

Hydrocarbon Gases of the Gorevoi Utes Underwater Oil-Gas Seep (Lake Baikal, Russia)¹

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Abstract—We investigated the molecular and stable isotope compositions of hydrocarbon gases of the Gorevoi Utes oil–gas seep (Lake Baikal) characterized by a simultaneous discharge of oil and gas from the lake floor. It has been found that these hydrocarbon gases are mostly thermogenic methane ($\delta^{13}\text{C}\text{-C}_1 = -53.9$ to -38.8‰ ; $\delta^{13}\text{C}\text{-C}_2 = -23.4$ to -33.3‰). At the same time, the gases have a minor amount of C_{2+} , seldom reaching 10%. The C_1/C_{2+} value varies from 9 to 2700, with the average value being 807, which is atypical of petroleum hydrocarbons. We suggest that degassing of oil leaking to the lake floor affects the molecular composition of such gases. Some secondary processes, primarily molecular fractionation of gas during its migration into the subsurface sediments and anaerobic biodegradation of methane homologues, contribute to the decrease in C_{2+} content.

Keywords: hydrocarbon gases, methane, oil, Lake Baikal

INTRODUCTION

Shallow and deep natural gas seeps have been found throughout the entire water area of Lake Baikal (Granin and Granina, 2002; Isaev et al., 2002, Granin et al., 2010). There are also underwater natural oil seepages, which are mainly concentrated along the southeastern coast, opposite the estuary of Stvolovaya, Bol'shaya and Malaya Zelenovskaya Rivers. In locations where seeps are found, oil forms films on the water surface in summer and oil spots on the ice in spring. Those natural oil seeps were thoroughly studied (Kontorovich et al., 1989, 2007; Kashirstev et al., 2006). No hydroacoustic anomalies as gas “acoustic flares” were detected at this place on the echosounder records.

In 2005, numerous oil spots (up to 1 m in diameter) were recorded in the Central basin of Lake Baikal (at 900 m water depth). The drops of this oil reached the surface forming rainbow patches on it. Echo sounding revealed an underwater acoustic anomaly in the form of gas flare ~500 m high. Higher methane levels were found in water samples collected in the immediate vicinity to the flare, thus suggesting that only gas is extracted.

Therefore, naturally occurring oil and gas found together in the same place have been first discovered on Lake Baikal on the site called Gorevoi Utes. This area is now thoroughly studied, including several dives of the MIR submersibles. In a previous work, the isotopic composition of methane was obtained (Kalmychkov et al., 2006). The data from the investigations of oil gathered near Gorevoi Utes (Kontorovich et al., 2007; Khlystov et al., 2007) and biota (Khlystov et al., 2009; Lomakina et al., 2014) were published as well.

This article presents the results from studies of hydrocarbon gases (HCG) from this unique site within Lake Baikal.

STUDY SITE AND METHODS

The underwater Gorevoi Utes oil-gas seep is located on the slope of the eastern shore in the Central Baikal basin (Fig. 1) near the Cape Gorevoi Utes at 870–920 m water depth (Khlystov et al., 2007; Granin et al., 2010).

Several geophysical studies revealed the geomorphological structure of the area (Khlystov et al., 2007). From geophysical surveys, we know that other geological structures except for the landslide, hosting a hill up to 10 m high and 50 m in diameter, are not found here. Gas flares were detected in close proximity to the hill. During the dive series of the MIR submersibles (2008–2009), numerous small bottom cone-shaped structures (to 1 m high and 1.5 m in diameter) consisting of bitumen, were found in the immediate vicinity

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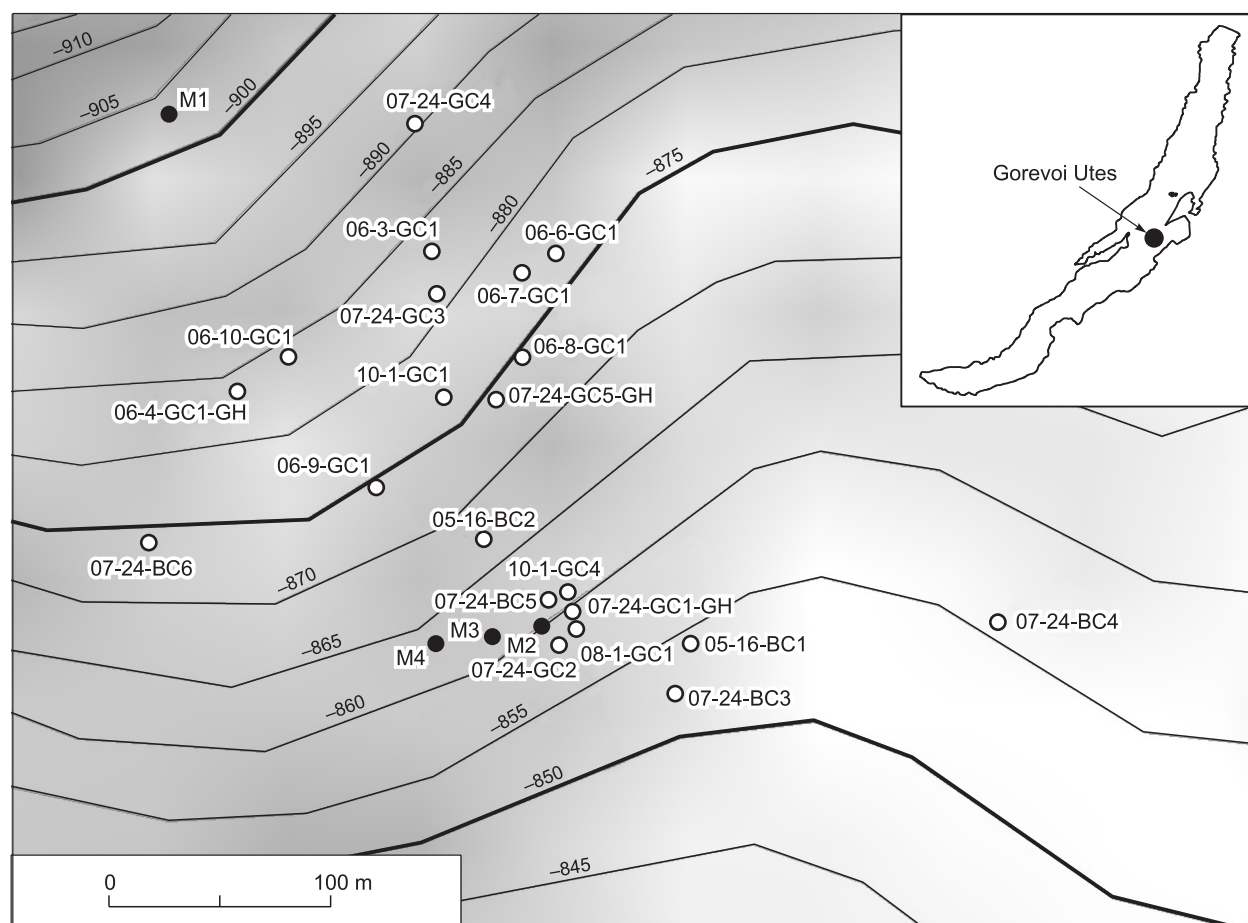


Fig. 1. Sampling sites of gas from sediments, Gorevoi Utes oil-gas seep.

of the Gorevoi Utes oil-gas seep (Khlystov et al., 2007; Sagalevich and Rimski-Korsakov, 2009). Some of those bottom structures are characterized by the simultaneous uploading of oil and gas (acting mounts). Gas bubbles were recorded on a flat bottom both in close proximity to bitumen mounts and away from them, thus frequently forming gas seeps (Khlystov et al., 2009).

Geophysical data suggest that oil is generated not in the sediments of the oil seep area but in the sediments occurring in the middle part of the lake and migrates towards the permeable zone of active faults on the eastern flank where oil is discharged (Khlystov et al., 2007).

The thermobaric conditions of the Gorevoi Utes oil-gas seep ($T = 3.3\text{ }^{\circ}\text{C}$, $P = 900\text{ atm}$) are most favorable for gas hydrate (GH) generation and the sites of gas uploading where the pore water is rich with methane are the places where gas hydrates are inevitably produced. Such compounds have been discovered in Lake Baikal (Khlystov et al., 2013).

The study area ($400 \times 400\text{ m}$) is shown in Fig. 1. The works were performed onboard the RV G.Yu. Vereshchagin. Sediment cores were retrieved using a gravity corer (GC) (5 m in length) and the Benthos benthic corer (BC) that provided the recovery of core up to 1.5 m long with an undisturbed

upper bed. Two cores (up to 20 cm long) were sampled using the equipment of the MIR submersible. Gas emitted as bubbles both from the even floor and acting bitumen structure was also sampled during the dives of the MIR submersibles. To collect and transport the gas to the surface we used a special trap (Egorov et al., 2010). Coordinates of sampling site were determined during the corer liftoff from the ground.

Hydrocarbon gases (HCG) in the sediments were analyzed by the headspace method (Bol'shakov and Egorov, 1987). The HCG concentration in the gas phase was analyzed on EKHO-PID chromatograph with plasma-ionization detector (2-m absorption column with the inner diameter of 2 mm, Porapak sorbent, isothermal regime, $T = 100\text{ }^{\circ}\text{C}$). Carbon isotope ratios ($\delta^{13}\text{C}$) of methane and ethane were determined using the Finnigan MAT 253 mass spectrometer equipped with a GC Trace chromatograph (capillary column Agilent Poraplot Q, 30 m, 0.32 mm, constant helium flux, $T = 30\text{ }^{\circ}\text{C}$) at the Laboratory of Isotope-Analytical methods of V.S. Sobolev Institute of Geology and Mineralogy, SB RAS (Novosibirsk). The $\delta^{13}\text{C}$ measurement accuracy was 0.5‰. Several samples were analyzed using the technique described in (Kalmychkov et al., 2006). Gas samples with methane concentrations of $>0.5\%$ were used for isotope analysis.

RESULTS AND DISCUSSION

The molecular and stable isotope compositions of HCG and GH from sediments of the oil-gas seep Gorevoi Utes are given in the Table. The main component of the gas is methane (C_1). Concentrations of its homologs C_2 – C_4 (C_{2+}) in gas samples from the cores vary from 0.04% to 1.22%. Gas hydrates (GH) show concentrations of C_{2+} varying between 0.12% and 0.70%, while gas, emitted as bubbles of the act-

ing bitumen mount (M4) and even floor (M3) has the concentrations of C_{2+} as 0.81% and 0.44%, respectively. The concentration of C_{2+} is slightly higher (2.14%) in gas from core M1 (Table 1).

Taking into account relatively low C_{2+} concentrations, we have to note gas from core M2 with C_{2+} concentration amounting to 10.3%. However, the analytical results of this sample do not reflect the true composition of the gas dissolved in pore waters as the core visually contained a great

Table 1. The molecular and stable isotope compositions of hydrocarbon gases from sediments, Gorevoi Utes oil-gas seep

Sample No.		Molecular composition HCG, %					C_1/C_2	C_1/C_{2+}	$\delta^{13}C-C_1, \text{‰}$	$\delta^{13}C-C_2, \text{‰}$
		C_1	C_2	C_3	$i-C_4$	$n-C_4$				
1	05-16 BC1 (35)	99.100	0.130	0.293	0.298	0.179	760	110	–44.23	–
2	05-16 BC2 (45)	98.781	0.842	0.199	0.118	0.060	117	81	–43.7	–23.4
3	06-3-GC1 (200-210)	99.335	0.241	0.190	0.179	0.055	412	149	–38.8	–
4	06-4-GC1 (30-40)	99.151	0.728	0.098	0.014	0.008	136	117	–42.4	–
5	06-4-GC1-GH (40-42)	99.759	0.232	0.005	0.002	0.001	429	414	–44.5	–
6	06-4-GC1-GH (42-44)	99.714	0.244	0.020	0.014	0.006	408	349	–44.3	–
7	06-6-GC1 (190-200)	99.916	0.084	–	–	–	1199	–	–48.3	–
8	06-7-GC1 (235-245)	99.620	0.376	0.003	0.001	–	265	262	–41.2	–
9	06-8-GC1 (210-220)	99.853	0.147	0.001	–	–	681	678	–46.9	–
10	06-9-GC1 (130-140)	99.757	0.090	0.076	0.031	–	1113	507	–45.3	–
11	06-9-GC1 (240-260)	99.733	0.114	0.076	0.031	0.046	878	373	–46.9	–
12	06-10-GC1 (210-220)	99.963	0.036	0.001	–	–	2755	2717	–40.8	–
13	07-24-BC1 (100-110)	99.924	0.075	–	–	–	1340	–	–52.2	–
14	07-24-BC3 (80-90)	99.894	0.061	0.040	0.004	–	1628	944	–41.8	–
15	07-24-BC5 (50-63)	99.947	0.053	–	–	–	1897	–	–53.9	–
15	07-24-BC6 (17-27)	99.878	0.122	–	–	–	821	–	–48.1	–
15	07-24-GC1 (22-24)	99.293	0.276	0.229	0.117	0.084	445	185	–42.3	–26.2
18	07-24-GC1-GH (25-35)	99.461	0.223	0.171	0.086	0.058	359	140	–42.3	–27.3
19	07-24-GC2 (40-48)	99.848	0.110	0.042	–	–	905	657	–43.6	–
20	07-24-GC2-GH (80-95)	99.872	0.128	–	–	–	778	–	–42.4	–29.2
21	07-24-GC2 (120-130)	99.914	0.078	0.008	–	–	1283	1164	–43.8	–
22	07-24-GC3 (40-50)	99.921	0.079	–	–	–	1270	–	–51.5	–
23	07-24-GC3 (1145-155)	99.843	0.146	0.011	–	–	685	637	–43.8	–
24	07-24-GC3 (280-290)	99.356	0.105	0.221	0.258	0.060	950	154	–40.4	–
25	07-24-GC4 (140-150)	99.955	0.045	–	–	–	2230	–	–49.9	–
26	07-24-GC4 (240-250)	99.952	0.048	–	–	–	2063	–	–46.8	–
27	07-24-GC4 (290-300)	99.937	0.060	0.004	–	–	1668	1575	–44.6	26.0
28	07-24-GC5-GH (132-140)	99.878	0.115	0.007	–	–	868	821	–46.6	–
29	07-24-GC5-GH (140-170)	99.879	0.112	0.009	–	–	894	827	–45.2	–
30	08-1-GC1 (58-60)	99.917	0.083	–	–	–	1209	–	–50.9	–
31	08-1-GC1 (118-120)	99.833	0.167	–	–	–	598	–	–47.2	–
32	08-1-GC1 (313-315)	99.653	0.208	0.139	–	–	478	287	–40.4	–
33	M1 (14-16)	97.860	0.385	0.572	0.668	0.515	254	46	–43.3	–33.3
34	M2 (14-16)	89.699	0.847	3.266	3.454	2.734	106	9	–42.2	–29.5
35	M3	99.564	0.181	0.145	0.080	0.030	551	228	–43.7	–32.1
36	M4	99.189	0.332	0.221	0.123	0.136	299	122	–40.9	–28.2

Note. Row “Sample No.” gives in brackets sampling intervals (cm) for samples of gas dissolved in pore waters and gas hydrates. Samples No. 1–12 were analyzed using the procedure described in (Kalmychkov et al., 2006). M1, dive of submersible MIR-2, 17.08.09, Core 1. Sediment was sampled from the even floor. M2, dive of submersible MIR-2, 17.08.09, Core 2. Sediment was sampled in the immediate vicinity to acting bitumen structure. M3, dive of submersible MIR-2, 19.08.09. Gas bubbles from the even floor. M4, dive of submersible MIR-2, 20.08.09. Gas bubbles from the acting bitumen structure.

amount of oil. So, oil appeared to be present in the vial for the head-space analysis. Therefore, using the headspace technique we analyzed the gas dissolved in pore waters and oil. For this reason, the molecular composition of the M2 core sample was not taken into consideration.

The molecular composition of the gas dissolved in pore waters is heterogeneous. Several samples contain only ethane (C_2), some of them show the presence of *i*-butane and/or propane, and nearly a third of gas samples contain homologs from ethane to *n*-butane inclusive (Table 1). Most of such samples were collected from the cores where oil was present. Total concentration of propane and butane (C_{3+}) was higher with respect to ethane (Table 1). In sediments with no oil, the concentration of methane homologs decreases with increasing molecular weight (gas sample from core 06-GC-1, Table 1).

The average $\delta^{13}C$ value of the oil-gas seep (gas dissolved in pore waters, GH, gas bubbles) is -44.86‰ (min -53.90‰ , max -38.84‰); $\delta^{13}C$ of ethane varies between -23.4‰ and -33.3‰ (average is -28.3‰) (Table 1). Such $\delta^{13}C$ values of methane and ethane suggest that these gases are of thermogenic origin (Whiticar, 1999; Milkov, 2005) and can be formed at depths of 2–3 km from the lake floor, i.e., in the main petroleum formation zone (Kontorovich, et al., 2007). On Lake Baikal, gas with similar isotope characteristics is found in sediments of the underwater Posol'skaya Bank (Kalmychkov et al., 2017).

Note, that in the immediate vicinity of oil seeps close to the southeastern shore of Lake Baikal (estuary of Stvolovaya, Bol'shaya and Malaya Zelenovskaya Rivers), where gas is not uploaded, the sediments contain gases of microbial

origin only ($\delta^{13}C-C_1 = -71.6\text{‰} \div -64.3\text{‰}$, average = -69.63‰ ; $C_1/C_2 = 17,000 \div 10,9000$, average = 48,000).

In the Bernard diagram (Bernard et al., 1976) which is used to define the genetic nature of methane, most of the gas samples lie above the thermogenic field (Fig. 2). Such low C_{2+} concentrations are not typical of the gas associated with oil. In the crude oil reservoirs, gas occurs as a free gas phase (gas cap) and/or is dissolved in the oil. Such initial gas is typically characterized by high concentrations of methane homologs (Neruchev, 1998).

In the sediments collected off the Gorevoi Utes oil-gas seep, gas with low C_{2+} concentration is probably produced as a result of oil degassing when oil leaks onto the lake's floor. When oil migrates to subsurface sedimentary strata, the gas, enriched with methane is typically released because of the pressure decrease. As opposed to homologs, such gas is poorly soluble in oil. The emitted gas exists as an independent gas phase that is suggested from bubbles released from the lake's floor. Gas can migrate separately or in combination with oil.

Such a scenario probably explains low concentrations of methane homologs and heterogeneity of C_{2+} molecular composition. Low concentrations of methane homologs in the thermogenic gas can be also explained by a series of secondary processes such as mixing of thermogenic and microbial gases, molecular fractionation during migration, leading to C_{2+} segregation and anaerobic biodegradation of methane homologs. These processes take place in many gas systems, which release thermogenic gas, e.g., mud volcanoes (Etiope et al., 2009).

Mixing of thermogenic methane with microbial one, which is generated at shallow depths leads to the decrease of C_{2+} and $\delta^{13}C-C_1$ values in the mixture. This process proceeds through the entire thermogenic gas migration path extending from the source to the bottom surface. On Lake Baikal, the intense methane generation begins already in the uppermost subsurface sediments (Namsaraev et al., 1995). Therefore, gas sampled from the upper layers of the cores is contaminated by microbial methane that is well illustrated in Fig. 3. As it follows from this figure, the increase of C_1/C_2 ratio and decrease in $\delta^{13}C-C_1$ value are mainly related to the mixing of the ascending flow of the thermogenic gas with the microbial methane generated in uppermost sediments. The gas sampled from the bottom layers is less contaminated with microbial methane and holds important information on characteristics of gas, occurring in deeper layers of bottom sediments. Therefore, $\delta^{13}C$ values typical of thermogenic methane, collected from deeper layers of bottom sediments suggest that mixing does not much influence the characteristics of primary gas.

When gas migrates from the source to the sub-bottom sediments, molecular fractionation can lead to the decrease of methane homolog concentrations. Wherein, $\delta^{13}C-C_1$ values do not demonstrate significant variations. Mixing and molecular fractionation generally take place simultaneously.

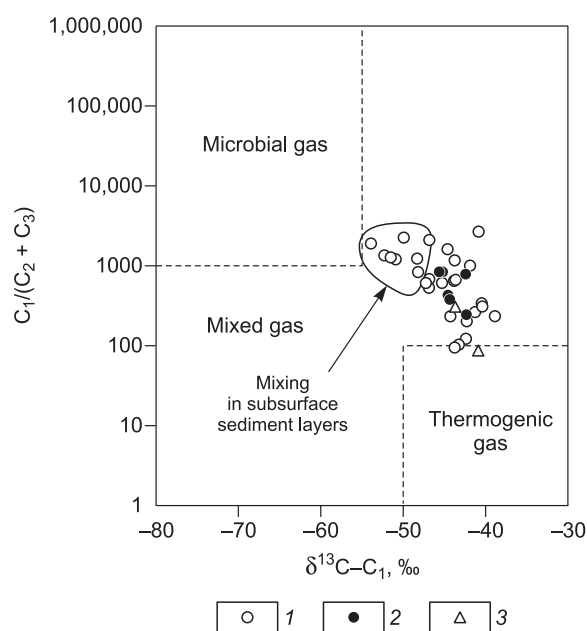


Fig. 2. Genetic characteristics of methane from sediments, Gorevoi Utes oil-gas seep from (Bernard et al., 1976). 1, gas, dissolved in pore waters; 2, gas hydrates; 3, gas bubbles.

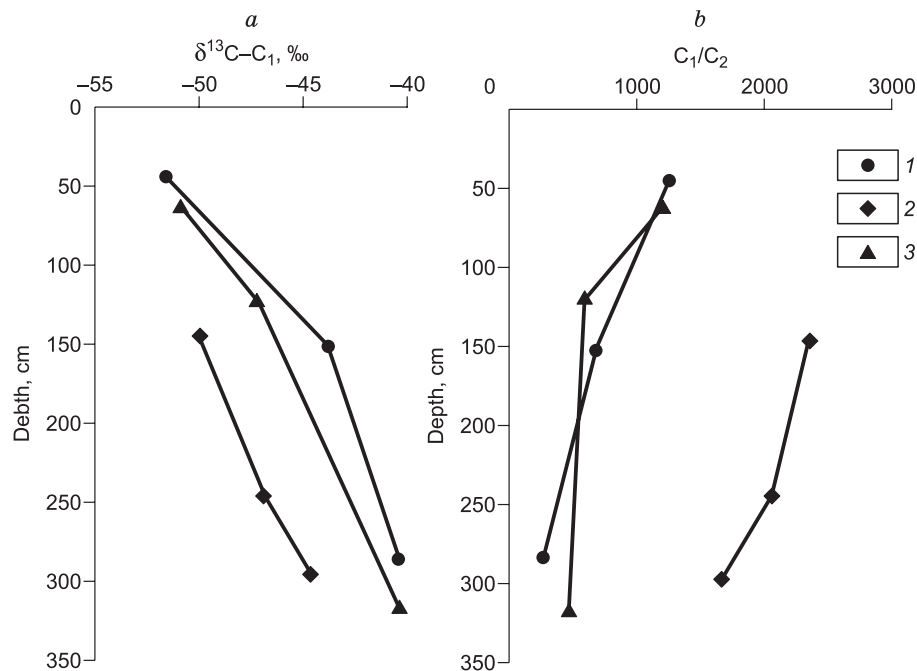


Fig. 3. Variations of $\delta^{13}\text{C}-\text{C}_1$ (a) and C_1/C_2 (b) values with the depth. 1, 07-24-GC-3; 2, 07-24-GC-4; 3, 08-1-GC-1.

The scheme from (Prinzhofer and Pernaton, 1997) based on the analysis of $\text{C}_2/\text{C}_1 - \delta^{13}\text{C}-\text{C}_1$ dependence is used to identify which process is dominating. In case of mixing of thermogenic and microbial methane, one can observe almost a linear dependence between C_2/C_1 ratio and $\delta^{13}\text{C}-\text{C}_1$ values. If the dominant process is molecular fractionation leading to C_{2+} removal, the dependence between these parameters is described as a convex curve.

Our data indicate that the linear dependence between C_2/C_1 and $\delta^{13}\text{C}-\text{C}_1$ is not available and we can observe almost vertical C_2/C_1 trend (Fig. 4), thus suggesting an important role of molecular fractionation during the gas migration into the uppermost sediments in the formation of the molecular composition of hydrocarbon gases from sediments of the Gorevoi Utes oil-gas seep. In our opinion, the significant heterogeneity in C_{2+} molecular composition is largely related to the molecular fractionation during the gas migration from several localities at different depths, where gas is separated from oil.

Decrease in C_{2+} content in the thermogenic gas can be partly explained by the anaerobic biodegradation of methane homologs, which is accompanied by the preferential removal of *n*-alkanes (propane, *n*-butane, and others) (James and Burns, 1984; Pallasser, 2000; Katz et al., 2002; Vandr  et al., 2007; Huang and Larter, 2014). Methane and ethane are less affected by the microbial community.

The gas unaffected by bacterial reworking in the methane-*n*-butane series shows a monotonous increase of $\delta^{13}\text{C}$ value (James and Burns, 1984). During this bacterial decomposition, this regularity is disturbed and the correspond-

ing curve has a broken shape, which is an indicator of the biodegradation of methane homologs.

$\delta^{13}\text{C}$ of methane homologs was analyzed only in a few samples due to their low concentrations in the gas. The analysis was performed using the technique described in (Ha-

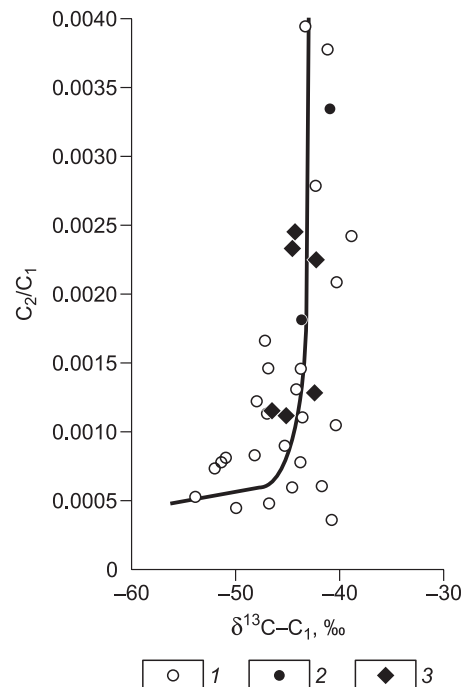


Fig. 4. $\text{C}_2/\text{C}_1 - \delta^{13}\text{C}-\text{C}_1$ diagrams from (Prinzhofer and Pernaton, 1997). 1, gas, dissolved in pore waters; 2, gas bubbles; 3, gas hydrates.

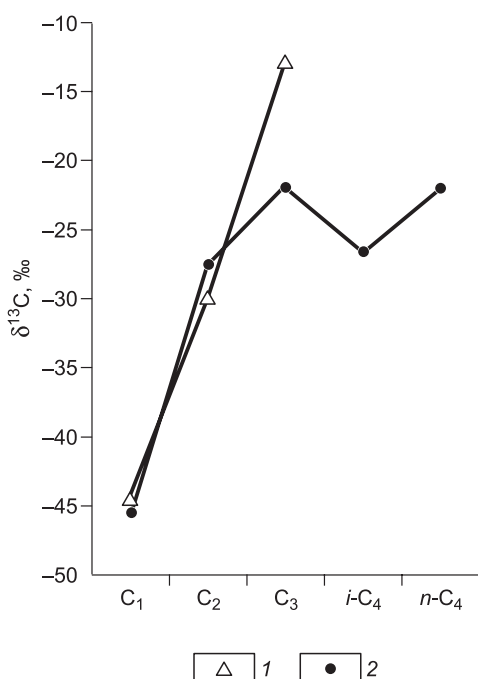


Fig. 5. $\delta^{13}\text{C}$ homologs of methane. 1, gas, dissolved in pore waters (10-1-GG-1); 2, hydrate gas (10-1-GG-4).

chikubo et al., 2015), which allows the determination of $\delta^{13}\text{C}$ at homolog concentrations $<0.1\%$ with respect to methane.

The results of $\delta^{13}\text{C}$ determination in methane homologs (Fig. 5) show that propane and *n*-butane are anomalously enriched in ^{13}C relative to ethane and *i*-butane. This fact indicates that *n*-alkanes were subjected to the bacterial reworking.

It should, however, be noted that $\delta^{13}\text{C}-\text{C}_3$ values in gas, dissolved in pore waters, are markedly higher than those in gas hydrates (-12.8% and -21.9% , respectively). Sampling sites of gas dissolved in pore waters (10-1-GC-1) and GH (10-1-GC-4) are located approximately 100 m from each other. The difference in the carbon isotope composition of propane can unlikely be explained by irregular distribution of microorganisms responsible for the alkane biodegradation in the sediments. In our opinion, this difference can be largely related to a different power of the ascending gas flows at those sampling sites. At large gas flows the bacterial reworking of hydrocarbon gases is less, as the microbial community does not have enough time to rework great abundances of those hydrocarbons.

Therefore, $\delta^{13}\text{C}-\text{C}_3$ values in GH, whose formation requires high methane concentration in pore waters, i.e., large gas flow from below, are markedly lower than those values in gas, dissolved in pore waters.

CONCLUSIONS

We reported the molecular and stable isotope compositions of hydrocarbon gases from sediments of the underwater Gorevoi Utes oil-gas seep.

The obtained data showed that sediments of this area contain methane of thermogenic origin. At the same time, the samples contain a small C_{2+} admixture that is not typical of gas associated with oil. Therefore, we suggest that such gas is produced from oil degassing when it leaks to the lake's floor.

Some secondary processes, primarily molecular fractionation during the gas migration into the subsurface sediments, may be also responsible for the decrease of C_{2+} concentrations. The anaerobic biodegradation of methane homologs can play a certain role in formation of the molecular composition of hydrocarbon gases.

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