



Coexistence of structure I and II gas hydrates in Lake Baikal suggesting gas sources from microbial and thermogenic origin

Masato Kida,¹ Oleg Khlystov,² Tamara Zemskaya,² Nobuo Takahashi,¹ Hirotsugu Minami,¹ Hirotohi Sakagami,¹ Alexey Krylov,¹ Akihiro Hachikubo,¹ Satoshi Yamashita,¹ Hitoshi Shoji,¹ Jeffrey Poort,³ and Lieven Naudts³

Received 26 September 2006; revised 27 October 2006; accepted 7 November 2006; published 16 December 2006.

[1] We report the field observation of hydrate deposits of different crystal structures in the same cores of a mud volcano in the Kukuy Canyon. We link those deposits to chemical fractionation during gas hydrate crystallization. Gas composition and crystallographic analyses of hydrate samples reveal involvement of two distinct gas source types in gas hydrate formation at present or in the past: microbial (methane) and thermogenic (methane and ethane) gas types. The clathrate structure II, observed for the first time in fresh water sediments, is believed to be formed by higher mixing of thermogenic gas. **Citation:** 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.

1. Introduction

[2] Gas hydrates (GHs) are natural gas reservoirs in ice-like crystalline solids; they are stable in pore spaces of submarine/sublacustrine sediments at water depths greater than about 500 m. Gas hydrates near the bottom are related to sites of enhanced fluid venting, such as cold seeps, vents, mud volcanoes, and other structures. Lake Baikal is the deepest rift lake in the world and the only fresh water environment from which gas hydrates have been recovered [Kuzmin et al., 1998; Van Rensbergen et al., 2002]. Lake Baikal, with a water depth of up to 1622 m, was formed in an active continental rift environment in Central Asia. Thick accumulations, probably of Oligocene and Neogene synrift sediments, underlie three deep-water basins [Golmshtok et al., 2000]. The presence of gas hydrates in those sediments was first suggested by the observation of a bottom-simulating reflector (BSR) on multichannel seismic reflection profiles [Hutchinson et al., 1992]. In 1997, methane hydrate samples were obtained from the 225-m-long Baikal Drilling Project (BDP) well at the southern Baikal basin. The GHs from sub-bottom depths of 121 and 161 m contained guest gases, mainly of methane (99% of total hydrocarbons) with delta ¹³C values between -58‰ and -68‰ [Kuzmin et al., 1998], which indicates a microbial origin for the gas.

[3] The GHs near the lake bottom were found at places associated with methane seeps. The first shallow hydrates were discovered in a seep called Malenky in the southern

Baikal basin [Van Rensbergen et al., 2002; Matveeva et al., 2003; Klerkx et al., 2003]. Gas from the hydrate samples consisted mainly of methane of microbial origin, similar to those from the BDP well. Recently, GH-bearing structures were also discovered at the central basin of Baikal [Khlystov, 2005; Kalmychkov et al., 2005; De Batist et al., 2005]. In the mud volcano K-2 in the Kukuy Canyon, GHs of mixed genesis (bacterial + thermogenic) with considerable admixture of ethane (13.4%) were detected [Kalmychkov et al., 2005], which has allowed prediction of the presence of hydrates with clathrate structure II [Khlystov, 2005]. The present study shows detailed characteristics of the GHs sampled from this mud volcano during an international collaborative field investigation of the Kitami Institute of Technology, Japan and the Limnological Institute SB RAS, Russia in the autumn of 2005, onboard of RV G. Yu. Vereshchagin. Measurements of gas compositions and isotopic compositions on carbon and hydrogen were taken from dissociated gas samples of hydrates. Crystal structures were detected using ¹³C NMR measurements. All data were incorporated to elucidate possible GH formation processes in-situ in sublacustrine sediments.

2. Materials and Experimental Methods

[4] The GH-bearing sediment cores were obtained respectively at water depths of 930 m and 938 m from two sites, K2St2GC1 and K2St2GC6 (Figure 1). The GH fractions were stored and transported in a dry-shipper at liquid nitrogen temperature. Gas compositions of hydrocarbons of C₁-C₃ in dissociated gas samples from hydrates were measured using gas chromatograph (GC-14B; Shimadzu Corp.) equipped with a thermal conductivity and a flame ionization detector with a column (Sunpak-S; Shimadzu Corp.). Heavier hydrocarbons of C₄-C₉ were analyzed using a gas chromatograph (GC-14B; Shimadzu Corp.) equipped with a flame ionization detector with a capillary column (TC-1; GL Sciences Inc.) and a gas chromatograph (263-30; Hitachi Ltd.) with a flame ionization detector equipped with a column (VZ-7; GL Sciences Inc.). Isotopic compositions of δ¹³C and δD were measured using an isotope apparatus (DELTA plus XP; Thermo Finnigan). The ¹³C NMR spectra for determination of clathrate hydrate structure were measured with an NMR spectrometer (100 MHz, JNM-AL400; JEOL) equipped with the probe for solid samples (SH40T6; JEOL), using cross polarization and magic angle spinning (CP-MAS) technique. The hydrate samples were introduced into a zirconia sample tube (6 mm diameter, 22 mm length; JEOL) in liquid N₂. The measurement temperature was maintained

¹Kitami Institute of Technology, Kitami, Japan.

²Limnological Institute, Siberian Branch of the Russian Academy of Sciences, Irkutsk, Russia.

³Renard Centre of Marine Geology, Ghent University, Ghent, Belgium.

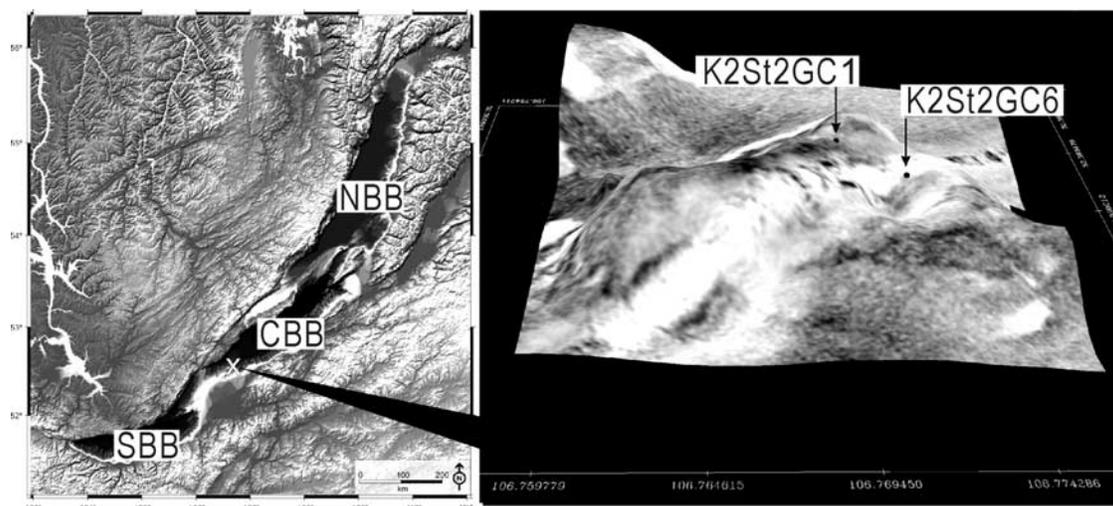


Figure 1. Shaded-relief DTM of the Baikal Rift Zone, constructed by compiling SRTM-derived topography data with bathymetry data from Lake Baikal [INTAS Project 99-1669 Team, 2002] with indication of the three basins (SBB, Southern Baikal Basin; CBB, Central Baikal Basin; NBB, Northern Baikal Basin). The locations of the cores are shown on a 3D image of the K-2 mud volcano draped with side-scan sonar mosaic; depths are compiled from echosounder recordings.

at 163 K using a variable temperature unit and a cooling vessel (JEOL). The spinning rate of the sample tube was 2.5–3.9 kHz. Values of ^{13}C chemical shift were determined using adamantane as an external reference material and a methyl carbon peak at 298 K was set at 29.472 ppm [Hayashi and Hayamizu, 1991].

3. Results and Discussion

[5] The stratigraphy of the recovered cores from two sites of K2St2GC1 and K2St2GC6 in a mud volcano in the Kukuy Canyon is shown in Figure 2. At K2St2GC1, a core of 135 cm was recovered with GH layers at two levels: 97–105 cm (designated as layer A in Figure 2a) and 115–135 cm (B in Figure 2a). The upper hydrate layer comprised 1–7-mm-diameter joint granules. The lower layer mostly comprised massive hydrates, containing a few large granules. The lithological composition of the overlying sediments is described in Figure 2a: dark-gray diatomaceous silty clay, covered with numerous degassing cracks and swellings and soft authigenic carbonates. At K2St2GC6, a core of 252 cm sediments was retrieved with GH occurring in the bottom part of the section (225–252 cm). The GH was present as three thin inclined layers (designated as C, D and E in Figure 2b), separated by thin layers of sediments. The top layer exhibits a fine structure of granules, but the bottom hydrates are massive with rare granules on edges. The lithological composition of sediments differs slightly from that in K2St2GC1, but degassing cracks, swelling and soft authigenic carbonates were equally present.

[6] Table 1 shows the hydrocarbon compositions of dissociated gases from seven hydrate samples retrieved at the Kukuy mud volcano. Two hydrate samples, A1 and E1, contained about 15% ethane, whereas five others (B1–B5) from layer B contained ethane of less than 5%. All hydrate samples contain much heavier hydrocarbons up to C_9 hydrocarbons at trace levels, suggesting some connection of the investigated structure to oil fields [Kontorovich et al., 1989] at some depth.

[7] The clathrate hydrate structure is known to depend on the molecular species trapped in its crystal [Sloan, 2003]. If the guest gas comprises methane and ethane mixtures, both clathrate hydrate structures I and II might be formed, depending on the mixing ratio [Subramanian et al., 2000a; Uchida et al., 2002; Takeya et al., 2003]. Also, CP-MAS ^{13}C NMR spectroscopy was used to determine the clathrate hydrate structure from all seven hydrate samples (CP-MAS ^{13}C NMR spectra are shown in Figure 3). The profile of sample A1 showed three peaks at chemical shifts of 6.25 ppm, -4.24 ppm, and -8.12 ppm, which are respectively attributed to ethane molecules in large cages of structure II, methane molecules in small cages of

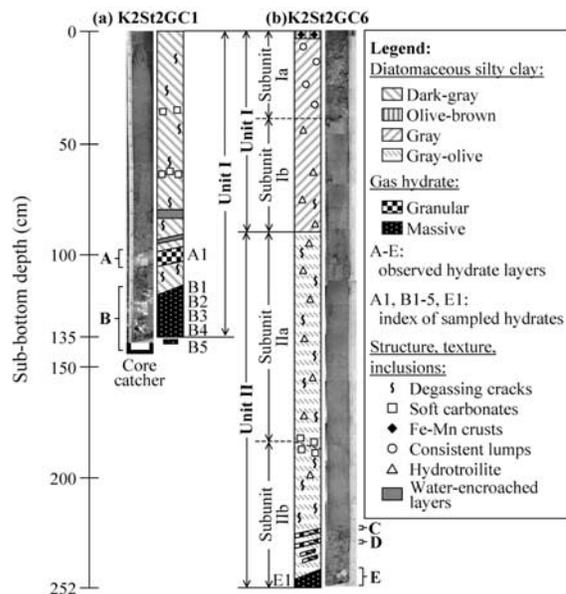


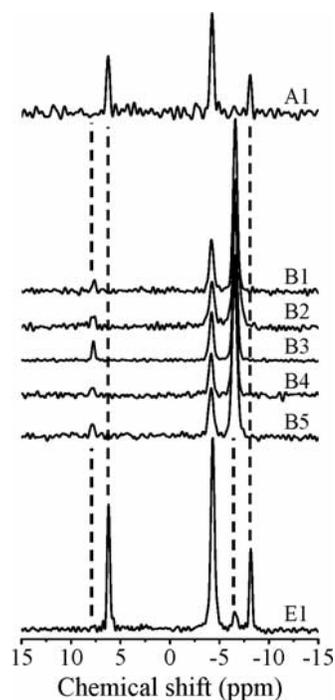
Figure 2. The stratigraphy of sediment cores recovered from the Kukuy mud volcano: (a) K2St2GC1 and (b) K2St2GC6.

Table 1. Hydrocarbon Compositions of Dissociated Gases From Seven Hydrate Samples Recovered From the Kukuy Mud Volcano^a

Sample	Layer						E1
	A		B				
	A1	B1	B2	B3	B4	B5	
Methane/%	85.1	98.5	96.9	96.8	95.7	97.4	85.6
Ethane/%	14.9	1.49	3.09	3.09	4.24	2.25	14.3
Propane/%	0.022	0.006	0.013	0.013	0.002	0.140	0.017
Isobutane/%	0.005	0.001	0.001	0.003	0.001	0.131	0.012
n-butane/%	0.001	<0.001	<0.001	0.001	<0.001	0.008	0.001
Neopentane/%	0.030	<0.001	0.002	0.002	0.001	0.014	0.026
Isopentane/%	<0.001	<0.001	0.001	0.002	0.001	0.003	<0.001
Cyclopentane/%	<0.001	<0.001	<0.001	0.024	0.002	0.002	<0.001
n-pentane/%	ND	ND	<0.001	<0.001	<0.001	<0.001	ND
n-hexane/%	<0.001	ND	ND	0.000	ND	ND	ND
∑C ₆ others/%	<0.001	<0.001	0.008	0.004	0.001	0.001	<0.001
∑C ₇ -C ₉ /%	<0.001	0.001	0.009	0.013	0.004	0.004	ND

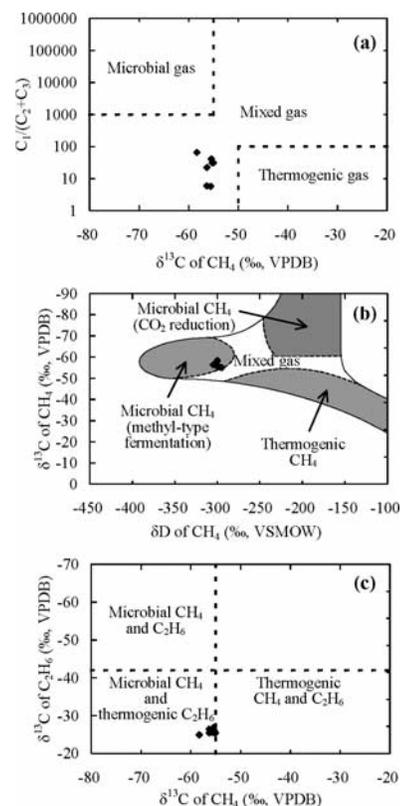
^aND means the component was not detected.

structure II, and methane molecules in large cages of structure II. Figure 3 shows that the profile of sample B1 differed from that of sample A1. The three ¹³C NMR peaks occurred at 7.66 ppm, -4.19 ppm, and -6.62 ppm, which are respectively attributed to ethane molecules in large cages of structure I, methane molecules in large cages of structure I, and methane molecules in small cages of structure I. In analogy with synthetic clathrate structure-I and structure-II reported [Subramanian *et al.*, 2000a], this shift in peaks suggests that samples from hydrate layer A include only structure II and from B only structure I. However, sample E1 shows four peaks at 6.21 ppm, -4.34 ppm, -6.52 ppm, and -8.17 ppm, which are respectively attributed to ethane molecules in large cages of structure II, methane molecules in small cages of

**Figure 3.** CP-MAS ¹³C NMR spectra of seven hydrate samples recovered from the Kukuy mud volcano.

structures I and II, and methane molecules in large cages of structure I, and methane molecules in large cages of structure II. This profile indicates clearly that sample E1 includes both clathrate structures I and II.

[8] Analyses of the isotope ratios of both CH₄ and C₂H₆ released from the hydrate samples revealed almost constant values for all seven samples ($\delta^{13}\text{C}$ of CH₄ between -55.0 and -58.3‰, δD of CH₄ between -295 and -305‰, $\delta^{13}\text{C}$ of C₂H₆ between -24.9 and -26.9‰, and δD of C₂H₆ between -217 and -241‰). In Figures 4a-4c, we plotted different relations between isotopic ratios and gas composition of the hydrates to determine the origin of the natural gases. Figure 4a shows that all samples are located in the field of mixed microbial and thermogenic gases. The methane gas appears in the field of microbial origin produced by methyl-type (acetic) fermentation [Whiticar, 1999; Milkov, 2005]; but is very close to the field of mixed gases (Figure 4b). This is the first reported information about GH formed from methane that has been generated as a result of

**Figure 4.** Calcification of the dissociated gases from seven hydrate samples recovered from the Kukuy mud volcano: (a) relationship between carbon isotope composition ($\delta^{13}\text{C}$) of CH₄ and the ratio $C_1/(C_2 + C_3)$, (b) relationship between hydrogen (δD) and carbon isotope composition ($\delta^{13}\text{C}$) of CH₄, and (c) relationship between carbon isotope composition ($\delta^{13}\text{C}$) of CH₄ and C₂H₆. The ratios of $C_1/(C_2 + C_3)$ were determined using gas chromatography. The stable carbon and hydrogen isotopic composition are defined respectively as $\delta^{13}\text{C} = \left\{ \left(\frac{^{13}\text{C}/^{12}\text{C}}{(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}} \right) - 1 \right\} \times 1000$ (‰) and $\delta\text{D} = \left[\left(\frac{^2\text{H}/^1\text{H}}{(^2\text{H}/^1\text{H})_{\text{VSMOW}}} \right) - 1 \right] \times 1000$ (‰).

methyl-type fermentation. The ethane, on the other hand, is apparently of thermogenic origin, as indicated by its higher values in $\delta^{13}\text{C}$ of C_2H_6 (Figure 4c).

[9] These findings suggest that the hydrates in one and the same Kukuy mud volcano have characteristics that imply two gas source types. One source delivers methane from microbial origin by methyl-type fermentation. This implied source concurs with earlier reports for hydrates from the BDP well [Kuzmin *et al.*, 1998] and the Malenky structure [Van Rensbergen *et al.*, 2002]. On the other hand, thermogenic methane and ethane are associated with deep oil fields. Gases from these two sources mix within venting fluids with different ratios, forming clathrate structures I and II at the same (E) or different (A and B) sub-bottom depths. Because of mixing of gases from thermogenic and microbial sources, the hydrate-bound methane at the K-2 mud volcano is heavier in ^{13}C of about 10‰ in comparison to pure bacterial hydrate-bound methane obtained from the Malenky structure and BDP well. Based on a similar methane-carbon and methane-hydrogen isotopic composition in all GH layers of both cores, we can conclude that the mixing ratio of thermogenic and microbial methane was the same during formation of the investigated GH layers. The existence of two layers containing only structure I hydrate (B) and structure II (A) are explainable using fractionation of methane and ethane in the venting fluid by gas flow through some faults. On the other hand, the coexistence of structures I and II was observed under artificially controlled systems by Subramanian *et al.* [2000b] and Takeya *et al.* [2003], where the possibility of a kinetic effect for the mixed condition of the two structures was suggested [Takeya *et al.*, 2003]. Layer E might be the first example of chemical fractionation indicated from laboratory experiments by Takeya *et al.* [2003] related to coexistence of structure-I and structure-II hydrates formed from a mixture of methane and ethane gases.

[10] **Acknowledgments.** This work was supported by funding agencies in Japan (Japan Society for the Promotion of Science KAKENHI 14254003, 15550060, and 17550069, the Ministry of Education, Culture, Sports, Science and Technology KAKENHI 15760640, and the Kitami Institute of Technology Presidential Grants 2003 and 2005) and in Russia (the Integration project of RAS SB 58).

References

- De Batist, M., *et al.* (2005), Mud volcanoes, gas seeps and gas hydrates in Lake Baikal—A review, paper presented at Fourth Vereshchagin Baikal Conference, Limnol. Inst. of the Siberian Branch of the Russ. Acad. of Sci., Irkutsk, Russia, 26 Sept. to 1 Oct.
- Golmshtok, A. Y., A. D. Duchkov, D. R. Hutchinson, and S. B. Khanukaev (2000), Heat flow and gas hydrates of the Baikal rift zone, *Int. J. Earth Sci.*, *89*, 193–211.
- Hayashi, S., and K. Hayamizu (1991), Chemical shift standards in high-resolution solid-state NMR (^{13}C , ^{29}Si , and ^1H nuclei), *Bull. Chem. Soc. Jpn.*, *64*, 685–687.
- Hutchinson, D. R., A. J. Golmshtok, L. P. Zonenshain, T. C. Moore, C. A. Scholz, and K. D. Klitgord (1992), Depositional and tectonic framework of the rift basins of Lake Baikal from multichannel seismic data, *Geology*, *20*, 589–592.
- INTAS Project 99-1669 Team (2002), A new bathymetric map of Lake Baikal [CD-ROM], open-file report, *Renard Cent. of Mar. Geol.*, Ghent Univ., Ghent, Belgium.
- Kalmychkov, G. V., A. V. Egorov, and O. M. Khlystov (2005), Isotope characteristics of Baikal methane (Russia, eastern Siberia), paper presented at Fourth Vereshchagin Baikal Conference, Limnol. Inst. of the Siberian Branch of the Russ. Acad. of Sci., Irkutsk, Russia, 26 Sept. to 1 Oct.
- Khlystov, O. M. (2005), New finds of gas hydrates in Lake Baikal, paper presented at Fourth Vereshchagin Baikal Conference, Limnol. Inst. of the Siberian Branch of the Russ. Acad. of Sci., Irkutsk, Russia, 26 Sept. to 1 Oct.
- Klerkx, J., *et al.* (2003), Methane hydrates in surface layer of deep-water sediments in Lake Baikal (in Russian), *Dokl. Akad. Nauk*, *393*, 822–826.
- Kontorovich, A. E., D. I. Drobot, and R. N. Presnova (1989), Geokhimiya naftidov i problema genezisa Baikalskoi nefi (in Russian), *Sov. Geol.*, *2*, 21–29.
- Kuzmin, M. I., *et al.* (1998), First find of gas hydrates in sediments of Lake Baikal (in Russian), *Dokl. Akad. Nauk*, *362*, 541–543.
- Matveeva, T. V., L. L. Mazurenko, V. A. Soloviev, J. Klerkx, V. V. Kaulio, and E. M. Prasolov (2003), Gas hydrate accumulation in the subsurface sediments of Lake Baikal (eastern Siberia), *Geo Mar. Lett.*, *23*, 289–299.
- 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.
- Sloan, E. D., Jr. (2003), Fundamental principles and applications of natural gas hydrates, *Nature*, *426*, 353–359.
- 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.
- 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.
- Takeya, S., Y. Kamata, T. Uchida, J. Nagao, T. Ebinuma, H. Narita, A. Hori, and T. Hondoh (2003), Coexistence of structure I and II hydrates formed from a mixture of methane and ethane gases, *Can. J. Phys.*, *81*, 479–484.
- Uchida, T., S. Takeya, Y. Kamata, Y. I. Ikeda, J. Nagao, T. Ebinuma, H. Narita, O. Zatssepina, and B. A. Buffett (2002), Spectroscopic observations and thermodynamic calculations on clathrate hydrates of mixed gas containing methane and ethane: Determination of structure, composition and cage occupancy, *J. Phys. Chem. B*, *106*, 12,426–12,431.
- 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.
- Whiticar, M. J. (1999), Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, *Chem. Geol.*, *161*, 291–314.

A. Hachikubo, M. Kida, A. Krylov, H. Minami, H. Sakagami, H. Shoji, N. Takahashi, and S. Yamashita, Kitami Institute of Technology, Kitami, Hokkaido 090-8507, Japan. (kidama@mail.kitami-it.ac.jp)

O. Khlystov and T. Zemskaya, Limnological Institute, Siberian Branch of the Russian Academy of Sciences, 3, Ulan-Batorskaya St., P.O. Box 4199, Irkutsk 664033, Russia.

L. Naudts and J. Poort, Renard Centre of Marine Geology, Ghent University, Krijgslaan 281-S8, Ghent B-9000, Belgium.