN SEA

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ABSTRACT

We investigated molecular and stable isotope compositions of hydrate-bound gas and dissolved gas in pore water in sediment cores that were retrieved from the eastern margin of Japan Sea to clarify the gas origin and to understand the formation process of shallow gas hydrate accumulated in this area. Hydrate-bearing sediment cores were retrieved from Umitaka Spur and Joetsu Knoll in the Joetsu Basin during a cruise onboard R/V *Marion Dufresne* in June 2010. Hydrate-bound hydrocarbons were primarily thermogenic at Umitaka Spur. On the contrary, those at Joetsu Knoll partly contain microbial methane (C_1) because ^{13}C and deuterium (D) are both depleted and close to the field of microbial C_1 via CO_2 reduction. Depth profiles of C_1 in the sediments showed a minimum concentration of ^{13}C at a depth, corresponding to the SMI depth. C_1 concentration in the sediments increased dramatically beneath the SMI depth. $\delta^{13}C$ of C_1 increased slightly with depth in a deeper layer, whereas δD of C_1 decreased. A high concentration of neopentane ($_{neo}C_5$, 2,2-dimethylpropane) was detected near the depths of gas hydrates. Because $_{neo}C_5$ cannot be encaged in the crystallographic structure I hydrate, it could be discharged from the hydrate crystal during the formation process and remain in the sediment.

Keywords: gas hydrate, Japan Sea, stable isotope, methane, neopentane

INTRODUCTION

Gas hydrates are crystalline clathrate compounds composed of water and gas molecules that are stable at low temperatures and high partial pressures of each gas component. Natural gas hydrates exist in near-surface sediments associated with active gas plumes that vent from a sea or lake floor. Recently, gas hydrate samples were retrieved from Umitaka Spur and Joetsu Knoll in the eastern margin of the Japan Sea [1], where gas venting has been observed by echo-sounder images [2]. The behavior of gas hydrate systems in shallow sediment layers has been studied relative to pore water geochemistry [3, 4]. $\delta^{13}C$ of methane (C_1) in hydrate-bound and seep gases ranged from −50 to −30 ‰VPDB, suggesting a thermogenic origin [1], however, little information is available for about ethane (C_2), propane (C_3), and other hydrocarbons. Although C_1 is the major component of hydrate-bound gases, C_2 and C_3 increase the stability of gas hydrates because of their low equilibrium pressures [5] and their ability to change the crystallographic structure from structure I (sI) to structure II (sII) [6, 7]. Natural gas hydrates of sII discovered worldwide [8–11] contain a significant amount of C_2 and C_3. C_1 and C_2 mixed-gas hydrates discovered in Lake Baikal belong to the sII gas hydrate group and contain

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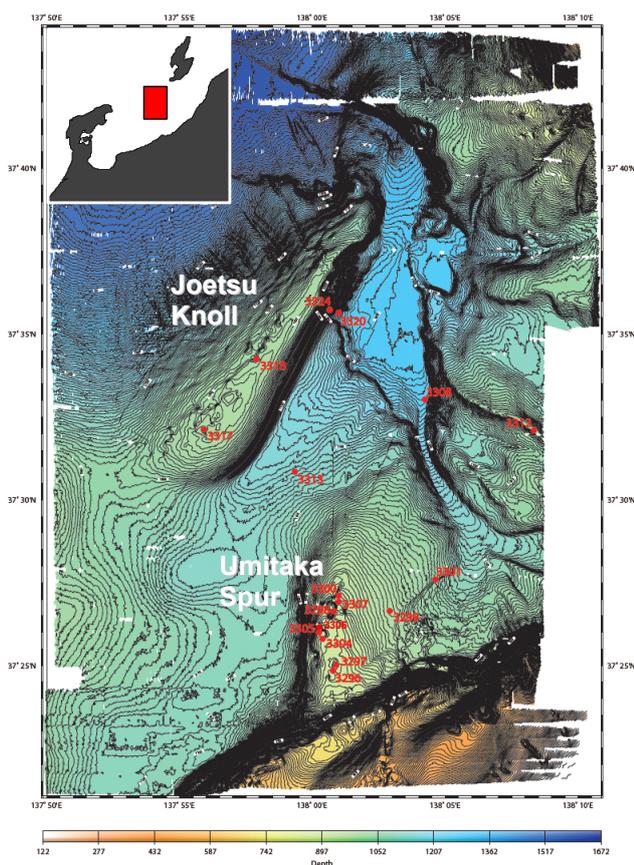
Figure 1 Coring sites of the MD179 cruise: Umitaka Spur and Joetsu Knoll in the Joetsu Basin, Japan Sea.

several hundred ppm of neopentane ($_{neo}C_5$, 2,2-dimethylpropane) [12, 13]. Structure H gas hydrates recovered from northern Cascadia Margin, offshore Vancouver Island [14], can encage large guest molecules. Because thermogenic gas generally contains heavier hydrocarbons, we will clarify the manner in which these hydrocarbons ascending from a deep layer are trapped by gas hydrate formations, dissolve into pore water, and escape to the sea floor. In this study, we investigated molecular and stable isotope compositions of hydrate-bound gas and dissolved gas in pore water in sediment cores that are retrieved from Umitaka Spur and Joetsu Knoll in order to clarify the gas origin and to understand the formation process of the shallow gas hydrate accumulated in this area.

SAMPLING METHODS

The location map of the coring sites of the MD179 cruise is shown in Figure 1. Seventeen sediment

cores were retrieved from the Joetsu Basin during the cruise onboard R/V *Marion Dufresne* in June 2010. A 20–50 m long Calypso giant piston corer enabled us to obtain sediment cores up to 40 m in length. A Calypso square box corer (CASQ, 25 cm × 25 cm square section, 12 m in length) was also used. Hydrate-bearing cores MD10-3305G and MD10-3306 (placed 300 m apart) were retrieved from Umitaka Spur. MD10-3305G was retrieved by a simple gravity corer without a piston coring system. MD10-3317 and MD10-3318C retrieved from Joetsu Knoll also contained gas hydrates. All samples except MD10-3318C that were retrieved using the CASQ corer lost the top part of their sediment layers because the gas hydrates dissociated in the corer and displaced the top part during the recovery process on board.

Hydrate bound gases were collected using a plastic syringe and stored in 5 mL vials sealed with butyl septum stoppers [15–17]. We placed each hydrate sample into a 50 mL plastic syringe, pushed the cylinder to reduce the dead volume, and attached the syringe to a vial with a needle. An additional needle was attached to the vial to flush the air inside. Each vial was then filled with hydrate-bound gas with no sediment particles or pore water present.

The dissolved gases in the pore water were extracted by a headspace gas method whereby 10 mL of sediment, a 9.5 mL saturated aqueous solution of NaCl, and a 0.5 mL preservative (benzalkonium chloride, 10 wt% aqueous solution [18]) were introduced into a 25 mL vial to create a 5 mL headspace. The headspace was flushed with helium because the carrier gas used in gas chromatography was also helium, thereby reducing air contamination. The vials were shaken well and stored upside-down until the gas analysis stage.

SAMPLE ANALYSES

The experimental setup for gas analysis was the same as that used in our previous study [15, 16]. Molecular compositions of hydrocarbons were determined using a gas chromatograph (Shimadzu GC-14B) equipped with a thermal conductivity detector for detecting CO_2, H_2S, and high concentrations of C_1, and a flame ionization detector was used for detecting low concentrations of hydrocarbons (C_2–C_5), along with a packed column (Shimadzu Sunpak-S). The two instruments were connected in series. Carbon and hydrogen isotopes of hydrocarbons were measured

Table 1 Molecular and isotopic compositions of hydrate-bound gases.

| Core No.	Molecular composition						Isotopic composition (‰VPDB&VSMOW)				
	C_1 (%)	C_2 (%)	C_3 (%)	CO_2 (%)	H_2S (%)	$C_1/(C_2+C_3)$	$d^{13}C$ C_1	$d^{13}C$ C_2	$d^{13}C$ C_3	$d^{13}C$ CO_2	dD C_1
MD10-3305G	98.0970	0.0292	0.0019	1.1047	0.7672	3158	-36.6	-17.9	5.8	14.3	-166.7
MD10-3305G	98.2636	0.0270	0.0020	1.1771	0.5303	3389	-36.0	-18.2	5.7	18.0	-164.1
MD10-3305G	98.1732	0.0301	0.0017	1.2623	0.5327	3086	-36.0	-18.2	5.9	19.5	-164.0
MD10-3305G	99.7694	0.0331	0.0018	0.1957	n.d.	2859	-34.6				-166.7
MD10-3306							-35.7	-18.1	4.8	23.8	-166.9
MD10-3306	99.1224	0.0292	0.0020	0.8464	n.d.	3176	-37.3	-18.4	6.3	20.3	-164.0
MD10-3317	99.3054	0.0171	0.0001	0.6421	0.0353	5783	-56.4	-31.7		9.7	-194.1
MD10-3317	99.3126	0.0153	0.0001	0.6319	0.0401	6446	-54.6	-31.8		11.6	-194.6
MD10-3317	99.4114	0.0172	0.0001	0.5714	n.d.	5758	-54.8	-31.9		8.5	-193.9
MD10-3317	99.8707	0.0171	0.0001	0.1122	n.d.	5810	-54.8				-193.7
MD10-3317	99.2852	0.0205	0.0001	0.6605	0.0337	4819	-57.1	-31.4		9.1	-193.6
MD10-3317	99.8774	0.0211	0.0001	0.1014	n.d.	4713	-55.4				-194.9
MD10-3317	99.9506	0.0216	0.0001	0.0277	n.d.	4603	-54.8				-193.8
MD10-3318C	99.8069	0.0148	0.0011	0.1772	n.d.	6257	-44.0	-21.3	4.0		-188.9
MD10-3318C	99.0927	0.0421	0.0005	0.5066	0.3582	2328		-22.8	4.5	17.4	-187.9
MD10-3318C	99.8849	0.0456	0.0004	0.0691	n.d.	2172	-44.3	-24.5			-190.3
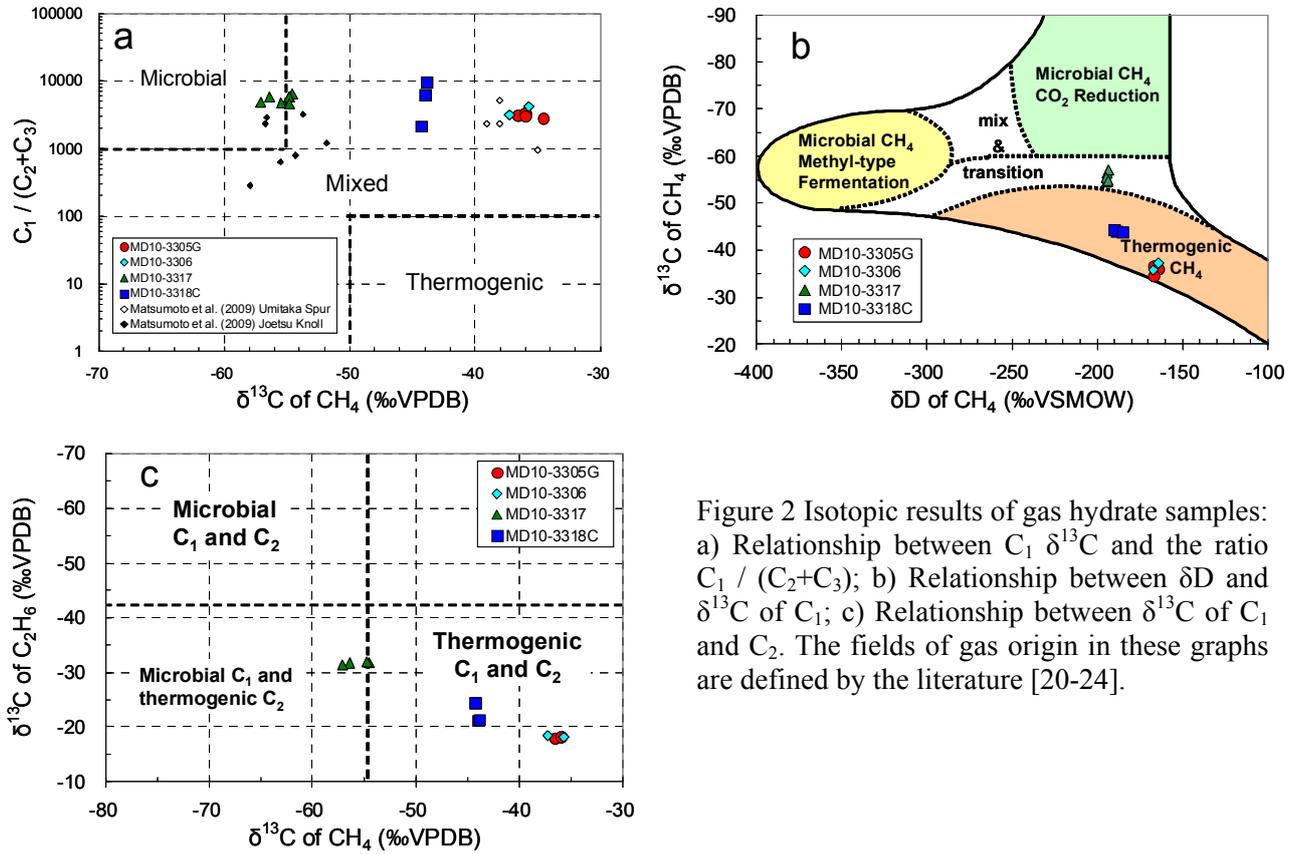
Figure 2 Isotopic results of gas hydrate samples: a) Relationship between C_1 $\delta^{13}C$ and the ratio $C_1 / (C_2+C_3)$; b) Relationship between δD and $\delta^{13}C$ of C_1; c) Relationship between $\delta^{13}C$ of C_1 and C_2. The fields of gas origin in these graphs are defined by the literature [20-24].

using a continuous-flow isotope-ratio mass spectrometer (CF-IRMS, Thermo Finnigan DELTA plus XP) with a Supelco Carboxen-1006 PLOT capillary column (30 m × 0.32 mm inner diameter). To avoid air contamination in samples with low C_1 concentration, a Supelco Carboxen-1010 PLOT capillary column (30 m × 0.32 mm inner diameter) was also used. A Varian Poraplot Q capillary column (27.5 m × 0.32 mm inner

diameter) was used for higher hydrocarbons (C_5–C_8). Stable isotope compositions are reported in terms of δ values (‰).

RESULTS AND DISCUSSION

Hydrate-bound gases

Molecular and isotopic compositions of hydrate-bound gases are summarized in Table 1. Generally,

C_1 was the main component of the gas hydrates, comprising more than 98 %, and concentrations of C_2, C_3, and CO_2 were in the range 148–456 ppm, 1–20 ppm, and 0.03–1.26 %, respectively. Some gas samples contained negligible amounts of H_2S, up to 0.77 %. Based on these gas compositions, the crystallographic structure of the gas hydrates was estimated to be sI, and this was confirmed for the samples from Umitaka Spur by PXRD [19].

The relationship between the isotopic ratio and molecular composition of hydrate-bound gas is shown in Figure 2. According to the Bernard diagram [20], the data of MD10-3305G, 3306, and 3318C were plotted in a mixed gas field while that of MD10-3317 was plotted on the border between microbial and mixed gases. $\delta^{13}C$ of C_1 widely ranged from −57.1 to −34.6 ‰, while $C_1 / (C_2 + C_3)$ concentration ranged from 2,200 to 6,400. These data agree well with those obtained by a previous research [1].

On the contrary, stable isotopes of C_1 displayed thermogenic origin, with the exception of MD10-3317 (Figure 2b). Hydrate-bound C_1 from Umitaka Spur were plotted in a typical thermogenic field. Both depletions in $\delta^{13}C$ and δD imply presence of microbial C_1 via CO_2 reduction mixed with thermogenic C_1 at Joetsu Knoll. Distribution of $\delta^{13}C$ of C_2 in the range −31.9 to −17.9 ‰ indicates a thermogenic origin at each site (Figure 2c). Therefore, the discrepancy in Figure 2a was caused mainly by the depletion of C_2 and C_3.

In Umitaka Spur, seismic profiles revealed prominent gas chimneys in the sediment layers, which suggests that thermogenic gas ascended from a deeper layer [1]. Isotopic evidence indicated thermogenic origin of C_1 and C_2. Although hydrate-bound thermogenic gas contains a significant amount (sometimes more than 10 %) of C_2 and C_3, as reported in Gulf of Mexico [8, 9], northern Cascadia Margin offshore Vancouver Island [10], and Caspian Sea [11], the composition of C_2 was only several hundred ppm and that of C_3 was minimal as stated above. Several theories based on these results have been proposed: (1) fractionation at the upward migration [25]; (2) formation of C_2-rich gas hydrates in the deeper layer [1]; and (3) adsorption of C_2 and C_3 to the sediment layer at the process of migration [18].

Gas concentration profiles in sediment

The depth profiles of dissolved hydrocarbons (C_1–C_3) in sediment are shown in Figure 3. High C_1 flux caused shallow sulfate-methane interface
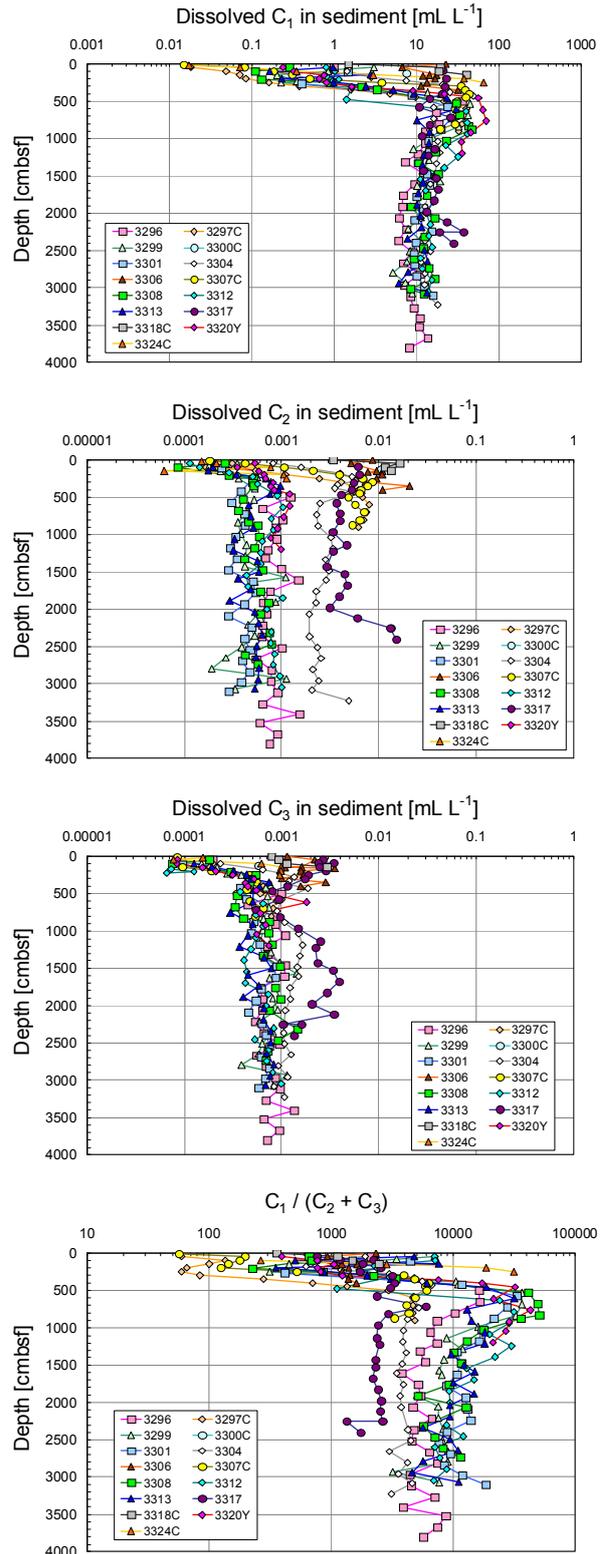

Figure 3 Depth profiles of C_1, C_2, and C_3 concentration dissolved in sediment (pore water) and gas ratio $C_1 / (C_2 + C_3)$. Horizontal axis shows the dissolved volume in sediment at standard temperature (298.15 K) and pressure (101.325 kPa).
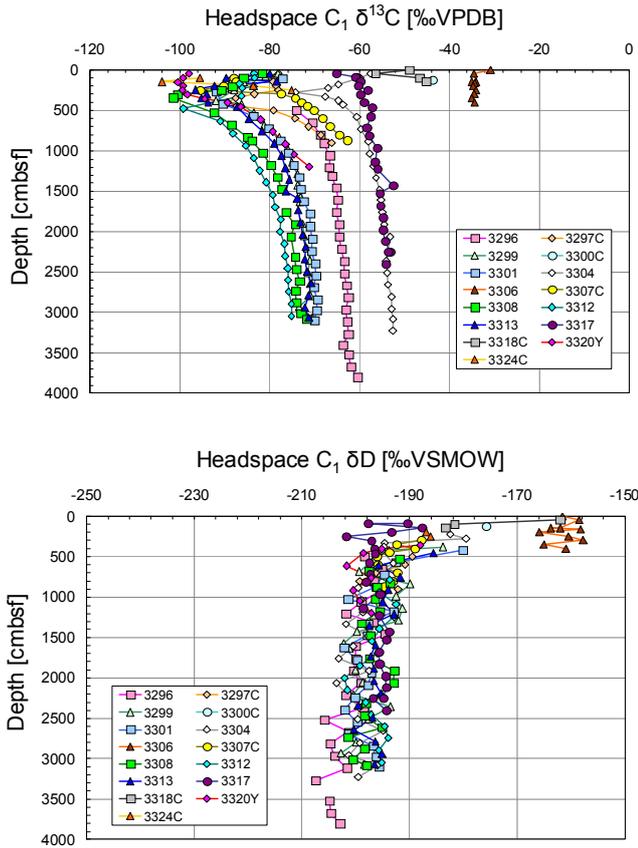
Figure 4 C_1 Isotopic profiles of dissolved gas in pore water (sediment).

Table 2 Molecular and isotopic compositions of dissolved gas in pore water for hydrate-bearing cores. DMB: dimethylbutane; n.d.: not determined.

Core	MD10-3306				MD10-3318C
Depth (cmbsf)	150	200	295	400	150
Molecular composition (%)					
C_1	40.6927	42.3098	41.4039	28.4440	86.9438
C_2	0.0211	0.0264	0.0255	0.0153	0.0289
C_3	0.0037	0.0039	0.0037	0.0022	0.0063
$_{neo}C_5$	0.1946	0.1298	0.1862	0.0830	0.0760
CO_2	59.0879	57.5301	58.3807	71.4555	6.6473
H_2S					6.2977
$C_1/(C_2+C_3)$	1640	1393	1422	1624	2469
C_2/C_3	6	7	7	7	5
Isotopic composition ($\delta^{13}C$ ‰VPDB)					
$\delta^{13}C$ of C_1	-33.9	-34.6	-34.4	-34.3	-45.3
$\delta^{13}C$ of C_2	-47.3	-32.9	-21.5	-21.1	-24.8
$\delta^{13}C$ of C_3	4.5	4.5	3.9	2.9	8.8
$\delta^{13}C$ of $_iC_4$	2.6	4.4		2.3	1.1
$\delta^{13}C$ of $_{neo}C_5$	-23.0	-23.3	-22.8	-23.2	-21.4
$\delta^{13}C$ of 2,2DMB	-18.3	-19.0	-19.3	-18.6	-15.7
$\delta^{13}C$ of 2,3DMB	-21.9	-20.5		-21.6	
$\delta^{13}C$ of $_nC_6$	-23.0	-22.6		-23.0	
$\delta^{13}C$ of $_nC_7$	-28.1	-26.6		-27.4	
$\delta^{13}C$ of $_nC_8$	-26.4				
$\delta^{13}C$ of CO_2	n.d.	n.d.	n.d.	n.d.	-10.2
Isotopic composition (δD ‰VSMOW)					
δD of C_1	-162.0	-165.9	-157.8	-161.0	-183.4
δD of $_{neo}C_5$	-125.5	-124.2	-132.8	-124.5	-119.4

(SMI) depths in this area [4, 26]. C_1 concentration profiles indicate that SMI depths were distributed at around 2–5 m depth and dissolved C_1 drastically increased with depths lower than the SMI depth. Peaks of dissolved C_1 concentration appeared at around 5–8 m depth and decreased thereafter. Concentration of dissolved C_2 in hydrate-bearing cores was nearly one order higher than that of other cores, and MD10-3297C, 3304, and 3307C cores retrieved from Umitaka Spur were also C_2 rich. Concentration of dissolved C_3 in hydrate-bearing cores was relatively higher than that of other cores. Both concentrations of C_2 and C_3 were depleted in the surface layer (0–5 m depth) of non-hydrate cores. The gas ratio $C_1 / (C_2 + C_3)$ showed a peak near 5–8 m depth, which agrees with the peak of dissolved C_1. These results indicate high microbial activity (methanogenesis) just beneath the SMI depth.

It must be noted that the dissolved C_3 concentration of the MD10-3317 core was distinctively higher than that of the other cores. C_3

in the hydrate-bound gas was about 1 ppm (Table 1), possibly because contamination of dissolved gas in pore water adhered to the hydrate crystals. Because sI gas hydrates cannot encage C_3, it appears reasonable to assume that gas hydrates existing in the core (about 13 m and 23 m from the core top) discharged C_3 during their formation, and C_3 remained in the sediment.

On the other hand, the reason why up to 20 ppm of C_3 was detected in the hydrate-bound gas of other sediment cores (Table 1) requires further investigation. Existence of a small amount of C_3 in the hydrate-bound gas has been previously reported [12, 13, 15, 16], although PXRD, NMR, and Raman analysis indicated that the crystals belonged to the sI group. Two possibilities exist: contamination by the dissolved gas in pore water during the sampling procedure, or coexistence of sI and a small amount of sII gas hydrates [27, 28].

$\delta^{13}C$ of C_1 in dissolved gas in pore water showed negative peaks at the SMI depths (Figure 4). This depletion in $\delta^{13}C$ of C_1 was caused by anaerobic

oxidation of methane (AOM). AOM produces ^{13}C-depleted CO_2, and ^{13}C-depleted C_1 is also generated via microbial CO_2 reduction [29]. Below the SMI depths, the profiles of $\delta^{13}C$ of C_1 became asymptotic, and the values depended on each core. $\delta^{13}C$ of C_1 was high in the hydrate-bearing cores and decreased with distance from the gas hydrate retrieval site. The upward increase in profiles of $\delta^{13}C$ of C_1 was due to consumption of C_1 during oxidation in the surface layer. Although $\delta^{13}C$ of C_1 in non-hydrate cores displayed microbial origins, several cores retrieved from Umitaka Spur (MD10-3296, 3297, 3304, and 3307C) appeared to be affected by thermogenic C_1. On the contrary, depth profiles of δD of C_1 were almost identical to each other except the MD10-3306 core, which decreased gradually with depth. This tendency agrees fairly well with the δD profiles of pore water [4], because δD of C_1 is primarily decided by the δD of ambient water in the case of microbial C_1 via CO_2 reduction.

Neopentane and higher hydrocarbons
Molecular and isotopic compositions of dissolved gas in pore water for MD10-3306 and 3318C are shown in Table 2. The main components were CO_2 and C_1, and a high concentration of $_{neo}C_5$ (0.1–0.2%) was detected, although $_iC_4$, $_nC_4$, $_iC_5$, and $_nC_5$ were under the detection limit of the gas chromatograph. $_{neo}C_5$ can be encaged in the large cages of sII [30]; however, the detection of $_{neo}C_5$ in the hydrate-bound gas was only at trace levels. Accordingly, $_{neo}C_5$ could be discharged from the crystal during the formation process of sI gas hydrates and remain in the sediment.

Regarding isotopic compositions of hydrocarbons, $\delta^{13}C$ of C_1–C_8 were measured by the CF-IRMS. It should be noted that $\delta^{13}C$ of C_3 and $_iC_4$ were exceptionally high compared with $\delta^{13}C$ of other hydrocarbons. It is possible that light molecules of C_3 and $_iC_4$ were consumed by microbial activity, and $\delta^{13}C$ of the residual C_3 and $_iC_4$ increased [18]. The concentration of $_nC_4$ was under the detection limit of the analytical system. It is reasonable to assume that $_nC_4$ was consumed chiefly by microbial activity because $_nC_4$ is easier to decompose than $_iC_4$.

CONCLUSION
Molecular and isotopic compositions of hydrate-bound gas and dissolved gas in pore water were reported for samples retrieved from Umitaka Spur and Joetsu Knoll in the eastern margin of the Japan Sea. The hydrate-bound gas from Umitaka Spur was of typical thermogenic origin, and that from Joetsu Knoll partly contained microbial gas because ^{13}C and D were both depleted and close to the field of microbial C_1 via CO_2 reduction according to empirical classification. Depth profiles of $\delta^{13}C$ of dissolved C_1 in pore water registered minimum peaks at a depth corresponding to the SMI depth, and increased slightly thereafter; δD of dissolved C_1 decreased with depth. The molecular compositions of C_2 and C_3 were quite small compared with those of typical thermogenic gas, and that of $\delta^{13}C$ of C_3 and $_iC_4$ were exceptionally high. The questions to be solved focus on the manner in which microbial activities and inorganic processes affect these hydrocarbons in hydrate-bearing sediment systems. A high concentration of $_{neo}C_5$ was detected, which suggests that the $_{neo}C_5$ was discharged from the hydrate crystal during the formation process and remained in the pore water, because $_{neo}C_5$ cannot be encaged by sI gas hydrates. The concentration of dissolved C_3 in the hydrate-bearing core retrieved from Joetsu Knoll was higher than those of other cores, which also supports this theory.

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