Article

Molecular Indicators of Sources and Biodegradation of Organic Matter in Sediments of Fluid Discharge Zones of Lake Baikal

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Abstract: This paper performs a detailed study of a wide set of organic-geochemical proxies in 15 sediment cores collected from the main basins of Lake Baikal (the northern, the central and the southern) where processes of focused fluid discharge were detected. A variety of studied zones includes sites with gas and hydrothermal seepage, mud volcanoes with or without gas-oil fluid discharge, gas hydrates and authigenic carbonates. The composition of the dispersed organic matter and individual hydrocarbon molecular markers (n-alkanes, dimethyl alkanes, isoprenoids, steranes, terpanes and polycyclic aromatic hydrocarbons) testify to the input from predominantly allochthonous terrestrial and autochthonous microbial and algal sources. The studied sources, maturity and biodegradation parameters of organic matter vary significantly for areas with different fluid discharge. The composition of specific biomarkers including isoprenoids and immature hopanoids reflects the lateral and vertical changes of microbial activity in sediments associated with various environmental conditions. The identified types of terpanes distribution (mature, mixed and immature) correlate well with types of fluid discharge and attest to the development of various methanogenic and methanotrophic microbial communities in sediments. Moreover, the revealed specificity of microbial molecular markers distribution allowed us to suggest the fluid discharge processes in zones where they were not previously detected.

Keywords: dispersed organic matter; hydrocarbon molecular markers; sediments; fluid discharge zones; authigenic carbonates; gas hydrates; Lake Baikal

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1. Introduction

Lake Baikal is a unique ultra-deep freshwater inland reservoir characterized by a variety of liquid and gas fluid discharge zones detected in the main deep basins (the northern, the central and the southern), submarine elevations and shallow water areas [1–5]. Discharge processes include hydrothermal venting (HTh), oil (OS) and gas (GS) seepage, mud volcanism (MV) and associated gas hydrate (GH) and authigenic carbonates (Carb) that form due to various diagenetic, catagenetic, endogenous and circulation processes in sediments of the Baikal Rift Zone [3,6–10]. The favorable environments of sediment accumulation (rapid sedimentation, large amount of terrigenous input, coastal erosion, discharges and landslides), their enrichment in organic matter, high primary production in water and microorganisms activity in sediments also determine such a diversity of fluid discharge zones [10–13].

The unique biodiversity of Lake Baikal is largely determined by the multiple changes in climatic, tectonic and geochemical processes that characterize the development of this region during ancient and modern geological epochs [4,14,15]. It is important to note that microorganisms play a key role in sedimentary biochemical processes. They are involved in the generation of hydrocarbons (HCs) and the active biological transformation of their dispersed and concentrated forms [13,16–19]. Thus, the importance of multidisciplinary research of the processes that occur in sediments of fluid discharge zones is hard to overestimate.

Hydrocarbon molecular markers (MM or biomarkers) are components of the dispersed organic matter (OM) and chemical fossils that inherit the chemical structure of their biological precursors and, thus, are a universal link in the chain of the sequential transformation of OM: biopolymers–biomonomers–geomonomers–geopolymers [20–23]. Their usage allows for the determination of the OM origin including the input from biogenic and abiogenic sources, the level of OM transformation during thermal maturation and biodegradation as well as the influence of endogenous and exogenous processes. The study of biogenic MM, products of the transformation of prokaryotic cell components in sediments of Lake Baikal, is of special interest. These proxies are effective for studying both the microbial production input to the sediments of zones with or without fluid discharge (background) and the type of microbial activity (HCs generation or biotransformation).

In this study, we present the results of the distribution of a wide set of organic-geochemical proxies in the bottom sediments of all the geographic zones of Lake Baikal (the northern, the central and the southern basin, Academician Ridge). Special attention is paid to the group composition of OM and the detailed study of its molecular composition (linear *n*-alkanes *n*-C14–*n*-C39 and branched 3,5-, 3,6-, 3,7-dimethylalkanes, isoprenoids, steranes, tri- and tetracyclic terpanes, hopanes, polycyclic aromatic HCs–PAHs; Table S1). A significant volume of actual data makes it possible to compare the organic-geochemical characteristics of sediments from zones with all the types of fluid discharge known in Lake Baikal: hydrothermal venting, mud volcanism and gas seepage, accompanied by the occurrence of gas hydrates, authigenic carbonates and oil. Moreover, the comparative study of areas with and without detected fluid discharge demonstrates a significant discrepancy in the group and molecular composition of OM. Thus, sampling across a wide range of underwater environmental conditions and the complex study of the origin of OM and transformation based on a wide set of molecular fingerprints provide a novel understanding of the geochemical state of bottom sediments of the fluid discharge zones of Lake Baikal. The study of organic-geochemical characteristics through the sediment section allows detecting the influence of different geological processes on OM biodegradation and microbial activity.

2. Geological Setting of Lake Baikal Sampling Sites

The northern Basin of Lake Baikal was sampled in the area of the low-temperature hydrothermal vent in Frolikha Bay (site 1, 2; Figure 1; Table 1; [18,24–29]) and in the background area near the Barguzinsky Nature Reserve (site 3; Figure 1; Table 1). The fluid discharge center of low-temperature hydrotherm (up to 16 °C) of Frolikha Bay is associated with regional active faults. Microbial mats, which cover the surface sediments in the area of seepage, consist predominantly of colorless sulfur bacteria of the genus *Thioploca* [26,30]. Methane-producing archaea [28] and methanotrophic bacteria [13] as well as various benthic organisms, hydrobionts and fish fauna, which form a unique biological community based on chemosynthesis [18,25], were also found in the surface layer of sediments. The gas fluid consists predominantly of methane of mixed microbial-thermogenic origins (with the possible admixture of endogenous [7]). Sediments are enriched in sulfates due to the oxidation of sulfides by bacteria of the *Thioploca* genus [27]. The organic matter of bottom sediments has a low level of thermal maturity [31].

Figure 1. Sampling sites in the northern, central and southern basins of Lake Baikal classified by the type of the focus fluid discharge process and expeditionary year.

Table 1. Main characteristics of samples and their organic geochemical parameters.

Core #	Sampling Intervals, cm	Coordinates N	Coordinates W	Lithological Description	Content in Sediment, % CaCO ₃	TOC	OM	EOM1	Content in OM, % EOM2	HA	ROM
Northern Baikal											
1	<i>n</i> = 2: 0–10; 25–35	55.52	109.78	Frolikha Bay (low-temperature hydrothermal seep) Diatomaceous silt with hydrotroilite; -//-	0.00–0.00 0.00	0.6–0.9 0.7	1.1–1.6 1.3	2.3–2.6 2.5	—	—	—
2	<i>n</i> = 2: 5–15; 137–147	55.52	109.76	-//-; Turbidite with sand layers	0.00–0.33 0.17	1.5–2.0 1.8	2.8–3.6 3.2	1.5–2.5 2.0	—	—	—
3	<i>n</i> = 3: 5–15; 62–72; 110–120	54.46	109.06	Background area near the Barguzinsky Nature Reserve Oxidized layer, silt with hydrotroilite; silt with sand	0.00–0.33 0.17	0.5–1.5 1.0	0.9–2.7 1.8	1.3–1.8 1.6	—	—	—
Central Baikal											
4	<i>n</i> = 3: 0–3; 3–16; 16–27	53.88	108.61	Background area near the Ushkany Islands (Fe-Mn crusts) Diatomaceous silt; -//-; Oxidized clay layer with hydrotroilite	0.08–0.33 0.22	0.2–1.2 0.8	0.3–2.2 1.5	0.3–1.9 1.0	1.2–3.3 2.2	0.0–22.0 10.1	75.2–94.8 86.7
5	<i>n</i> = 3: 10–20; 40–50; 120–130	53.50	108.00	Academician Ridge, mud volcano Mud volcanic breccia; -//-; -//- Academician Ridge, background area	0.00–0.17 0.08	0.8–0.9 0.9	1.5–1.7 1.6	1.1–1.2 1.1	1.4–3.4 2.4	4.6–11.0 8.6	84.4–92.0 87.9

Table 1. Cont.

Core #	Sampling Intervals, cm	Coordinates		Lithological Description	Content in Sediment, %			Content in OM, %			
		N	W		CaCO ₃	TOC	OM	EOM1	EOM2	HA	ROM
6	<i>n</i> = 2: 5–15; 95–105	53.50	108.07	Diatomaceous silty-clay with hydrotroilite; -/-/- Gorevoy Utes, oil seepage	0.00–0.67 0.33	1.3–2.0 1.7	2.4–3.7 3.0	1.1–1.3 1.2	—	—	—
7	<i>n</i> = 2: 10–20; 100–120	53.30	108.40	Diatomaceous silt with oil; Grey clay with oil	0.08–0.42 0.25	1.2–3.8 2.5	2.3–6.9 4.6	17.0–41.3 29.2	33.9–7.1 5.5	2.2–20.8 11.5	49.4–58.3 53.8
8	<i>n</i> = 6: 0–15; 50–60; 60–70; 100–110; 190–200; 300–310	53.30	108.39	Diatomaceous silt with oil; Diatomaceous silt; -/-/-; -/-/-; Clay with hydrotroilite; -/-/-	0.08–0.33 0.17	1.0–4.8 2.5	1.8–8.7 4.5	1.4–47.9 12.1	1.9–5.9 4.0	1.0–20.2 11.4	38.4–90.0 72.5
9	<i>n</i> = 2: 0–10; 110–120	53.00	107.90	Silty clay; Silty clay with GH Kitami, mud volcano	0.17–0.17 0.17	0.8–0.9 0.9	1.5–1.7 1.6	1.1–2.9 2.0	1.6–2.8 2.2	6.2–60.4 33.3	36.9–88.1 62.5
10	<i>n</i> = 2: 10–20; 50–65	52.60	107.40	Diatomaceous silt with oil; Grey clay Cape Tolsty, oil seepage	0.00–0.08 0.04	1.6–3.1 2.4	3.0–5.7 4.3	0.6–1.6 1.1	0.8–2.1 1.5	15.9–27.8 21.9	68.5–82.6 75.6
11	<i>n</i> = 3: 0–15; 30–40; 86–96	52.59	106.73	Diatomaceous silt with breccia; Clay with carbonates; Clay with GH Kukuy, mud volcano, gas hydrates	0.08–0.58 0.28	1.0–1.3 1.2	1.9–2.4 2.2	1.4–2.2 1.7	1.6–4.3 2.7	3.8–7.4 11.0	76.9–92.5 84.5
Southern Baikal											
12	<i>n</i> = 5: 5–15; 20–30; 86–96; 100–110; 193–203	52.00	106.00	Posolsky canyon-1, hydrate hill Diatomaceous silt with hydrotroilite; -/-/-; -/-/-; -/-/-; Silty clay	0.00–0.50 0.22	1.0–2.7 1.7	1.8–4.9 3.0	0.9–1.6 1.2	1.8–2.4 2.1	4.9–22.4 11.9	74.2–92.1 84.8
13	<i>n</i> = 3: 0–15; 40–50; 80–90	51.92	105.63	Malenky, mud volcano Diatomaceous silt with breccia; -/-/-; Clay with pebbles	0.08–0.08 0.08	0.8–1.0 0.9	1.4–1.9 1.6	1.0–2.1 1.6	2.6–4.4 3.7	4.7–28.9 17.1	67.5–86.9 77.7
14	<i>n</i> = 3: 10–20; 75–85; 120–135	51.60	104.90	Kedr, mud volcano, gas hydrates Diatomaceous silt; Gas- and water enriched clay; -/-/- with carbonates	0.08–0.33 0.19	0.7–1.6 1.1	1.3–2.8 2.0	0.8–1.3 1.1	1.4–1.8 1.6	0.8–8.8 5.9	88.6–96.6 91.4
15	<i>n</i> = 6: 0–10; 20–30; 45–55; 95–105; 120–130; 166–174	51.61	104.90	Diatomaceous silt with hydrotroilite; -/-/-; Silty clay with sand and carbonates; -/-/-; -/-/- (no carb.); -/-/-	0.08–0.08 0.08	0.5–1.2 0.7	1.0–2.1 1.3	0.6–1.3 0.8	1.6–3.6 2.2	4.3–13.5 7.5	83.6–93.6 89.5

The first core collected from the Academician Ridge contains mud breccia (site 5, Figure 1; Table 1; [32,33]) and the second is from the background area without any detected signs of deep fluid migration (site 6, Figure 1; Table 1). Hemipelagic sediment accumulation in this and other basins of the lake is supplied by the significant input of products of aquatic plants like phytoplankton and diatoms [7,34,35]. Sediments from the area of mud volcanic activity (“AcademRidge” [32]) are enriched with gas and contain gas hydrate layers and mud volcanic breccia of late Miocene–early Pliocene age. However, the ubiquitous overlapping of sediments with the thick layer of Holocene diatomic silt indicates the absence of modern volcanic activity. The study of microbial diversity in sediments of the region has revealed organotrophic, thionic, sulfate-reducing bacteria and methanogenic archaea. It is important to note that the last one is found at all the depths studied (up to 100 m), except the lowest layer [36].

Sediments from the central Basin were collected from sites with liquid oil discharge (site 7, 8—Gorevoy Utes and site 10—Cape Tolsty; Figure 1; Table 1; [37–41]), gas seeps and mud volcanoes, where gas hydrates were detected (mud volcano Kitami—site 9 and Kukuy—site 11; Figure 1; Table 1; [42,43]). Oils from the discharge zones of the central and the southern Baikal are generally well studied and their composition is comparable to those of the Cretaceous and earlier ages (most likely the Oligocene–Early Miocene) from other deep-sea freshwater reservoirs [39,40]. Liquid oil discharges to the water as a consequence of vertical migration along the permeable zones of tectonic faults [44]. It forms bitumen mounds at the lake bottom and slicks on its water surface that are rapidly transformed by local oil-oxidizing bacteria [42,45]. Sediments in zones of oil discharge are permeated with oil channels and enriched with gas (predominantly methane of thermogenic origin with a small admixture of microbial). The main source of Baikal oil is OM of freshwater reservoirs with a high content of land plant components. Biological diversity in zones of oil discharge

forms due to the growth of macro- and meiofaunal communities and microorganisms, which use HCs as a main carbon source [13,18].

The studies of methane fluid discharge in the central and the southern basins of the lake evidence the predominantly microbial origin of gas [7,43]. Several hydrate-bearing mud volcanoes were detected in the area of Kukuy canyon [3,46]. While methane, seeping in the discharge zone, is predominantly thermogenic, in the adjacent area, it may have a mixed microbial-thermogenic origin. The same mixed genesis is also characteristic for methane from the gas hydrate-bearing Kitami mud volcano [7,47].

The study of the southern basin included the sampling of sediments from the mud volcano Malenky (site 13, Figure 1, Table 1; [6,7,13,28,48–50]) and gas hydrate-bearing sediments from the mud volcano Kedr (site 14, 15, Figure 1, Table 1; [49,51,52]). The former study of gas fluid from the MV Malenky [6] has suggested its possible migration from the deep strata. However, the analysis of isotopic carbon and nitrogen composition of benthic animals has revealed their vital dependence on the methane carbon source [18], and the study of the isotopic composition of methane has indicated its microbial origin [7]. Gas hydrates and authigenic carbonates were detected in sediments of the MV Kedr. It was also shown that the area around the MV has moundy bottom relief with pockmarks, which testify to the gas fluid discharge from greater depths [52]. Moreover, the coal-bearing beds of the Tankhoy Formation of the Oligocene–Miocene age in this part of the lake may serve as a source of gas for hydrates formation. Methane and its homologues associated with gas hydrates of the MV Kedr have a thermogenic or secondary-microbial genesis that differs from the other hydrate-bearing zones of the lake due to the active biodegradation processes. These data are consistent with the presence of molecular markers of anaerobic methanotrophic archaea in sediments [49].

One more sediment core from the southern basin of the lake is located to the south of the Selenga river delta (site 12, Figure 1; Table 1) in the region of the gas hydrate mound (Posolsky Canyon-1; [47]) near the Posolsk Bank where methane seeps and gas hydrates were detected [3,7,13,17,49,50,53–55]. According to the studies of the focused fluid discharge zone in this area, methane has a mixed thermogenic-microbial origin [7]. Results of the radioisotope research have shown the presence of both aerobic and anaerobic methane oxidation processes in the Posolsk Bank sediments [17,56]. The detected archaea genus *Methanoperedenaceae* (ANME 2d) and bacterial phylum *Methylophilum* (NC10) are the most possible microbes for the aerobic methane oxidation in this and other regions of Lake Baikal. This process is often accompanied by nitrate, nitrite, Fe(III) or Mn (IV) reduction [49].

3. Materials and Methods

3.1. Sample Collection and Pretreatment

Sediment samples for the study were collected during several scientific research cruises of LIN SB RAS onboard the R/V “G.Yu. Vereshchagin” to Lake Baikal in 2017–2020 (15 cores, 47 samples; Figure 1; Table 1). The data were classified according to the geographical position of stations and the absence or presence of detected fluid discharge near sampling sites. The cores collected from zones where fluid discharge was not detected we have considered as a background. Sediment samples were collected using a 3 m gravity corer with a plastic liner (i.d. 100 mm). All the cores were sampled according to the lithological structure. Samples were kept in sterile boxes at -18°C until the laboratory investigation. Sample preparation included freeze-drying (Scanvac CoolSafe Freeze Dryer), grinding (Retsch RM-200), sieving to a fraction of 0.25 mm (Retsch AS-200) and taking 100 g of averaged subsamples (25%) for OM extraction.

3.2. Organic-Geochemical Analysis

Details of the analytical procedure have been described in [23,57,58] and can be summarized as follows: the content of organic (TOC) and carbonate (CaCO_3) carbon definition; Soxhlet extraction of the dissolved part of dispersed OM from sediments with chloroform

(EOM1—non-polar extractable organic matter) and sulfur removing; Soxhlet re-extraction of sediments with ethanol/benzene (1:2 *v/v*) for polar components of organic matter elicitation (EOM2); humic acids (HAs) extraction and calculation of the part of insoluble residual organic matter (ROM). The study of group composition of EOM1 included its fractionation into oils (hydrocarbons—HCs), resins and asphaltenes, and further oils fractionation into aliphatic (saturated—SAT) and aromatic (AR) components. The molecular composition of HCs (n-alkanes, isoprenoids, dimethylalkanes, tri- and tetracyclic terpanes, hopanes, steranes and polycyclic aromatic hydrocarbons—PAHs; Table S1) were studied using the method of gas chromatography-mass spectrometry (GC-MS) carried out on an HP5973/HP6850 Agilent Technologies MSD [57,58]. All compounds were assigned by the comparison of their retention times and mass spectra with those of external standards (Supelco 47,930-U, 46955-U, 49451-U; Chiron AS 2634.27-5UG, AS 0613.30-100-10, AS 2616.31-10UG, AS 2635.27-5UG, AS 0976.29-10-IO, AS 2646.30-10UG, AS 9876.16-50-IO, AS 9877.16-50-IO, AS 1693.16-500-IO, AS 0651.20-K-IO, S-4063-100-5 T), NIST and WILEY libraries and/or with published data [59–63].

4. Results and Discussion

4.1. Group Composition of the Extractable Organic Matter

The studied sediments from the northern, central and southern Basin of Lake Baikal are represented predominantly by diatomaceous silts typical for the modern Holocene sedimentation. The age of the bottom layers of cores from the Academician Ridge is an exception and is theoretically estimated as the Late Pleistocene due to the low sedimentation rates in the region (ca. 0.09 mm/year; [11,64]). However, the real age of sediments in cores collected from zones of fluid discharge, and especially regions with mud volcanic activity, may differ from the theoretical estimation due to the upward migration of the ancient rock material to the bottom surface. The importance of this phenomenon is confirmed by numerous findings of mud breccia inclusions in the studied sediment sections. The wide distribution of diagenetic iron sulfide inclusions (hydrotroilite) in the studied cores indicates processes of sulfate reduction, that in Lake Baikal are associated predominantly with a high methane concentration and its generation in sediments [65–67]. Special attention should be paid to the sediment cores with oil inclusions (site 7, 8, 10), authigenic carbonates and gas hydrates (site 9, 11, 14, 15) collected from the zones with focused fluid discharge.

The content of carbonate carbon (CaCO_3) in sediments is less than 0.67% (Table 1) that is associated with low content and lability of biogenic CaCO_3 in the water column of the lake [68]. The concentration of TOC and OM varies from 0.2 to 4.8% and from 0.3 to 8.7%, correspondingly (Table 1), reaching the expected maximum in oil-bearing layers of sediments from Gorevoy Utes and Cape Tolsty, and also in sediments from the hydrothermal zone of the Frolikha Bay. Significant variations in the group composition of OM (EOM1 from 0.3 to 47.9% and ROM from 96.6 to 36.9%; Table 1) also reflect the difference between sites with fluid discharge and/or high bioproductivity from the background regions. In contrast to oil-bearing sediments, where the decrease of ROM is accompanied by the growth of the EOM1, the deep layers of the core from MV Kitami show the sharp increase of HAs (up to 60%). This agrees with the upward migration of clay deposits enriched in terrigenous OM in the area of mud volcanism. This conclusion agrees with the relatively high concentrations of HAs in the surface sediments of mud volcanoes Malenky, Kukuy and Kedr, where the presence of mud breccia was detected. The ratio EOM1/EOM2 is less than one in most of the samples, except oil-bearing sediments, and indicates the input of oxidized OM with a relatively low level of thermal maturity [69,70].

The content of TOC-normalized EOM1 (β ; Table 2) shows values less than 6% in most of the samples attesting to the syngenetic type of bituminous components of OM and the host rock [69,71,72]. The exception is sediments enriched in oil (sites 7 and 8), where bituminous components are of epigenetic origin (β up to 86%). Oils (HCs) and resins dominate in the group composition of the EOM1 in most samples. The proportion of

aliphatic fraction in HC composition is higher than aromatic ($Al/Ar > 1$), attesting to the general uniformity of OM sources in the lake sediments.

4.2. Geochemical Characteristic of Molecular Markers

4.2.1. N-Alkanes and Isoprenoids

The total content of molecular markers (n-alkanes, steranes, terpanes, PAHs) varies significantly (from 271 to 10977 ng/g dry weight (dw); Table 2) depending on the geographic location and presence/absence of signs of the fluid discharge. The relatively high content is detected in zones of the oil show (site 8), mud volcanism (site 11, 13, 14), hydrothermal venting (site 1, 2) and in the surface sediments of the hydrate hill (site 12), where the active fluid discharge is not detected. Herewith, different components lead to an increase in the total content of molecular markers. Thus, n-alkanes predominate in the composition of MM from mud volcanoes Kukuy, Malenky, Kedr, and in the region of the hydrate hill Posolsky canyon-1. Terpanes show maximum content in sediments from Frolikha Bay and oil show Gorevoy Utes (site 8). PAHs are the main components in some layers of the cores from MV Malenky and Gorevoy Utes (site 7), where the total content of MM is relatively low.

Most *n*-alkane profiles show a bimodal distribution with a significant predominance of high molecular weight (HMW) components *n*-C₂₇–*n*-C₃₁ of terrigenous origin—foliar, conifer plants and grass ($TAR > 1$; Table 2; [73–75]) and with relatively low maturity level ($CPI_{22-30} > 2$ in most samples, except site 7, 8; Figure 2; Table 2). The growth of *n*-C₁₆ and *n*-C₁₈ homologues in the composition of the low molecular weight (LMW) n-alkanes in most studied sites ($OEP_{17-19} < 1$; Table 2) may attest to the processes of microbial transformation of algal detritus or the input of microbial OM [76–79]. Herewith, the possibility of even-number n-alkanes input with petroleum HCs is extremely low due to the absence of their maximum in the studied profiles of oil-bearing sediments.

Table 2. Main organic-geochemical parameters of OM and its molecular components.

Core #	Sampling Interval, cm	β, % ¹	% in EOM ²		Al/Ar ³	ΣMM ⁴	% from ΣMM ⁵			Pr/Ph ⁶	OEP ⁷	OEP ⁷	TAR ⁸	CPI ⁹	Ret ¹⁰	MPI ¹¹	
			HCs	Resins		ng/g	n-Alk.	Ster.	Terp.	PAH	17-19	27-31			%ΣPAH		
Northern Baikal																	
Frolikha Bay (low-temperature hydrothermal seep)																	
1	0–10	4.2	11.3	76.1	8.5	² 486.8	34.7	0.0	55.0	10.3	0.8	0.7	6.0	9.8	5.2	0.0	0.3
	25–35	4.7	13.2	76.1	1.5	² 486.8	38.5	0.0	49.6	12.0	0.8	0.8	5.9	5.9	4.9	0.0	0.3
2	5–15	2.7	8.8	82.5	8.1	² 564.7	73.7	0.0	14.8	11.5	0.9	0.5	5.5	4.7	3.9	1.4	0.3
	137–147	3.6	7.7	83.1	1.0	¹ 433.1	67.9	0.0	22.1	10.0	0.9	0.7	6.9	13.1	4.9	0.5	0.2
Background area near the Barguzinsky Nature Reserve																	
3	5–15	2.4	37.2	61.9	9.2	¹ 182.9	67.5	0.4	3.5	28.6	1.0	0.5	3.8	2.0	2.3	3.4	0.3
	62–72	3.3	10.5	80.0	6.0	¹ 425.3	72.4	0.0	8.0	19.5	1.0	0.5	4.2	3.4	2.2	1.8	0.3
	110–120	2.7	19.2	79.4	6.0	878.7	82.6	0.0	1.4	16.0	1.1	0.6	5.3	2.2	2.8	2.4	0.4
Central Baikal																	
Background area near the Ushkany Islands (Fe-Mn crusts)																	
4	0–3	1.2	20.3	75.7	2.7	¹ 836.9	89.9	0.1	6.9	3.2	1.4	0.9	6.1	9.4	3.1	6.1	0.6
	3–16	0.6	34.1	61.4	2.5	¹ 479.0	94.6	0.4	2.7	2.4	0.8	0.8	6.8	7.3	3.0	14.4	0.9
	16–27	3.5	36.8	52.7	5.5	¹ 584.1	93.0	0.2	4.2	2.8	1.1	0.9	4.9	9.2	2.8	8.5	0.8
Academician Ridge, mud volcano																	
5	10–20	2.1	15.7	81.7	2.6	902.6	54.3	0.0	4.0	41.8	3.0	0.5	6.2	15.2	3.4	0.4	0.5
	40–50	2.2	17.2	80.2	1.7	859.5	55.6	0.0	4.1	40.3	2.7	0.4	5.6	13.2	3.2	0.8	0.6
	120–130	1.9	15.5	82.9	3.8	959.2	56.8	0.0	4.2	39.0	2.6	0.5	5.6	14.6	3.3	0.4	0.4
Academician Ridge, background area																	
6	5–15	2.3	19.0	79.9	7.3	¹ 472.3	72.3	0.2	5.1	22.3	1.1	0.5	4.3	4.8	2.6	2.2	0.3
	95–105	2.0	19.1	79.4	6.2	² 168.3	69.3	0.3	6.5	24.0	0.9	0.5	4.6	3.9	2.7	1.6	0.4

Table 2. Cont.

Core #	Sampling Interval, cm	β, % ¹	% in EOM ^{1 2}		Al/Ar ³	ΣMM ⁴ ng/g	% from ΣMM ⁵			PAH	Pr/Ph ⁶	OEP ⁷ 17-19	OEP ⁷ 27-31	TAR ⁸	CPI ⁹	Ret ¹⁰ %ΣPAH	MPI ¹¹
Gorevoy Utes, oil seepage																	
7	10–20	30.9	52.1	45.2	1.2	1066.6	16.6	1.9	18.4	63.0	1.6	0.8	1.7	3.4	1.4	0.0	1.2
	100–120	75.2	50.8	46.1	4.6	801.2	5.7	0.9	8.9	84.5	3.2	0.6	0.5	0.1	1.4	0.0	1.3
8	0–15	87.2	57.9	36.5	1.2	3610.1	33.2	2.4	48.2	16.2	0.0	1.5	0.4	5.6	1.3	0.0	0.3
	50–60	12.0	64.7	33.8	2.0	10976.8	51.0	2.0	44.4	2.6	0.0	1.9	0.8	16.5	2.0	0.0	0.3
	60–70	20.7	67.6	29.8	1.6	2475.9	14.4	3.5	69.9	12.2	2.2	2.1	0.7	1.4	2.1	2.3	0.0
	100–110	2.6	23.0	70.9	2.5	2966.9	68.3	0.2	17.7	13.8	1.3	2.5	1.1	14.6	2.7	2.4	0.3
	190–200	5.9	27.4	69.6	2.3	3797.5	71.4	0.4	17.8	10.4	1.6	3.0	1.0	11.7	2.6	0.6	0.3
	300–310	3.8	19.8	71.8	3.0	4969.4	77.8	0.3	13.7	8.3	1.4	3.4	1.2	19.3	2.9	0.4	0.9
Kitami, mud volcano																	
9	0–10	5.3	12.7	86.4	3.3	1536.8	59.2	0.3	9.1	31.4	1.7	0.5	7.1	13.8	3.8	0.0	0.4
	110–120	2.1	9.2	89.3	3.0	1458.3	85.0	0.0	1.2	13.8	1.6	1.4	10.2	16.5	5.5	0.0	0.5
Cape Tolsty, oil seepage																	
10	10–20	2.9	10.4	84.9	4.0	2531.5	67.0	0.4	4.6	28.0	1.2	0.6	6.9	17.0	4.5	0.0	0.4
	50–65	1.1	22.1	75.8	1.9	747.4	48.6	0.5	16.3	34.6	1.8	0.5	7.0	13.9	4.1	0.0	0.4
Kukuy, mud volcano, gas hydrates, carbonates																	
11	0–15	2.6	10.1	87.6	5.3	7826.2	89.2	0.0	2.3	8.5	1.4	1.0	8.2	41.8	4.0	0.3	0.5
	30–40	4.0	12.6	85.8	10.3	8116.5	94.6	0.0	2.4	3.0	1.8	1.1	8.6	26.9	4.0	1.5	0.5
	86–96	2.7	7.8	90.7	3.4	8598.0	81.4	0.0	2.1	16.5	1.9	1.2	8.2	37.0	3.9	0.3	0.5
Southern Baikal																	
Posolsky canyon-1, hydrate hill																	
12	5–15	2.1	8.3	87.5	4.0	1896.3	65.5	0.3	4.4	29.8	1.7	0.6	7.1	14.7	4.2	3.1	0.4
	20–30	1.8	9.0	89.7	4.0	6962.4	98.0	0.0	0.2	1.8	1.2	1.0	7.6	41.7	4.0	1.5	0.3
	86–96	2.1	10.2	88.7	8.0	1060.5	93.1	0.0	1.3	5.5	1.3	0.8	7.8	32.4	3.9	1.8	0.3
	100–110	1.7	9.2	89.6	4.5	954.2	82.6	0.0	4.8	12.7	1.4	0.6	7.2	20.7	4.3	2.3	0.4
	193–203	2.9	10.9	86.9	4.5	1175.7	91.4	0.0	2.1	6.5	1.6	1.1	8.2	33.0	4.2	1.2	0.3
Malenky, mud volcano																	
13	0–15	1.9	15.8	80.0	1.8	3058.5	91.2	0.0	4.0	4.8	1.5	1.0	8.5	36.5	4.0	2.7	0.4
	40–50	2.9	11.8	83.0	8.5	3619.6	94.2	0.0	4.3	1.6	1.4	1.1	7.7	21.9	3.9	0.0	0.2
	80–90	3.8	23.3	72.7	2.5	292.4	14.0	0.0	0.0	86.0	0.9	1.3	3.2	7.1	1.8	0.0	0.3
Kedr, mud volcano, gas hydrates, carbonates																	
14	10–20	2.3	12.3	83.9	2.0	3783.0	75.6	0.4	14.9	9.1	1.1	0.8	7.1	11.2	3.7	1.5	0.7
	75–85	2.3	8.8	81.9	2.6	6350.8	77.5	0.0	17.0	5.4	1.9	1.0	7.8	17.5	4.4	1.5	0.6
	120–135	1.4	10.0	85.0	2.0	2842.9	85.8	0.0	7.1	7.1	0.5	0.9	7.5	41.0	3.4	0.5	0.6
15	0–10	2.4	24.8	67.4	1.5	785.6	84.8	0.0	12.8	2.4	0.9	0.7	7.1	16.8	3.6	1.6	0.3
	20–30	1.3	12.9	78.2	2.5	271.1	82.6	0.0	12.7	4.8	0.8	0.6	9.9	11.8	4.6	1.5	0.4
	45–55	1.7	12.1	81.3	1.6	442.5	87.7	0.0	6.7	5.5	1.1	0.8	10.8	28.7	4.6	0.0	0.3
	95–105	1.4	19.2	73.1	3.0	766.5	93.1	0.0	5.6	1.3	1.1	0.8	10.1	18.4	4.1	0.0	0.3
	120–130	1.0	14.3	79.4	2.3	543.1	93.6	0.0	5.0	1.4	0.9	0.8	10.2	25.8	4.4	0.0	0.3
	166–174	1.0	16.2	76.5	2.3	579.2	94.1	0.0	4.4	1.5	0.9	0.8	9.0	22.9	3.8	0.0	0.4

¹ β = (EOM1/TOC) * 100%; ² Composition of EOM1 fraction (HCs—oils, Resins and the residual component—asphaltenes; the sum is 100%); ³ Al—aliphatic HCs, Ar—aromatic HCs; ⁴ Total content of molecular markers (MM); ⁵ Relative content (%) of the main groups of MM: n-Alk.—n-alkanes, Ster.—steranes, Terp.—terpanes, PAH—polycyclic aromatic HCs; all the components of groups of n-alkanes, steranes (regular and dia-), terpanes (tri- and tetracyclic, mature hopanes, immature hopanes and hopenes) and PAHs are listed in Table S1. ⁶ Pr—pristane, Ph—phytane; ⁷ OEPn = (n-Cn-2 + 6 × n-Cn + n-Cn+2)/(4 × n-Cn-1 + 4 × n-Cn+1); OEP17-19 = (OEP17 + OEP19)/2; OEP27-31 = (OEP27 + OEP29 + OEP31)/3; ⁸ TAR = (n-C27 + n-C29 + n-C31)/(n-C15 + n-C17 + n-C19) [80,81]; ⁹ CPI = 2*(n-C23 + n-C25 + n-C27 + n-C29)/(n-C22 + 2*(n-C24 + n-C26 + n-C28) + n-C30) [81]; ¹⁰ Relative content of retene in total PAH, %; ¹¹ MPI1 = 1.5*(3MP + 2MP)/(P + 9MP + 1MP) [81].

Figure 2. Relative distribution of *n*-alkanes *n*-C₁₃—*n*-C₄₀ (%) in the OM of bottom sediments of Lake Baikal. The most representative lines are selected to display *n*-alkanes distribution in layers of one sediment core with similar chromatographic profiles.

The most prominent maximum of *n*-C₁₆, *n*-C₁₈ homologues is detected in bottom sediments of the northern Baikal and Academician Ridge, and also in the hydrothermal region Frolikha, where the red-ox environmental conditions ($Pr/Ph < 1$; Table 2) may promote the reduction of carboxyl groups of fatty acids of the local biota. The predominance of odd-number LMW *n*-alkanes *n*-C₁₅—*n*-C₁₉ (OEP17–19 up to 3.4, site 8; Table 2) is detected in some oil-bearing layers of the Gorevoy Utes area, that together with the maximum of *n*-C₂₀ and *n*-C₂₅ and the absence of the HMW homologues *n*-C₂₆—*n*-C₃₈ may attest to the active biodegradation. The presence of the unresolved complex mixture (UCM) on the TIC chromatographic profiles of sites 7 (10–120 cm) and 8 (0–70 cm; Figure 3a) confirms this assumption [82].

The sharp increase of HMW *n*-alkanes content (*n*-C₃₅—*n*-C₃₉) in OM of sediments from the Gorevoy Utes (site 8) is a unique phenomenon that requires special attention (Figure 2). Quite possibly, the homologue *n*-C₃₉ peak is just an element in a series of *n*-C₃₅₊ *n*-alkanes, which full length we do not see due to the GC method restrictions. Such distribution is a characteristic of the asphaltene fraction of crude oils [83] but was not found in fresh and biodegraded oils of lake Baikal where the content of HMW homologues *n*-C₃₀₊ sharply decreases [84]. However, the presence of UCM, total absence of isoprenoids, high level of *n*-alkanes maturity ($CPI \leq 2$; Table 2) and decrease of *n*-C₃₅—*n*-C₃₉ homologues content with depth in the studied samples (site 8, 0–15, 50–60 cm) may indicate aerobic

biodegradation processes which lead to the partial loss of lower MW and the preservation of higher MW *n*-alkanes [85].

Isoprenoid HCs (pristane and phytane) are detected in all samples, except surface sediments of Gorevoy Utes (site 8), and their content reaches maximum values for the region in the deeper layers of site 7 (100–120 cm) and 8 (60–70 cm). Values of the isoprenoid ratio (Pr/Ph from 0.5 to 3.2; Table 2), which is a traditional indicator of the red-ox environments [81], show significant variations between the studied sites and indicate the changes in conditions of sedimentation from reducing to moderately oxidizing. Herewith, the increased content of pristane may be associated with the additional input of highly mature OM of kerogen [86]. The highly reducing conditions of sedimentation are detected in sediments of hydrothermal vent Frolikha and some layers of sediments from MV Malenky and Kedr, which are likely associated with liquid and gas fluid discharge. The wide range of values demonstrated on the Connan–Cassou diagram (Figure 3b; [87,88]) attests to the mixed, predominantly terrigenous origin of the OM in the region. The highest level of OM thermal maturity is detected at the bottom layers of the core from Gorevoy Utes, in sediments from MV Kukuy, Kedr (site 15) and in the upper part of the core from MV Malenky. According to the diagram (Figure 3b), the highest level of biodegradation show sediments from the Academician Ridge (site 5, MV), the lower part of the cores 14 (MV Kedr) and 10 (oil show Cape Tolsty) and the surface sediments of core 4 (the northern Baikal).

Figure 3. (a) Total ion chromatogram showing the distribution of aliphatic components in OM of Gorevoy Utes (site 8) surface sediments. Abbreviations of *n*-alkanes and hopanes are defined in Table 1S. (b) A cross-plot of pristane/*n*-C17 (Pr/*n*-C17) versus phytane/*n*-C18 (Ph/*n*-C18) (modified after [89]) shows a difference in facies and OM maturity between the studied sediment cores (averaged values for several layers of one core are shown, see legend). (*) Values are out of the chart area.

Variations in isoprenoid parameters reflect the influence of focus fluid discharge processes on the vertical migration of the ancient material enriched in thermally mature OM to the bottom surface. Moreover, the scatter of data allows detecting layers of sediments from the fluid discharge zones with active biodegradation associated with high biodiversity and favorable environmental conditions [18,90].

4.2.2. Terpanes and Steranes

A high concentration of terpanes in which hopanes are the major constituents (Figure 4a) reflects the input of prokaryotic OM [81] and is detected in some layers of Frolikha Bay

sediments, Gorevoy Utes, Cape Tolsty and MV Kedr (Table 2). The molecular composition of terpanes is one of the most interesting characteristics of OM of Lake Baikal because it reflects the unique biodiversity and development of the microbial communities in the sediments of the lake.

Figure 4. (a) Examples of the three main types of terpanes distribution (chromatogram of m/z 191 for the most representative samples): mature (I), mixed (II) and immature (III). Mass spectra of the most rare and specific hopane components are shown here in the insets and in Figure 5. All abbreviations are defined in Table S1. (b) Group characteristics of terpanes of all the sites (total terpanes normalized values of tri- and tetracyclic terpanes, mature and immature hopanes, in %). Components of each group are listed in Table S1. The averaged values for several layers of one core are shown (see Y-axis labels). *) The number of chromatogram type – I, II or III (Figure 4a) is indicated in the left vertical column.

The “mature” type of terpanes distribution (number I, Figure 4a) is the most frequent characteristic of OM of the pelagic sediments of different marine and freshwater basins but is detected only in sediments from oil shows Gorevoy Utes (site 7, 8) and Cape Tolsty (site 10). The low content of immature hopanes in the OM of sediments from the northern Baikal (site 4) and in the surface clay of MV Kitami (site 9), which sediment section contain a gas hydrate, allows to attribute them to the mature type too. The main characteristics of the molecular composition of the mature type of Lake Baikal terpanes include stable forms of trisnorhopanes – Ts and Tm ($Ts/(Ts+Tm) \geq 4$; Figures 4a and 6a), the series of H29-H35 $\alpha\beta$ -hopanes with high values of homohopanes ratio $H31\ S/(S+R) \geq 0.4$ (Figures 4a and 6a), significant content of C30 moretane (stable $\beta\alpha$ geohopane) and C30 diahopane, which forms during the oxidative catalytic transformation of hopenes in a clayey environment [81]; Figure 4a, inset). The gradual increase of mature hopane components deep in the sediments of the northern Baikal basin (site 4) is likely associated with the low sedimentation rate and local diagenetic processes. This agrees with the highest content of tri- and tetracyclic terpanes ($Tt23/H30$ up to 0.4)—the structures stable to biodegradation that originate from freshwater or marine algae and land plant sources [91]. The surface layer of the core from MV Kitami (site 9) does not contain diatomaceous silt and is represented by clay deposits likely due to the uplift migration or redeposition of the ancient material enriched in OM of post-diagenetic maturity level. Thus, the “mature” type of terpane distribution in the surface layer of the core is consistent with this assumption.

Figure 5. Mass spectra of hopane structures (m/z 191) characteristic of the mixed and immature type of terpane profiles of Lake Baikal sediments: (a)—C30 neohop-13(18)-ene; (b)—X, Hopene with the unknown structure; (c)—C32 bishomohopene; (d)—C31 2-methylhopane.

Figure 6. Cross plots of thermal maturity parameters based on: (a) trisnorhopanes (Ts and Tm) and H31 homohopanes distribution (m/z 191); (b) isomerisation at asymmetric centers of C29 steranes (m/z 217). The averaged values for several layers of one core are shown (see legend). Maturity trend lines are adapted from [81]; all abbreviations are listed in Table S1.

Terpane profiles of most Baikal sediments are represented by the less mature forms that, for convenience, are marked here as mixed (II) and immature (III) types of distribution (Figure 4a). The predominance of immature $\beta\beta$ -hopanes and hopenes in the mixed type of distribution is accompanied, however, by the input of mature constituents. This may be due to the inflow of clay particles with terrigenous runoff, erosion and redeposition of ancient sediments and an uplift of the mud breccia to the bottom surface. The mixed type is characteristic for most Lake Baikal sediments and it does not show significant variations in components, only in their ratios (Figure 7). In contrast to the mature type, in the mixed type, the less stable structures—22,29,30-trisnorhop-17(21)-ene (Te) and 17 β (H)-22,29,30-trisnorhopane (Tb) predominate in the composition of trisnorhopanes. The content of mature components (H29–H31 $\alpha\beta$, moretane C29 $\beta\alpha$ and gammacerane) is significantly lower than the less stable structures—C29 $\beta\beta$ hopane, 17 β (H)-hop-20(21)-ene, C30 neohop-13(18)-ene, C32 homohopene, 2-methyl-17 α (H),21 β (H)-hopane and hopene, with an unidentified structure (X; Figures 4a and 5b).

Figure 7. Input of immature hopanes to the OM of sediments of Lake Baikal. The vertical rows of data are arranged according to the studied core intervals. Individual hopanes are normalized to the total content of hopanes ($\Sigma\text{Hopanes} = \Sigma\text{mature, mixed, immature hopanes, all compounds}$ are listed in Table S1). The intervals with focused fluid discharge are marked as oil—oil channel; HTh—hydrothermal vent; GH—gas hydrate; Breccia—mud volcanic breccia; Gas—gas-bearing layer; Carb—authigenic carbonates; ?—no detected fluid discharge, but the data attest to the growth of microbial activity. I, II, III—type of terpanes distribution according to Figure 4a.

Most of these structures are specific markers of prokaryotic OM of the early diagenetic stage of transformation. For example, such rare structures as hop-20(21)-enes (Figure 4a, the inset), whose precise origin is still incompletely understood, may be generated by catalytic oxidation of the less stable bacterial marker—diploptene (hop-22(29)-ene) in the clayey environment [60,92]. The stronger oxidation leads to the formation of neo-13(18)-ene from diploptene (Figures 4a and 5a; [93]). Both products are detected in immature coals and source rocks and are characteristic of the OM of most sediments of Lake Baikal, except areas with oil discharge (Gorevoy Utes and Cape Tolsty) and the lower part of the section of the northern basin (site 4). Variations in their relative content attest to the different

stages of diploptene transformation likely associated with the presence of a clay catalyst. The maximum values are detected in zones with mud volcanic activity and in layers that contain mud breccia, gas or liquid fluid (HTh vent Frolikha; MV Academician Ridge; MV Kukui; MV Malenky; MV Kedr; Figure 7). This agrees with their formation during microbial generation and biodegradation of OM. Other immature structures detected in most sediments of the lake are C30 hopene with an unidentified structure (Figures 4a and 5b) and two intensive peaks located between H32 and H33 homohopanes on the chromatogram (m/z 191), identified as C32 homohopene and 2-methylhopane (Figure 5c,d; [59,61]).

Parfenova et al. [61] have described the molecular structure of homohopene detected in the organic-rich limestones of the Sinyaya Formation (Lower Cambrian) and its homologues series was found in the mid-Cretaceous silty sandstones and mudstones of Hokkaido [94]. The nature of these compounds is still incompletely understood, but there is an assumption about their origin from bacteriohopanepolyol, which is a component of bacteria living in water, soil and sediments [95]. It is important to note that the revealed homologue of homohopene comes later on the chromatogram (m/z 191) than the described C31 compound [61], and most likely has 32 carbon atoms. According to the scheme suggested in [95], the C32 homologue is one of the most stable forms of homohopenes that can be found in the OM of the diagenetic level of transformation.

There is much more information about the structure and distribution of 2-methylhopanes for today. Thus, their main precursors, 2-methylhopanepolyols, are widespread in the ancient deposits, modern microbial mats and bacterial cultures [59,96–98]. It was shown that these compounds are genetically associated with cyanobacteria and/or methylotrophs [59]. Herewith, cells of cyanobacteria often generate more stable C32 2-methylhopanes, while in sediments of Lake Baikal, only C31 homologue was detected (Figures 4a and 6d). Moreover, all sediments with a mixed and immature type of terpane distribution contain gammaceran that is traditionally considered a product of tetrahymanol, a component of marine and freshwater sediments, photosynthetic sulfur bacteria and ferns, which occurs in stratified oxygen-poor water environments [99,100]. However, the experimental study of gammaceran formation in conditions characteristic for the HCs generation zone (80°C, 5 mpa) has revealed another possible source for this compound in the sediments of Lake Baikal. It was shown that the enrichment of sediments with the biomass of Baikal diatom *Ulnaria acus* (*Synedra acus*) leads to the OM composition changes and gammacerane formation in initially clean samples [54]. Received data agree with the result of [101] that has shown gammacerane formation from protozoa biomass feeding on cyanobacteria and microorganisms in various paleoenvironments. Moreover, gammacerane is the main biomarker of lacustrine oils and bitumen, including the “Green River” petroleum deposit in China, where the main sources of OM are algal detritus and bacteria [81].

The last immature type of terpane distribution (III; Figure 4a) was detected only in the Frolikha Bay sediments. The main characteristic of this type of profile is the total absence of tri- and tetracyclic terpanes and mature hopanes and a high content of immature constituents such as Tb, hop-17(21)-ene, hop20(21)-ene and neo-13(18)-ene, which testifies to the intensive input of microbial OM to the sediments (Figures 4a,b and 7). Previous studies [31,102] have shown that the anomaly increase of the content of the other diploptene transformation product C30 hop-17(21)-ene in mud breccia of MV Kedr may be due to the development of chemoorganotrophic microorganisms, which use metabolic products of methanotrophic and, possibly, methanogenic bacteria [103]. Despite the unexpected absence of C30 hop-17(21)-ene in sediments of sites 14 and 15 (MV Kedr), in this study, the low concentration of this compound was detected in surface sediments of oil discharge zones (Gorevoy Utes and Cape Tolsty, site 7, 10) in the bottom layer of the core from southern Baikal (Posolsky canyon-1, site 12) and in gas hydrate-bearing sediments (Kukuy, site 11; Figure 7). The unexpected appearance of the hop-17(21)-ene structure in the sediment core from the background region of northern Baikal (site 3) likely attests to the unrevealed processes of fluid discharge. All these data confirm the assumption about the link between the content of hop-17(21)-ene in the OM of sediments and the microbial

activity in zones of focus' fluid discharge and also may indicate such processes in zones where they were not detected previously.

Steranes are minor components of the OM of Lake Baikal's bottom sediments (Table 2) and are represented predominantly by ethylcholestanes (C_{29}) that indicate the input of OM from land plant sources likely associated with clay minerals. It is important to note that the presence of low mature terrigenous components of n-alkanes ($OEP_{27-31} \geq 5$ for most samples; Table 2) and the total absence of steranes in some layers of sediments likely attests to the level of OM transformation insufficient for their generation that agrees with the previous results [31]. Sediments with a significant content of C_{29} steranes (Figure 6b) differ by level of OM thermal maturity and biotransformation. Thus, the most thermally mature steranes were detected in the OM of background sediments of central Baikal (site 4; Figure 6b), and the most biodegraded OM of eukaryotic genesis was found in Gorevoy Utes sediment core (site 7) and in the surface of MV Kedr (site 14).

4.2.3. Polycyclic Aromatic Hydrocarbons

The contribution of PAHs (all compounds are listed in Table S1) to the composition of molecular markers of OM varies from 1.3 to 86% and the maximum values are detected in sediments from Academician Ridge MV, Gorevoy Utes and MV Malenky (sites 5, 7 and 13 correspondingly). Phenanthrene and its C1-C4 alkyl homologues, cadalene, retene and perylene are the main constituents of PAHs of most Lake Baikal sediments and only samples from oil discharge zones show minimum values of perylene. The input of these compounds attests to the mixed biogenic-petrogenic origin of OM. Thus, cadalene and retene are derivatives of sesqui- and diterpenoids produced by higher plants [62,104]. The formation of perylene is usually associated with the transformation of terrigenous and/or marine OM during microbial processes in reducing environments, or the release of water fungi products during the destruction of wood [105–107]. Previous studies have shown that phenanthrene structures may be associated with diterpene transformation [108] or may form by the dehydrogenation of sterols [109]. The ratio of diterpenoid diagenetic products, methylphenanthrenes (MPI1; Table 2; [110]), is based on different thermodynamic stability and bioavailability of the main four isomers (3MP, 2MP, 9/4MP, 1MP). The values of MPI1 reflect the level of OM transformation [81] and point to the wide scatter of its thermal maturity in samples of Lake Baikal—from immature diagenetic (site 1, 137–147 cm) to the late oil catagenetic stage (site 7, 10–120 cm) with a predominance of early and peak oil generation stages in most of the studied samples. However, the strong association of phenanthrene structures with the mineral matrix of terrigenous rocks should be considered.

The distribution and origin of retene in the sediments of Lake Baikal is an important issue that requires special attention. An experimental study has shown that the destruction of algal biomass accompanied by the development of microbial communities in the area of methane seepage may lead to retene formation [54,90,111]. However, in this study, the increased content of retene (up to 2% of total PAHs; Table 2) is detected in sediments of background zones of the lake (site 3, 4, 6) and only in some layers of cores from fluid discharge zones (site 8, 12, 13). High retene concentration in sediments of the background zones may be due to several reasons. The first is input with terrigenous clay minerals, and the second and the most probable is the destruction of diatom *Ulnaria acus* (*Synedra acus*) in the surface layer of sediments. This diatom is one of the dominant phytoplankton species, which produces the bulk of primary production of the lake [112]. Despite the fact that retene is conventionally considered a marker of coniferous plants [104], it is often absent in terrestrial petroleum and may be found in sediments and bitumen enriched in algal OM. The previous data on retene generation from algae with the assistance of microorganisms [113,114] agree with the recent experimental result on diatomic biomass destruction by the local microbial community of Lake Baikal [54]. The typical mesophilic bacteria of genus *Arthrobacter* and *Solirubrobacter* belonging to the phylum *Actinobacteria*, and genus *Sphingomonas* represented by the class α -*Proteobacteria* were dominant in thermobaric conditions of the experiment. The specified taxa have flexible metabolism, which

helps them to function not only in mesophilic conditions but also adapt to the temperature increase during burial and fluid circulation [115]. The destruction of OM and associated retene formation in the bottom sediments of Lake Baikal may be due to the functioning of the dominant taxa *Chloroflexi*, *Ca. Atribacteria* (OP9), *Deinococcus-Thermus*, *Acidobacteria*, *Ca. Aminicenantes* (OP9), *Ca. Latescibacteria*, *Ca. Saccharibacteria*, *Planctomycetes* and *Firmicutes* [54]. The third reason for the increase of retene concentration in the background regions of Baikal is aerosol transport of combustion products after the extensive wildfires around the lake's coasts. The eolian input of retene to the northern part of the lake from northern Siberia is up to 0.33 ng/m³ and is determined predominantly by the combustion of *Pinus sylvestris* and *Larix sibirica*, constituting 80% of the forest [116].

4.2.4. Dimethylalkanes

Besides the traditional set of molecular markers, a series of methylated alkanes (3,5-, 3,6-, 3,7-dimethylalkanes – DMA, m/z 99, 113, 127; Figure 8) were also identified in bottom sediments of Lake Baikal. These structures have been previously detected in OM of recent and partially lithified deposits of Siberia and the Russian Platform [63,117,118] and in sediments of the Academician Ridge of Lake Baikal [111]. Precursors of these compounds with a high probability are di- and tetraether lipids of archaea and bacteria [63,119].

Figure 8. Example of summary mass chromatogram of n-alkanes and 3,5-, 3,6-, 3,7-dimethylalkanes (m/z 71, 99, 113 and 127 correspondingly) in bottom sediments of MV Kedr (upper line) and mass spectra of DMAs according to their characteristic ions (bottom line).

The received data on the distribution of 3,6-DMA (only even homologues) and 3,7-DMA (only odd homologues) agree with the previous research [63], but the series of 3,5-DMA in the OM of bottom sediments of Lake Baikal contains both odd and even-chained homologues that were not detected previously. The ubiquitous distribution of these compounds in the sediments of the lake (even their low content) allows us to define them as a background geochemical characteristic. However, their total absence in the OM of some sediment cores collected from the fluid discharge zone (site 7, 10–120 cm; 8, 0–70 cm;

9, 110–120 cm; 13, 80–90 cm; 12, 193–203 cm) is also informative and has the potential to be a tool for the anomaly detection.

4.3. Specificity of OM in Zones of Authigenic Carbonates Formation

The study of OM and hydrocarbon molecular proxies in sediment cores with layers containing authigenic carbonates (Kukuy, site 11; Kedr, site 14, 15) gives a new way to understand the conditions of their formation in the specific environment of Lake Baikal. According to the present conception [9,49,51,120,121], the formation of authigenic carbonates of Lake Baikal is associated with microbial methane generation processes. Acetoclastic methanogenesis is one of the most probable processes of methane formation in anaerobic conditions of freshwater reservoirs, but it shows less evidence in Lake Baikal sediments than the hydrogenotrophic way. Thus, acetate-ion was not detected in the pore water of sediment cores from MV Malenky (up to 139 cm) and Kedr (152 cm; [49]). The isotopic composition of siderites from zones of the focus fluid discharge [120] points to their enrichment in ^{13}C compared to methane and ethane. This allows us to consider the microbially transformed OM of bottom sediments as the initial source of HCO_3^- . Herewith, it is important to note that processes of methane generation, anaerobic methane oxidation (AOM) and authigenic carbonates formation are spatially separated in the sediment section, which complicates the search of their common molecular proxies. The received results on the group and molecular composition of the dispersed OM in bottom sediments with authigenic carbonates and gas hydrates inclusions (MV Kukuy, site 11; MV Kedr, site 14, 15) allows us to emphasize the following:

1. The increased content of EOM2 (ethanol-benzene extract; $\text{EOM1/EOM2} < 0.4$) is detected in layers of sediments from MV Kukuy and Kedr (11, 0–15 cm; 15, 20–55 cm, 120–174 cm). The same or higher contents are characteristic of MV Malenky (13, 40–50 cm), where carbonate inclusions were also found [9,120], MV from the region of Academician Ridge (5, 40–50 cm) and in two upper layers of the background core with Fe-Mn crusts from northern Baikal (4, 0–16 cm). The use of ethanol-benzene instead of a chloroform solvent allows us to extract more polar components of OM, which contain alcohol, ester and acid groups including fatty acids, resinous substances, terpenoids, waxes, polyphenols and carbohydrates, etc. [122,123] Thus, the increased content of oxidized components in sediments of these areas point to the lower level of OM maturity [124,125].

2. A significant content of humic acids (up to 60%) is detected in most of the sediments of Lake Baikal. Previous studies [126–128] have shown that degradation of OM with a high content of HAs may lead to the increase of molecular H_2 rather than acetate in the anoxic sedimentary environment and a corresponding shift to the hydrogenotrophic methanogenesis instead of the acetoclastic way. This is consistent with the results of radioisotope research and cultivation [48,126,129]. Vertical migration of clay deposits with the mud volcanic breccia in sediment cores from MV of the Academician Ridge (site 5), MV Kitami (site 9) and MV Malenky (site 13) determines the growth of HAs concentration with depth and is accompanied by the absence of acetate-ion. However, sediment cores enriched in authigenic carbonates and gas hydrates from the MV Kukuy and Kedr show a significant decrease of HAs content with depth, herewith the acetate concentration is still under the detection limits in these layers (0.1 mg/L). Thus, we can make a preliminary conclusion that humification is probably not the unique reason for acetate decrease in sediments of the deep-water zone of Lake Baikal.

3. The high content of immature molecular markers of prokaryotic origin (hopanes and hopenes) in the OM of sediment cores from MV Kedr and Kukuy (Figure 4a) is consistent only with the values detected in the sedimentary OM of hydrothermal vent site Frolikha (site 1, 2) and may testify to the high microbial activity in the sediment section [129]. Herewith, the increase of content and diversity of immature hopane structures with depth confirms the assumption of the existence of a larger methane generation zone in these regions.

5. Conclusions

The study of a wide set of organic-geochemical proxies in bottom sediments collected from all the geographic zones of Lake Baikal (northern, central and southern basins, Academician Ridge) allowed us to reveal the most effective molecular indicators of hydrocarbon migration in areas of the focused fluid discharge. The complex analysis of hydrocarbon molecular markers distribution (n-alkanes, dimethylalkanes, isoprenoids, tri- and tetracyclic terpanes, hopanes, steranes and PAHs) has shown that the general characteristics of the OM of sediments indicate the predominant input from terrigenous (allochthonous) and algal/microbial (autochthonous) sources and the unique composition of molecular proxies. Herewith, the composition of HC molecular markers in bottom sediments of the focus fluid discharge zones (liquid and gas seepage, oil shows, hydrothermal venting, mud volcanism and associated gas hydrates and authigenic carbonates) varies significantly due to the environmental conditions and local microbial activity. Thus, the specific immature hopane structures are identified in sediments of sites with the detected vertical migration of the mud breccia to the bottom surface due to microbial activity (MV Kukuy, Kitami, Malenky, Kedr). The increased content of microbial OM is associated with gas-bearing intervals of these cores, which also contain gas hydrates and authigenic carbonates. The maximum of microbially degraded OM in deposits from the regions with oil discharge is registered both at the top (Cape Tolsty) and at the bottom (Gorevoy Utes) of sediment sections and points to the development of different archaea and bacterial communities. The unique distribution of immature hopane structures defined in bottom sediments of the hydrothermal vent site Frolikha attests to the active development of chemoorganotrophic microorganisms that most likely use methane as the main carbon source. The analysis of OM in sediment layers enriched in authigenic carbonates and gas hydrates point to the specificity of its group and molecular characteristics (the growth of polar lipids fraction content, changes in HAs distribution through the core, specific immature hopane profiles), but the significant increase of knowledge in this field is still required to make more reliable conclusions. It is interesting to note that different molecular signs of microbial activity were registered in the OM of sediment cores without any signs of fluid discharge (northern Baikal background) and with high probability indicate the presence of undetected anomalies in these regions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/geosciences12020072/s1>, Table S1: list of compounds (molecular ions) and their abbreviation.

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