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GEOCHEMISTRY

Genetic Types of Methane from Lake Baikal

G. V. Kalmychkov[a], A. V. Egorov[b],
Academician of the RAS M. I. Kuz'min[a], and O. M. Khlystov[c]

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Elucidation of issues concerning the genesis of Baikal methane is constrained by the almost complete absence of data on the contents of methane (C_1), its homologues (C_{2+}), and its carbon isotopic composition ($\delta^{13}C_{CH_4}$). Alekseev et al. [1] reported some $\delta^{13}C_{CH_4}$ data on gas seeps near the southeastern coast of the lake, as well as information obtained during the International Baikal Drilling Project [2, 3]. This project included study of the carbon isotopic composition of methane and the content of ethane in gas seep from sediments in the entire sequence of bottom sediments recovered by deep-water boreholes (maximum depth of the section is 600 m, borehole BDP-98). Only bacterial methane was identified during these studies. However, the genesis of Baikalian methane cannot be judged from data on three sites of the lake where deep-water boreholes were drilled.

Therefore, in 2003–2005, the contents of methane, its homologues, and $\delta^{13}C_{CH_4}$ values were systematically determined in gases released from the Lake Baikal sediment and in gases from the coastal thermal springs.

The works were carried out over the entire area of the lake (Fig. 1). Special attention was given to gas seeps on the lake floor in both shallow- and deep-water parts of Baikal.

In the coastal (shallow-water) part of Lake Baikal, we studied gas from several ice holes, which represent polynyas (ice-free water areas) typically formed at the end of March–beginning of April due to intense gas release from the lake floor [4, 5]. The water depth here is no more than 30–40 m.

Gas seeps in the deep-water part of Baikal have been studied since the 1990s after the detection of seismoacoustic traces of gas seeps from the lake floor. Complex geophysical works in the Southern depression of the lake at a depth of ~1400 m revealed several morphologically distinct uplifts up to 40 m high and 800 m across with gas conduits and high heat flow [6, 7]. It was later established that the sediments contain mud-volcanic breccia. This fact made it possible to classify the discovered structures as submarine mud volcanoes.

We studied in detail the Malen'kii and Bol'shoi volcanoes in the Southern depression of Baikal, as well as the K-2 mud volcano in the Kukui submarine canyon (Middle depression) area. In all these structures, the subsurface sediments contain gas hydrates (GH).

We studied various types of gas: (i) gas released from sediments; (ii) gas released during the decomposition of GH; and (iii) gas bubbles from ice holes and thermal springs located on the coast.

Bottom sediments were sampled with benthic gravity corers (BGC), which allow us to recover cores with undisturbed upper sedimentary layers, as well as a gravity corer (GC), which allows us to recover sediment cores up to 3 m long.

Gas was extracted from sediment by phase-equilibrium degassing [8]. The content of methane and its homologues in a gas phase was determined by a KhPM-2 chromatograph equipped with a flame-ionization detector on board the research vessel. The $\delta^{13}C_{CH_4}$ values were measured on a VG OPTIMA (ISOTECH) (Fisions) mass spectrometer equipped with a device for preliminary chromatographic separation of the gas sample.

The studies showed that $\delta^{13}C_{CH_4}$ of the Baikal methane varies from –16.1 to –77.5 ‰. The C_1/C^{2+} ratio is within 5.7–65 000.

Data presented in Fig. 2 indicate the presence of three known genetic (bacterial, thermal, and endogenous) types of methane. The bacterial methane is most typical of Lake Baikal and any other basin.

[a] *Vinogradov Institute of Geochemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1a, Irkutsk, 664033 Russia; e-mail: gkalm@igc.irk.ru*
[b] *Shirshov Institute of Oceanology, Russian Academy of Sciences, Nakhimovskii pr. 36, Moscow, 117997 Russia; e-mail: avegorov@sio.rssi.ru*
[c] *Limnological Institute, Siberian Division, Russian Academy of Sciences, ul. Ulan-Batorskaya 3, Irkutsk, 664033 Russia; e-mail: oleg@lin.irk.ru*

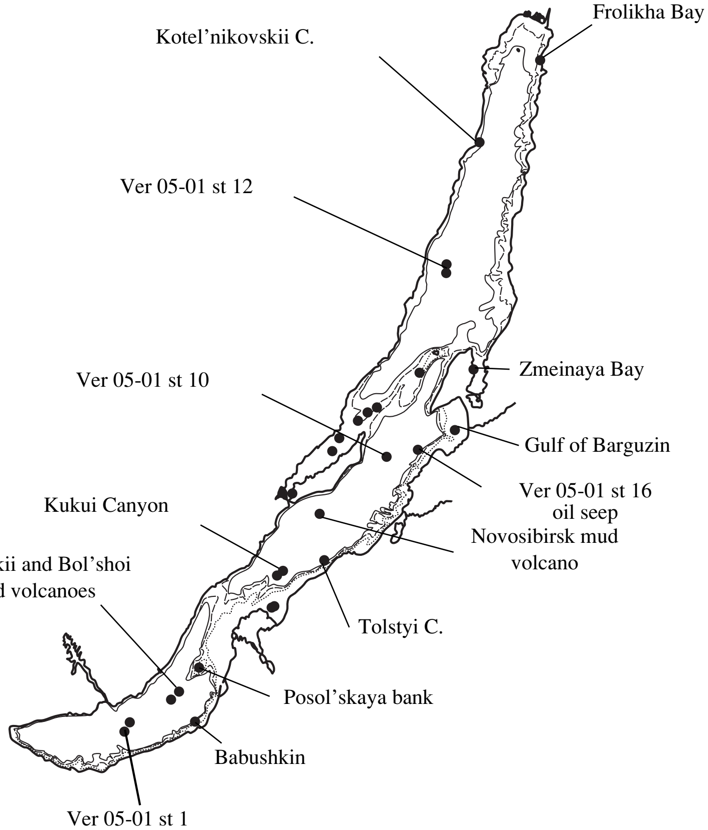

Fig. 1. Location scheme of gas sampling stations.

The *bacterial methane* of Lake Baikal has a light carbon isotopic composition ($\delta^{13}C_{CH_4}$) from –64 to –77.5‰ and insignificant traces of heavy hydrocarbons in gas (C_1/C_{2+} = 790–65 000). Three clusters with different C_1/C_{2+} ratios (1–3) can be distinguished in the bacterial methane field (Fig. 3).

The first cluster with a relatively high content of C_{2+} (mainly ethane) involves free gas samples taken from the cores of deep-water boreholes BDP-96 and BDP-98, which were drilled at the submarine Akademicheskii Ridge (C_1/C_{2+} = 790–1250; sampling interval 11.4–600 m [2, 3]), as well as gas extracted by us from the upper 3-m-thick sedimentary layer at the BDP-98 drilling site (C_1/C_{2+} = 2000–2600).

The second cluster (C_1/C_{2+} = 2700–7000) includes gas from seeps on the lake floor in both shallow-water (gas bubbles from ice holes) and deep-water (submarine Malen'kii and Bol'shoi mud volcanoes, gas released from sediment, and gas obtained by decomposition of GH) parts of Lake Baikal.

The third cluster (C_1/C_{2+} > 10000) contains gases from quiet parts of Lake Baikal, with no significant gas seepage from the lake floor.

We believe that the compositional differences of hydrocarbon gases are governed by the nature of methane-generating organic matter. They finally depend on specific sedimentation conditions in different areas of Baikal. In particular, hemipelagic sediments accumulated on the Akademicheskii Ridge are similar to the oceanic deep-water sediments enriched in water plant remains (primarily, plankton). In the deep-water sectors of the lake with high sedimentation rates up to avalanche sedimentation, the bottom sediments are enriched in the terrigenous organic component.

The C_1/C_{2+} ratio is presumably affected by mixing of gases formed in different conditions. It is highly possible that the values of the C_1/C_{2+} ratio obtained for gases sampled near vent sites fall into the intermediate zone (Fig. 3) because of their mixing.

Thermal methane was discovered by us for the first time in Baikal in gas obtained by decomposition of GH, which was found in the sediments of a K-2 mud volcano located in the submarine Kukui canyon area (Fig. 1). The ethane content in the sample was 13.4 vol %. The $\delta^{13}C_{CH_4}$ value was –51.6‰ at C_1/C_{2+} = 5.7. Gas released from sediments in contact with the hydrate-bearing layer had different characteristics: $\delta^{13}C_{CH_4}$ = –52‰ at C_1/C_{2+} = 37.7.

It should be noted that the Baikal gas hydrates, which were discovered during the drilling of deep-

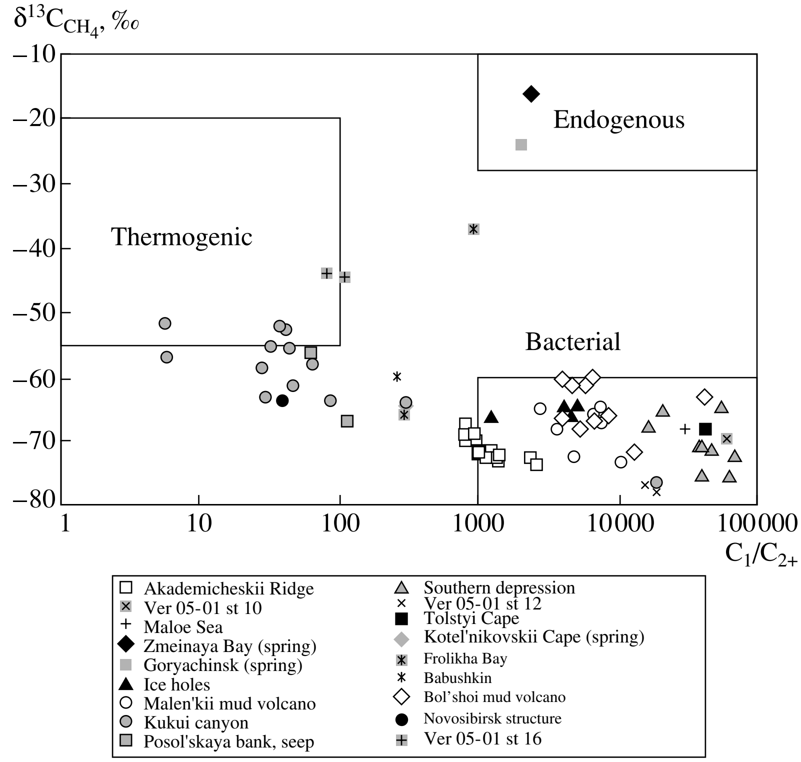

Fig. 2. Generalized $\delta^{13}C_{CH_4}$–C_1/C_{2+} diagram (fields of bacterial, thermogenic, and endogenous methanes are shown according to [9, 10]).

water borehole BDP-97 [11] at a depth of 121 and 161 m, as well as in the subsurface sediment layer [12], had a KC-1 structure and contained traces of heavy hydrocarbons. The extremely high, at least for Baikal, ethane content in GH from the Kukui canyon indirectly testifies to the KC-2 structure [13].

Thermal methane was also found in gas released from sediments at Ver 05-01 St 16 at a water depth of 900 m (Fig. 1). This station detected oil seeps at the lake floor and a powerful gas jet distinctly recorded by echo-sounder. Two 70-cm-long cores of bottom sediments were recovered by a benthic bottom corer. The sediments exhibited signs of gas saturation. Gas extracted from the sediments had the following characteristics: $\delta^{13}C_{CH_4}$ = –44.2‰, C_1/C_{2+} = 110 for core BGC-1; $\delta^{13}C_{CH_4}$ = –43.7‰, C_1/C_{2+} = 81 for core BGC-2. Gas from Ver 05-01 St 16 has high contents of propane and butane, whereas gases from other stations have negligible contents of these components relative to ethane.

In the Kukui canyon, thermogenic methane occurs only in sediments taken immediately near the mud volcano center. CH_4 has a mixed (bacterial + thermogenic) genesis already at an insignificant distance (50–100 m) from the center. Such methane is characterized by the lower content of heavy hydrocarbons and lighter carbon isotopic composition ($\delta^{13}C_{CH_4}$) varies from –57.6 to –63.9‰, C_1/C_{2+} = 30–300).

In addition to the Kukui canyon, the mixed methane was found in gases released as bubbles from the lake floor in the Babushkin area ($\delta^{13}C_{CH_4}$ = –59.7‰, C_1/C_{2+} = 258) and Kotel'nikovskii Cape ($\delta^{13}C_{CH_4}$ = –64.2‰, C_1/C_{2+} = 293). Mixed genesis was also identified for methane released from sediments in the Novosibirsk structure ($\delta^{13}C_{CH_4}$ = –64.2‰, C_1/C_{2+} = 40.2) and in the gas griffon located on the Posol'skii bank ($\delta^{13}C_{CH_4}$ = –66.6‰, C_1/C_{2+} = 118).

Endogenous methane was identified only in free gas from the thermal spring located near the water level in Zmeinaya Bay ($\delta^{13}C_{CH_4}$ = –16.1‰). Earlier, endogenous methane was found in springs near the settlement of Goryachinsk ($\delta^{13}C_{CH_4}$) = –24‰). It should be noted that these are nitrogen-rich springs with a methane content of no more than 2% [14].

Gas separated from sediments taken near a submarine hydrothermal spring in Frolikha Bay located in the northern area of the lake had the following characteris-

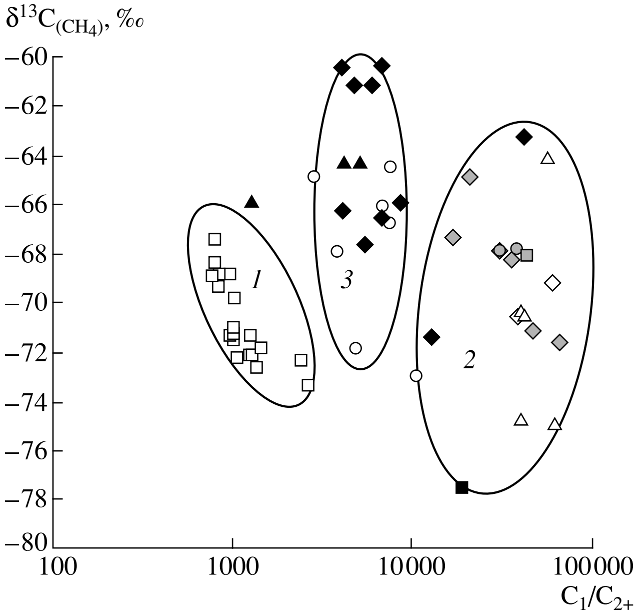

Fig. 3. $\delta^{13}C_{CH_4}$–C_1/C_{2+} diagram (fields of bacterial methane, symbols are shown in Fig. 2).

tics: $\delta^{13}C_{CH_4}$ = –36.8‰, C_1/C_{2+} = 916. The obtained results indicate that the gas contains an admixture of thermogenic or even endogenous methane. Additional study of the carbon isotopic composition of methane from this area is needed to determine its genesis.

Thus, all three known genetic types of methane were identified at Baikal. The most abundant (bacterial) methane occurs in most samples. Thermogenic methane occurs in gas seeps on the lake floor. Endogenous methane was determined only in the coastal thermal springs. Methane of mixed (thermogenic + bacterial) origin was identified in many samples taken from shallow-water gas seeps (ice holes) and in sediments from submarine mud volcanoes.

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