

Isotopic composition of dissolved inorganic carbon in subsurface sediments of gas hydrate-bearing mud volcanoes, Lake Baikal: implications for methane and carbonate origin

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Abstract We report on the isotopic composition of dissolved inorganic carbon (DIC) in pore-water samples recovered by gravity coring from near-bottom sediments at gas hydrate-bearing mud volcanoes/gas flares (Malenky, Peschanka, Peschanka 2, Goloustnoe, and Irkutsk) in the Southern Basin of Lake Baikal. The $\delta^{13}\text{C}$ values of DIC become heavier with increasing subbottom depth, and vary between -9.5 and $+21.4\%$ PDB. Enrichment of DIC in ^{13}C indicates active methane generation in anaerobic environments near the lake bottom. These data confirm our previous assumption that crystallization of carbonates (siderites) in subsurface sediments is a result of methane generation. Types of methanogenesis (microbial methyl-type fermentation versus CO_2 -reduction) were revealed by determining the offset of $\delta^{13}\text{C}$ between dissolved CH_4 and CO_2 , and also by using $\delta^{13}\text{C}$ and δD values of dissolved methane present in the pore waters. Results show that both

mechanisms are most likely responsible for methane generation at the investigated locations.

Introduction

Dissolved inorganic carbon (DIC) is the major inorganic carbon form in most natural waters. DIC comprises three principal species, H_2CO_3 , HCO_3^- , and CO_3^{2-} . Their relative abundance is mainly a function of pH. DIC is related to many biogeochemical processes, including methane fermentation, methane oxidation, and carbonate precipitation or dissolution. Isotopic characterization of carbon in the DIC pool is important for a wide variety of scientific studies related to gas hydrate research.

Lake Baikal, eastern Siberia, is the largest freshwater reservoir in the world, and the only freshwater lake known

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to contain gas hydrates. First samples of methane hydrates were recovered in 1997 from 121 and 161 m below the lake floor (mblf) in borehole BDP-97 (Baikal Drilling Project), drilled in the southern part of Lake Baikal (Kuzmin et al. 1998). Subsequent sidescan sonar and seismic observations conducted in the Southern Basin in 1999 resulted in the discovery of a number of elevated structures (Malenky, Malyutka, Bolshoi, Stary) characterized by the distortion of the acoustic signal (Vanneste et al. 2001; van Rensbergen et al. 2002). In March 2000, first near-bottom methane hydrates were sampled at the Malenky mud volcano (van Rensbergen et al. 2002; Klerkx et al. 2003; Matveeva et al. 2003). During the following intensive coring of the mud volcanoes within the Southern Basin, subsurface gas hydrates were found in the Bolshoy, Malyutka, and Peschanka mud volcanoes, and Goloustnoe Flare. In the Central Basin, subsurface gas hydrates were recovered from the K-0 flare, K-2 mud volcano, and St. Petersburg mud volcano (e.g., Khlystov 2006). Investigations of the isotopic composition of carbon and hydrogen in the hydrocarbon gases dissolved in pore water and in gas hydrates indicate that most of the methane was produced due to methyl-type fermentation (Kida et al. 2006; Hachikubo et al. 2009, 2010, this issue).

Gas hydrate accumulations in submarine fluid discharge areas commonly contain authigenic carbonates (e.g., Greinert et al. 2001; Lein 2004). Their genesis is usually explained by the anaerobic bacterial oxidation of methane (e.g., Martin et al. 1996; von Rad et al. 1996; Greinert et al. 2001). However, bottom sediments of Lake Baikal are practically carbonate-free, because of the low alkalinity and calcium content of the lake water (Knyazeva 1954). As a consequence, the pore waters are undersaturated with respect to calcite formation (Mizandrontsev 1975). Mizandrontsev (1975) was the first to suggest that carbonates in the deepwater sediments of Lake Baikal could be formed as rhodochrosite, accounting for the enrichment of Mn in the sediments. Small granules of this mineral were later found at a thermal spring in Frolikha Bay, in the northern part of Lake Baikal (Callender and Granina 1992; Granina 2008). In the BDP-98 well at Academican Ridge, microconcretions (less than 1 mm in diameter) of siderite and rhodochrosite were found at depths of 100–600 mblf (Drilling Project Group 2000). It was suggested that their formation was due to methanogenesis (Sapota et al. 2006). As a result of the intensive study of the mud volcanoes during the last several years, authigenic carbonates, in the form of siderite, were found in subsurface sediments of the Malenky and K-2 mud volcanoes (both containing gas hydrates), and the Irkutsk structure (without gas hydrates). The ^{13}C values of these siderites (+1.9 to +21.9‰ PDB) indicate that their formation is due to methanogenesis (Krylov et al. 2008a; this study).

$\delta^{13}\text{C}$ values of DIC in Lake Baikal waters are reported to be lighter than -20‰ (Prokopenko and Williams 2005), but to our knowledge such data are yet to be published for the pore waters of mud volcanoes in Lake Baikal. In this paper we report the first results dealing with the isotopic composition of DIC in the subsurface sediments of several methane seepage structures/mud volcanoes. These data would help to understand the mechanism of methane generation/oxidation and carbonate formation in Lake Baikal mud volcanoes.

Materials and methods

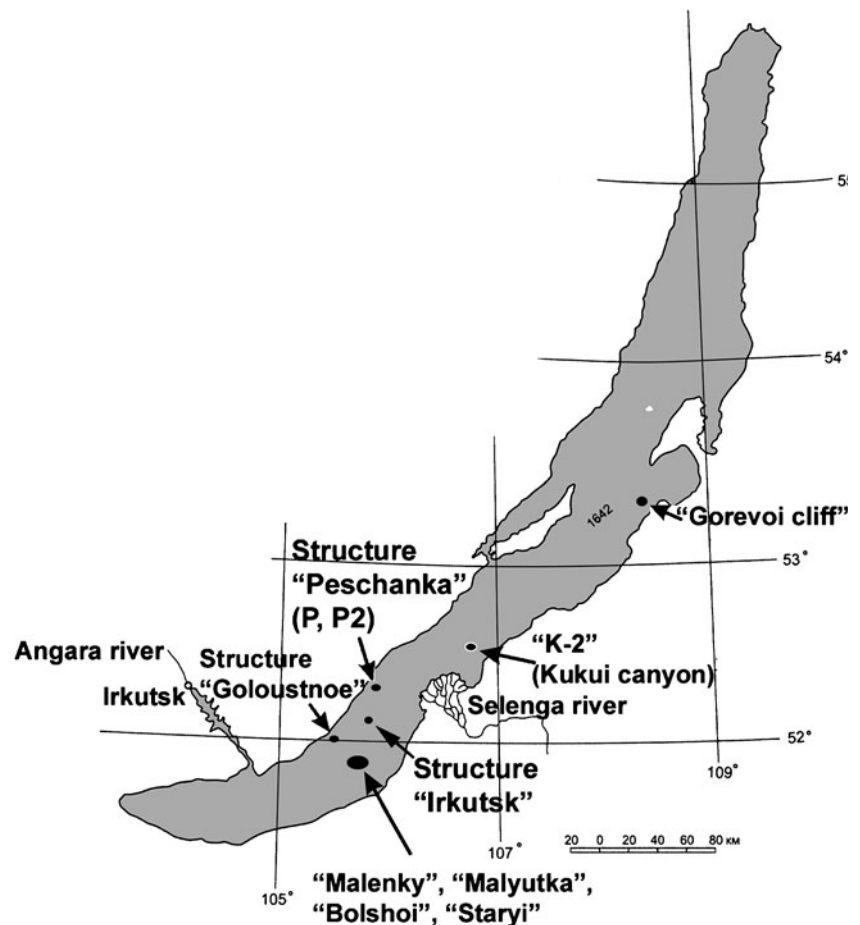
The sediment cores studied in the present work were retrieved in the Southern Basin of Lake Baikal, with a 3- and 5-meter gravity corer onboard the RV *G.Yu. Vereshchagin* in 2007, and during an ice expedition in 2008. The following structures/mud volcanoes were cored (Fig. 1): Malenky (cores 2007St1GC4, 2007St1GC5, and reference core 2007St10GC2), Peschanka (core 2007St2GC14, and reference core 2007St4GC1), Peschanka 2 (core 2007St2GC5), Irkutsk (core 2007St6GC1), and Goloustnoe (cores 2008St8w-GC7, 2008St8wR-GC2, 2008St8wH-GC3, and 2008St8wF-GC1).

Gas hydrates were observed in cores 2007St1GC4 (“nodule-type” hydrates at 117–127 and 230 cm below lake floor), 2007St1GC5 (“plate-like” hydrates at 67–74 and 77–79 cmlf), 2007St2GC5 (inclined thin layers and “plate-type” hydrates at 273–323 and 406–426 cmlf), 2007St2GC14 (inclined thin layers of hydrates at 127–133, 150–154, 211–217, and 246–288 cmlf), 2008St8wR-GC2 (“plate-type” hydrates at the core bottom), 2008St8w-GC7 (“plate-type” hydrates at the core bottom), and 2008St8wH-GC3 (“plate-type” hydrates at 86 cmlf).

Pore-water samples for investigating the isotopic composition of DIC were squeezed from the sediments and filtered through 0.2- μm filters shortly after core recovery, and stored in liquid nitrogen. CO_2 gas samples were obtained immediately from the sediments after core recovery, using the vacuum degassing system onboard the RV *G.Yu. Vereshchagin*. CO_2 samples were not taken at the Goloustnoe structure. Dissolved CH_4 samples were obtained from the pore waters using the common “head space” method; methane was not taken from core 2007St6GC1, Irkutsk. Soft siderite nodules, varying in size from 0.5 to 3 cm, were recovered from cores 2007St1GC4, Malenky (seven samples) and 2007St6GC1, Irkutsk (one sample).

The isotopic composition of DIC, siderites, CH_4 , and CO_2 gas was measured at the New Energy Resources Research Center of the Kitami Institute of Technology, by means of a CF-IRMS (Delta Plus XP; Thermo Finnigan).

Fig. 1 Location map of DIC and siderite sampling sites in Lake Baikal



DIC measurements were carried out using a gas-bench system according to the method developed and described by Torres et al. (2005). The $\delta^{13}\text{C}$ isotopic composition of CO_2 and CH_4 was determined using a mass spectrometer connected to a gas chromatographer. The CO_2 gas for the determination of the isotopic composition of the siderites was obtained from the completed reaction of carbonates (1–3 mg) with pure H_3PO_4 at 70°C during 14 h. The $\delta^{13}\text{C}$ values are given relative to the VPDB scale, using NBS-19 as standard.

The mineralogical composition of the carbonates was determined at the Kitami Institute of Technology by powder X-ray diffraction analyses (Rigaku RINT-1200, monochromatic Cu K-alpha radiation). Internal quartz was used as a standard for peak correction.

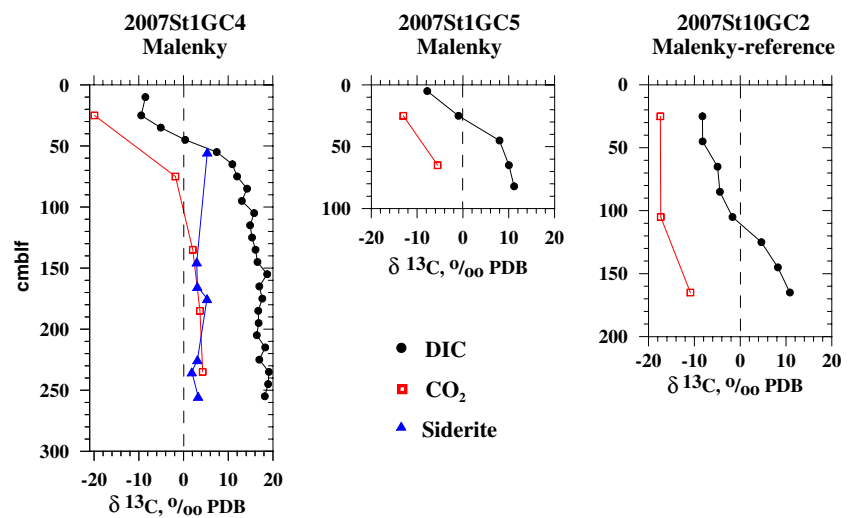
Results and discussion

Isotopic composition of carbon ($\delta^{13}\text{C}$) in DIC, CO_2 , and siderites

The $\delta^{13}\text{C}$ values of DIC, CO_2 , and siderites are shown in Figs. 2, 3, and 4 (cf. Table 1). $\delta^{13}\text{C}$ values of DIC and CO_2

(Figs. 2, and 3) become heavier with increasing depth below the lake floor (blf), from minimum values of (respectively) -9.5 and -19.9‰ in core 2007St1GC4 (Malenky), to maximum values of (respectively) $+21.4$ and $+4.7\text{‰}$ in core 2007St2GC5 (Peschanka 2). The isotopic separation of $\delta^{13}\text{C}$ between DIC and CO_2 also increases with depth at all investigated sites (cf. at the Goloustnoe Flare, CO_2 gas was not sampled; Fig. 5a). This offset is presumed to be an artifact of CO_2 outgassing during sediment recovery, and varies from 6.7‰ in the upper layers of core 2007St4GC1 (reference site for Peschanka mud volcano), to 21.7‰ in the bottom layer of core 2007St10GC2 (reference site for Malenky mud volcano). The average values of the DIC– CO_2 $\delta^{13}\text{C}$ offset vary between 11‰ in core 2007St4GC1, and 16.9‰ in core 2007St10GC2 (Table 1). The theoretical equilibrium carbon isotope fractionation between DIC and gaseous CO_2 was calculated based on the equation of Zhang et al. (1995), applying a subbottom sediment temperature of 3.5°C . The obtained value of 10.1‰ is usually smaller (with a few exceptions in the uppermost layers) than the observed $\delta^{13}\text{C}$ DIC– CO_2 offset. For comparison, an isotopic offset of about 12.5‰ between the $\delta^{13}\text{C}$ values of CO_2 gas and DIC was reported for Blake Ridge (Paull et al. 2000).

Fig. 2 Vertical distribution of $\delta^{13}\text{C}$ values of DIC, CO_2 , and siderite in the Malenky mud volcano



The strong enrichment in ^{13}C of DIC at layers deeper than ca. 50–100 cmblf (Figs. 2, 3, and 4) indicates active methanogenesis. During methane generation, the carbon isotopic fractionation between CH_4 and CO_2 may reach 80‰, with CO_2 becoming ^{13}C -rich (Rosenfeld and Silverman 1959). Thus, methane generation is the reason for the ^{13}C -enrichments in both siderites (e.g., Krylov et al. 2008a, b) and DIC. The $\delta^{13}\text{C}$ values of siderites in core 2007St1GC4 (Malenky) vary between +1.9 and +5.3‰ PDB. The uppermost siderite sample, located at 55 cmblf, has a $\delta^{13}\text{C}$ value similar to that of DIC, +5.3 and +7.4‰, respectively

(Fig. 2). The lower siderite samples, by contrast, have $\delta^{13}\text{C}$ offsets to DIC of around 13–15‰, which is obviously too high for isotopic fractionation. Thus, we speculate that the siderite in this core was formed higher up in the sediment column, close to the depth of slightly positive $\delta^{13}\text{C}$ values of DIC, and then was buried in deeper sediment layers due to sedimentation. The difference in $\delta^{13}\text{C}$ values between siderite (+11.7‰) and DIC (+5.4‰) in the Irkutsk structure is elevated, and probably caused by depletion in ^{13}C of DIC with time, after siderite has formed. It was reported by Krylov et al. (2008a) that the theoretical difference in $\delta^{13}\text{C}$

Fig. 3 Vertical distribution of $\delta^{13}\text{C}$ values of DIC and CO_2 in the Peschanka and Peschanka 2 mud volcanoes

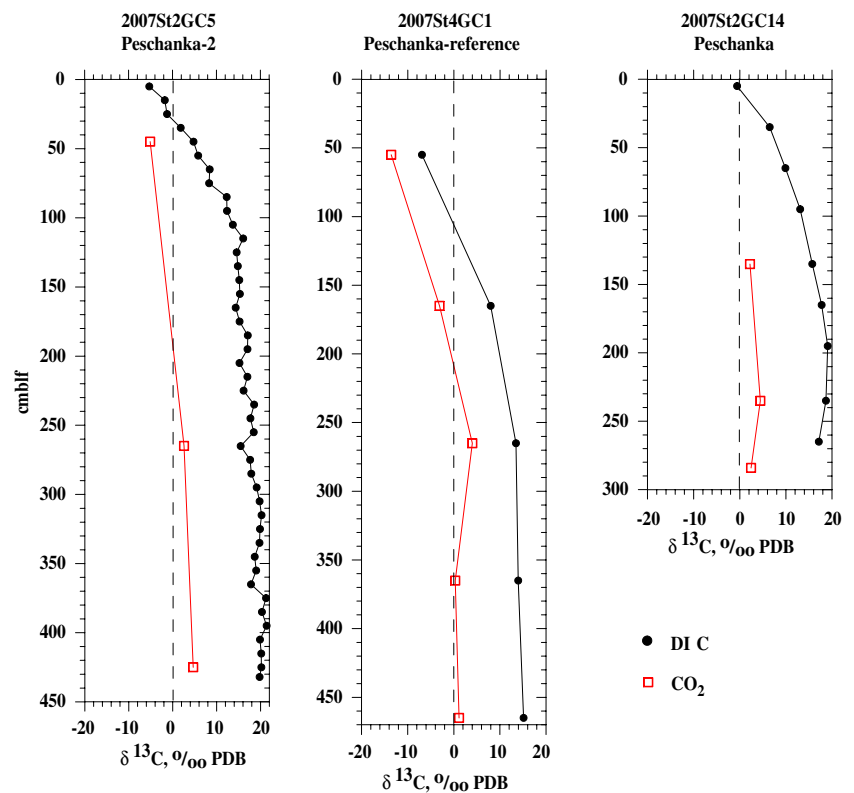
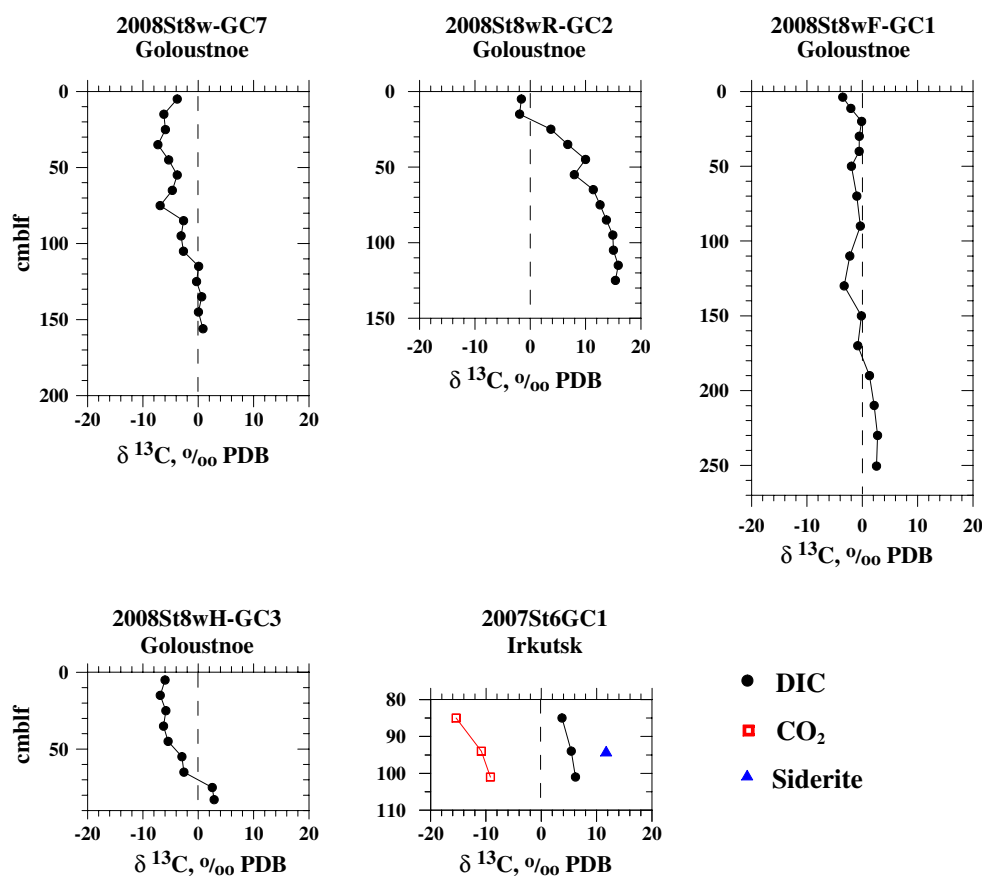


Fig. 4 Vertical distribution of $\delta^{13}\text{C}$ values of DIC, CO_2 , and siderite in the Goloustnoe Flare and Irkutsk mud volcano



between CH_4 and siderite in freshwater environments of Lake Baikal is expected to be about 59–74‰. This is in good agreement with the observed data for core 2007St1GC4, Malenky ($\delta^{13}\text{C}$ methane -63.4 to -69.9 ‰, siderite $+1.9$ to $+5.3$ ‰, difference 65.3 to 75.2‰).

Isotopic composition of carbon ($\delta^{13}\text{C}$) in methane

Intensive study of the isotopic composition of carbon ($\delta^{13}\text{C}$) in methane from Lake Baikal sediments have allowed to distinguish the following genetic types: microbial, thermogenic, and endogenous (Kalmychkov et al. 2006). The $\delta^{13}\text{C}$ values of CH_4 dissolved in pore water of our stations vary between -61.4 ‰ (2007St2GC5, Peschanka 2) and -86.9 ‰ (2007St4GC1 reference for Peschanka; Fig. 6, Table 1), and indicate a microbial origin (e.g., Whiticar 1999). CH_4 in the reference cores is depleted in ^{13}C , in comparison with methane from the mud volcanoes. This might be a consequence of considerable admixture of deeper methane within the mud volcanoes. Two groups of methane $\delta^{13}\text{C}$ profiles were observed (Fig. 6). The first group includes profiles with $\delta^{13}\text{C}$ values that become gradually lighter with decreasing depth, but turn to heavier values in the uppermost layers (2007St1GC4 in the Malenky mud volcano, 2007St10GC2 at the reference site for Malenky, and

2007St4GC1 at the reference site for Peschanka). The second group includes profiles with $\delta^{13}\text{C}$ values that become gradually lighter near the uppermost layers (2007St1GC5 in Malenky, 2007St2GC5 in Peschanka 2, 2007St2GC14 in Peschanka, and 2008St8wR-GC2 and 2008St8wF-GC1 in Goloustnoe). It is not clear to which group the two cores from the Goloustnoe structure (2008St8w-GC7 and 2008St8wH-GC3) belong, since the isotopic values of $\delta^{13}\text{C}$ were not measured in the uppermost parts of these cores. The carbon isotopic composition of the methane profiles often parallels the DIC isotopic values (Figs. 2, 3, 4, and 6).

Methane oxidation

The most probable reason for the enrichment in ^{13}C of CH_4 in the uppermost sediment layers of marine sediments is the process of anaerobic oxidation of methane (AOM; e.g., Whiticar 1999; Valentine and Reeburgh 2000). When methane diffuses upward in marine sediments, it is oxidized under anaerobic conditions by sulfate in a molar ratio of 1:1, mediated probably by consortia of archaea and sulfate-reducing bacteria (e.g., Boetius et al. 2000; Orphan et al. 2001):



Table 1 Average, minimum, and maximum $\delta^{13}\text{C}$ values of DIC, CO_2 , siderite, and CH_4 , as well as offsets between DIC and CO_2 , and between CO_2 and CH_4 in the mud volcanoes of Lake Baikal

	$\delta^{13}\text{C}$ (‰ PDB)				$\delta^{13}\text{C}$ offset (‰)	
	DIC	CO_2	Siderite	CH_4	DIC– CO_2	CO_2 – CH_4
2007St1GC4, Malenky						
Average	12.3	–2.3	3.6	–65.2	13.2	62.2
Min.	–9.5	–19.9	1.9	–69.9	10.4	50.0
Max.	19.1	4.3	5.3	–63.4	14.8	69.0
Number (<i>n</i>)	25	5	7	24	5	4
2007St1GC5, Malenky						
Average	4.1	–9.3		–65.9	13.8	53.6
Min.	–7.8	–13.0		–68.1	12.0	
Max.	11.2	–5.5		–64.2	15.6	
Number (<i>n</i>)	5	2		7	2	1
2007St10GC2, Malenky reference						
Average	–0.5	–15.2		–71.3	15.5	56.4
Min.	–8.2	–17.4		–75.0	9.2	52.3
Max.	10.9	–10.9		–63.7	21.7	60.4
Number (<i>n</i>)	8	3		15	3	2
2007St2GC5, Peschanka 2						
Average	14.8	0.7		–65.1	12.7	66.3
Min.	–5.3	–5.1		–74.0	9.9	62.8
Max.	21.4	4.7		–61.4	15.5	68.7
Number (<i>n</i>)	44	3		43	3	3
2007St2GC14, Peschanka						
Average	13.0	3.0		–65.2	13.9	67.9
Min.	–0.6	2.2		–71.8	13.5	67.2
Max.	19.1	4.5		–63.5	14.2	68.5
Number (<i>n</i>)	9	3		29	2	3
2007St4GC1, Peschanka reference						
Average	8.7	–2.3		–75.4	11.0	73.5
Min.	–6.9	–13.6		–86.9	6.7	70.9
Max.	15.1	4.0		–70.2	14.0	77.6
Number (<i>n</i>)	5	5		50	5	5
2007St6GC1, Irkutsk						
Average	5.1	–11.8	11.7		16.9	
Min.	3.8	–15.4			15.4	
Max.	6.2	–9.2			19.1	
Number (<i>n</i>)	3	3	1		3	
2008St8w-GC7, Goloustnoe						
Average	–3.2			–65.9		
Min.	–7.3			–73.7		
Max.	0.8			–63.6		
Number (<i>n</i>)	16			12		
2008St8wR-GC2, Goloustnoe						
Average	9.5			–63.8		
Min.	–1.9			–70.0		
Max.	15.9			–62.0		
Number (<i>n</i>)	13			13		
2008St8wF-GC1, Goloustnoe						

Table 1 (continued)

	$\delta^{13}\text{C}$ (‰ PDB)				$\delta^{13}\text{C}$ offset (‰)	
	DIC	CO_2	Siderite	CH_4	DIC- CO_2	CO_2 - CH_4
Average	-0.5			-63.8		
Min.	-3.5			-65.5		
Max.	2.8			-61.9		
Number (<i>n</i>)	16			15		
2008St8wH-GC3, Goloustnoe						
Average	-3.4			-66.1		
Min.	-6.9			-71.0		
Max.	2.9			-62.8		
Number (<i>n</i>)	9			8		

The light isotope ^{12}C of CH_4 in the uppermost sediments is oxidized more rapidly than the heavy isotope, ^{13}C , enriching the residual methane in ^{13}C (e.g., Whiticar and Faber 1986; Whiticar 1999). As a result, $\delta^{13}\text{C}$ values of

CH_4 become heavier in the top parts of the sediment column.

However, this mechanism, widely distributed in the marine environment, cannot be directly adopted for explanation of the

Fig. 5 **a** Vertical distribution of $\delta^{13}\text{C}$ DIC- CO_2 offset (ϵ_c). **b** Vertical distribution of $\delta^{13}\text{C}$ CO_2 - CH_4 offset (ϵ_c); values ranging between 40 and 55 characterize methane generation through methyl-type fermentation (Whiticar 1999)

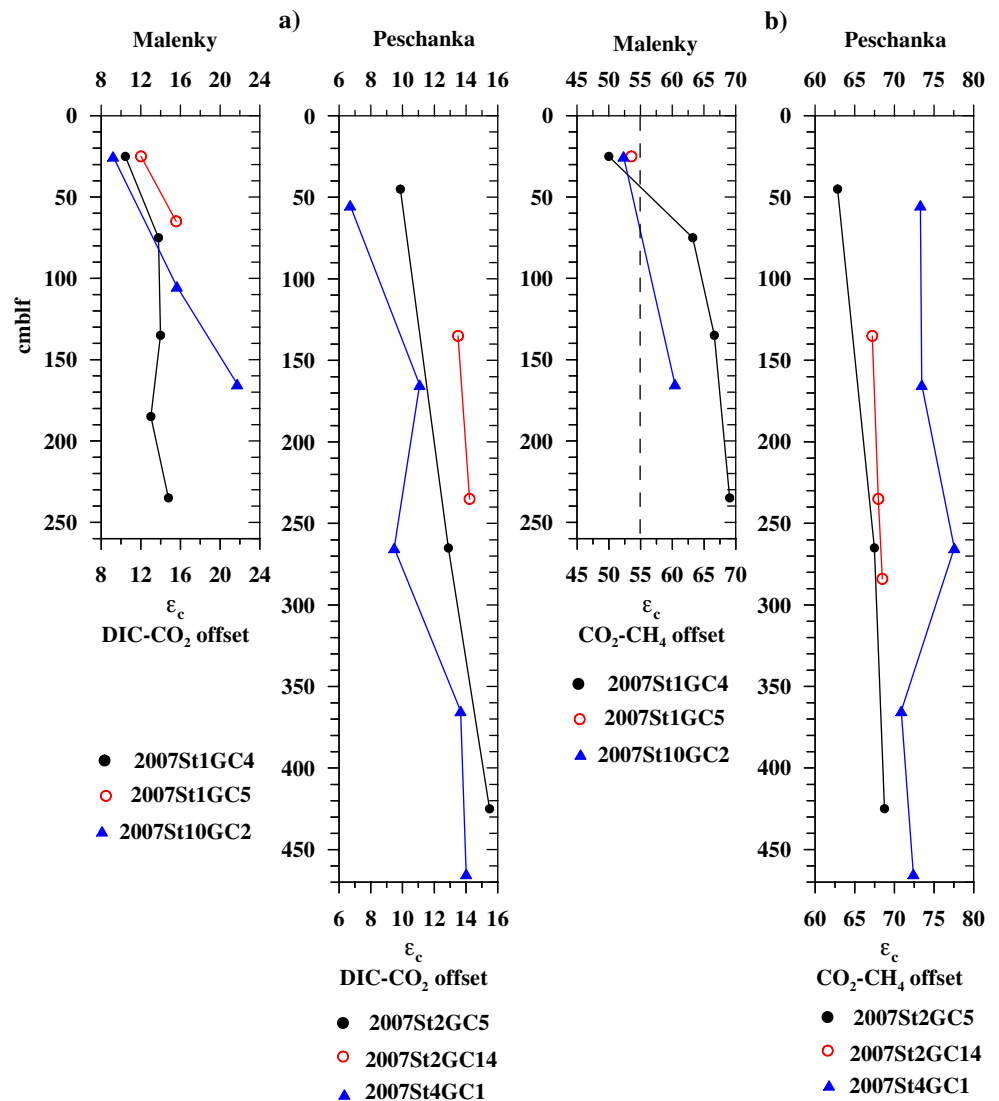
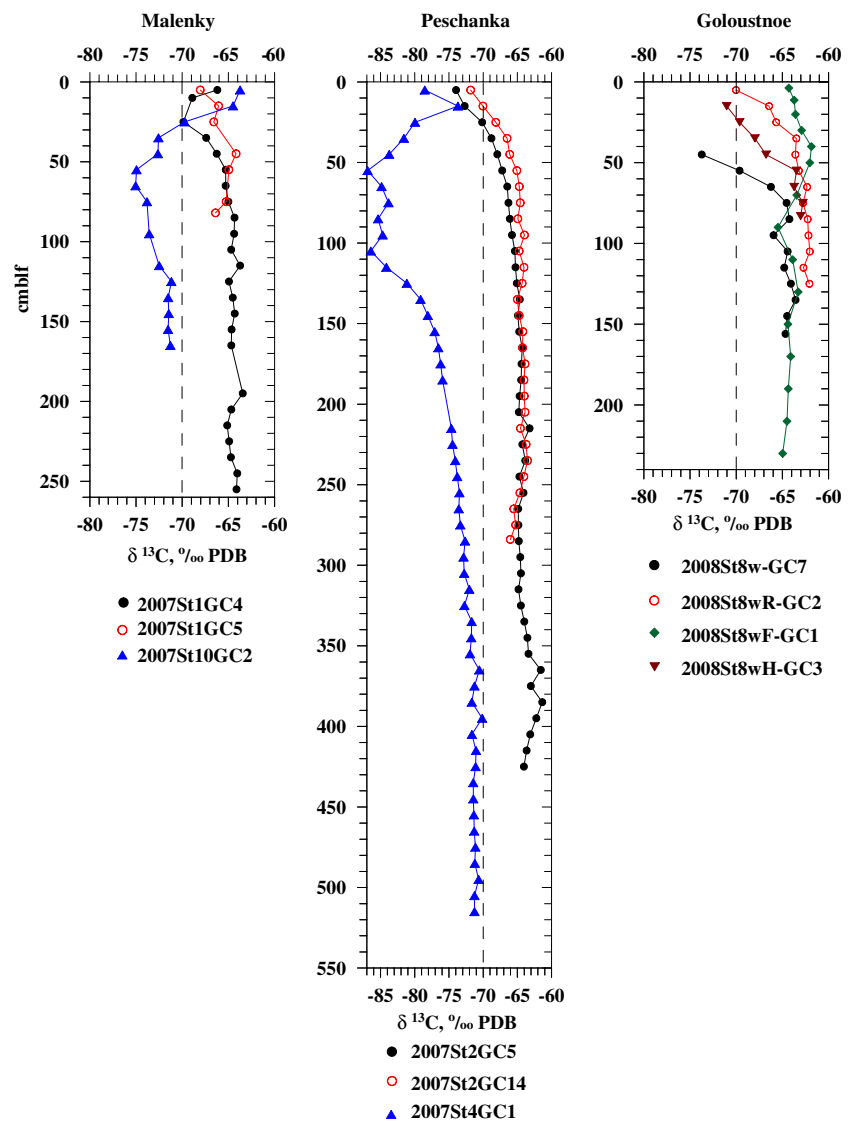


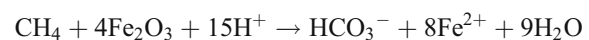
Fig. 6 Vertical distribution of $\delta^{13}\text{C}$ values of methane dissolved in pore water. Methane formed through bacterial methyl-type fermentation has $\delta^{13}\text{C}$ values heavier than -70‰ (Whiticar 1999)



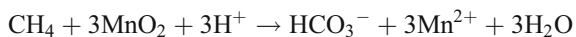
behavior of our first group of $\delta^{13}\text{C}$ (CH_4) profiles (Fig. 6), because sulfate concentrations in freshwater are considerably lower than in seawater.

For AOM maintenance, sulfate concentrations should exceed the threshold of 0.2 mM, below which sulfate-reducing bacteria become sulfate-limited (e.g., Alperin et al. 1992; Whiticar 1999). The sulfate-reduction zone in Lake Baikal's freshwater environment is generally insignificant; background concentrations of sulfate in the pore waters of the Southern Basin are around 0.07 mM (Granina et al. 2001). Concentrations of sulfate have been published for the Malenky mud volcano, and are often below 0.2 mM, but in some cores much higher concentrations reaching 15 mM were recorded, which is sufficient for AOM maintenance (Matveeva et al. 2003; Pogodaeva et al. 2007; Zemskaya et al., unpublished data). A deep source of sulfate has been suggested as an explanation for the observed anomalies (Granina et al. 2001; Matveeva et al.

2003). The sulfate concentrations measured in cores 2007St1GC4 and 2007St10GC2 belonging to the first group, and in core 2007St2GC5 belonging to the second group (Fig. 6) do not exceed 0.11 mM. Evidently, mechanisms other than AOM are needed to explain the oxidation of methane in this anaerobic freshwater environment. One possible candidate involves reactive iron and manganese oxides, which are present in considerable amounts in the uppermost sediments of Lake Baikal (Granina et al. 2004; Granina 2008), and in the mud volcanoes sediments (Krylov et al. 2008b). A possible contribution of Mn and Fe oxides to methane oxidation was already reported for Blake Outer Ridge sediments (Matsumoto 1989), and for methane-seep sediments from the Eel River Basin in California (Beal et al. 2009). The possible reactions are



and



^{13}C -depleted carbon obtained from CH_4 oxidation is added to the DIC pool. Another important source of carbon for DIC is the oxidation of organic matter.

Methanogenic pathways

In cores 2007St1GC5 (Malenky), 2007St2GC5 (Peschanka 2), 2007St2GC14 (Peschanka), 2008St8wR-GC2 (Goloustnoe), and 2008St8wF-GC1 (Goloustnoe), which all belong to the second group, methane in the uppermost sediment section becomes gradually depleted in ^{13}C (Fig. 6). Such change in the isotopic composition of methane is usually caused by processes involved in methane generation (e.g., Whiticar 1999; Paull et al. 2000). It is well known, however, that AOM prevents methane generation via CO_2 -reduction and acetate fermentation, since sulfate-reducing bacteria out-compete methanogens for H_2 and acetate (e.g., Alperin et al. 1992). In the presence of non-limiting sulfate concentrations, sulfate-reducing bacteria maintain acetate and H_2 concentrations at levels too low to support the growth of methanogenic bacteria. By implication, there are two possible explanations for the $\delta^{13}\text{C}$ and CH_4 changes in the uppermost sediments in the cores of the second group: either only small amounts of methane are generated here from the non-competitive substrate, or AOM via sulfate reduction does not occur or is highly restricted.

Methane production rates are usually highest immediately below the sulfate reduction zone (e.g., Alperin et al. 1992; Whiticar 1999). This was confirmed for the Malenky mud volcano where the maximum activity of the methane-generating microorganisms was located 100 cmblf, immediately below the peaks of sulfate-reduction activity (Klerkx et al. 2003). Thus, newly generated methane enriched in ^{12}C might migrate upward, and if methane-generating rates exceed rates of sulfate reduction, then the vertical distribution of $\delta^{13}\text{C}$ values might be similar to those observed in the second group. Thus, we speculate that anaerobic methane oxidation in near-bottom sediments of the studied cores belonging to the second group is likely outweighed by the processes of methane generation and/or upward methane migration.

The range of isotope separation between CO_2 and CH_4 (ϵ_c) can be used to determine the methane genesis pathway via CO_2 -reduction (ranges from 49 to over 100, with values most commonly around 65 to 75), or from methylated substrate (40–55; Whiticar 1999). In the cores discussed here, the isotopic offset (ϵ_c) between CO_2 and CH_4 generally increases with depth, and varies between 50 (2007St1GC4, Malenky) and 77.6 (2007St4GC1, reference

site for Peschanka; Fig. 5b). Most values correspond to “ CO_2 -reduction”, and only three values from the upper parts of cores 2007St1GC4, 2007St1GC5, and 2007St10GC2 (all from Malenky) correspond to methane generation from a “methylated substrate”. Alternatively, a decrease of the CO_2 – CH_4 offset in the upper sediments of the Malenky mud volcano (around 25 cmblf; Fig. 5b) might be caused by methane oxidation processes, rather than by a shift from CO_2 -reduction to methyl-type fermentation (see Whiticar 1999).

However, the most common method for determining the methane generation pathway is based on $\delta^{13}\text{C}$ vs. δD diagrams (Whiticar et al. 1986; Whiticar 1999). $\delta^{13}\text{C}$ and δD values of our CH_4 samples vary between –86.9 and –61.4‰, and between –323.7 and –284.9‰, respectively. Based on these data, almost all samples can be classified as microbially produced by methyl-type fermentation; samples from the reference cores and upper layers of several other cores with $\delta^{13}\text{C}$ values lighter than –70‰ (Fig. 6) can be classified only as microbially produced, without further specification. It is important to note that an origin of hydrate-bound methane resulting from methyl-type fermentation has already been reported by Kida et al. (2006) and Hachikubo et al. (2009) for the K-2 mud volcano, Central Baikal Basin, and by Hachikubo et al. (2010, this issue) for the Central and Southern Basins. Interestingly, when using the results from an experiment on methane generation via both CO_2 -reduction and methyl-type fermentation pathways in freshwater environments by Sugimoto and Wada (1995), our CH_4 samples plot in the field of CO_2 -reduction in the δD vs. $\delta^{13}\text{C}$ diagram. Hornibrook et al. (1997) comment that in comparison with a natural setting, the high H_2 concentration in the culture experiments of Sugimoto and Wada (1995) may have affected the magnitude of hydrogen isotope partitioning, and led to the observed discrepancies compared to the model of Whiticar et al. (1986).

The reason for the difference in methane generation determination obtained by the methods mentioned above is not clear. Probably, methane generated in Lake Baikal sediments takes place both through CO_2 -reduction and methyl-type fermentation. It has been stated that acetate fermentation is responsible for about 70% of methanogenesis in freshwater environments, and that the utilization of other methylated substrates and/or CO_2 reduction can account for the remainder (e.g., Whiticar 1999). Unfortunately, information about acetate concentration in the near-surface sediments of Lake Baikal is limited to that of Namsaraev and Zemskaia (2000) who report values of 0.25–5.9 mg/l. This is not sufficient to produce enough methane and bicarbonate required for, among others, siderite precipitation (Krylov et al. 2008a). Krylov et al. (2008a) speculate that the generation of most of the CH_4 , CO_2 , and HCO_3^- observed in the mud volcanoes occurs

from acetate within the upper few hundred meters of sediment that is transported upward with ascending fluids. The new data on CH₄ generation pathways here presented, based on the $\delta^{13}\text{C}$ difference between CO₂ and CH₄, contradict these earlier interpretations based on δD and $\delta^{13}\text{C}$ isotope values of methane. It is clear that further investigations are required for reliable determination of methane generation pathways in Lake Baikal.

Concluding remarks

Investigation of the isotopic composition of DIC and CO₂ is important to characterize mechanisms of methane generation/oxidation, carbonate formation, etc. The $\delta^{13}\text{C}$ distributions of DIC and CO₂ in the mud volcanoes of the Southern Basin of Lake Baikal show strong enrichment in ^{13}C of DIC, which testifies that methane generation is active at shallow subbottom depths in the investigated mud volcanoes. Methane generation is suspected even in the uppermost sediments of the second group of $\delta^{13}\text{C}$ (CH₄) profiles. The determination of methane generation pathways was performed based on both (1) $\delta^{13}\text{C}$ CO₂–CH₄ offset values, and (2) $\delta^{13}\text{C}$ and δD values of methane (Whiticar 1999). The uncertainty regarding the obtained results is most likely caused by site-specific intermixing of CO₂-reduction and methyl-type fermentation pathways, due to fluid migration. Further investigations are required for reliable determination of methane generation pathways in Lake Baikal.

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