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Organic Geochemistry and Microfossils of the Upper Jurassic and Lower Cretaceous Strata in the Lower Reaches of the Olenek River (Northeastern Framing of the Siberian Platform, Arctic Siberia)

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Abstract—The organic-geochemistry data reveal two levels in the reference Upper Jurassic–Lower Cretaceous section of the lower reaches of the Olenek River: lower (Volgian–lower Boreal Berriasian (diasterene)) and upper (Boreal Berriasian–Valanginian (hopane)). The Volgian beds are composed of clays with abundant prasinophytes *Leiosphaeridia* and *Tasmanites* and various dinocyst assemblages and have the highest content of organic carbon (C_{org}), up to 9%. Isoprenoids, in particular, pristane and phytane, are highly predominant among aliphatic hydrocarbons; their content is more than three times higher than that of coeluting *n*-alkanes, which is typical of buried chlorophyll-containing plankton (dinocysts and prasinophytes). Sedimentological, biofacies, and paleoecological analyses show that the highly carbonaceous beds of the Buolkalakh Formation formed under oxygen deficit conditions. An integrated analysis demonstrated that the pristane/phytane ratio does not always reliably reflect the reducing or oxidizing conditions of organic-matter accumulation and diagenesis. The discrepancy between the geochemical identification of organic matter according to the pristane/phytane ratio and the biofacies and sedimentological data is due to the low catagenetic maturity of OM. The Volgian was marked by a significant transgression of the Anabar–Lena sea, which was gradually changed by a successive regression of its basin at the end of this stage and in the Boreal Berriasian. The C_{org} contents in the coastal and subcontinental sediments decreased. Diasterenes and 4-methyldiasterenes disappeared from the balance of biomarker molecules, and the portion of hopanoids increased. Aerobic environments prevailed in the subbottom waters. Earlier, three biomarker horizons were identified according to geochemical criteria in the synchronous sections of Anabar Bay (Laptev Sea coast): terpane, diasterene, and hopane ones. In the section of the Olenek basin, the upper two horizons are well identified by specific biomarkers, and the lower one is absent because of the sedimentation break. Stratigraphic analysis of the location of these geochemical levels in different parts (and bathymetric zones) of the Anabar–Lena basin shows their diachronous formation. According to all geological and geochemical criteria, the Volgian Stage and the lower beds of the Boreal Berriasian Stage of this basin have a high petroleum potential. In the axial zone of the basin and, especially, on the Laptev Sea shelf, there were probably favorable conditions for the generation and accumulation of hydrocarbons genetically related to the Upper Jurassic highly carbonaceous rocks.

Keywords: Jurassic and Cretaceous; organic geochemistry; biomarkers; microfauna; terrestrial and marine palynomorphs; Arctic Siberia; Lena–Anabar basin

INTRODUCTION

The Upper Jurassic organic-rich sediments deposited in the Boreal and Arctic basins are the main source of hydrocarbons in the North and Norwegian Seas, the Barents shelf, and West Siberia (Leith et al., 1992; Kontorovich, 2004; Nikitenko, 2009). The Upper Jurassic and Cretaceous strata are widely distributed in the north of East Siberia (northern margin of the Siberian Platform) and are relatively well-studied in the marginal depressions. In this region, parallel stratigraphic zonal schemes have been developed for different groups of macro- and microfauna as well as marine and terrestrial palynomorphs (Beizel et al., 1976; Zakharov et al., 1997; Shurygin et al., 2000; Nikitenko et al., 2008, 2011, 2013, 2015a,b, 2018; Peshchevitskaya, 2010; Dzyuba, 2012; Shurygin and Dzyuba, 2015).

Marginal depressions occupied the area of the former carbonate platform complicated by early Proterozoic rift structures. During the Carboniferous (Visean), an extensive passive continental margin developed along the margin of the Siberian Craton that subsequently (late Mesozoic) transformed into the Verkhoyansk–Kolyma fold system with marginal troughs on the periphery as a result of the collision between the North American and Siberian Plates (Parfenov and Kuzmin, 2001).

This study presents the results of the continuing long-term investigations of the Jurassic and Cretaceous microbi-

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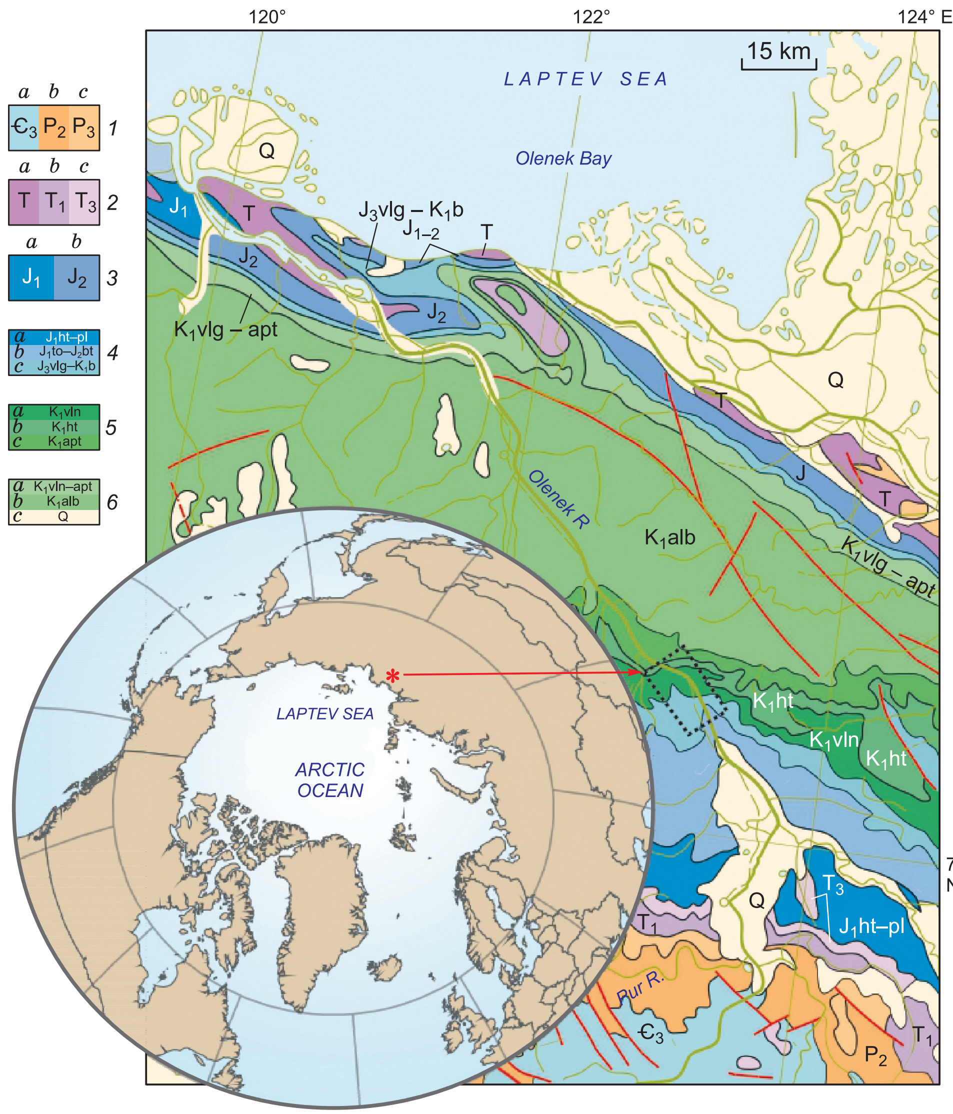
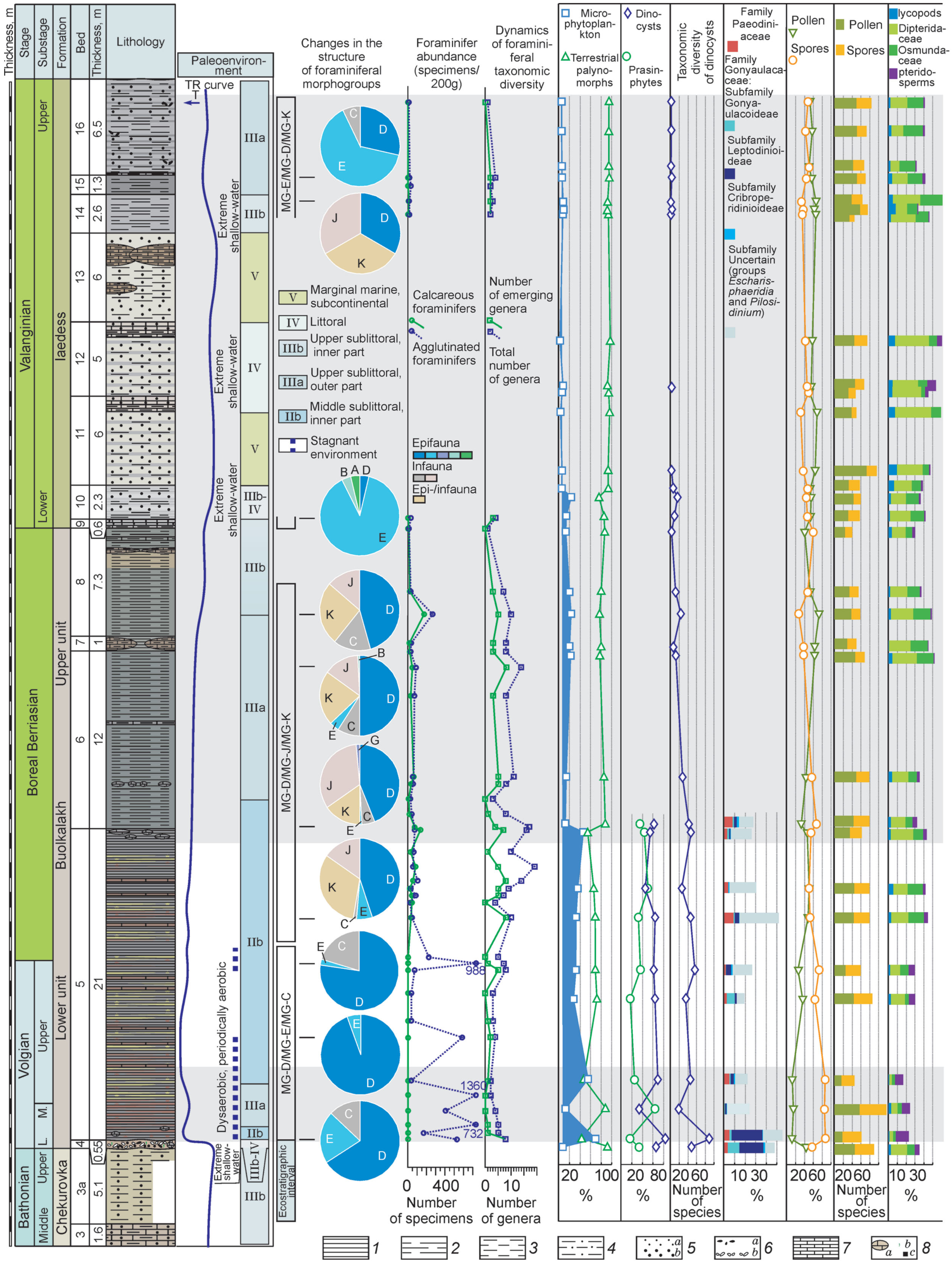


Fig. 1. Location of the reference Upper Jurassic and Lower Cretaceous section on the left bank of the Olenek River (platform flank of the Lena–Anabar basin, modified after Kovalev (2006). *1–6*, ages: *1*, Cambrian (*a*), Middle Permian (*b*), upper Permian (*c*); *2*, Triassic (*a*), Lower Triassic (*b*), Upper Triassic (*c*); *3*, Lower Jurassic (*a*), Middle Jurassic (*b*); *4*, Hettangian–Pliensbachian (*a*), Toarcian–Bathonian (*b*), Volgian–Boreal Berriasian (*c*); *5*, Valanginian (*a*), Hauterivian (*b*), Aptian (*c*); *6*, Valanginian–Aptian (*a*), Albian (*b*), Quaternary (*c*).

ota and dispersed organic matter (OM) from coastal sections along the Laptev Sea and the northern margin of the Siberian Platform. The first results of geochemical studies of the Anabar Bay section were published in Kashirtsev et al. (2018). In these sections, three biomarker horizons were identified according to the predominant distribution of certain hydrocarbon biomarkers: terpane (upper Oxfordian--Kimmeridgian), diasterene (upper Middle Volgian–base of the Valanginian), and hopane (Lower Valanginian). Along with the identification of biomarker molecules, the goal of this study was to assess both lateral and vertical variation of “geochemical facies” and microfossil assemblages throughout the Anabar–Lena basin.

The section studied is located on the platform flank of the Lena–Anabar basin in the Olenek River basin (Fig. 1). The Mesozoic strata in this region lie subhorizontally or dip gently to the north (1–3°). They are composed of Triassic, Jurassic, and Boreal Berriasian marine successions as well as Valanginian, Hauterivian, and Aptian–Albian marginal marine, subcontinental, and continental successions. Along the left bank of the Olenek River, the Upper Jurassic and Lower Cretaceous Buolkalakh Formation (Fig. 1) rests on the siltstone and sandstone beds of the Chekurovka Formation (Middle Jurassic, Bathonian), which contain a basal sand member with lenses of conglomerate (Fig. 2). The thickness of this member varies from 0.3 to 2 m in different sections. Conglomerate is composed of well-rounded pebbles, sandstone boulders, and calcareous nodules from the Chekurovka Formation. The basal member is overlain by a layer of black thinly laminated clays (Volgian–lower Boreal Berria-



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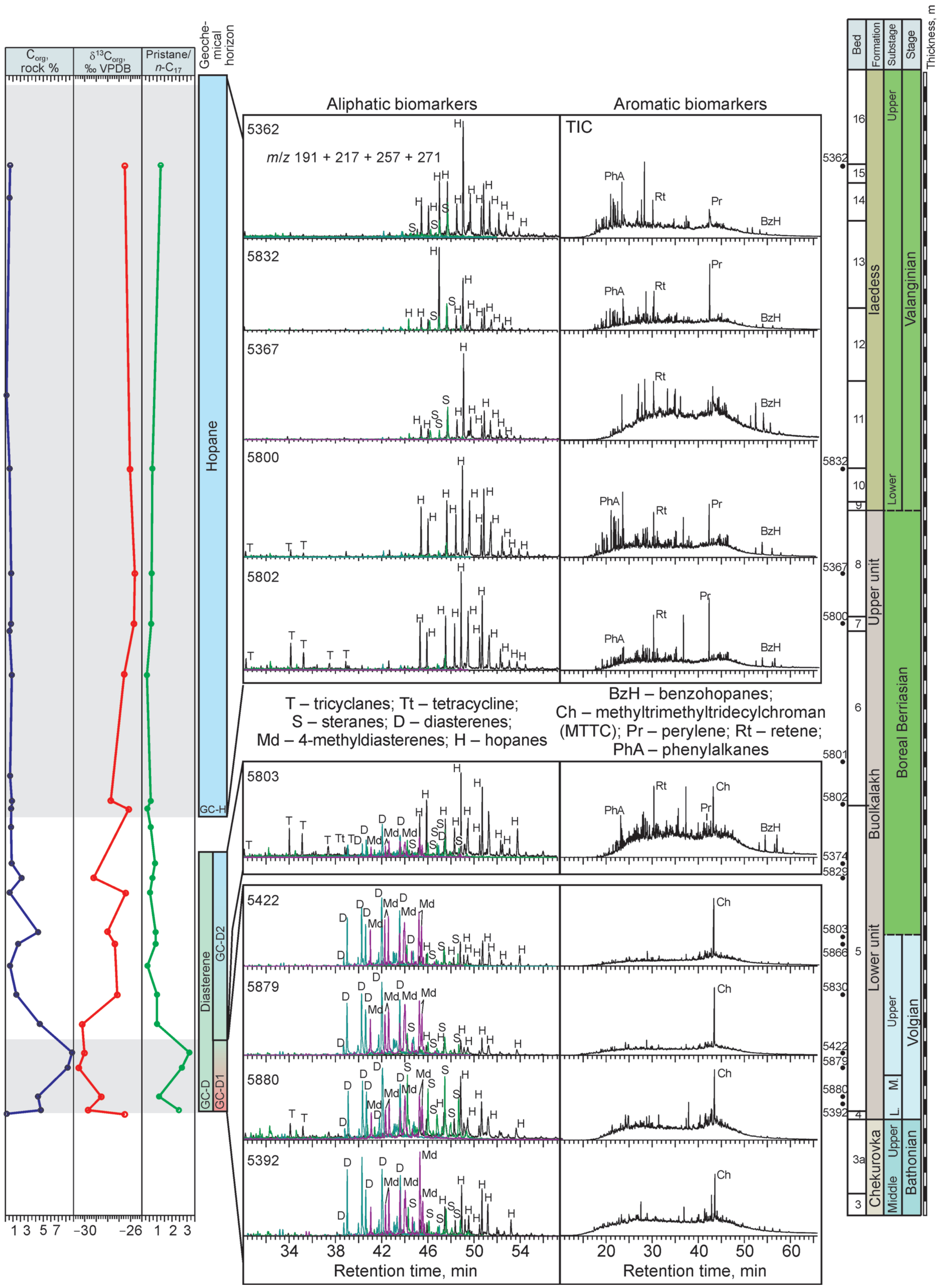

Fig. 2. Lithostratigraphy, paleoenvironments, taxonomic diversity, and structure of microbenthic communities, marine and terrestrial palynomorphs and biogeochemical characteristics of organic matter in the reference Upper Jurassic and Lower Cretaceous section, Olenek River. *1*, argillite-like clay; *2*, clayey silt; *3*, silt; *4*, sandy silt; *5*, *a*, sand; *b*, gravelstone; *6*, *a*, pebble; *b*, conglomerate; *7*, calcareous concretion layer; *8*, *a*, calcareous and siderite nodules; *b*, glauconite; *c*, pyrite.

sian), which is replaced by gray clays and silts at the top of the Boreal Berriasian. The Buolkalakh Formation contains abundant remains of ammonites, foraminifera, and marine and terrestrial palynomorphs (Nikitenko et al., 2018). The overlying Iaedaes Formation (Valanginian–Lower Hauterivian) is represented by shallow marine, coastal, and subcontinental light gray sandstones and gray siltstones.

MATERIALS AND METHODS

Twenty samples of argillaceous and silty rocks were collected for a biogeochemical study from the Olenek River section, which spans the Volgian–Lower Valanginian. The samples used in this study were first crushed using a ball mill and then separated into several portions. One portion of each sample was treated with 10% hydrochloric acid and used for determination of total organic carbon (C_{org}, % per rock) and stable carbon isotopic composition ($\delta^{13}C$, ‰). The second portion was used for determination of Rock Eval pyrolysis data (S_1, S_2, HI, and T_{max}). The remaining portion of the sample was used for multiple cold bitumen extraction with chloroform and subsequent centrifugation. After the asphaltenes were removed by precipitation using excess petroleum ether, the malthene fraction of bitumen was extracted and then separated into resins, aliphatic and aromatic hydrocarbons by liquid chromatography using an alumina–silica gel column.

The aliphatic and aromatic fractions were analyzed by gas chromatography–mass spectrometry using the Agilent GC/MS system consisting of an HP6890 gas chromatograph interfaced with an Agilent 5973N mass selective detector and HPG 1034 ChemStation software for data analysis. The chromatograph was equipped with the HP-5MS capillary column (length 30 m and inner diameter 0.25 mm) and operated in constant flow mode (at 1 mL/min) with helium as carrier gas. The injector temperature was 300 °C, and samples were injected in splitless mode. The temperature program was 100–290 °C at 4 °C/min, held at 290 °C for 30 min. The instrument was operated with an electron energy of 70 eV and a temperature of 250 °C. Identification of the individual compounds on mass chromatograms (TIC) and mass fragmentograms (*m/z* is the ratio of the mass of an ion to its charge) was done on the basis of NIST-08 library search (over 130,000 mass spectra of organic compounds), by comparing with literature data and reconstruction of structures based on the nature of ion fragmentation during electron impact.

Geochemical and biofacies characterization of the section. The analysis of geochemical data (Fig. 2; Table 1) enabled us to distinguish two levels in the studied section, which are characterized by the dominant type of hydrocarbon biomarkers. The stratigraphic studies (Nikitenko et al., 2018) show that the lower level corresponds to the Volgian and the lowermost Boreal Berriasian and the upper level corresponds to the Boreal Berriasian–Valanginian.

Below we provide some geochemical characteristics of the lower level (Volgian–lowermost Boreal Berriasian (diasterene)) of the Olenek River section. The argillaceous rock samples from the Lower–base of the Upper Volgian interval are characterized by the highest C_{org} contents (4.3–8.8% per rock) (Fig. 2; Table 1), which tend to decrease in the uppermost Volgian interval (1.5 and 0.6%). At the same time, the interval with the highest organic carbon content has a high hydrogen index (HI) values, up to 250 mg HC/g C_{org}, indicating a relatively high hydrocarbon generative potential (Lopatin and Emets, 1987; Peters et al., 2005). This interval also tends to exhibit the lightest (from –28.5 to 30.5‰) carbon isotope values (Fig. 2; Table 1) as compared with the overlying and underlying sequences. All samples of chloroform bitumen extracts, including organic-rich samples, contain >50% resins and asphaltenes and up to 40% aliphatic and aromatic compounds. The aliphatic fraction of bitumen is represented mainly by *n*-alkanes with maxima at C_{25}–C_{27} and a marked odd-to-even number predominance (CPI $\gg$ 1), which is consistent with the parameter T_{max} values and indicates uniformly low (protocatagenesis) maturity of organic matter (Table 1). A markedly high ratio (up to threefold) of pristane and phytane isoprenoids to coeluting C_{17} and C_{19} *n*-alkanes (Fig. 2; Table 1) is one of the distinctive features of the distribution of acyclic hydrocarbons. This biomarker distribution generally reflects the abundance of chlorophyll-containing phytoplankton in the photic layer of the water column (Volkman et al., 2015). As shown below, the high concentration of phytoplankton in the sediment may also contribute to the formation of some aromatic compounds. Depending on the redox conditions in a stratified water column or sediments, phytol in chlorophyll can be readily reduced to phytane via hydrophytol or oxidized to phytanic acid, which is then decarboxylated to pristane (Tissot and Welte, 1978). Therefore, the ratio of these isoprenoids is commonly used to reconstruct environmental redox conditions during deposition and diagenesis. Our previous study shows that pristane/phytane ratios cannot reliably reflect the redox conditions during accumulation and diagenesis of organic matter, which were reconstructed based on sedimentological, biofacies, and paleoecological criteria. Thus, as indicated by the above data, the lower organic carbon-rich layers of the Buolkalakh Formation deposited under oxygen deficiency, though the elevated values of the pristane/phytane ratio may be indicative of a neutral to oxic depositional environment. At the same time (see below), the presence of methanotrophic biomarkers, as well as palynological and microfaunistic assemblages, suggests the development of stagnant conditions during deposition of clays and organic matter in the lower geochemical level of the studied section (Nikitenko et al., 2018). The observed discrepancy between geochemical results in diagnostics of organic matter using pristane/phytane ratios, on the one hand, and biofacies and sedimentological data, on the other, can be related to the low catagenetic maturity level of organic matter (Volkman and Maxwell, 1986; Goncharov et al., 2011).

Table1. Geochemical characteristics of organic matter from Upper Jurassic–Cretaceous sediments, Olenek River

Sample location (outcrop, bed, m from the base (B)/ top (T))	Lab sample no.	C_{org}, % per rock	Pyrolysis data		Carbon isotope composition ($\delta^{13}C_{org}$), ‰	Aliphatic biomarkers, % of the aliphatic fraction				Biomarker ratios				Aromatic biomarkers, % of the aromatic fraction	
			T_{max}, °C	HI, mg HC/g C_{org}		Steranes (St) *m/z* 217	Diasterenes (Dst) *m/z* 257	Methyldiasterenes (Mdst) *m/z* 271	Terpanes *m/z* 191	CPI	Pristane/ phytane	Pristane/ n-C_{17}	Steranes C_{29}/C_{27}	Chromans MTTC	Retene (Rt)
09H-14O-15-T	5362	0.62	442	51.00	–26.5	14.36	2.41	0.00	83.22	2.01	2.27	1.20	12.05	0.01	2.55
09H-14O-10-T	5832	0.58	438	52	–26.0	23.94	3.01	0.58	72.48	1.74	1.65	0.73	2.74	0.03	3.14
09H-14O-8-3B	5367	0.79	439	35	–25.6	21.98	2.36	1.02	74.64	2.18	1.00	0.71	5.31	0.01	2.89
09H-14O-7-0.5B	5800	0.74	439	28	–25.7	8.03	2.94	0.94	88.09	2.03	1.44	0.58	6.05	0.01	3.33
O14-6-3T	5801	0.86	440	29	–26.5	16.80	0.83	0.00	82.38	2.11	0.77	0.36	3.35	0.01	1.94
O14-6-B	5802	1.03	442	34	–27.7	8.59	2.71	0.90	87.79	2.33	0.86	0.58	5.46	0.01	3.41
O14-5-T	8661	0.76	437	26	No data	14.56	0.74	0.07	84.63	2.03	0.49	0.36	2.97	0.36	7.61
O14-5-1.5T	8663	0.77	435	26	–26.7	19.30	4.35	1.98	74.37	2.12	0.19	0.61	2.28	0.32	4.03
09H-14O-5-17B	5374	0.81	435	34	–26.8	11.17	6.66	3.66	78.51	2.09	1.50	0.90	5.31	1.2	3.45
O14-5-16B	5829	2.17	440	25	–29.2	17.43	12.03	6.34	64.20	2.05	1.23	0.70	3.31	3.80	3.39
O9H-14O-5-15B	8660	0.58	433	37	–26.4	20.13	1.90	0.63	77.35	1.89	0.23	0.60	2.59	N.d.	N.d.
O14-5-12.3B	5803	4.33	438	17	–28.0	19.29	13.04	9.45	58.23	2.06	0.98	0.93	2.16	4.31	2.31
09H-14O-5-11.5B	5366	1.57	421	16	–27.3	22.42	4.24	3.36	69.98	1.94	0.90	0.98	2.71	2.92	2.51
O14-5-10B	8664	0.63	425	19	–26.3	24.91	1.72	4.31	69.06	1.68	0.62	0.35	N.d.	N.d.	N.d.
O14-5-8B	5830	1.46	440	22	–27.1	26.52	12.96	9.85	50.67	2.03	1.03	1.21	1.37	2.66	1.03
O14-5-6B	8662	4.59	428	92	–30.2	20.55	26.75	25.81	26.88	2.22	1.44	1.40	0.84	2.46	1.32
09H-14O-5-4B	5422	8.81	418	264	–30.0	13.00	34.77	31.30	20.94	1.98	1.24	3.15	0.98	20.31	0.92
O14-5-3B	5879	8.21	417	256	–30.5	12.88	40.20	32.81	14.11	2.15	1.40	2.62	0.97	22.49	1.19
O14-5-1B	5880	4.29	418	40	–28.5	29.18	26.40	17.30	27.12	2.40	1.08	1.13	1.24	7.01	1.37
09H-14O-5-B	5392	4.57	420	208	–29.7	15.01	35.90	22.72	26.37	2.13	2.00	2.49	0.94	10.48	0.96

Note. HI, Hydrogen index; $T_{max,}$ the maximum hydrocarbon yield resulting from kerogen cracking; CPI (carbon preference index), ratio of odd- to even-numbered alkanes.

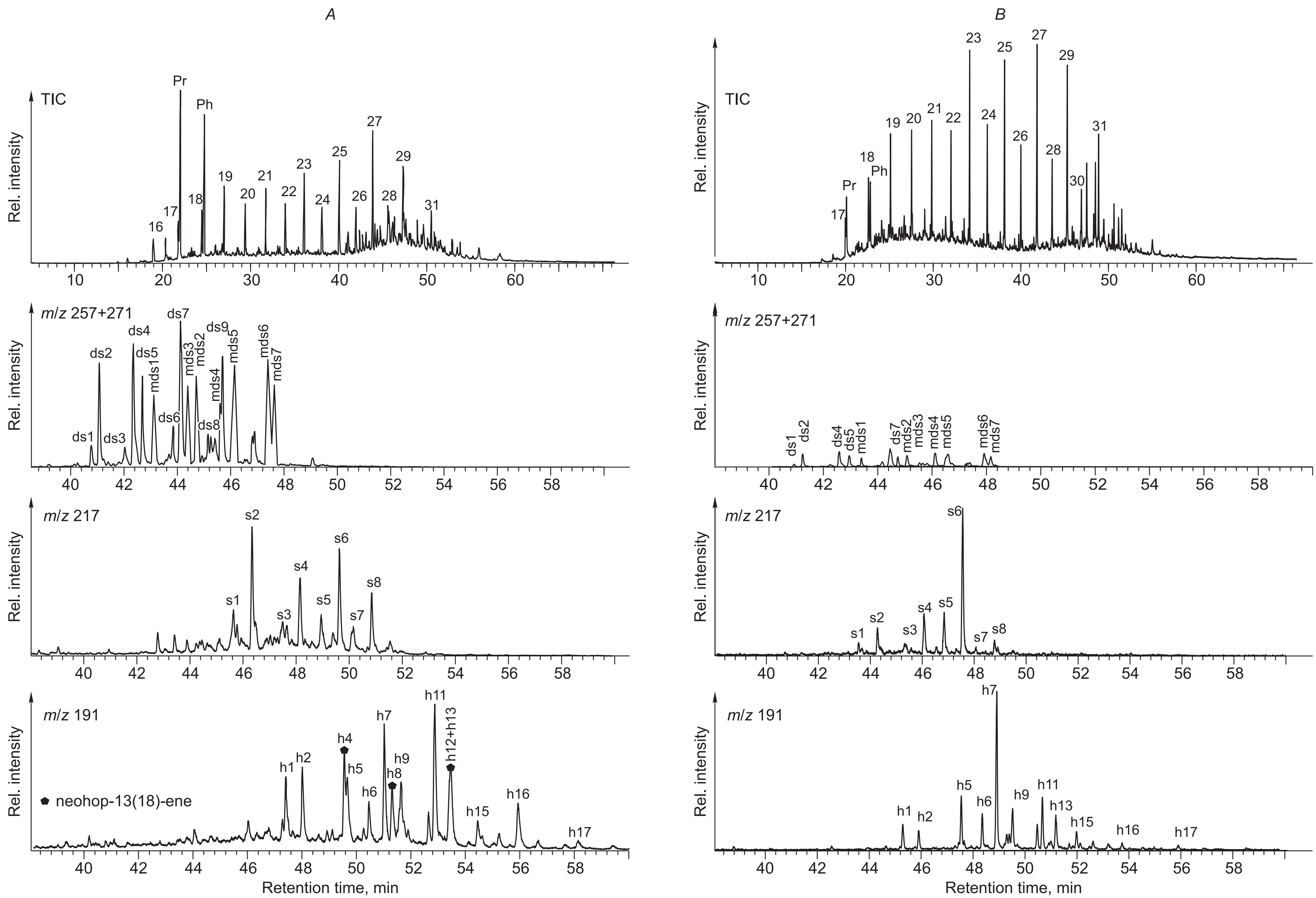

Fig. 3. Total ion current (TIC), *m/z* 191 (hopanoid), and *m/z* 257 + 271; 217 (steroid) mass chromatograms showing the distribution of biomarker hydrocarbons in the aliphatic fractions of bitumen extracts. *A*, sample 5879 from the base of the Upper Volgian (diasterene horizon); *B*, sample 5367, uppermost Boreal Berriasian (hopane horizon).

Diasterenes and 4-methyldiasterenes dominate over all other polycyclic biomarkers at the base of the Buolkalakh Formation, as can be clearly seen on the composite mass chromatograms for four fragment ions: *m/z* 191 (tricyclanes and hopanoids), *m/z* 217 (steranes), *m/z* 257 (diasterenes), and *m/z* 271 (4-methyldiasterenes) (Figs. 2, 3; Table 2). In this interval, the total amount of diasterenes to the sum of all polycyclic biomarkers may be greater than 60%. The formation of diasterenes and 4-methyldiasterenes in this interval at low maturity levels can be related to diagenetic transfor-

Table 2. Identification of diasterenes, steranes, and hopanoids on mass chromatograms (Fig. 3)

Peak	*m/z*	Formula	Hydrocarbon
Diasterenes			
ds1	257, 370	$C_{27}H_{46}$	20S-10β–diacholest-13(17)-ene
ds2	257, 370	$C_{27}H_{46}$	20S-10α–diacholest-13(17)-ene
ds3	257, 370	$C_{27}H_{46}$	20R-10β–diacholest-13(17)-ene
ds4	257, 370	$C_{27}H_{46}$	20R-10α–diacholest-13(17)-ene
ds5	257, 384	$C_{28}H_{48}$	20S-10β–24-methyldiacholest-13(17)-ene
ds6	257, 384	$C_{28}H_{48}$	20S-10α–24-methyldiacholest-13(17)-ene
ds7	257, 384	$C_{29}H_{50}$	20S-10α–24-ethyldiacholest-13(17)-ene
ds8	257, 384	$C_{29}H_{50}$	20R-10β–24-ethyldiacholest-13(17)-ene
ds9	257, 384	$C_{29}H_{50}$	20R-10α–24-ethyldiacholest-13(17)-ene
4-methyldiasterenes			
mds1	271, 384	$C_{28}H_{48}$	20S-10α–4-methyldiacholest-13(17)-ene
mds2	271, 384	$C_{28}H_{48}$	20R-10α–4-methyldiacholest-13(17)-ene
mds3	271, 398	$C_{29}H_{50}$	20S-10α–4-methyl, 24-dimethyldiacholest-13(17)-ene
mds4	271, 412	$C_{30}H_{52}$	20S-10β–4-methyl, 24-ethyldiacholest-13(17)-ene
mds5	271, 412	$C_{30}H_{52}$	20S-10α–4-methyl, 24-ethyldiacholest-13(17)-ene
mds6	271, 412	$C_{30}H_{52}$	20R-10β–4-methyl, 24-ethyldiacholest-13(17)-ene
mds7	271, 412	$C_{30}H_{52}$	20R-10α–4-methyl, 24-ethyldiacholest-13(17)-ene
Steranes			
s1	217, 372	$C_{27}H_{48}$	20S-17α-cholestane
s2	217, 372	$C_{27}H_{48}$	20R-17α-cholestane
s3	217, 386	$C_{28}H_{50}$	20S-17α-methylcholestane
s4	217, 386	$C_{28}H_{50}$	20R-17α-methylcholestane
s5	217, 400	$C_{29}H_{52}$	20S-17α-ethylcholestane
s6	217, 400	$C_{29}H_{52}$	20R-17α-ethylcholestane
s7	217, 414	$C_{30}H_{54}$	20S-17α-propylcholestane
s8	217, 414	$C_{30}H_{50}$	20R-17α-propylcholestane
Hopanoids			
h1	191, 370	$C_{27}H_{46}$	17α(H),21β(H)-trisnorhopane (Tm)
h2	191, 370	$C_{27}H_{46}$	17 (H),21β(H)-trisnorhopane
h3	191, 384	$C_{28}H_{48}$	17α(H),21β(H)-28-norhopane
h4	191, 396	$C_{29}H_{48}$	Neonorhop-13(18)-ene
h5	191, 398	$C_{29}H_{50}$	17α(H),21β(H)-norhopane
h6	191, 398	$C_{29}H_{50}$	17β(H),21α(H)-norhopane
h7	191, 412	$C_{30}H_{52}$	17α(H),21β(H)-hopane
h8	191, 410	$C_{30}H_{50}$	Neohop-13(18)-ene
h9	191, 412	$C_{30}H_{52}$	17β(H),21α(H)-hopane (moretane)
h10	191, 426	$C_{31}H_{54}$	17α(H),21β(H)-homohopane (22S)
h11	191, 426	$C_{31}H_{54}$	17α(H),21β(H)-homohopane (22R)
h12	191, 424	$C_{31}H_{52}$	Neohomohop-13(18)-ene
h13	191, 426	$C_{31}H_{54}$	17β(H),21α(H)-homohopane (homomoretane)
h14	191, 440	$C_{32}H_{56}$	17α(H),21β(H)-bishomohopane (22S)
h15	191, 440	$C_{32}H_{56}$	17α(H),21β(H)-bishomohopane (22R)
h16	191, 424	$C_{31}H_{54}$	17β(H),21β(H)-homohopane
h17	191, 424	$C_{32}H_{56}$	17β(H),21β(H)-bishomohopane

mation of buried organic matter, including sterols and 4-methylsterols via catalysis of clay minerals. Most researchers consider diasterenes that formed during middle stages of diagenetic degradation of organic matter as transitional to regular steranes and diasteranes at later diagenetic and early catagenetic stages (Petrov et al., 1985; Peakman and Maxwell, 1987). The presence of 4-methyldiasterenes in the Volgian bitumens is apparently associated with dinoflagellates producing specific dinosterols (4-methylsterols) with methyl substituents at C-4, C-23 and a double bond at C-22. The origin of 4-methylsteranes appears to be firmly established by a correlation between abundant dinoflagellate cysts in Maoming strata that are enriched in these compounds (Brassell et al., 1985). In the Olenek River section, the presence of 4-methyldiasterenes correlates well with palynological data: In the Volgian interval, dinoflagellate cysts reach the highest abundance and diversity among microphytoplankton communities (Fig. 2).

The composition and distribution of hopanoids in the Volgian–Valanginian interval reflect a low degree of thermal maturity of organic matter. This is the most clearly seen in organic matter from the Volgian layers, where the regular hopanes with the biological configuration 17β(H),21β(H) were identified along with methanotrophic neohop-13(18)-enes (Fig. 3; Table 2). The presence of methanotrophic bacteria, as well as the preservation of their metabolites and diasterenes in the sediments of this interval, is apparently due to the development of anoxic and dysaerobic conditions during intensive microbial reworking of planktonic organic matter. This is also reflected in the composition of palynological assemblages, which are dominated by thin translucent particles of detritus and phytodebris strongly affected by destruction (Fig. 4).

In the aromatic fraction of bitumen extracts with a predominance of diasterenes in the aliphatic fraction (diasterene horizon) have anomalously high concentrations of methyltrimethyltridecylchromans (MTTC) in the alpha-forms *m/z* 149 → 414 (Figs. 2, 5; Table 2). The stereochemistry of the identified MTTC is known to be almost identical to that of the various forms of tocopherols (vitamin E) but differs from the latter in the absence of a hydroxyl group on the aromatic ring. Therefore, it can be logically assumed that

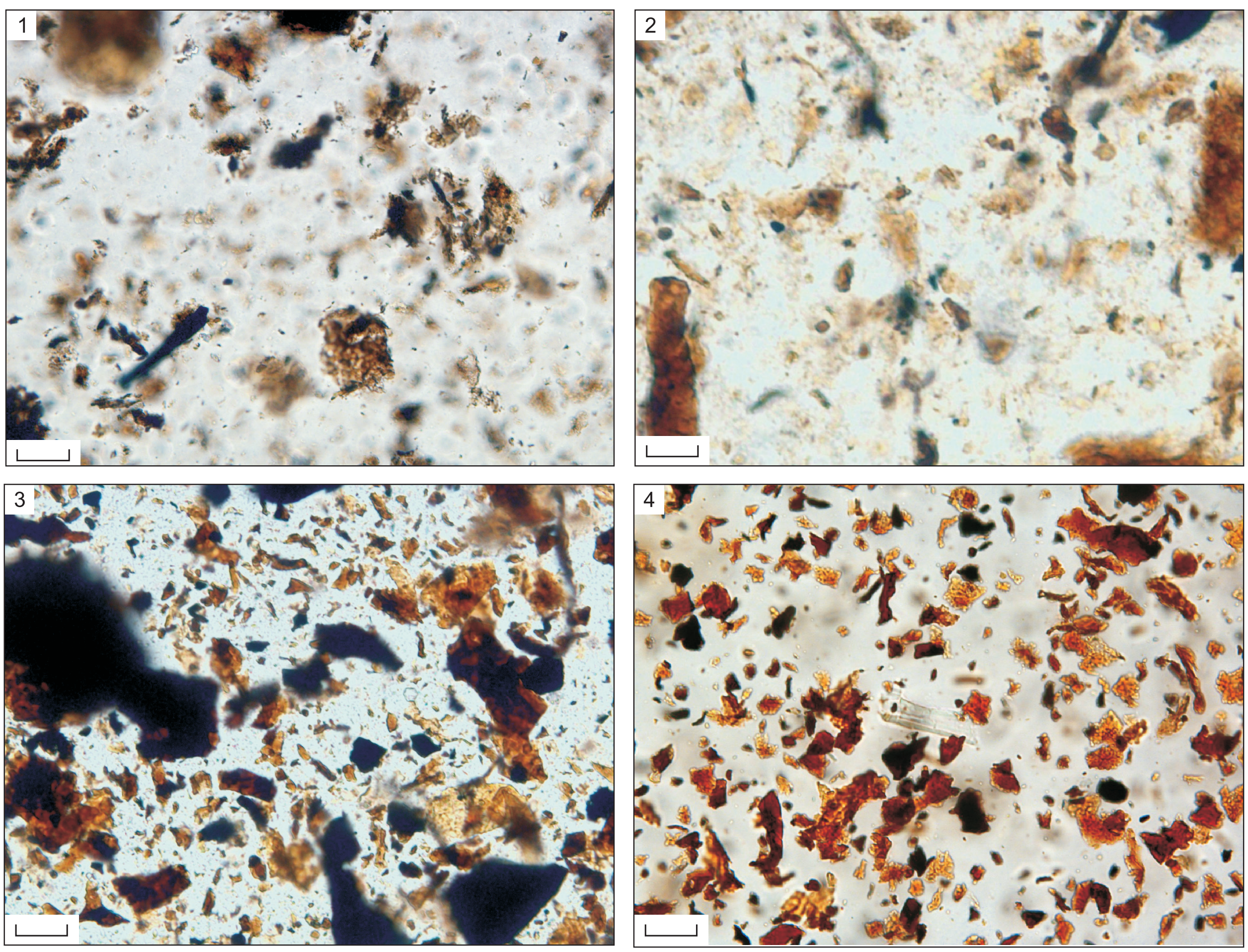

Fig. 4. The overall composition of palynological samples from the Olenek River section. Scale bar 25 μm. 1, Sample from bed 5, 4 m from the base, Volgian Stage; 2, sample from bed 5, 17 m from the base, Boreal Berriasian; 3, sample from bed 10, 1.5 m from the base, Valanginian; 4, sample from bed 15, top, Valanginian.

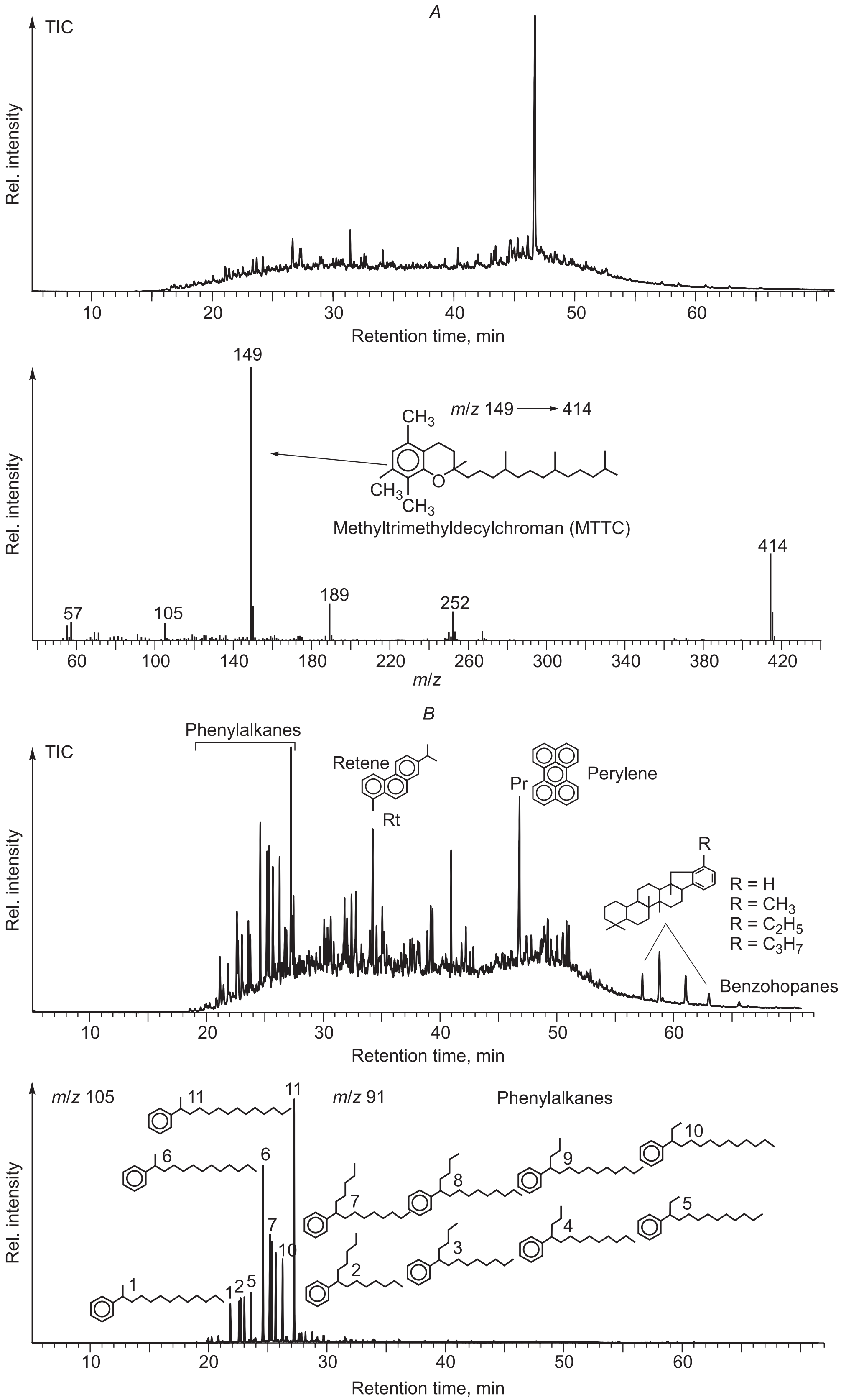

Fig. 5. Total ion current (TIC) and *m/z* 91 + 105 mass chromatograms showing the distribution of phenylalkanes in the aromatic fraction: *A*, sample 5879 from the base of the Upper Volgian (diasterene horizon) (below is the base peak); *B*, sample 5800 from the upper layers of the Boreal Berriasian (hopane horizon).

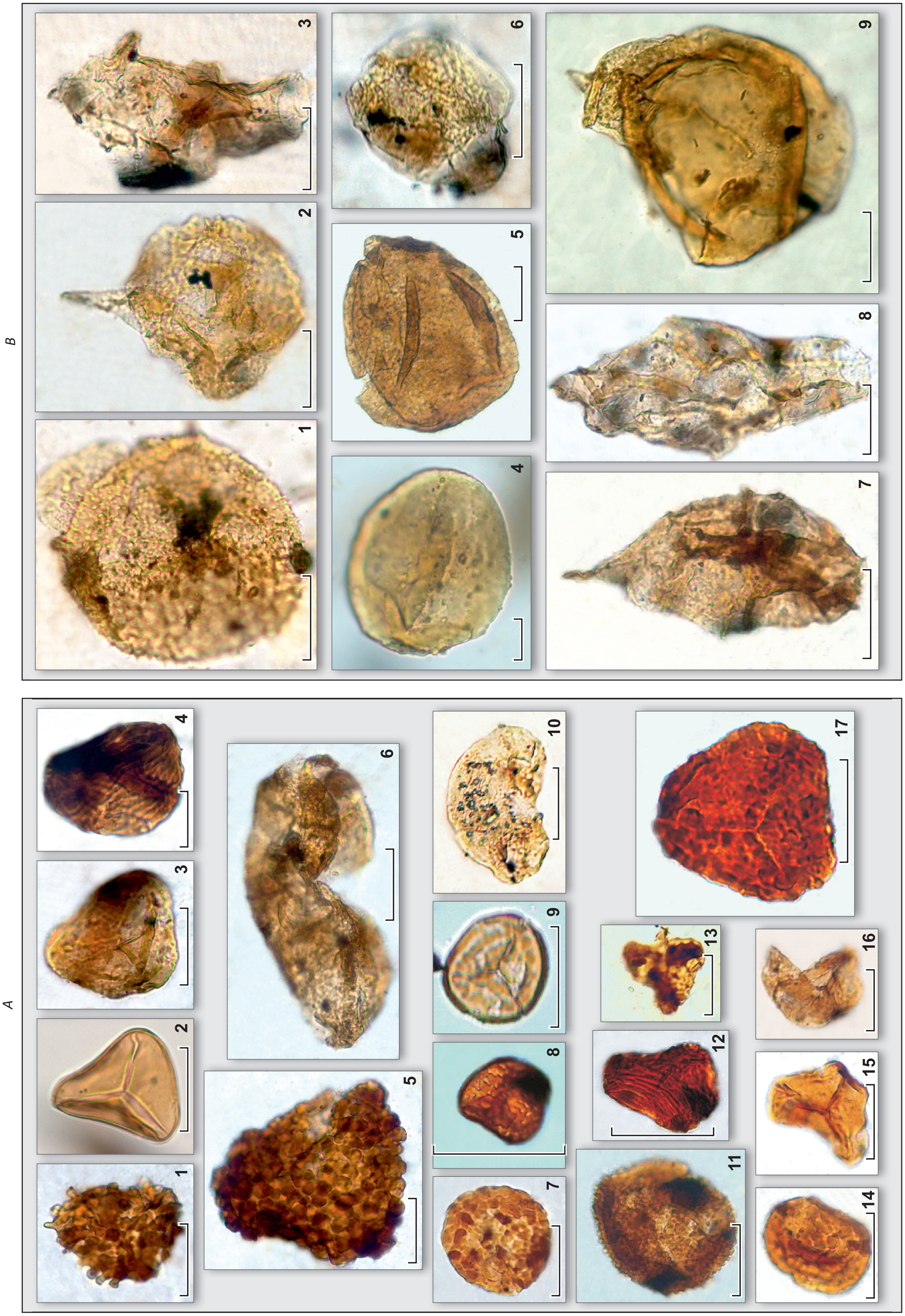

Fig. 6. Palynomorphs from the Volgian, Berriasian, and Valanginian, Olenek section. All specimens from outcrop 14. Scale bar 25 μm. *A*, Spores and pollen of terrestrial plants: 1, *Neoraistrickia bacculifera* (Maljavkina) Iljina, bed 5, top, Boreal Berriasian; 2, *Cyathidites minor* Couper, bed 11, 1 m from the base, Lower Valanginian; 3, *Cyathidites* sp., bed 5, top, Berriasian; 4, *Plicatella exilioides* (Maljavkina) Bondarenko, bed 10, top, Lower Valanginian; 5, *Trilobosporites gibberulus* (Kara-Murza) Pocock, bed 5, top, Boreal Berriasian; 6, *Pseudopicea magnifica* Bolchovitina, bed 7, 0.5 m from the base, Boreal Berriasian; 7, *Selaginella granata* Bolchovitina, bed 5, top, Boreal Berriasian; 8, *Klukisporites foveolatus* Pocock, bed 12, 2 m from the base, Lower Valanginian; 9, *Stereisporites congregatus* (Bolchovitina) Schulz, bed 11, 1 m from the base, Lower Valanginian; 10, *Pinus subconcinua* Bolchovitina, bed 5, base, Volgian; 11, *Baculatisporites comaumensis* (Cookson) Potonie, bed 6, 3.5 m from the base, Boreal Berriasian; 12, *Cicatricosisporites ludbrookiae* Dettmann, bed 14, 1.5 m from the base, Valanginian; 13, *Eboracia granulosa* (Tralau) Timoshina, bed 5, 15 m from the base, lowermost Boreal Berriasian; 14, *Dejerseysporites verrucosus* (Pocock) McKellar, bed 6, 3.5 m from the base, Boreal Berriasian; 15, *Dictyophyllidites harrisii* Couper, bed 8, 1.5 m from the base, Boreal Berriasian; 16, *Taxodiaceaepollenites* sp., bed 6, base, Boreal Berriasian; 17, *Trilobosporites valanjinensis* (Kara-Mursa) Döring, bed 14, 1.5 m from the base, Valanginian; *B*, microphytoplankton: 1, *Trichodinium ciliatum* (Gocht) Eisenack et Klement, bed 5, base, Volgian; 2, *Paragonyaulacysta* sp., bed 5, 11.5 m from the base, uppermost Volgian; 3, *Tubotuberella apatela* (Cookson et Eisenack) Ioannides, bed 6, 3.5 m from the base, Boreal Berriasian; 4, *Tasmanites* sp., bed 5, 2 m from the base, Volgian; 5, *Batiacasphaera norvickii* (Burger) Lentin et Williams, bed 5, 17 m from the base, lowermost Boreal Berriasian; 6, *Dingodinium* sp., bed 5, 15 m from the base, lowermost Boreal Berriasian; 7, *Paragonyaulacysta ?borealis* (Brideaux et Fisher) Stover et Evitt, bed 6, 3.5 m from the base, Boreal Berriasian; 8, *Tubotuberella rhombiformis* Vozzhennikova, bed 6, 3.5 m from the base, Boreal Berriasian; 9, *Scriniodinium multistratum* Lebedeva et Pestchevitskaya, bed 6, 15 m from the base, lowermost Boreal Berriasian.

MTTC homologs form from the diagenetic dehydration of tocopherols; however, some researchers suggest that this reaction is kinetically unlikely (Sinninghe Damsté et al., 1987). Li et al. (1995) supposed that the formation of MTTC during diagenesis can be the result of condensation reactions of chlorophyll and alkylphenols. It seems very likely that a similar process occurred during diagenesis in organic matter from the sediments of Volgian age as a result of the interaction of chlorophyll (phytoplankton) with alkylphenols. The latter are the precursors of phenylalkanes, which are abundant in organic matter from the Berriasian–Valanginian sediments (Fig. 5). Accordingly, phenylalkanes are much less abundant in the Volgian layers, since MTTC were derived from these precursors. The oldest chromans were found in a crude oil of Neoproterozoic age from India (Dutta et al., 2013). It is quite natural that the chlorophyll contained in cyanobacteria and prasinophytes, known from the Precambrian, played a significant role in their formation (Rozanov and Astafieva, 2008).

Geochemical features, such as the increased organic matter contents and an unusual distribution of hydrocarbon biomarkers from the Volgian clays, appear to be the result of the geodynamic conditions in the study area, paleogeography, paleoclimate, and bioproductivity of the Anabar–Lena sea and the adjacent continent. The biofacies analysis of terrestrial palynomorph assemblages from the Olenek region revealed a moderately warm and humid climate in Volgian time, which is typical of the Siberian–Canadian paleofloristic region (Nikitenko et al., 2015a,b, 2018). The palynological spectra composition shows a large number of Boreal taxa and the large amount of hygrophilous plant spores (Figs. 2, 6*A*).

As noted above, the beginning of the Volgian transgression in the Olenek section was marked by deposition of the basal member of the Buolkalakh Formation, which is composed of sands and sandstones with lenses of conglomerates containing pebbles, sandstone boulders, and fragments of belemnite rostra. The basal member of the Buolkalakh Formation erosively overlaps the Chekurovka sandstones and contains terrestrial palynomorphs and dinocyst assemblages, belonging to the subfamilies Leptodinioidea (*Scriniodinium*, *Meiourogonyaulax*, *Leptodinium*, *Ambonosphaera*, *Sirmiodinium*, *Occisucysta*) and Gonyaulacoidea (mostly *Tubotuberella*), usually characteristic of the middle part of the neritic zone (Wilpshaar and Leereveld, 1994; Leereveld, 1995; Nikitenko et al., 2015b). High dinocyst abundance in the basal member may be related to redeposition of Kimmeridgian deep-water sediments (Nikitenko et al., 2018).

At the base of the clay-rich interval of the Buolkalakh Formation, the microphytoplankton assemblages are characterized by high abundance and diversity and contain dinocysts of the families Gonyaulacaceae and Pareodiniaceae, which is indicative of the neritic zone (Figs. 2, 6*B*). The results of the microfaunal analysis indicate deposition in shallow and moderately deep-water environments of the upper and middle sublittoral environments farther seaward in the

Volgian and at the base of the Boreal Berriasian. At the base of layer 5, carbon-rich clays contain differentiated foraminiferal assemblages typical of the inner part of the middle sublittoral zone (Nikitenko et al., 2018). These assemblages are characterized by the absence of an obvious dominant species and typical representatives include *Ammodiscus*, *Dorothia*, and *Recurvoides*, whereas *Spiroplectammina*, *Kutsevella*, *Trochammina*, and *Bulbobaculites* are rare (morphogroups MG-E, MG-C, and MG-D, overwhelming predominance of epifauna). Poor foraminiferal assemblages of Middle Volgian age are represented by rare *Trochammina*, *Kutsevella*, and *Evolut* (morphogroup MG-D, epifauna) (Fig. 2), probably suggesting that the environment was mainly associated with the outer part of the upper sublittoral zone with stagnant conditions. In the late Volgian and earliest Boreal Berriasian, the foraminiferal assemblages become more diversified and contain only agglutinated species, such as *Recurvoides*, *Evolutinella*, and *Gaudryina*, and few *Ammodiscus*, *Glomospirella*, and *Arenoturrispirillina* (morphogroups MG-E, MG-C, and MG-D, overwhelming predominance of epifauna) (Fig. 2). It should be noted that bacteriophages and scavengers play a significant role in the microbenthic community structure, which also confirms bacterial activity, as indicated by geochemical data and, indirectly, by biofacies analysis of palynological assemblages. Foraminiferal assemblages are characterized by a strong dominance of epifaunal species, with only rare (early Volgian and early Boreal Berriasian) representatives of a shallow infauna (morphogroup MG-C). This indicates predominantly anoxic conditions within the sediment layers and dysaerobic conditions within the sediment surface and bottom water layers.

Unstable paleoenvironments in the middle and late Volgian are evidenced by variations in the taxonomic composition of dinocyst assemblages and the quantitative relationship between different groups of microphytoplankton. This period was marked by a decrease in dinocysts diversity, which, nevertheless, remained high enough (15–26 genera), as well as by a periodic predominance of prasinophytes of the genera *Leiosphaeridia* and *Tasmanites* in microphytoplankton assemblages, which are regarded as an indicator of stagnant conditions (Figs. 2, 6). Their presence in fine-grained sediments is often considered an indicator of anoxic or dysaerobic bottom-water conditions (Jarvis et al., 1988; Tyson, 1995; Guy-Ohlson, 1996; Jansonius and McGregor, 1996; Ilyina et al., 2005). A prolific bloom of microalgae requires the abundance of nutrients and relatively warm climate conditions. Note that a period of slight climatic warming in the Late Volgian time is reconstructed from an increase in the portion of thermophilic components in the structure of spore and pollen assemblages (Nikitenko et al., 2018). Plankton assemblages with high abundances of prasinophytes often correlate with reduced salinity and enhanced supply of waters rich in biogenic components from the continent. In our case, the abundance of *Leiosphaeridia* in the Volgian sediments suggests a significant increase in photic zone productivity and, as a result, the burial of organic matter in sediments and its microbial degradation, which can cause further oxygen depletion in the bottom layers (Bujak and Mudge, 1994; Ilyina et al., 2005; Nikitenko et al., 2018). It should be noted that in West Siberia, the prasinophytes *Leiosphaeridia* appear to be widespread in the sections of the Bazhenov Formation (top of the Lower Volgian–base of the Boreal Berriasian), which was deposited far offshore in a deeper-water environment (Shurygin et al., 2000; Kontorovich et al., 2019). The abundance of biogenic elements in the Bazhenov Sea can be explained by its epicontinental nature, when the regional supply of nutrients from the continent into deep open-sea waters and their further dispersal by currents was limited. The concentration of biogenic elements in the Olenek region of the Anabar–Lena sea can be explained by the formation of a bay with relatively quiet conditions, which caused reduced mixing of local waters with open-sea waters. This is confirmed by lithological data and the structure of microbenthic communities (Nikitenko et al., 2018).

The composition and distribution of individual hydrocarbons in organic matter from sediments in the Boreal Berriasian and, particularly, Valanginian sections change during marine regression. By analogy with the coeval section of Anabar Bay (Kashirtsev et al., 2018), the hopane horizon (Boreal Berriasian–Valanginian) is recognized here based on the ratio between aliphatic biomarkers. This stratigraphic level is characterized by a considerable decrease in the organic carbon content, and most samples show C_{org} values <1% (Fig. 2; Table 1). In contrast to the diasterene horizon, the ratio between isoprenoids and *n*-alkanes (mainly C_{25} or C_{27}) shows a decrease in the aliphatic fraction of bitumen extracts (Fig. 2; Table 1). That is, the ratio of pristane/phytane to coeluting *n*-alkanes usually does not exceed 1. Diasterenes and 4-methyldiasterenes are almost absent, while hopanoids become more abundant. It was found that hopanoids occur in the biological (17β(H),21β(H)) configuration, but unsaturated methanotrophic neohop-13(18)-enes disappear. In foraminiferal communities, infaunal taxa may constitute >50% of the assemblage (Nikitenko et al., 2018); bioturbation becomes more obvious with numerous occurrences of trace fossils. This indicates aerobic, well-oxygenated environments in the surface sediment layer and bottom waters, which is consistent with geochemical evidence.

In bitumen extracts, the predominance of C_{29} ethylcholestanes among all steranes usually reflects a greater contribution from terrestrial organic matter, i.e., the increasingly prevailing role of lipid components of terrestrial plant remains. Where the Volgian clays grade to more silty sediments and sands of the Boreal Berriasian and Valanginian, significant variations in the organic matter composition are reflected in the hydrocarbon-type composition of aromatic fractions, as indicated by the higher concentration of phenylalkanes, phenanthrenes, perylene, retene, and benzohopanes compared to that of chromans (MTTC) (Figs. 2, 5). It is assumed that phenylalkanes can be synthesis products of archaea, including the terrestrial thermophilic archaebacterium *Thermoplasma acidophilum*, and benzohopanes probably form by cyclization and aromatization of the homohopanoid side chain during early diagenesis (Ellis et al., 1996; Peters et al., 2005).

Otto and Simoneit (2001) suggested that retene and perylene are inherited from the lipid components of higher plant remains; for example, their bioprecursors are found in conifer resins. All samples from the Boreal Berriasian and Valanginian intervals of the Olenek section show only a slight increase in the concentrations of retene and perylene, though palynological data indicate that conifers were widely distributed in the terrestrial plant communities in areas adjacent to the Olenek region of the Anabar–Lena basin (Nikitenko et al., 2018). In the Boreal Berriasian and Valanginian, the percentage of conifer pollen decreases. It is assumed that the retreat of the sea gave rise to costal lowland plains favorable to the growth of hydrophilous mosses and cyatheacean and dipteridacean ferns. In the overall composition of palynological specimens from the Valanginian interval, the regressive events are documented by an increase in the portion of dense opaque detritus particles, which are interpreted to be microscopic fragments of carbonized wood (Fig. 4). Like conifers, the Mesozoic cyatheacean and dipteridacean ferns are believed to be mostly treelike ferns (Grushvitskii and Zhilin, 1978; Van Konijnenburg-Van Cittert, 2002). The presence of small concentrations of retene and perylene in the studied samples suggests that conifers were not dominant in terrestrial forests of the Olenek region during the late Boreal Berriasian and Valanginian, which is also consistent with palynological data. Slightly higher concentrations of these compounds as compared with organic-rich Volgian samples cannot be explained by an increase in the relative abundance of conifers in plant communities, but rather reflects a regressive phase and a larger input of wood debris from the continent as a source of organic matter.

It should be noted that using certain geochemical characteristics (a predominance of the same type of biomarker hydrocarbons) enabled us to identify three geochemical horizons (from the bottom upward) in the reference Upper Jurassic and Lower Cretaceous section of Anabar Bay: terpane (upper Oxfordian–Kimmeridgian), diasterene (upper Middle Volgian–base of Valanginian), and hopane (Lower Valanginian) (Kashirtsev et al., 2018). As shown above, in the coeval sections of the Olenek River, the upper two horizons (diasterene and hopane) are well identified by specific biomarkers, and the lower (terpane) horizon is absent because of the sedimentation break (from uppermost Bathonian to Lower Volgian).

The analysis of the stratigraphic position of these geochemical horizons in different parts (and bathymetric zones) of the Anabar–Lena basin reveals their diachronous nature (Fig. 7). The diasterene horizon is correlated with the Volgian and lowermost Boreal Berriasian in the Olenek section or with the uppermost Middle Volgian–base of the Valanginian in the deep-water section of Anabar Bay. The hopane horizon is correlated with the uppermost Boreal Berriasian–Valanginian in the Olenek section and with the Lower Valanginian in the Anabar Bay section. The diachronism of these geochemical horizons can be associated with the lateral and temporal variations in stagnant environments, which led to the development of anoxic and dysaerobic conditions in the surface sediment and bottom water layers. A similar situation is typical of the West Siberian basin (Kontorovich et al., 2019).

Thus, the identification of geochemical horizons using stratigraphic and lateral variations in the same type of biomarker hydrocarbons can be used as a certain correlative tool for reconstructing the geochemical environment of formation of sediments and their subsequent transformation.

CONCLUSIONS

The following conclusions can be drawn based on the synthesis of sedimentological, faunal, and palynological data combined with geochemical data on fossil organic matter from the Upper Jurassic and Lower Cretaceous sections in the lower reaches of the Olenek River.

In the Volgian time, the Anabar–Lena sea was an area that experienced a series of intensive transgressive events. The high concentrations of dispersed organic matter (up to 8% in some layers) in the lower units of the clay-dominated Buolkalakh Formation (Volgian–lowermost Boreal Berriasian) and the presence of a specific suite of biomarker hydrocarbons are interpreted to have originated from chlorophyll-containing phytoplankton (prasinophytes and dinocysts). Increased production of phytoplankton suggests the enhancement of nutrient supply in the neritic zone of the Anabar–Lena paleobasin, which probably constituted a small bay in the Olenek region with quiet conditions that prevented the rapid inflow of biogenic elements into the open sea and their subsequent dispersal. Bacterial degradation of abundant organic matter in the sediments favored the development of periodically dysaerobic bottom-water conditions and, thus, the preservation of high concentrations of isoprenoids, diasterenes, methanotrophic hopenes, and chromans in the composition of organic matter.

The second half of the Boreal Berriasian was marked by the onset of marine regression, as indicated by variations in the lithology, structure of faunal and palynological assemblages, and typical biomarker hydrocarbons. This level is characterized by the absence of diasterenes, hopenes, and chromans as well as by the dominance of ethylcholestane among regular steranes. This can be explained by increased contribution of terrestrial detritus and palynomorphs to the organic matter composition.

Organic-geochemistry data reveal two geochemical horizons in the studied section: the diasterene (Volgian–lowermost Boreal Berriasian) and hopane (Boreal Berriasian–Valanginian). Earlier, three biomarker horizons were identified in the coeval Anabar Bay section (Laptev Sea coast) based

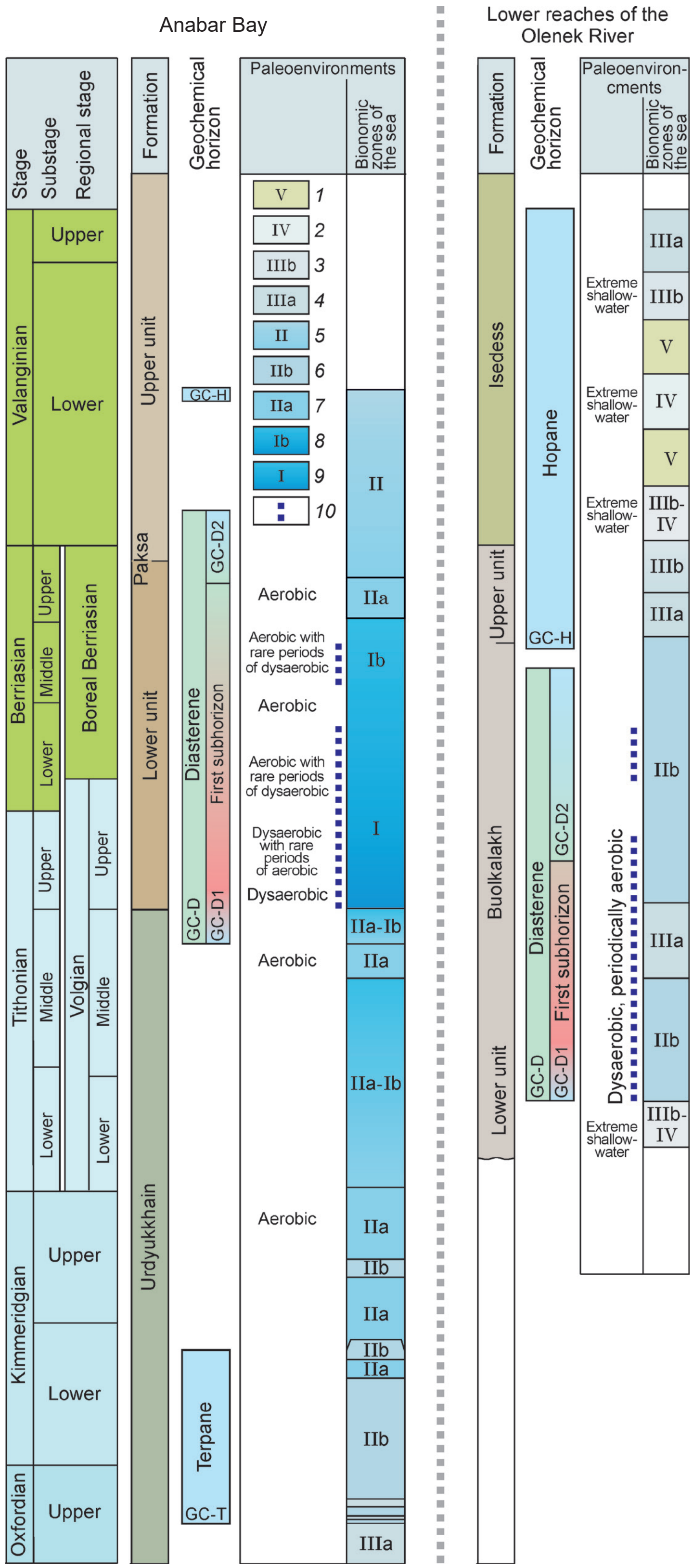

Fig. 7. Stratigraphic position of geochemical horizons in the Anabar Bay (Nikitenko et al., 2015b; Kashirtsev et al., 2018) and Olenek River sections. *1*, Coastal and subcontinental settings; *2*, littoral; *3*, upper sublittoral, inner part (proximal shallow-water conditions); *4*, upper sublittoral, outer part (distal shallow-water conditions); *5*, middle sublittoral (moderately deep water); *6*, middle sublittoral, inner part (proximal moderately deep-water conditions); *7*, middle sublittoral, outer part (distal moderately deep-water conditions); *8*, lower sublittoral, inner part (proximal relatively deep-water conditions); *9*, lower sublittoral (conditions of relative deep water); *10*, stagnant environments.

on the specific geochemical criteria: terpane (uppermost Oxfordian–Kimmeridgian), diasterene (uppermost Middle Volgian–base of the Valanginian), and hopane (Lower Valanginian), according to the prevailing distribution of biomarker hydrocarbons characteristic of these levels. In the Olenek section, the upper two horizons are well identified by specific biomarkers, while the lower (terpane) horizon is absent because of the stratigraphic hiatus from upper Bathonian to Lower Volgian. Thus, the analysis of the stratigraphic position of the diasterene and hopane horizons in different parts of the Anabar–Lena basin reveals their diachronous nature.

According to geological and geochemical criteria, the Volgian interval and the lower part of the Boreal Berriasian of the Anabar–Lena basin have a high petroleum potential. However, these rocks did not reach the oil window because of insignificant basinal subsidence and moderate pressure–temperature conditions that existed along the margins of the Siberian Platform during regional geodynamic evolution. At the same time, the most favorable conditions for generation and accumulation of hydrocarbons genetically related to Upper Jurassic and Lower Cretaceous carbon-rich rocks existed in the axial part of the trough (Lower Lena depression) and, especially, on the shelf of the Laptev Sea during the development of the passive continental margin.

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