MOLECULAR AND ISOTOPIC COMPOSITIONS OF HYDRATE-BOUND HYDROCARBONS IN SUBSURFACE SEDIMENTS FROM OFFSHORE SAKHALIN ISLAND, SEA OF OKHOTSK

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ABSTRACT

We report molecular and isotopic compositions of hydrate-bound gas and dissolved gas in pore water that were obtained from new seepage sites offshore of Sakhalin Island in the Sea of Okhotsk. In the framework of the Sakhalin Slope Gas Hydrate (SSGH) project, we obtained shallow sediment cores from the southern area of the Lavrentyev Fault in 2009 and 2010. Empirical classification of stable isotopes $\delta^{13}C$ of methane (C_1) and ethane (C_2) and δD of C_1 indicate a microbial origin. Concentration profiles of dissolved C_1 in the pore water suggest a shallow sulfate-methane interface (SMI). SMI depths of hydrate-bearing cores were estimated as 30–50 cmbsf and those of gas-rich cores with no gas hydrates were approximately 2 m. Although molecular compositions of hydrate-bound gases were nearly the same in the northern and southern areas of the Lavrentyev Fault, C_1 stable isotopes in the southern area were more depleted than those in the northern area — nearby 6 ‰ for $\delta^{13}C$ and 7 ‰ for δD — which suggests a great increase in active microbial processes in the shallow sediment. It was found that approximately 5 ‰ of the isotopic difference between δD in hydrate-bound and dissolved gas in pore water is due to isotopic fractionation during the formation of gas hydrates.

Keywords: gas hydrate, Sea of Okhotsk, stable isotope, methane, ethane

INTRODUCTION

Near-surface gas hydrates in the Sea of Okhotsk were first discovered northwest of Paramushir Island in 1986 [1, 2] and northeast of Sakhalin Island in 1991 [3, 4], where gas plumes vent from the sea floor. Geological, geophysical, and geochemical approaches to the Okhotsk gas hydrates were summarized by Ginsburg and Soloviev [5]. Stable isotopes of methane (C_1) in a gas hydrate sample obtained from the "Obzhirov Flare" located offshore of Sakhalin Island [3] suggested its microbial origin via CO_2 reduction. Pore water geochemistry data from the Russian–German project KOMEX (Kurile-Okhotsk Sea Marine Experiment) revealed that the gas hydrate was produced from an upward-migrating fluid [6]. Hydrate-bearing seepage structures were investigated from 2003 to 2006 within the

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framework of the CHAOS (hydro-Carbon Hydrate Accumulations in the Okhotsk Sea) project, and gas hydrate samples were obtained from nine seepage structures distributed in the northern area of the Lavrentyev Fault [7–10]. According to empirical classifications [11–13], molecular and isotopic compositions of the hydrate-bound gases obtained at each site offshore of Sakhalin Island primarily indicate a microbial origin via CO_2 reduction [14]. Because $\delta^{13}C$ in C_2 ranged from −40.8 to −27.4 ‰, it was concluded that hydrate-bound gas contains a small amount of thermogenic gas [14].

Isotopic compositions of hydrate-bound gases provide information to identify their gas sources and to assess migration and formation of gas hydrates. Because isotopic fractionation of hydrocarbons occurs during the formation of gas hydrates [15], isotopic differences between the hydrate-bound gas and dissolved gas in pore water provide information to determine whether the current gas in pore water is the source of the hydrate-bound gas [14, 16].

The Sakhalin Slope Gas Hydrate (SSGH) project began in 2007 [17, 18], and sediment cores were retrieved in 2009 and 2010 from the southern area of the Lavrentyev Fault during the LV47 and LV50 cruises [19, 20]. It has been hypothesized that C_1 in the southern area of the Lavrentyev Fault could be thermogenic because several gas chimneys in the sediment ascend from the lower layer of the bottom-simulating reflector (BSR) [19]. In this study, we report the results of gas analysis for hydrate-bound gas and dissolved gas in pore water that were obtained from the new seepage sites offshore of Sakhalin Island in the Sea of Okhotsk.

STUDY AREAS

SSGH-09 and SSGH-10 projects were conducted offshore Sakhalin Island in the Sea of Okhotsk during LV47 and LV50 cruises in 2009 and 2010, respectively, onboard R/V *Akademik M. A. Lavrentyev* (LV) (Figure 1). The main focus for the SSGH project is the southern area of the Lavrentyev Fault, whereas the former project, CHAOS, focused on its northern area. Three hydrate-bearing sediment cores (LV50-29HC, LV50-31HC, and LV50-33HC) were obtained from the southern area of the Lavrentyev Fault. A
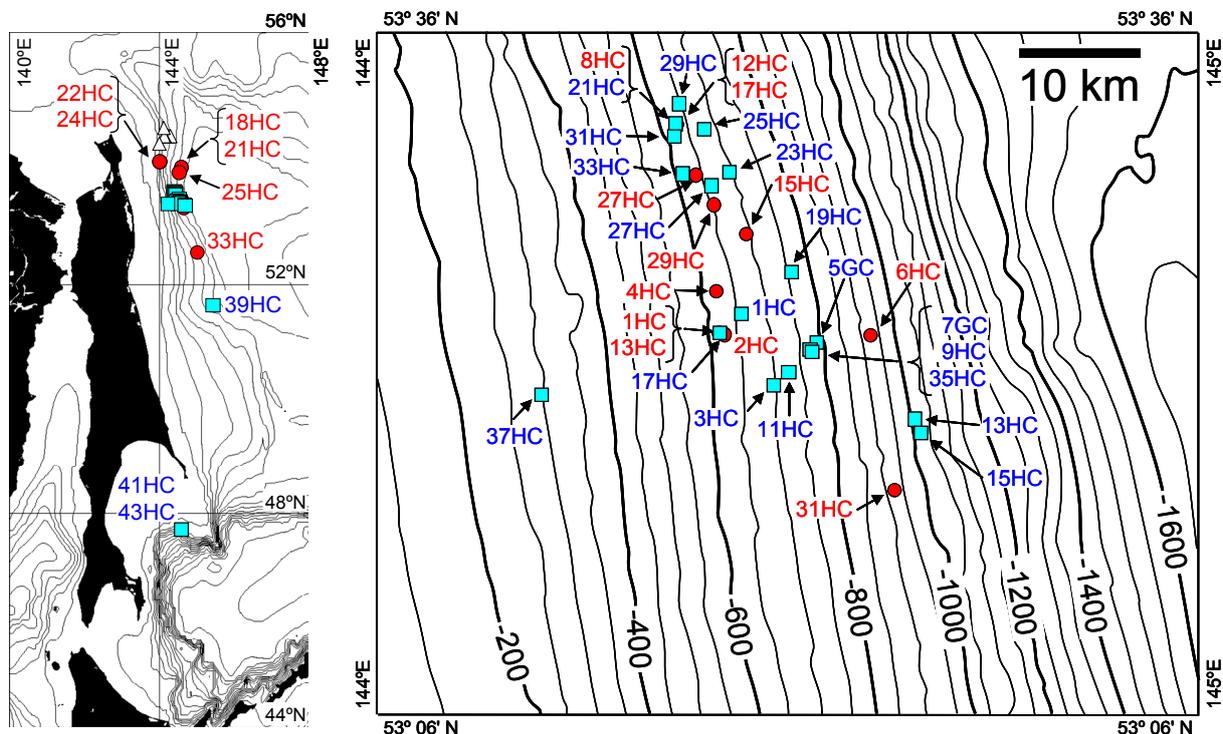

Figure 1 Location map of coring sites offshore of Sakhalin Island in the Sea of Okhotsk. Red circles represent sampling sites of the LV47 cruise in 2009. Blue squares represent those of the in LV50 cruise in 2010. LV50-22HC and LV50-24HC were obtained from the Lavrentyev Fault zone. Open triangles represent seepage structures investigated in LV32, LV36, and LV39 cruises from 2003 to 2006 [14] in the northern area of the Lavrentyev Fault.

gas hydrate sample discovered in the core LV47-24HC was obtained at the seepage structure "Dungeon" in the Lavrentyev Fault zone [19]. Two reference cores (LV47-33HC and LV50-39HC) were obtained to check the baseline concentration of dissolved C_1 in the pore water. Cores LV50-41HC and LV50-43HC were retrieved to investigate a new site off Cape Terpeniya (Cape Patience). Other sediment cores were gas-rich in deeper layers, but no gas hydrate was discovered. Sediment cores were retrieved using a gravity corer (GC) and a hydrostatic corer (HC), 10.5 m and 5.5 m long, respectively, and an inner diameter of 0.125 m.

SAMPLING METHODS

Hydrate-bound gases were collected using a plastic syringe onboard the ship and stored in 5 mL vials sealed with butyl septum stoppers [14]. We placed each hydrate sample in a 50 mL plastic syringe, pushed the cylinder to reduce the dead volume, and attached the syringe to a vial using a needle. Another needle was attached to the vial to flush the air inside. Each vial was then filled with hydrate-bound gas devoid of sediment particles or pore water.

The dissolved gases in the pore water were extracted by a headspace gas method whereby 10 mL of sediment and a 10 mL saturated aqueous solution of NaCl were introduced into a 25 mL vial to create headspace. In the LV47 cruise, the headspace was flushed by N_2. After the vial was agitated by shaking thoroughly, a second vacuumed 8 mL vial was attached via a needle, and a saturated aqueous solution of NaCl was added to the 25 mL vial using a syringe to obtain only the headspace gas [19, 21]. In the LV50 cruise, a 0.5 mL preservative (benzalkonium chloride [22], 10 wt% aqueous solution) was introduced into the 25 mL vial. The vials were then thoroughly shaken and stored overturned.

SAMPLE ANALYSES

The experimental setup for analyzing the gas was the same as that used in our previous study [14, 16]. Molecular compositions of hydrocarbons (from C_1 to C_3), CO_2, and H_2S were determined using a gas chromatograph (Shimadzu GC-14B) equipped with a thermal conductivity detector for detecting high concentrations of hydrocarbons, CO_2, and H_2S, and a flame ionization detector for detecting low concentrations of hydrocarbons, along with a packed column (Shimadzu Sunpak-S).
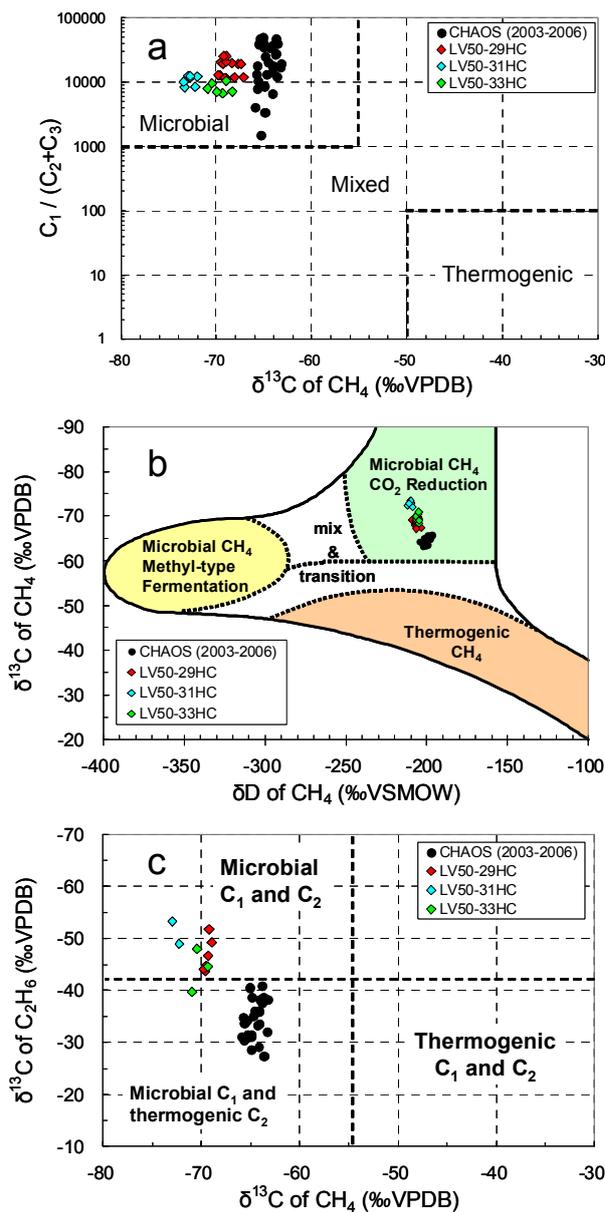

Figure 2 Isotopic results of gas hydrate samples: a) relation between C_1 $\delta^{13}C$ and the ratio C_1 / (C_2+C_3), b) relation between δD and $\delta^{13}C$ of C_1, c) relation between $\delta^{13}C$ of C_1 and C_2. The fields of gas origin in these graphs are according to [12, 13, 23–25]. Solid circles represent samples retrieved from the north area of the Lavrentyev Fault [14].

The two instruments were connected in series. Carbon and hydrogen isotopes of C_1 and C_2 were measured using a continuous-flow isotope-ratio mass spectrometer (CF-IRMS, Thermo Finnigan DELTA plus XP) with a Supelco Carboxen-1006
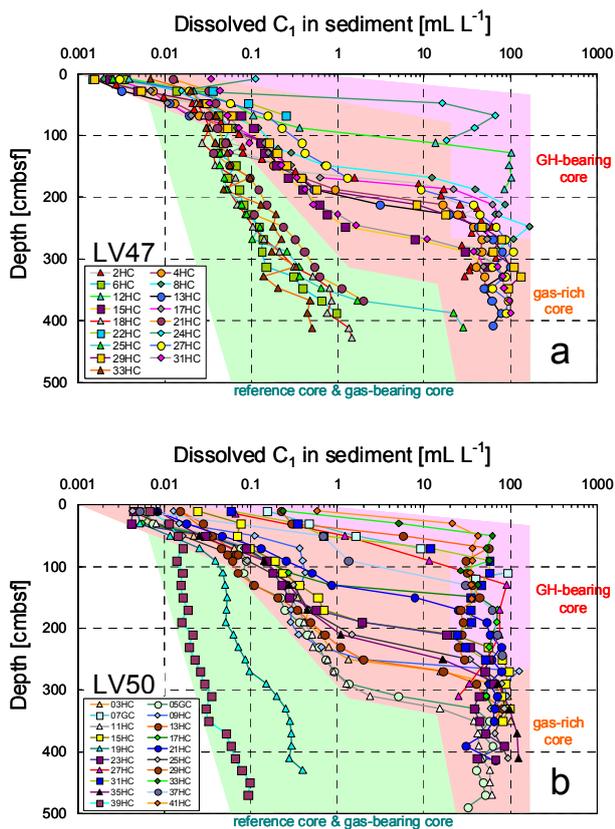
Figure 3 Depth profiles of C_1 concentration dissolved in sediment pore water: a) data from the LV47 cruise (SSGH-09); b) data from the LV50 cruise (SSGH-10).

PLOT capillary column (30 m × 0.32 mm inner diameter). To avoid air contamination in low-concentration samples of C_1, a Supelco Carboxen-1010 PLOT capillary column with the same dimensions also was used. The backflush system of the gas chromatograph combined with the CF-IRMS enabled us to separate low-concentration C_2 (less than 0.1 vol %) from C_1 and to measure the isotopes of C_2. Stable isotope compositions were reported in terms of δ values (‰).

RESULTS AND DISCUSSION

Hydrate-bound gases

We focused on hydrate samples of LV50-29HC, LV50-31HC, and LV50-33HC retrieved from the southern area of the Lavrentyev Fault. C_1 was the main component of the gas hydrate (99.6 ± 0.6 %), and concentrations of C_2, C_3, CO_2, and H_2S were 86 ± 36 ppm, 1 ± 0 ppm, 0.05 ± 0.07 %, and 0.3 ± 0.5 %, respectively. The gas composition shows that the crystallographic structure of these gas hydrates is cubic structure I.

Figure 2 shows the relationship between the isotopic ratios and molecular composition of hydrate-bound gases. All the gas samples were located in a microbial gas field [24] had $C_1 / (C_2 + C_3)$ composition in the range from 7,000 to 25,000, and that of $\delta^{13}C$ in C_1 in the range from −73.5 to −67.1 ‰ (Figure 2a). $\delta^{13}C$ of C_1 from the southern area was about 5 ‰ lower than that from the northern area. δD of C_1 provided additional information for interpreting the gas origin, as shown in Figure 2b, that the hydrate-bound C_1 belongs to a field of microbial origin via CO_2 reduction [12, 13]. δD of C_1 from the southern area was about 7 ‰ lower than that from the northern area. Figure 2c shows the relationship between $\delta^{13}C$ of C_1 and C_2. The boundaries between thermogenic and microbial origins were based on a previous research [23, 25]. The distribution of $\delta^{13}C$ of C_2 ranged from −46.8 to −39.7 ‰ indicating a microbial origin of C_2, whereas C_2 from the northern area shows thermogenic origin [14].

In the northern area of the Lavrentyev Fault, pore water geochemistry suggested the existence of upward fluid infiltration at several seepage structures [6, 26], and the geothermal gradient at the sea floor was greater than that of the background value [7]. Seismic cross sections obtained from the southern area indicate BSR, and many gas chimneys formed below the depth of the BSR [19]. Although the hydrate-bound gas from the southern area was expected to be thermogenic, isotopic evidence indicated that both C_1 and C_2 appear to be microbial.

Depth profiles of dissolved gases in pore water

Figure 3 shows the depth profiles of dissolved C_1 in pore water. Horizontal axis shows the dissolved volume in sediment at standard temperature (298.15 K) and pressure (101.325 kPa). Hydrate-bearing sediment cores could not be retrieved from the southern area in the LV47 cruise; only LV47-24HC from the Lavrentyev Fault zone contained gas hydrates with a high C_1 concentration. LV50-29HC, LV50-31HC, and LV50-33HC contained gas hydrates after a depth of 100 cm, and the C_1 concentration increased dramatically with depth. These C_1 profiles of hydrate-bearing cores suggest a shallow sulfate-methane interface (SMI). SMI depth was estimated to be 30–50 cm from the sea
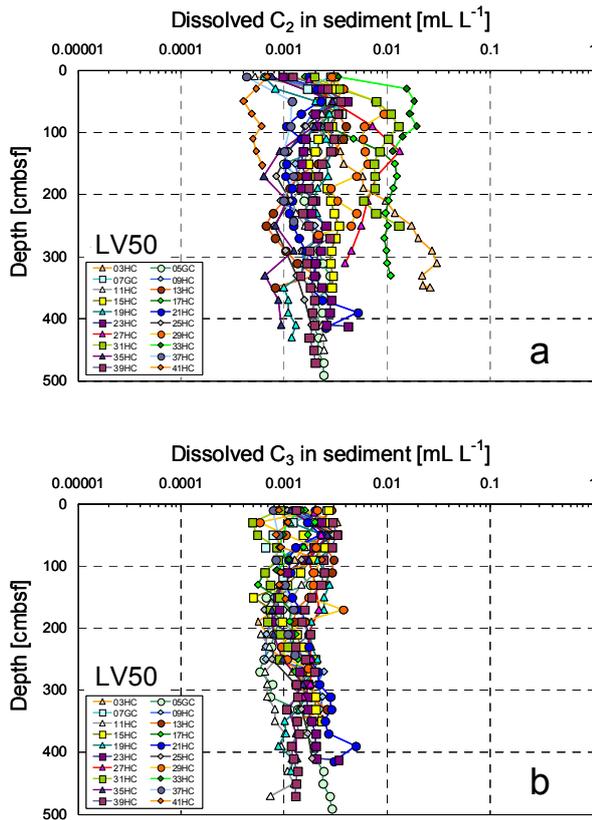
Figure 4 Depth profiles of C_2 and C_3 concentrations dissolved in sediment pore water from the LV50 cruise (SSGH-10): a) profiles of C_2; b) profiles of C_3.

Figure 5 Relation between $\delta^{13}C$ and δD of C_1 in hydrate-bound sediment cores.

floor in the case of hydrate-bearing cores and approximately 2 m from the sea floor in the case of gas-rich cores with no gas hydrate. The maximum concentration of C_1 in the sediment was about 100 mL L^{-1}; however, this could be an underestimation because dissolved gas can easily escape from the gas-rich layers of the sediment core.

Conversely, reference cores LV47-33HC and LV50-39HC showed low C_1 concentration. The profiles of two sediment cores retrieved from the southern area, LV47-6HC and LV50-19HC, were similar to the reference cores, even for the gas seepage area.

The depth profiles of C_2 and C_3 are plotted in Figure 4. C_2 concentrations of the three hydrate-bearing cores were greater than that of other gas-rich and reference cores. The preferential inclusion of C_2 in the hydrate phase indicates that the gas hydrate enriched C_2, and C_2 concentration in the
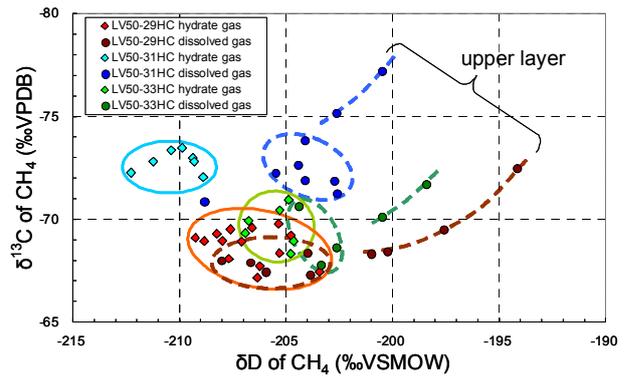
dissolved gas decreased. However, $C_1 / (C_2 + C_3)$ composition of hydrate-bound gas and dissolved gas in pore water were 7,000–25,000 and 1,800–6,500, respectively; therefore C_2 composition of dissolved gas was approximately three times larger than that of hydrate-bound gas. C_2 solubility in water is larger than that of C_1. Therefore, quantitative mass balance is a topic for further investigation.

LV50-03HC, LV50-17HC, and LV50-27HC cores were also C_2 rich. Because $\delta^{13}C$ of C_2 in the dissolved gas of LV50-03HC was -33.0 ± 2.5 ‰, dissolved C_2 could be affected by thermogenic gas. $\delta^{13}C$ of C_2 of other cores was more depleted. C_3 concentration in the dissolved gas was relatively small (Figure 4b), and stable isotopes cannot be measured.

The LV50-41HC core retrieved from the new site off Cape Terpeniya, southeast of Sakhalin Island, showed a much higher C_1 concentration and lower C_2 concentration; $C_1 / (C_2 + C_3)$ composition was in the range from 12,000 to 34,000. It is expected that gas hydrates will be discovered in this area during subsequent investigations.

Isotopic difference between hydrate-bound gas and dissolved gas in pore water

Isotopic fractionation of carbon and hydrogen in C_1 and C_2 during the formation of gas hydrates has been previously investigated [15]. Before 2007, little attention was paid to the isotopic fractionation between guest molecules of gas hydrates and gas bubbles/dissolved gas. Regarding mixed-gas hydrates, gas fractionation can occur between light and heavy guest molecules because the equilibrium pressures of their pure hydrates

slightly differ from each other. δD of hydrate-bound gas becomes several permil (4.8 ± 0.4 ‰ for C_1 and 1.1 ± 0.7 ‰ for C_2) lower than that of the original gas, whereas $\delta^{13}C$ of hydrate-bound and original gases remains almost constant [15]. These isotopic differences in δD are sufficiently small for discussing the source types of hydrate-bound gases using the $\delta^{13}C$ - δD diagram [12, 13]. Figure 5 shows the isotopic difference between hydrate-bound and dissolved gases of each hydrate-bearing sediment core. In LV50-31HC, δD of C_1 of hydrate gas was about 5 ‰ lower than that of dissolved gas in pore water, whereas $\delta^{13}C$ of C_1 of both gases was almost constant. Based on the results of laboratory experiments [15], we concluded that hydrates in the LV50-31HC core were formed from the current gas dissolved in pore water. On the contrary, the difference between δD in hydrate-bound and dissolved gases is negligible for LV50-29HC and LV50-33HC cores to be explained by isotopic fractionation. These results suggest that the gas in the pore water is not the source of gas hydrates in these cores.

CONCLUDING REMARKS

We reported molecular and isotopic compositions of hydrate-bound gas and dissolved gas in pore water that were obtained from sediment cores offshore of Sakhalin Island in the Sea of Okhotsk. The hydrate-bound C_1 was determined to be microbial in origin via CO_2 reduction in the southern area of the Lavrentyev Fault. Hydrate-bound gas also contained a small amount of microbial C_2, although hydrate-bound C_2 was reported as thermogenic origin in the northern area of the Lavrentyev Fault [14]. The difference between δD of C_1 in hydrate-bound gas and dissolved gas in pore water was analyzed, and we observed that the isotopic difference was caused by fractionation during the formation of gas hydrates.

ACKNOWLEDGMENTS

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