Natural gas hydrates with locally different cage occupancies and hydration numbers in Lake Baikal

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[1] Knowledge of cage occupancies and hydration numbers (n) of naturally occurring gas hydrate in a local environment is important for the improvement in global estimates of hydrate-bound natural gas. We report on local differences in cage occupancies and hydration number of gas hydrates from Lake Baikal. Natural gas hydrates of both structures I and II (sI and sII) and ranging in composition from pure CH_4 to mixed gas hydrate containing up to 15% C_2H_6 are compared. The average hydration numbers are $n = 6.1$ for the sI CH_4 hydrates recovered from the Malenky and Bolshoy mud volcanoes, $n = 6.2$ for the sI hydrates, containing $3-4\%$ C_2H_6 recovered from the K-2 mud volcano, and $n = 6.9$ for the sII hydrate containing about 15% C_2H_6 recovered from the K-2 mud volcano. The differences in hydration number are due to the differences in the small cage occupancy of CH_4 among the samples studied.

1. Introduction

[2] Natural gas hydrates (NGHs), which are present in marine and lacustrine sediments at water depths greater than about 500 m and permafrost layers, act as a large natural gas reservoir because of their widespread occurrence. NGH is an ice-like crystalline clathrate compound that contains natural gas components in its polyhedral cages, which consist of hydrogen-bonded water molecules. Gas hydrate is a nonstoichiometric compound, expressed by the formula $G \cdot nH_2O$, where G and n are gas component and hydration number, respectively. The three main crystallographic structures of NGH are structure I (sI), structure II (sII), and structure H (sH) [*Sloan*, 2003]. The crystallographic structure of NGH depends on the encaged components [*Davidson et al.*, 1986; *Uchida et al.*, 1999; *Lu et al.*, 2007].

[3] The cage occupancy is defined as a ratio: (number of cages occupied by guest molecules)/(number of total cages). Both ^{13}C NMR and Raman techniques have been applied widely to estimate cage occupancies, not only of synthetic gas hydrates but also of NGHs [*Ripmeester and Ratcliffe*, 1988; *Sum et al.*, 1997; *Uchida et al.*, 1999; *Tulk et al.*, 1999; *Subramanian et al.*, 2000a, 2000b; *Uchida et al.*, 2002; *Ripmeester et al.*, 2005; *Kim et al.*, 2005; *Lu et al.*, 2005; *Kida et al.*, 2007]. The cage occupancies are estimated from the integrated intensities of ^{13}C NMR signals or Raman peaks from encaged gases using a statistical thermodynamic model [*van der Waals and Platteeuw*, 1959]. Furthermore, cage occupancies enable us to give the hydration number defined as the number of water molecules per guest molecule. The assumption of single occupancy for all cages gives us ideal hydration numbers of 23/4 for sI, 17/3 for sII, and 17/3 for sH. The abundance of gas hydrate in sediments can be calculated from the hydration number and the density of gas hydrate under the conditions studied [*Lu et al.*, 2005]. However, global estimations of the amount of natural gas in NGHs have been typically based on assuming fixed ideal hydration number of CH_4 hydrate ($n = 23/4$) [*Kvenvolden*, 1995]. Crystals of NGHs mainly contain CH_4. They also contain smaller quantities of heavier hydrocarbons such as C_2H_6, C_3H_8, and i-C_4H_{10} and nonhydrocarbons such as CO_2 and H_2S depending on the local environment [*Davidson et al.*, 1986]. A Knowledge of hydration numbers in various environments should improve global estimates of the amount of natural gas trapped in gas hydrate crystals. However, cage occupancies and hydration numbers of NGHs are poorly understood.

[4] The hydration number can be estimated by direct measurements of the gas-water ratio obtained by dissociation of the gas hydrate. However, NGHs generally contain frozen water [*Takeya et al.*, 2006]. Therefore, direct measurements have the potential to overestimate hydration numbers, since it is difficult to distinguish water from gas hydrate crystals from that frozen water. As an alternative to direct measurement, ^{13}C NMR or Raman techniques are convenient for estimation of cage occupancies and hydration number without considering the excess frozen water. Since they do not measure the excess frozen water, those values are estimated from integrated intensities ratio of peaks from guest molecules interacting with host water molecules. Under the coexistence of three phases, gas, hydrate, and ice, the ^{13}C NMR or Raman signals from the encaged gases are separated from signals of the gas phase [*Sum et al.*, 1997; *Subramanian et al.*, 2000b]. In particular, in the case of mixed gas system, the ^{13}C NMR technique gives us high-resolution signals from mixed gas hydrates compared with Raman spectroscopy.

[5] For NGHs containing CH_4 as a main component, the n values of 5.91 (via direct measurement) for the Middle America Trench (off Guatemala) sample [*Handa*, 1988], 6.2 (via Raman) for the Blake Ridge (off South Carolina) sample [*Uchida et al.*, 1999], 6.1–6.3 (via ^{13}C NMR and Raman) for the Mallik sample [*Ripmeester et al.*, 2005], 6.11 (via ^{13}C NMR) for the Hydrate Ridge (off Oregon) samples [*Kim et al.*, 2005], 6.1 (via ^{13}C NMR and Raman) for the offshore Vancouver Island samples [*Lu et al.*, 2005], and 5.900 (via X-ray diffraction) for the offshore Vancouver Island sample [*Udachin et al.*, 2007] have been reported. Furthermore, naturally occurring mixed gas hydrates containing heavier hydrocarbons have been discovered in the Caspian Sea [*Ginsburg et al.*, 1992], the Gulf of Mexico [*Davidson et al.*, 1986], the Gulf of Cadiz [*Mazurenko et al.*, 2002], the Cascadia margin [*Lu et al.*, 2007], and other places, but attempts to estimate the n value are reported for mixed gas hydrate recovered from the Gulf of Mexico [*Handa*, 1988]. The Gulf of Mexico sample contained 66% CH_4, 2.9% C_2H_6, 14.7% C_3H_8, 3.7% i-C_4H_{10}, and trace amount of heavier hydrocarbons [*Davidson et al.*, 1986]. Handa used the gas-water ratio for the estimation and reported the n value of 8.2 for the sample. The differences in the hydration numbers between the natural mixed gas hydrate and the natural CH_4 hydrates reported could be due to those in gas compositions. On the other hand, it has been
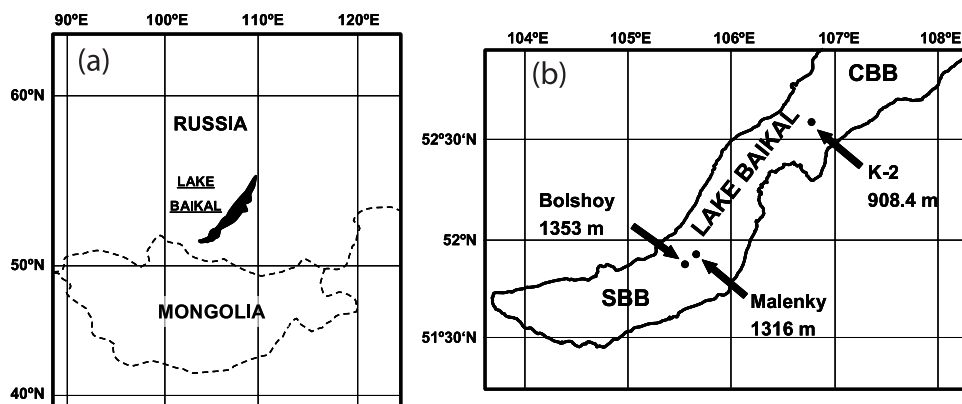
Figure 1. Map of Lake Baikal: (a) location of Lake Baikal and (b) location and water depth of the study sites. The Malenky and Bolshoy mud volcanoes are located in the southern Baikal Basin (SBB); the K-2 mud volcano is located in the central Baikal Basin (CBB).

pointed out that the *n* value of the mixed gas hydrate was overestimated because a portion of the water originally present in the sample was converted into ice during the various handling procedures for several measurements conducted on the same sample at different laboratories [*Handa*, 1988]. Recently, estimation of guest molecular distribution in single crystal lattice of the sII NGH containing CH_4, C_2H_6, and C_3H_8 recovered from the offshore Vancouver Island was attempted by X-ray diffraction technique based on the assumption of full cage occupancy [*Udachin et al.*, 2007].

[6] The purpose of the present study is to obtain occupation factors of gas hydrates formed from natural gases with different gas compositions. In this study, the NGHs recovered from different areas in Lake Baikal were studied. Lake Baikal is the only fresh water environment where NGHs have been recovered [*Kuzmin et al.*, 1998]. In Lake Baikal, NGHs form from microbial gas and from thermogenic gas in the southern Baikal Basin (SBB) and from gas associated with deep oil fields in the central Baikal Basin (CBB) [*Kuzmin et al.*, 1998; *Kida et al.*, 2006]. We attempted to estimate cage occupancies and hydration numbers of pure CH_4 and mixed CH_4-C_2H_6 hydrates locally formed in different areas in Lake Baikal.

2. Materials and Experimental Method

[7] Gas hydrate-bearing sediment cores were recovered from three study sites, the Malenky and Bolshoy mud volcanoes in the SBB and the K-2 mud volcano in the CBB of Lake Baikal (Figure 1), which were obtained by gravity coring. The field investigations were carried out in 2005 and 2006 in the framework of an international collaboration of

the Kitami Institute of Technology, Japan and the Limnological Institute SB RAS, Russia. The hydrate fractions were stored and transported at liquid nitrogen temperature using a dry-shipper. Photographs of the hydrate-bearing sediments are presented in Figure 2. Massive or small piece of NGHs were found in silty clay in the cores recovered. The Malenky core was obtained at 51°55.223′N, 105°38.109′E, and water depth of 1316 m. The core had a length 124 cm and the hydrate (sample A) was obtained from the sub bottom depth interval of 111–124 cm. The 104-cm-long Bolshoy core was obtained at 51°52.779′N, 105°33.337′E, and water depth of 1353 m. The hydrate, which was obtained from the 87–99 cm of the core, is denoted as sample B. The K-2 core was obtained at 52°35.473′N, 106°46.284′E, and 908.4 m water depth. The core was 295 cm long. The hydrates were obtained from three intervals: 250–258 cm (sample C-1), 269–273 cm (sample C-2), and 274–279 cm (sample C-3).

[8] A portion of the hydrates stored in a dry-shipper was decomposed in a small vessel to analyze molecular and isotopic compositions ($\delta^{13}C$ and δD) of hydrocarbons in the released gas. The experimental methods of the gas analyses were already detailed in our previous paper [*Kida et al.*, 2006]. The confidence limits of the measurements of hydrocarbon composition are 0.005% for C_1–C_3 hydrocarbons and 0.0005% for C_4–C_9 hydrocarbons, which were determined by duplicate analyses of standards. The analytical precision of $\delta^{13}C$ is 0.1‰ and that of δD is 0.6‰ [*Hachikubo et al.*, 2007].

[9] The ^{13}C single-pulse NMR spectra for identifications of encaged hydrocarbons, determination of clathrate hydrate structure, and estimation of cage occupancies and hydration number were mea-
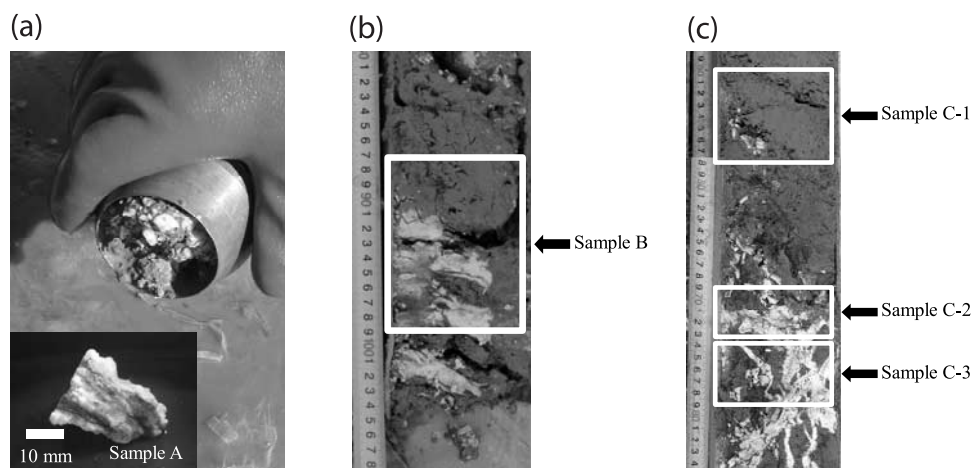
Figure 2. Close-up photographs of the hydrate-bearing sediment cores recovered from the three study sites. (a) Photograph of the bottom of the core recovered from the Malenky structure, displaying white massive gas hydrates. Sample A was collected from the massive gas hydrates. (b) Close-up core photograph of the interval of 80–108 cm below the lake floor of the core recovered from the Bolshoy structure. (c) Close-up core photograph of the interval of 246–297 cm below the lake floor of the core recovered from the K-2 mud volcano. Samples studied were obtained from inside of the white frame in Figures 2b and 2c.

sured using an NMR spectrometer (100 MHz, JNM-AL400; JEOL) equipped with the probe for solid samples (SH40T6; JEOL). The hydrates were introduced into a zirconia sample tube (6 mm diameter, 22 mm length; JEOL) in liquid nitrogen. All spectra were measured at 171 K using cooled dry nitrogen gas. The values of the ^{13}C chemical shift were determined using adamantane as an external reference material with the methyl carbon peak at 298 K set at 29.472 ppm [*Hayashi and Hayamizu*, 1991]. On the basis of results of a previous study [*Kida et al.*, 2007], ^{13}C single-pulse NMR measurements were carried out under the following conditions: ^{13}C pulse length 5.5 μs (90°), pulse delay time 50 s for complete relaxation

Table 1. Molecular and Isotopic Compositions of Hydrocarbon in Dissociated Gases From Five Hydrate Samples Recovered From Lake Baikal[a]

	SBB Basin		CBB Basin: K-2 Site		
	Malenky Site: Sample A	Bolshoy Site: Sample B	Sample C-1	Sample C-2	Sample C-3
Molecular Composition					
Methane/%	99.97	99.98	85.22	96.74	96.24
Ethane/%	0.03	0.02	14.69	3.24	3.72
Propane/%	<0.01	<0.01	0.02	<0.01	<0.01
Isobutane/%	ND	<0.001	0.005	0.006	0.007
n-butane/%	ND	<0.001	0.001	0.001	0.001
Neopentane/%	ND	<0.001	0.064	0.001	0.001
Isopentane/%	<0.001	<0.001	<0.001	0.004	0.007
Cyclopentane/%	<0.001	<0.001	ND	ND	ND
n-pentane/%	ND	ND	<0.001	<0.001	<0.001
n-hexane/%	ND	ND	<0.001	ND	ND
ΣC_6 others/%	ND	<0.001	ND	0.004	0.009
$\Sigma C_7 - C_9$/%	ND	<0.001	<0.001	0.004	0.005
$C_1/(C_2 + C_3)$	3593	4732	6	30	26
Isotope Composition					
$\delta^{13}C$ of methane/‰	−66.6	−66.5	−57.4	−57.6	−57.0
δD of methane/‰	−304	−302	−303	−303	−304
$\delta^{13}C$ of ethane/‰	ND	ND	−25.9	−26.4	−26.1
δD of ethane/‰	ND	ND	−216	−200	−200

[a]ND means that the component was not detected.

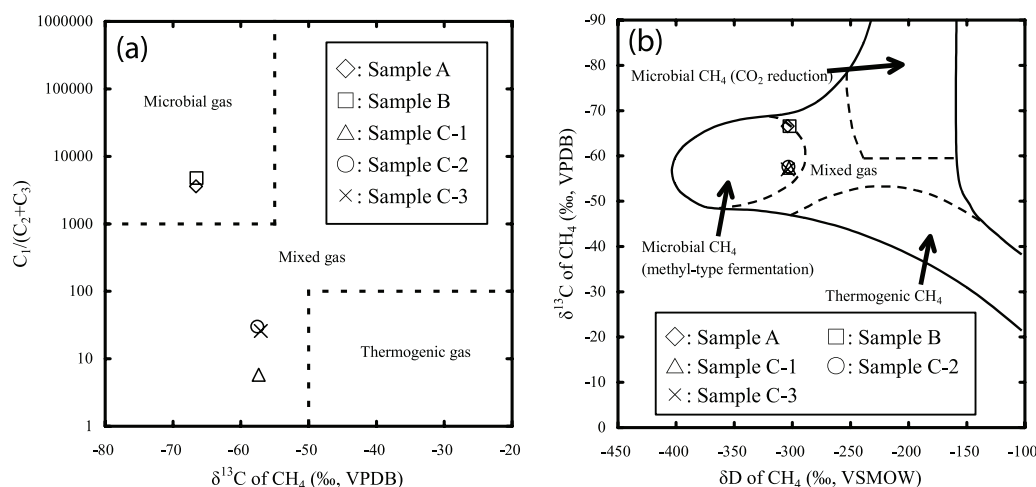**Figure 3.** (a) Relationship between carbon isotope composition ($\delta^{13}C$) of CH_4 and the ratio $C_1/(C_2 + C_3)$. (b) Relationship between hydrogen (δD) and carbon isotope composition ($\delta^{13}C$) of CH_4.

of the samples, number of acquisitions 80–264, and spinning rate 3.4–4.1 kHz at the magic angle.

3. Results and Discussion

3.1. Composition and Isotopic Signature of the Baikal Hydrates

[10] The molecular and isotopic compositions of hydrocarbons in dissociated gas from five hydrate samples recovered from the SBB and CBB in Lake Baikal are presented in Table 1. Also, two different relationships between isotopic ratios and compositional ratio of $C_1/(C_2 + C_3)$ in the released gas are shown in Figure 3, based on studies by *Bernard et al.* [1976] and *Whiticar* [1999]. Samples A and B recovered from Malenky and Bolshoy in the SBB contained over 99.9% CH_4. Figure 3 shows the gases were of microbial origin by methyl-type (acetic) fermentation. The characteristics of hydrocarbons trapped in the gas hydrate samples A and B resembled those of the samples recovered during the Baikal Drilling Project (BDP) at the SBB in 1997 [*Kuzmin et al.*, 1998]. For samples C-1, C-2, and C-3 from the CBB, high concentrations of CH_4 and C_2H_6 were detected. The concentration ratios CH_4/C_2H_6 differed considerably from each of the three samples: the ratio CH_4/C_2H_6 of sample C-1 was 85.22/14.69, whereas those of samples C-2 and C-3 were, respectively, 96.74/3.24 and 96.24/3.72. The isotope values for CH_4 and C_2H_6 trapped in the three hydrate samples were almost constant, and were similar to those obtained from the same area during our study conducted in 2005 [*Kida et al.*, 2006]. Figure 3 indicates that the gas hydrates

in the K-2 mud volcano were formed by mixing of microbial and thermogenic gas.

3.2. Crystal Structure of the Baikal Hydrates

[11] The ^{13}C single-pulse NMR spectra of NGH samples recovered from Lake Baikal are depicted in Figure 4. Sample A, recovered from Malenky in the SBB, showed two peaks at −4.29 ppm and
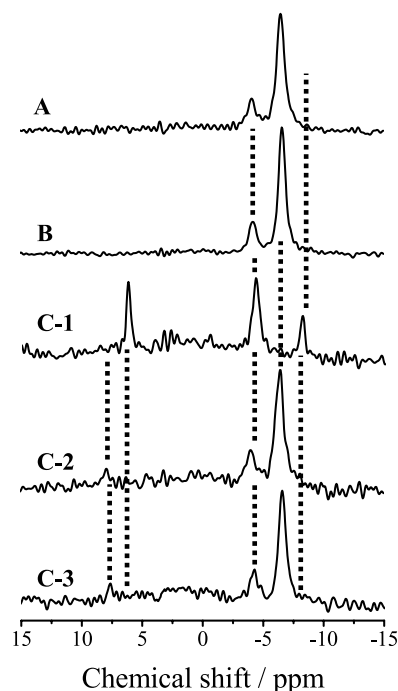

Figure 4. The ^{13}C single-pulse NMR spectra of five hydrate samples recovered from Lake Baikal.

Table 2. Summary of Cage Occupancies and Hydration Numbers of Five Hydrate Samples Recovered From Lake Baikal[a]

	SBB Basin		CBB Basin: K-2 Site		
	Malenky Site: Sample A	Bolshoy Site: Sample B	Sample C-1	Sample C-2	Sample C-3
Crystal structure	I	I	II	I	I
CH_4/C_2H_6 composition in dissociated gas (%)	99.97/0.03	99.98/0.02	85.22/14.69	96.74/3.24	96.24/3.72
Small cage occupancy of CH_4, $\theta_{M,S}$	0.853 ± 0.030	0.818 ± 0.025	0.732 ± 0.031	0.775 ± 0.032	0.798 ± 0.080
Large cage occupancy of CH_4, $\theta_{M,L}$	0.975 ± 0.002	0.977 ± 0.001	0.574 ± 0.029	0.943 ± 0.013	0.916 ± 0.058
Large cage occupancy of C_2H_6, $\theta_{E,L}$	–	–	0.412 ± 0.026	0.036 ± 0.012	0.035 ± 0.004
Hydration number, n	6.09 ± 0.04	6.14 ± 0.04	6.94 ± 0.17	6.20 ± 0.05	6.17 ± 0.11

[a] The uncertainties are the standard deviations of duplicate determinations.

−6.62 ppm, which were attributed to CH_4 in small and large cages of sI, respectively, based on earlier studies on synthetic gas hydrates [*Ripmeester and Ratcliffe*, 1988; *Kida et al.*, 2007]. The unit cell of sI hydrate is constructed by 46 H_2O molecules (two small cages (12-hedrons) and six large cages (14-hedrons)) [*Sloan*, 2003]. Sample B recovered from Bolshoy in SBB yielded two peaks at −4.24 and −6.62 ppm, which were assigned respectively to CH_4 in small and large cages of sI as well as sample A. For samples recovered from the K-2 mud volcano in the CBB, sample C-1 showed three peaks at 6.21 ppm, −4.33 ppm, and −8.22 ppm, which are respectively attributed to C_2H_6 in large cages of sII, CH_4 in small cages of sII, and CH_4 in large cages of sII, similarly to the spectra of CH_4-C_2H_6 mixed gas hydrates already reported [*Subramanian et al.*, 2000a, 2000b; *Kida et al.*, 2006, 2007]. The unit cell of sII hydrate consists of 136 H_2O molecules (16 small cages (12-hedrons) and eight large cages (16-hedrons)) [*Sloan*, 2003]. The C-2 sample yielded three peaks at different positions from those of sample C-1. The three peaks of sample C-2 at chemical shifts of 7.91 ppm, −3.99 ppm, and −6.47 ppm, were attributed respectively to C_2H_6 in large cages of sI, CH_4 in small cages of sI, and CH_4 in large cages of sI. The spectrum of sample C-3 showed three peaks at the same positions as those of sample C-2, indicating the sI hydrate crystal structure. These ^{13}C NMR spectra indicated that sI and sII hydrates coexist in the core recovered from the K-2 mud volcano. This observation was similar to that in our previous report on hydrate-bearing cores recovered from the K-2 mud volcano [*Kida et al.*, 2006].

3.3. Cage Occupancies and Hydration Numbers of the Baikal Hydrates

[12] In the CH_4-C_2H_6 system, the values of small cage occupancy of CH_4 ($\theta_{M,S}$), large cage occupancy of CH_4 ($\theta_{M,L}$), and large cage occupancy of C_2H_6 ($\theta_{E,L}$) are given by relative occupancy ratios calculated by ^{13}C NMR signals from encaged CH_4 and C_2H_6, based on a statistical thermodynamic model [*van der Waals and Platteeuw*, 1959]. Details of this estimation have been described in the paper reported by *Kida et al.* [2007]. This method have several assumptions: free energy of the hydrate is independent of cage occupation, distortions of hydrate cages and guest-guest interactions are excluded, and each cage can contain one guest molecule [*Sloan*, 1998]. The hydrate formation temperature in this study was assumed to be the reported water temperature (276.6 K) of the bottom of Lake Baikal [*van Rensbergen et al.*, 2002]. The hydration number, n, is given by equation (1) for sI and equation (2) for sII.

$$n = \frac{23}{3(\theta_{M,L} + \theta_{E,L}) + \theta_{M,S}} \quad (1)$$

$$n = \frac{17}{(\theta_{M,L} + \theta_{E,L}) + 2\theta_{M,S}} \quad (2)$$

Here, the values of $\theta_{E,L}$ for samples A and B recovered from the SBB are not included because no signals from C_2H_6 were observed.

[13] The cage occupancies and hydration numbers of NGHs recovered from Lake Baikal are presented in Table 2. The cage occupancies of sample A (sI)

obtained from Malenky in SBB were estimated as $\theta_{M,S} = 0.853$ and $\theta_{M,L} = 0.975$. The value of n for sample A was 6.09, which resembles values reported for synthetic pure CH_4 hydrate ($n = 6.05 \pm 0.06$ [*Ripmeester and Ratcliffe*, 1988]) and NGHs containing CH_4 as a main component (n values of 6.11 for the Hydrate Ridge (offshore Oregon) sample [*Kim et al.*, 2005] and 6.1 for the offshore Vancouver Island samples [*Lu et al.*, 2005]). For sample B (sI) recovered from the SBB, the values of $\theta_{M,S}$, $\theta_{M,L}$, and n were 0.818, 0.977, and 6.14, respectively, which were almost consistent with those of sample A. The present results for samples A and B showed nearly full CH_4 occupation for large cages and the presence of some vacant small cages in sI hydrate. For sample C-1 (sII), recovered from the CBB, the cage occupancies were estimated as $\theta_{M,S} = 0.732$, $\theta_{M,L} = 0.574$, and $\theta_{E,L} = 0.412$. The sum of $\theta_{M,L}$ and $\theta_{E,L}$ was 0.986, reflecting that CH_4 and C_2H_6 almost entirely occupied the large cages in sII. The value of n for sample C-1 was 6.94, which is much greater than those for samples A and B with sI. Nevertheless, compared to the reported n value of 8.2 for the sII naturally occurring mixed gas hydrate recovered from the Gulf of Mexico, the value of n for sample C-1 (sII) was quite small. This difference in n values between sample C-1 and the Gulf of Mexico sample is inferred to result from the differences in gas composition. Furthermore, our value, which was estimated without considering the effect of excess water in the sample, is expected to differ greatly from the value estimated by Handa using the gas-water ratio. For sample C-2 (sI) recovered from the CBB, the values of $\theta_{M,S}$, $\theta_{M,L}$, and $\theta_{E,L}$ were, respectively, 0.775, 0.943, and 0.036. The sum of $\theta_{M,L}$ and $\theta_{E,L}$ was 0.979, indicating that the large cages of sI were almost at full occupancy level. The hydration number of sample C-2 was estimated as $n = 6.20$, which is slightly greater than those of samples A and B. The cage occupancies and hydration number of sample C-3 (sI) located directly below sample C-2 were almost identical to those of sample C-2 (sI), as listed in Table 2. The difference in the values of $\theta_{M,S}$ among the CH_4-C_2H_6 hydrates from the K-2 mud volcano are not large, but, in contrast, the differences in hydration number between them is quite large. This difference is due to the fact that number of small cages per a unit cell of sII is larger than that of sI.

4. Conclusions

[14] We reported on the qualitative and quantitative parameters of the hydrocarbon gases trapped in the NGHs of Lake Baikal. There are considerable amounts of both CH_4 and C_2H_6, were pointed out in the Baikal mud volcano hydrates, with pure CH_4 hydrates in southern Baikal Basin and mixed CH_4-C_2H_6 hydrates in central Baikal Basin. Their cage occupancies and hydration numbers were estimated using an optimal ^{13}C NMR method. All samples studied had small cage occupancy of CH_4 ranging from 0.732 to 0.853. Large cages were almost fully occupied by only CH_4 or two guest components of CH_4 and C_2H_6 for all samples. The difference in the values of $\theta_{M,S}$ among the NGHs studied resulted in large differences among the hydration numbers. The present study suggests that consideration of cage occupancies and hydration numbers of mixed gas hydrates in local environments can be used to improve global estimates of the amount of natural gas trapped in hydrate crystals.

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