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Model of formation of double structure gas hydrates in Lake Baikal based on isotopic data

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[1] We measured the isotopic compositions of methane (C_1) and ethane (C_2) of hydrate-bound gas and of dissolved gas in pore water retrieved from bottom sediments in Lake Baikal. Both structure I (sI:3% C_2) and II (sII:14% C_2) gas hydrates are observed in the same sediment cores in Kukuy K-2 mud volcano. We found that C_2 δD of sI gas hydrate is larger than that of sII, whereas C_1 $\delta^{13}C$, C_1 δD and C_2 $\delta^{13}C$ values are practically the same in both hydrate structures. $\delta^{13}C$ of C_1 and C_2 of hydrate-bound gas are several permil smaller than those in pore water, showing that the current pore water is not the source of gas hydrates. These findings lead to a new model where the sII gas hydrates were formed prior to the sI hydrates. **Citation:** Hachikubo, A., et al. (2009), Model of formation of double structure gas hydrates in Lake Baikal based on isotopic data, *Geophys. Res. Lett.*, 36, L18504, doi:10.1029/2009GL039805.

1. Introduction

[2] Natural gas hydrates are crystalline clathrate compounds composed of water and gas molecules that form in submarine/sublacustrine sediments when the pore water is saturated by gases at low temperature and high partial pressure of each gas component. Gas hydrates were first obtained from sub-bottom depths of 121 and 161m in the Baikal Drilling Project (BDP) well in the southern basin of Lake Baikal in 1997 [Kuz'min et al., 1998]. More recently, gas hydrates near the lake bottom were discovered in the mud volcanoes Malenky in the southern basin [Van Rensbergen et al., 2002] and Kukuy K-2 in the central basin [Khlystov, 2006; Kalmychkov et al., 2006], where gas-saturated fluids were discharged. While hydrate gas retrieved from the near surface sediments of Lake Baikal contained mainly microbial C_1 , high concentration of C_2 (13.4%) in the dissociated gas obtained in Kukuy K-2 was reported by Kalmychkov et al. [2006]. This indicated gas hydrate of mixed origin (microbial + thermogenic) and suggested the presence of structure II (sII) gas hydrates

[Kalmychkov et al., 2006]. Subramanian et al. [2000a, 2000b] showed that sII gas hydrates form at appropriate composition of C_1 and C_2 ; sII appear from 0.6–0.8% to 25–27.8% of C_2 composition in vapor phase at 274.2K. Kida et al. [2006] determined by CP-MAS ^{13}C NMR spectroscopy that the Kukuy K-2 hydrates that contained about 14–15% of C_2 belonged to sII, whereas the structure I (sI) gas hydrate contained about 3% of C_2 . They also pointed out that in the same cores the sI gas hydrates occur beneath the sII gas hydrates. In this study, gas compositions and isotopic ratios (^{13}C and D) were taken from hydrate-bound gas and also from dissolved gas in pore water. The aim of this work is to understand the formation process of the different crystal structures of gas hydrate in Kukuy K-2 mud volcano in Lake Baikal.

2. Materials and Methods

[3] Hydrate-bearing sediments were sampled in Lake Baikal using a gravity corer during cruises of RV G. Yu. Vereshchagin in September 2005 (VER05-03) and September 2006 (VER06-02). Cores were retrieved from the Kukuy K-2 (908–923 m water depth) and K-0 sites (427–435 m water depth) in the central Baikal basin in 2006 and from the Bolshoy, Malenky and Malyutka sites (1345–1375 m water depth) in the southern basin in 2005 (Figure 1). Gas hydrates were found in nine cores from K-2 (at sub-bottom depths of 90–330 cmblf), in two cores from K-0 (85–370 cmblf) and in seven cores from the southern basin sites (70–180 cmblf). Hydrate-bound gases were collected on-board by a syringe and filled into 5ml vial bottles. The dissolved gases in pore water were obtained by the headspace gas method. Hydrate-bound gases were also tapped in the laboratory from gas hydrate samples stored in a dry-shipper at liquid nitrogen temperature.

[4] For the isotopic analyses of carbon and hydrogen, a mass spectrometer (DELTA plus XP; Thermo Finnigan) was used. Isotopic compositions are reported as δ values defined as

$$\delta_{sample} = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000 \text{ (‰)} \quad (1)$$

where R denotes the ratio of $^{13}C/^{12}C$ or D/H, and δ values ($\delta^{13}C$ and δD) are given with reference to the VPDB and VSMOW standards, respectively. The analytical precision of $\delta^{13}C$ is 0.1‰ and that of δD is 0.6‰. Gas composition of hydrocarbons in all gas samples was measured using a gas chromatograph (GC-14B; Shimadzu Corp.) equipped with a thermal conductivity and a flame ionization detector with a

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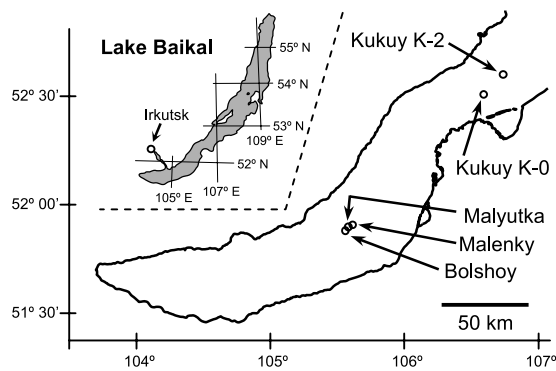


Figure 1. Location map of the coring sites in Lake Baikal where gas hydrate samples were retrieved.

packed column (Sunpak-S; Shimadzu Corp.). Raman spectra of the hydrate samples were obtained using a Raman spectrometer (RMP-210; JASCO Corporation) because the crystal structure can be determined by the Raman peak of the ν_3 C-C stretch for C_2 molecules [Subramanian *et al.*, 2000a].

3. Results

[5] Table 1 shows representative (median) values of gas composition. C_2 compositions are 1.2–4.5% (sI hydrates of Kukuy K-2) and 13.0–14.5% (sII hydrates of Kukuy K-2), respectively, and agree well with the results of gas composition reported by Kida *et al.* [2006]. Figure 2 shows the relation between the isotopic ratios and the gas composition of hydrate-bound gas from the different sampled sites in Lake Baikal. Gas samples obtained from Kukuy K-2 are located in the field of mixed microbial and thermogenic gas, whereas those obtained from the southern basin of Lake Baikal are in the field of microbial gas (Figure 2a). The C_1/C_2 ratios are clearly different for the sI and sII hydrates in Kukuy K-2 with the former widely distributed from 13 to 80 and the latter concentrated around 6. $C_1 \delta^{13}C$ ranges from -59.1 to -56.5‰ in Kukuy K-2, from -63.3 to -62.5‰ in Kukuy K-0 and from -66.2 to -64.6‰ in other sites of Baikal southern basin. There is no difference in $C_1 \delta^{13}C$ between sI and sII hydrates in Kukuy K-2. Based on the $\delta^{13}C$ - δD diagram of C_1 [Whiticar, 1999; Milkov, 2005] and as reported earlier by Kida *et al.* [2006], C_1 of Kukuy K-2 for both sI and sII appears in the field of microbial origin produced by methyl-type fermentation (Figure 2b). As C_1 samples from the other sites also belong to the same field, it is clear that microbial C_1 by methyl-type fermentation is dominant in Lake Baikal. $C_2 \delta^{13}C$ in Kukuy and Malyutka indicates a thermogenic origin (Figure 2c) and the data of $C_1 \delta^{13}C$ in Kukuy K-2 are close to the thermogenic field. This shows that thermogenic gas mixes partly with the microbial gas (mainly C_1) and/or anaerobic methane oxidation increases $C_1 \delta^{13}C$ in Kukuy K-2.

[6] Figure 3 shows $\delta^{13}C$ profiles of eight hydrate-bearing cores in Kukuy K-2 plotted against depth below the lake bottom. $C_1 \delta^{13}C$ of dissolved gas in pore water is low (-65‰) in the upper layer (35–70 cmblf) and increases with depth to a value of -55‰ . On the other hand, $C_1 \delta^{13}C$ of hydrate-bound gas ranges from -59 to -57‰ at 93 to

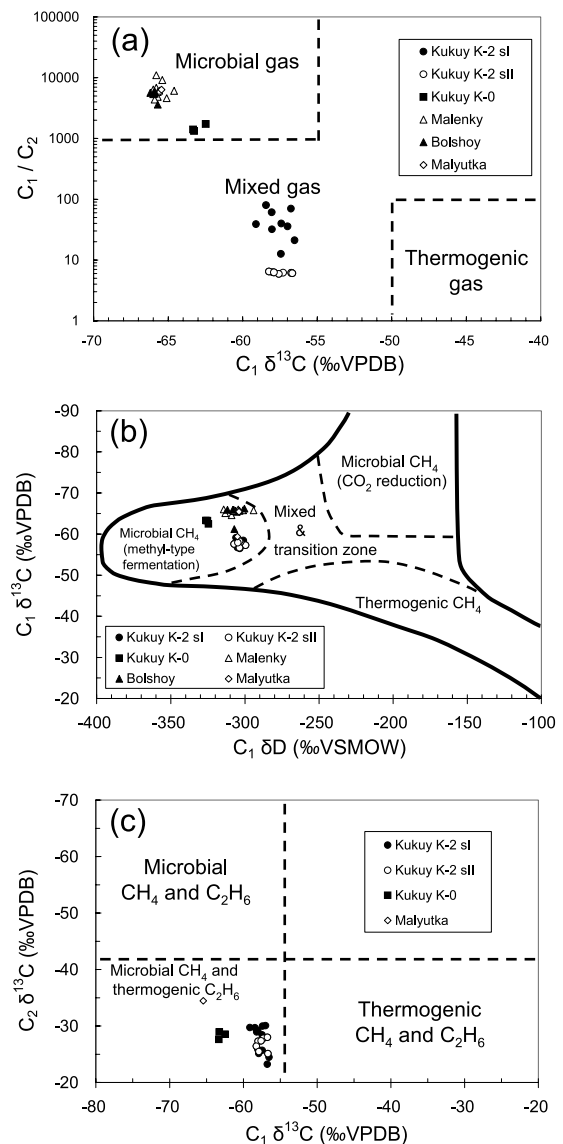


Figure 2. Isotopic results of gas hydrate samples obtained in Lake Baikal: (a) relation between $C_1 \delta^{13}C$ and the ratio C_1/C_2 , (b) relation between δD and $\delta^{13}C$ of C_1 , (c) relation between $\delta^{13}C$ of C_1 and C_2 . The fields of gas origin in these graphs are according to Whiticar [1999] and Milkov [2005].

334 cmblf and is several permil lower than that of dissolved gas in pore water. $C_2 \delta^{13}C$ from dissolved gas in pore water is almost constant with depth (from -26 to -24‰) for all sediment cores. That of hydrate-bound gas, on the contrary,

Table 1. Gas Composition of Hydrate-Bound Gas

Site	C_1 (%)	C_2 (%)	C_3 (ppm)	iC_4 (ppm)	nC_4 (ppm)
Southern Basin ^a	99.98	0.02	4	n.d. ^b	n.d. ^b
Kukuy K-0	99.91	0.09	18	n.d. ^b	n.d. ^b
Kukuy K-2 sI	97.2	2.8	62	28	4
Kukuy K-2 sII	85.7	14.2	203	26	5

^aBolshoy, Malenky and Malyutka.

^bn.d., not detected.

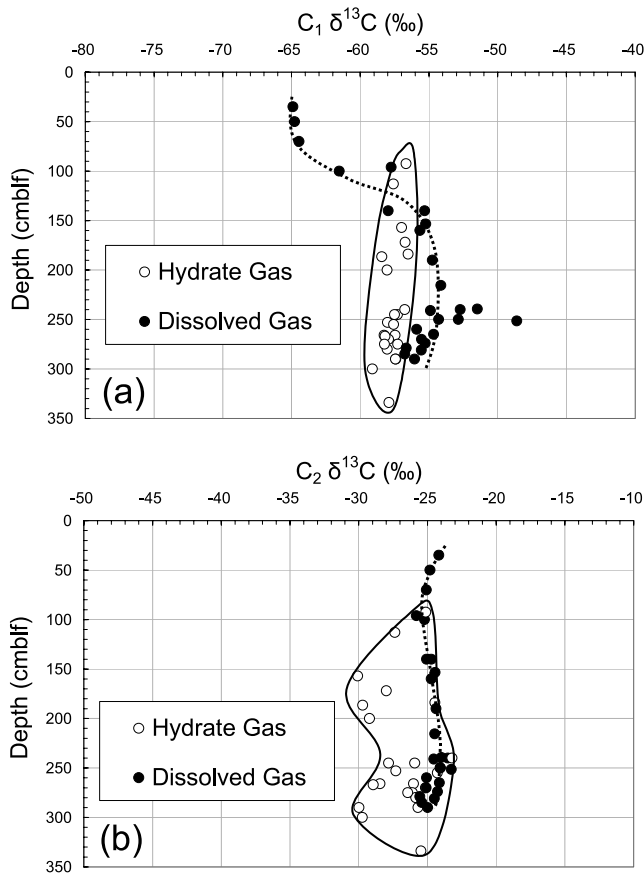


Figure 3. Isotopic profiles of (a) $C_1 \delta^{13}C$ and (b) $C_2 \delta^{13}C$ obtained from eight hydrate-bearing sediment cores in Kukuy K-2 mud volcano. Open circles: hydrate-bound gas, solid circles: dissolved gas in pore water.

ranges from -30 to -24‰ and is thus lower than that of dissolved gas.

[7] In all the sediment cores recovered from the Kukuy K-2 mud volcano the hydrates of sII are located in the upper part of the gas hydrate interval, and they occur as hydrate granules of several mm in diameter. Hydrates of sI, on the other hand, are massive and/or stratified, and found in the lower part of the gas hydrate interval. In most cases, a sediment layer of 3–13 cm separates the sII and sI hydrate intervals. This is illustrated in Figure 4a on a photograph of sediment core VER06-02 St2GC30. In this core granular sII hydrates are located in two layers, one at 91–98 cmbf (only traces) and the other from 115 to 123 cmbf. Hydrates of sI appear beneath the sII hydrates, as massive hydrates at 123–128 cmbf and 128–140 cmbf intervals, and as vertical “vein structure” from 140 to 260 cmbf. Figure 4b shows the depth profile of C_2 composition of hydrate-bound gas for this core. The two sII hydrate layers contain 14.2% and 13.0% of C_2 , respectively. On the other hand, C_2 composition of small massive and long vein hydrates (sI) is 1.4–3.2% and decrease with depth.

[8] Isotopic compositions are plotted against C_2 composition in Figures 5a–5d. $C_2 \delta D$ of sI hydrates is larger than that of sII hydrates, whereas $C_1 \delta D$, $C_1 \delta^{13}C$ and $C_2 \delta^{13}C$ in both hydrate structures are almost the same. $C_2 \delta D$ of sI

hydrates range from -196 to -211‰ , while those of sII show a more narrow range of -215 to -220‰ .

4. Discussion

[9] Isotopic fractionation of hydrocarbon gases during the formation of synthetic gas hydrates has been investigated by Hachikubo *et al.* [2007]. For gas hydrate samples produced in a pressure cell from gas and water, they

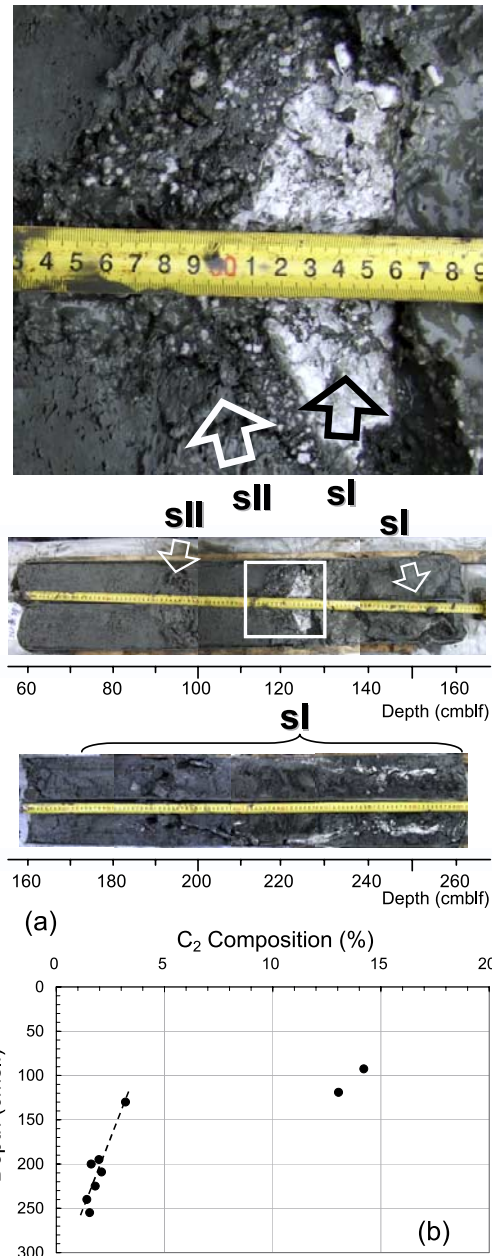


Figure 4. (a) Photo of a section of sediment core VER06-02 St2GC30 recovered from the Kukuy K-2 mud volcano in 2006 with indication of the intervals of sI and sII hydrates presence. (b) C_2 composition of hydrate-bound gas plotted against depth from the lake bottom: sI hydrates exist below 123 cmbf and C_2 composition decrease with depth. Broken line is the regression line for sI hydrates.

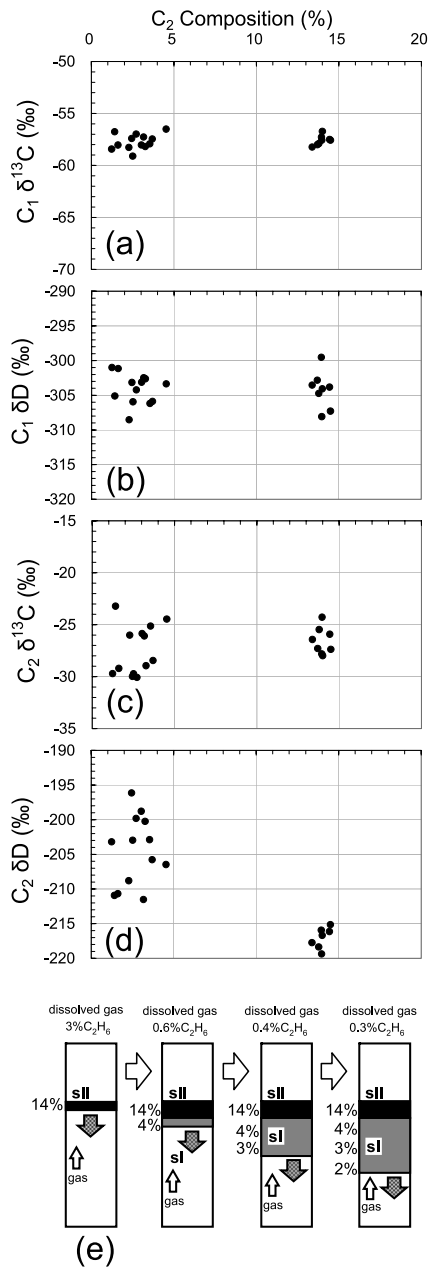


Figure 5. (a) $C_1 \delta^{13}C$, (b) $C_1 \delta D$, (c) $C_2 \delta^{13}C$ and (d) $C_2 \delta D$ plotted against C_2 composition. $C_2 \delta D$ of sI hydrate is larger than that of sII, though $C_1 \delta^{13}C$, $C_1 \delta D$ and $C_2 \delta^{13}C$ in both hydrate structures is almost the same. (e) Schematic model of the formation process of double structure gas hydrates in Kukuy K-2 mud volcano, Lake Baikal.

revealed that δD of hydrate-bound gas becomes several permil ($4.8 \pm 0.4\text{‰}$ for C_1 and $1.1 \pm 0.7\text{‰}$ for C_2) lower than that of the original gas, whereas $\delta^{13}C$ of hydrate-bound and original gases remains almost constant. Figure 3 shows that for the Kukuy K-2 samples $C_1 \delta^{13}C$ of hydrate gas ranges from -59 to -57‰ and is several permil lower than that of dissolved gas in pore water (about -55‰ below 140cmblf). For C_2 , $\delta^{13}C$ of hydrate gas was also lower than that of dissolved gas in pore water. Based on the results of our laboratory experiments [Hachikubo *et al.*, 2007], we can

thus conclude that the current gas dissolved in pore water is not the source of the gas hydrates in the Kukuy K-2 samples. The gas hydrate crystals in Kukuy K-2 were formed from C_1 ($\delta^{13}C$: -58‰) and C_2 ($\delta^{13}C$: -30‰) of dissolved/free gas different than the present. In a later stage the $\delta^{13}C$ of gas in pore water must have increased several permil and meanwhile and the concentrations of C_1 and C_2 dropped to under-saturation. This was possibly caused by changes in mud volcano activity, which could have altered the routes of gas supply and/or the mixing process between thermogenic and microbial gases.

[10] Our results as presented in Figures 4 and 5d allow to propose a model for the formation of the co-existing sI and sII gas hydrates in Kukuy K-2 mud volcano in Lake Baikal. First the sII gas hydrates were formed from supersaturated gas in pore water. Because of the preferential inclusion of C_2 in the hydrate phase, the concentration of C_2 in the remaining pore water decreased. Subsequently, the sI gas hydrates were formed from the low concentration of C_2 and increased $C_2 \delta D$ of gas hydrates. Although $C_1 \delta D$ in the hydrate phase must also be lower than that in the dissolved/free gas during the formation of hydrate, the difference of $C_1 \delta D$ between both structures is negligible due to abundance of C_1 compared with C_2 .

[11] Table 2 shows that the C_2 composition of the gas phase at corresponding depth of our hydrate samples and in equilibrium with the C_1 , C_2 and water system, is always lower. Moreover, Deaton and Frost [1946] showed that C_2 is enriched in the hydrate phase during formation of hydrate. As a result, the C_2 composition of the hydrate phase must always be larger than that of the gas phase. Assuming that the gas supplied by ascending fluids from deeper sediment layers was insufficient to maintain the C_2 concentration in the near-bottom sediments, we can propose the following scenario for the formation of gas hydrate in the near-surface (Figure 5e): nucleation of sII hydrate ($14\%C_2$) occurred rapidly from dissolved gas in pore water ($3\%C_2$) due to low equilibrium pressure. The C_2 concentration of dissolved gas was hereby reduced below the critical concentration of $0.6\text{--}0.8\%C_2H_6$ to form sII hydrates [Subramanian *et al.*, 2000b]. As a result, sI hydrate ($4\%C_2$) started to form, but this time more slowly due to the rather high equilibrium pressure. Because both C_2 concentrations of sI hydrate and dissolved gas decreased due to the preferential consumption of C_2 into hydrate phase, the range of C_2 compositions in sI hydrate became larger than those in sII hydrate as shown in Figures 2a and 4b. Isotope results in Figure 5d support this scenario: light C_2 molecules (C_2H_6)

Table 2. C_2 Composition of Gas and Hydrate Phases, Equilibrium Pressure and Crystal Structure at the Equilibrium State of the Ternary System Composed of C_1 , C_2 and Water at $276K^a$

C_2H_6 Composition (%)		Equilibrium Pressure (MPa)	Structure
Gas	Hydrate		
3.0	14.1	3.00	II
0.6	4.0	3.32	I
0.4	2.7	3.36	I
0.3	2.0	3.38	I
0.2	1.4	3.40	I

^aThese data are calculated by using CSMHYD Hydrate Program [Sloan, 1998].

were first concentrated in the sII hydrate and heavy C₂ molecules (C₂H₅D) remained in the dissolved gas and were consumed in the next stage of hydrate formation of sI.

[12] C₁ solubility in pore water with its hydrate is lower than that without hydrate under 278.15K and 10MPa [Handa, 1990]. For C₂ the solubility with its hydrate is not known for high pressure, but it is reasonable to assume a same trend. Using this assumption and measured water content and density data [Kataoka, 2009], we can calculate that 0.05m-thick layer of massive hydrate consumed the excess gas in about 10m of sediment layer. Therefore, the height of the “closed system” in Figure 5e is estimated at several tens of meters to form the gas hydrate layers in Figure 4a. The gas is probably provided by ascending free gas as Granin *et al.* [2007] observed gas seeps in all basins. Such free gas in the sediment can reduce the height of the closed system. We consider that the formation speed of the gas hydrate layer is relatively larger than the gas supply from deeper layer as the lake bottom is where low temperature and high pressure conditions are most suitable and surplus gas is abundant.

[13] Manakov *et al.* [2007] proposed an alternative model for the formation of the double-structure gas hydrates. They suggested that sI gas hydrates were formed first, then they partly dissolved due to insufficient gas supply, and finally reformed as sII gas hydrate from the dissolved gas. Their model agrees well with the enrichment process of C₂ [Deaton and Frost, 1946; Sloan, 1998], but it is not supported by our isotope data. It is debatable whether both processes can exist simultaneously at different places within Kukuy K-2 mud volcano and further studies are needed to find conclusive answers.

[14] **Acknowledgments.** This work was supported by funding agencies in Japan (Japan Society for the Promotion of Science KAKENHI 18206099 and 19550077, the Ministry of Education, Culture, Sports, Science and Technology KAKENHI 19740323), Flemish Fund for Scientific Research (FWO-Vlaanderen), Bilateral Flemish-Russian Federation Project, and the Integration project of RAS SB 58.

References

- Deaton, W. M., and E. M. Frost Jr. (1946), Gas hydrates and their relation to the operation of natural-gas pipe lines, *Monogr.* 8, U.S. Bur. of the Inter., Washington, D. C.
- Granin, N. G., R. Y. Gnatovsky, M. M. Makarov, and M. A. Yakup (2007), Gas seeps in Lake Baikal, paper presented at International Conference on Gas Hydrate Studies, Limnol. Inst., Russ. Acad. of Sci., Irkutsk, Russia, 3–8 Sept.
- Hachikubo, A., T. Kosaka, M. Kida, A. Krylov, H. Sakagami, H. Minami, N. Takahashi, and H. Shoji (2007), Isotopic fractionation of methane and ethane hydrates between gas and hydrate phases, *Geophys. Res. Lett.*, 34, L21502, doi:10.1029/2007GL030557.
- Handa, Y. P. (1990), Effect of hydrostatic pressure and salinity on the stability of gas hydrates, *J. Phys. Chem.*, 94, 2652–2657, doi:10.1021/j100369a077.
- Kalmychkov, G. V., A. V. Egorov, M. I. Kuz'min, and O. M. Khlystov (2006), Genetic types of methane from Lake Baikal, *Dokl. Akad. Nauk*, 411, 672–675.
- Kataoka, S. (2009), Soil properties of the gas hydrate-bearing sediments in Lake Baikal (in Japanese), Ph.D. thesis, 123 pp., Kitami Inst. of Technol., Kitami, Japan, 18 March.
- Khlystov, O. M. (2006), New findings of gas hydrates in the Baikal bottom sediments, *Russ. Geol. Geophys.*, 47, 979–981.
- Kida, M., *et al.* (2006), Coexistence of structure I and II gas hydrates in Lake Baikal suggesting gas sources from microbial and thermogenic origin, *Geophys. Res. Lett.*, 33, L24603, doi:10.1029/2006GL028296.
- Kuz'min, M. I., *et al.* (1998), The first find of gas-hydrates in the sedimentary rocks of Lake Baikal, *Dokl. Earth Sci.*, 362, 1029–1031.
- Manakov, A. Y., O. M. Khlystov, and A. G. Ogienko (2007), Unusual coexistence of cubic structure I and II natural gas hydrates in the same core mined at the K-2 mud volcano (Lake Baikal), paper presented at International Conference on Gas Hydrate Studies, Limnol. Inst., Russ. Acad. of Sci., Irkutsk, Russia, 3–8 Sept.
- Milkov, A. V. (2005), Molecular and stable isotope compositions of natural gas hydrates: A revised global dataset and basic interpretations in the context of geological settings, *Org. Geochem.*, 36, 681–702, doi:10.1016/j.orggeochem.2005.01.010.
- Sloan, E. D., Jr. (1998), *Clathrate Hydrates of Natural Gases*, 2nd ed., 705 pp., Marcel Dekker, New York.
- Subramanian, S., R. A. Kini, S. F. Dec, and E. D. Sloan Jr. (2000a), Evidence of structure II hydrate formation from methane + ethane mixtures, *Chem. Eng. Sci.*, 55, 1981–1999, doi:10.1016/S0009-2509(99)00389-9.
- Subramanian, S., A. L. Ballard, R. A. Kini, S. F. Dec, and E. D. Sloan Jr. (2000b), Structural transitions in methane + ethane gas hydrates—Part I: Upper transition point and applications, *Chem. Eng. Sci.*, 55, 5763–5771, doi:10.1016/S0009-2509(00)00162-7.
- Van Rensbergen, P., M. De Batist, J. Klerkx, R. Hus, J. Poort, M. Vanneste, N. Granin, O. Khlystov, and P. Krinitsky (2002), Sublacustrine mud volcanoes and methane seeps caused by dissociation of gas hydrates in Lake Baikal, *Geology*, 30, 631–634, doi:10.1130/0091-7613(2002)030<0631:SMVAMS>2.0.CO;2.
- Whiticar, M. J. (1999), Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, *Chem. Geol.*, 161, 291–314, doi:10.1016/S0009-2541(99)00092-3.
- A. Hachikubo, M. Kida, H. Minami, H. Sakagami, H. Shoji, and N. Takahashi, Kitami Institute of Technology, 165 Koen-cho, Kitami 090-8507, Japan. (hachi@mail.kitami-it.ac.jp)
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