

UDC 543.635

DOI: 10.15372/CSD2020227

Regularities of the Distribution of Hydrocarbon and Heteroatomic Compounds in the Dispersed Organic Matter of the Rocks in the Northern Part of West Siberia

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Abstract

The rocks of Lower Cretaceous section in four exploration wells at the oil-producing fields of the Yamalo-Nenets Autonomous District were investigated. Dispersed organic matter was characterised by the composition of hydrocarbons using gas chromatography – mass spectrometry (GC–MC). Steranes, hopanes, *n*-alkanes and isoprenoid alkanes, naphthalenes, phenanthrenes, sesquiterpanes, dibenzothiophenes and dibenzofurans, retene, cadalene and simonellit were identified. Metalloporphyrins and perylene were determined by means of spectrophotometry. It was shown that the sediments studied were deposited under suboxidative conditions in the sedimentation basin with a significant contribution of both phytoplankton and terrestrial vegetation to the initial organic matter. Sedimentation proceeded near the coastline of the sea or in a coastal water body, which was periodically flooded by the sea. The thermal maturity of the organic matter corresponds to the major zone of oil formation.

Keywords: organic matter, hydrocarbons, hopanes, steranes, sesquiterpanes

INTRODUCTION

For the sustainable development of Russia, the efficient use of natural energy resources is an urgent problem first of all for the oil and gas complex as the major motive force of the growth of Russian economy. The Yamalo-Nenets autonomous district (YaNAD) is situated in the northern part of the West Siberian oil and gas bearing province. Its territory holds the main prospected and expected resources of hydrocarbons in Russia. An increase in the production at the oil mining fields under development was predicted using the data obtained in the studies of the rocks from exploratory wells over these territories, which allows one to determine the directions of the rational use of natural resources and to provide their reproduction [1].

Relying on the data on the molecular composition of relic structures inheriting the major features of the structure of initial biological molecules, it is possible to obtain the notion of the main sources and conditions of sedimentation of the organic matter (OM) in sediments [2].

The goal of the work was to determine the facial-genetic assignment and specificity of diagenetic and catagenetic transformations of the rocks in the northern part of West Siberia through the investigation of the molecular composition of the OM disseminated in them.

EXPERIMENTAL

Materials

Sandstone, siltstone, silt-rich mudstone, argillite and coaly argillite of the Achimov complex

(lower Cretaceous) in the Nizhnepurovskiy District were investigated. The composition of normal and isoprenoid alkanes, phenanthrenes, steranes, hopanes, alicyclic and aromatic hydrocarbons was studied in order to determine the degree and conditions of the transformation of disseminated OM in the rocks. In the section of the studied sediments, the Sortym formation (K_1/srt) is distinguished, which is overlapped by the Tangal formation (K_1/tng , the Valanzhinian and Aptian stages). The southern margin of the territory was studied within the boundaries of the Yuzhno-Pyreynaya area (wells 213 and 227, samples 1-4 and 5-8, respectively), and the north-western part within the boundaries of the Urengoy area (wells 119 and 621, samples 9-13 and 14, respectively).

Methods of investigation

Organic components were isolated from the core material by extraction with a 7 % methanol solution in chloroform (chloroform extracted bitumen, CB) at 60 °C [3]. The molecular composition of organic compounds was studied by means of gas chromatography – mass spectrometry (GC-MS) using a magnetic DFS chromatograph – mass spectrometer (Thermo Scientific, USA) at the Tomsk Regional Equipment Sharing Centre of the Tomsk Scientific Centre, SB RAS. The content of specific structures was calculated from the areas of the corresponding peaks in the chromatograms using an internal standard and correction coefficients determined for each class of compounds according to the procedure presented in [4].

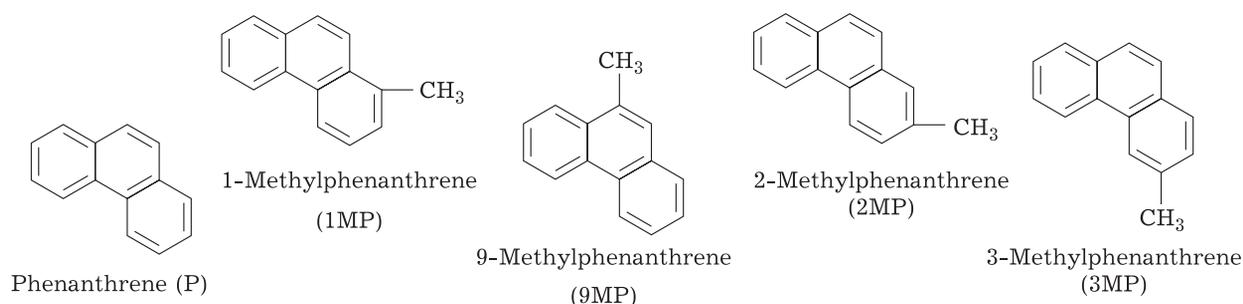
The content of metalloporphyrins and perylenes (Per) was determined by means of electron spectroscopy with the help of an SF-56 spectrophotometer (Russia) with the automatic registration of the spectrum by recording the intensities of absorption bands at 550 nm for nickel porphyrins (Ni-p), 570 nm for vanadyl

porphyrins (VO-p), and 435 nm for Per, and carrying out the calculations with extinction coefficients equal to $2.7 \cdot 10^4$, $2.9 \cdot 10^4$ and $4 \cdot 10^4$ L/(mol · cm), respectively.

To evaluate the degree of thermal transformation of the OM disseminated over the rocks, we studied the distribution and composition of phenanthrenes [5, 6], and used these data to calculate the methylphenanthrene index (MPI) according to equation $MPI = 1.5 (2MP + 3MP)/(P + 1MP + 9MP)$, and vitrinite reflectance (R_c) according to equation $R_c = 0.6 MPI + 0.4$ (Scheme 1).

RESULTS AND DISCUSSION

Characterising the OM of the section of Cretaceous rocks in the southern part of the territory under investigation (well 213), we may state that sample 1 (2724.2 m) is enriched with bituminous components. The value of pristine to phytane ratio (Pr/Ph) (Table 1) points to sub-oxidative conditions that existed in the sedimentation basin, while the composition of n-alkanes points to a mixed source of OM [7, 8], the composition of steranes – to non-marine settings of sedimentation, and hopanes – to lacustrine settings [9]. A substantial contribution from terrestrial plants into the initial OM of this interval is also confirmed by increased relative amounts of retene and especially cadalene (Fig. 1), as well as the presence of simonellite [10]. Lower along the section (sample 2, 3011.2 m) the rocks contain smaller amount of bitumoid, the initial organic material was sedimented in the sub-oxidative environment, but the presence of VO-p in the OM [11] (see Table 1) and the composition of steranes (Table 2, Fig. 2) provide evidence of the marine conditions of sedimentation, while the composition of n-alkanes confirms the prevailing contribution from phytoplankton into the formation of the OM. The rocks of samples 3



Scheme 1.

TABLE 1

Characterization of the studied rocks and the parameters of the composition of alkanes and heterocyclic compounds

Sample	Depth, m	Age/formation	CB, %	Pr/Ph	Pr/C ₁₇	Ph/C ₁₈	CPI	R _c	Content, nmol/g			Content, rel. %	
									VO-p	Ni-p	Per	DBF	DBT
The Southern zone													
1	2724.2	K ₁ /tng	0.23	1.9	0.52	0.34	1.49	0.64	0	0	0	23	7
2	3011.2	K ₁ /srt	0.12	1.8	0.59	0.48	1.08	0.66	116	0	0	8	4
3	3108.5	K ₁ /srt	0.15	1.7	0.52	0.56	1.03	0.77	90	0	0	26	9
4	3242.0	K ₁ /srt	0.07	0.9	0.54	0.60	1.04	0.55	179	0	0	18	2
5	3005.4	K ₁ /srt	0.07	1.4	0.45	0.51	0.86	0.54	57	0	0	7	3
6	3240.5	K ₁ /srt	0.04	1.3	0.51	0.47	1.01	0.54	0	0	0	0	2
7	3240.6	K ₁ /srt	0.11	1.0	0.69	0.54	1.32	0.54	100	173	0	11	3
8	3263.0	K ₁ /srt	0.09	1.5	0.52	0.51	1.00	0.65	0	0	0	9	5
The North-Western zone													
9	2653.9	K ₁ /tng	0.08	1.1	0.72	0.57	0.99	0.49	0	0	0	9	2
10	2743.1	K ₁ /tng	0.03	2.4	0.73	0.40	1.01	0.68	0	16	0	6	4
11	2758.1	K ₁ /tng	0.06	1.4	0.46	0.39	1.06	0.49	0	0	0	8	2
12	2792.3	K ₁ /tng	0.41	1.7	0.40	0.61	1.04	0.77	0	0	0	23	4
13	2879.5	K ₁ /tng	0.09	1.3	0.73	0.52	0.97	0.59	63	0	0	7	5
14	2707.8	K ₁ /tng	0.41	1.7	0.76	0.47	1.43	0.59	0	0	426	26	2

Note. CB is the concentration of bituminous components in rocks; DBF means dibenzofurans; DBT means dibenzothiophens; Pr/Ph is the ratio of pristine to phytane, Pr/C₁₇ and Ph/C₁₈ are the ratios of isoprenoid alkanes to normal ones, CPI is carbon preference index, R_c is the calculated vitrinite reflectance.

TABLE 2

Parameters of the composition of hopanes and steranes in the OM of rocks under investigation

Sample	Hopanes						C ₂₉ St/C ₃₀ H	Steranes					
	Content, rel. %			T _s /T _m	C ₂₈ /H	C ₂₉ /H		Content, rel. %			I/R	S/R	S/(S + R)
	C ₂₉	C ₃₀	C ₃₁					C ₂₇	C ₂₈	C ₂₉			
The Southern zone													
1	24	59	17	0.54	0.40	0.45	0.52	10	36	54	0.45	0.60	0.38
2	31	44	24	0.38	0.15	0.77	0.51	39	34	27	0.69	0.50	0.33
3	24	46	30	0.65	0.07	0.55	0.18	19	22	59	0.73	0.60	0.38
5	33	45	22	0.77	0.20	0.75	0.44	30	26	44	0.75	0.58	0.37
6	26	53	21	0.37	0.00	0.50	0.44	22	20	58	0.47	0.64	0.39
7	29	57	14	0.83	0.08	0.55	0.25	23	22	55	0.71	0.70	0.41
8	28	49	23	0.88	0.16	0.67	0.39	22	25	53	0.68	0.65	0.39
The North-Western zone													
9	36	34	30	0.39	0.00	0.93	0.24	–	–	–	–	–	–
10	32	37	31	0.81	0.12	0.85	0.71	23	36	41	0.80	0.72	0.42
11	33	35	32	0.43	0.18	0.95	0.28	21	26	53	–	–	–
12	36	48	16	0.51	0.38	0.75	0.47	29	21	50	0.60	0.52	0.34
13	34	39	28	0.65	0.17	0.87	0.25	29	21	49	0.97	0.53	0.35
14	25	52	23	0.67	0.06	0.48	0.18	18	33	49	0.48	0.55	0.36

Notes. 1. H – hopanes: C₂₉, C₃₀, C₃₁; T_s, T_m – trisnorhopanes; St – steranes: C₂₇, C₂₈, C₂₉; I and R – iso- and regular, S and R – stereoisomers; T_s/T_m – trisnorhopane ratio; C₂₈/H – the ratio of C₂₈ hopane to the sum of hopanes C₂₉, C₃₀, C₃₁; C₂₉/H – the ratio of C₂₉ hopane to the sum of hopanes C₂₉, C₃₀, C₃₁; C₂₉St/C₃₀H – the ratio of sterane C₂₉ to hopane C₃₀; I/R – the ratio of iso- and regular steranes; S/R and S/(S + R) – the ratios of S and R stereoisomers of steranes. 2. Dash means that the value was not determined.

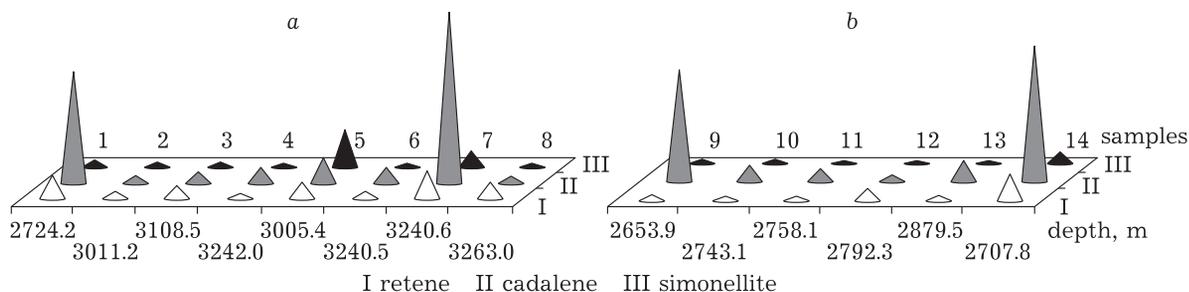


Fig. 1. Distribution of retene (I), cadalene (II) and simonellite (III) over the section of lower Cretaceous sediments in the southern (a) and north-western zone (b).

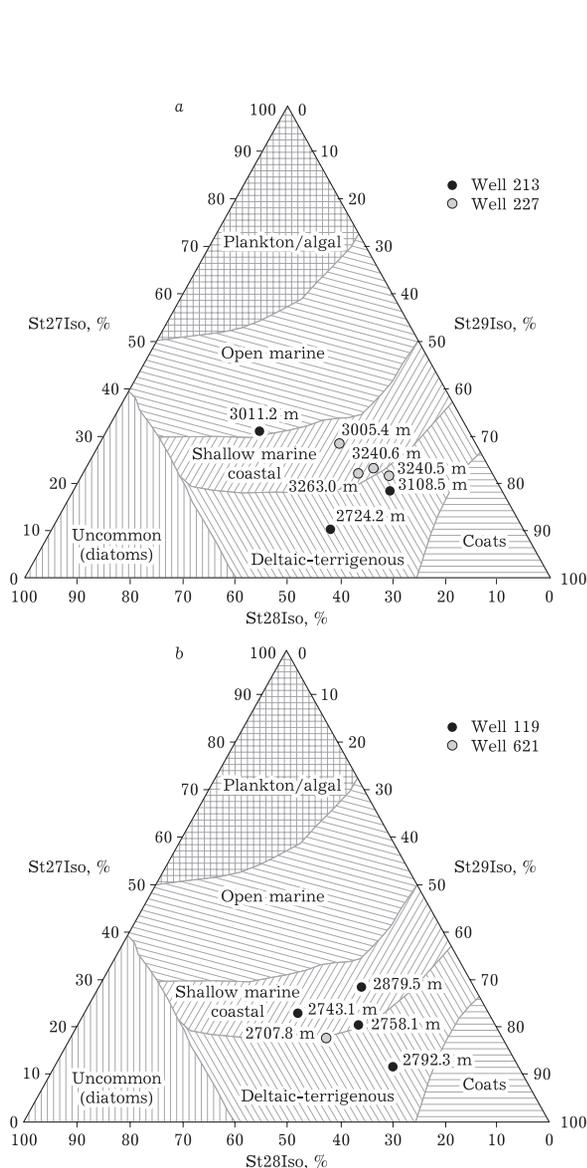


Fig. 2. Composition of steranes in the OM of rocks from the southern (a) and north-western zones (b). Interpretation according to [13]. Designations: St27, St28, St29 - steranes C_{27} , C_{28} , C_{29} .

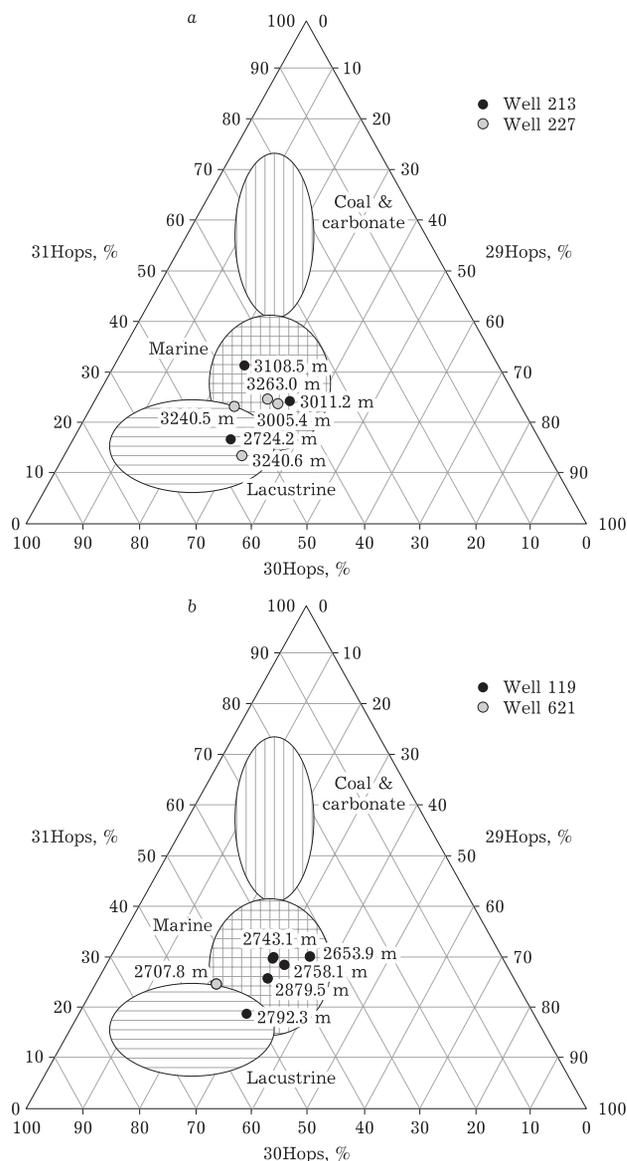


Fig. 3. Composition of hopanes of the OM in the rocks of the southern (a) and north-western zones (b). Interpretation according to [13]. Designations: Hops29, Hops30, Hops31 - hopanes C_{29} , C_{30} , C_{31} .

(3108.5 m) and 1 are close to each other in OM composition and sedimentation conditions. The value of Pr/Ph ratio suggests that the OM of sample 3 was sedimented under sub-oxidative conditions too. The composition of steranes and their decreased amount with respect to hopanes ($C_{29}St/C_{30}H$, see Table 2) point to the continental genesis of the OM. A substantial contribution from terrestrial plants into the composition of the OM is also evidenced by the composition of *n*-alkanes, but the presence of a definite amount of VO-p and increased content of sulphur-containing compounds – dibenzothiophenes (DBT) – point to possible occasional income to seawater into sedimentation basin. Bitumoid content in the rocks of sample 4 (3242.0 m) decreased. Initial organic matter was deposited in the reducing (Pr/Ph = 0.9) marine (the presence of VO-p) environment (see Table 1). According to the data on the composition of *n*-alkanes, the source of the OM was mainly phytoplankton.

Thermal transformation of the OM in sample 1 with respect to the parameters of alkane composition is characterized as immature (CPI = 1.49), and the value of R_c corresponds to catagenesis stage MK_1 . Down along the section (samples 2–4), thermal maturity of the OM increases, CPI coefficient approaches 1, and the value of R_c corresponds to catagenesis stage MK_2 . However, the parameters related to the composition of steranes and hopanes characterize the OM as less mature (see Table 2, Figs. 2 and 3).

Changes in the conditions of OM accumulation downward the section (well 227, samples 5–8) are evidenced by the variations in the amount and composition of bitumoids. For example, the organic material of sample 5, represented mainly by phytoplankton, was deposited under the sub-oxidative shallow sea conditions as suggested by the composition of steranes (see Table 2, Fig. 2), which is confirmed by the presence of VO-p and by the composition of hopanes (see Tables 1 and 2). Lower along the section (sample 6), the conditions were changing from sub-oxidative to reducing, vanadyl and nickel complexes of porphyrin disappeared, the content of cadalene and retene in the OM (that is, the fraction of terrestrial organic material) decreased sharply. According to the data on the composition of steranes, organic material was accumulating in the shallow coastal zone of the sea, while the data on the composition of hopanes suggest that accumulation proceeded in a coastal lake in occasional contacts with the sea. For sample 7, the reducing conditions of OM

burial were detected, along with the presence of hetero compounds (metalloporphyrins, dibenzothiophenes and dibenzofurans). The organic matter of sample 8 originating mainly from phytoplankton was deposited under sub-oxidative conditions of a shallow sea. The parameters of the composition of alkanes, steranes and hopanes characterize the OM of the lower part of the section in the southern zone as close to mature, the value of R_c corresponds to the stage of catagenesis MK_1 , and in the lower part it reaches MK_2 .

In general, substantial variations of the conditions of sediment accumulation and the source that supplied the OM to the sediments are observed in the section of Cretaceous sediments in the southern zone of the territory. The degree of thermal transformation of the OM corresponds mainly to catagenesis stage MK_1 , and in the lower part of the section to MK_2 [12].

Characterising the rocks of the north-western zone (wells 119, 621), one should stress that the OM of the rocks of sample 9 contain rather small amount of bituminous components (see Table 1) in which only trace amounts of steranes were detected. Hopanes are present in rather low concentration too. Metalloporphyrins are absent. The value of Pr/Ph ratio (1.1) provides evidence of the reducing conditions of OM accumulation. The composition of alkanes points to phytoplankton as the major source of the OM, while the composition of hopanes points to the marine conditions of sediment accumulation. Lower along the section (sample 10), a decrease in the amount of bituminous components and changes of the conditions of sediment accumulation to oxidative (Pr/Ph = 2.4, see Table 1) were detected. The data on the composition of steranes (see Fig. 2) and hopanes (see Table 2, Fig. 3) indicate that initial OM was deposited in a shallow sea, and organic components were supplied into the sediments by phytoplankton and bottom algae (the fraction of C_{15} – C_{21} homologues is high in the composition of *n*-alkanes). The content of bituminous components in sample 11 is low, the Pr/Ph value (1.4) points to sub-oxidative conditions of sedimentation, the composition of alkanes points to phytoplankton as the main source of the OM, and the composition of steranes is the evidence of shallow marine sedimentation conditions. In the rocks of sample 12 (2792.5 m), the concentration of bituminous components is substantially higher. The organic material was accumulated under sub-oxidative conditions (Pr/Ph = 1.7). An increased content of naphthalenes is detected in bitumoid, and also (in

comparison with the overlying rocks) retene, which is the evidence of the contribution from the terrestrial flora (see Fig. 1, b), however, the composition of *n*-alkanes corresponds to the dominating contribution from phytoplankton into the initial OM of the sediment. According to the data on the composition of steranes, the OM was accumulated in an intracontinental water reservoir (see Fig. 2); according to the data on the composition of hopanes (see Fig. 3), this water reservoir had been a lake. Lower along the section, the content of bitumoid in the rocks (sample 13) is again low. The organic matter was accumulated in the sediments under the conditions close to reductive (Pr/Ph =

1.3). The presence of VO-p, the composition of steranes and hopanes point to the marine conditions of the deposition of initial OM, the source of which was phytoplankton and bottom algae.

The rocks of sample 14 (well 621) are enriched with bituminous components with a substantial fraction of naphthalenes. The high content of retene and cadalene, as well as the presence of simonellite in the OM, provide evidence of the substantial contribution from terrestrial plants into the initial organic matter, and the composition of *n*-alkanes suggests a significant contribution from phytoplankton. The presence of perylene points to the shallow sedimentation basin, while

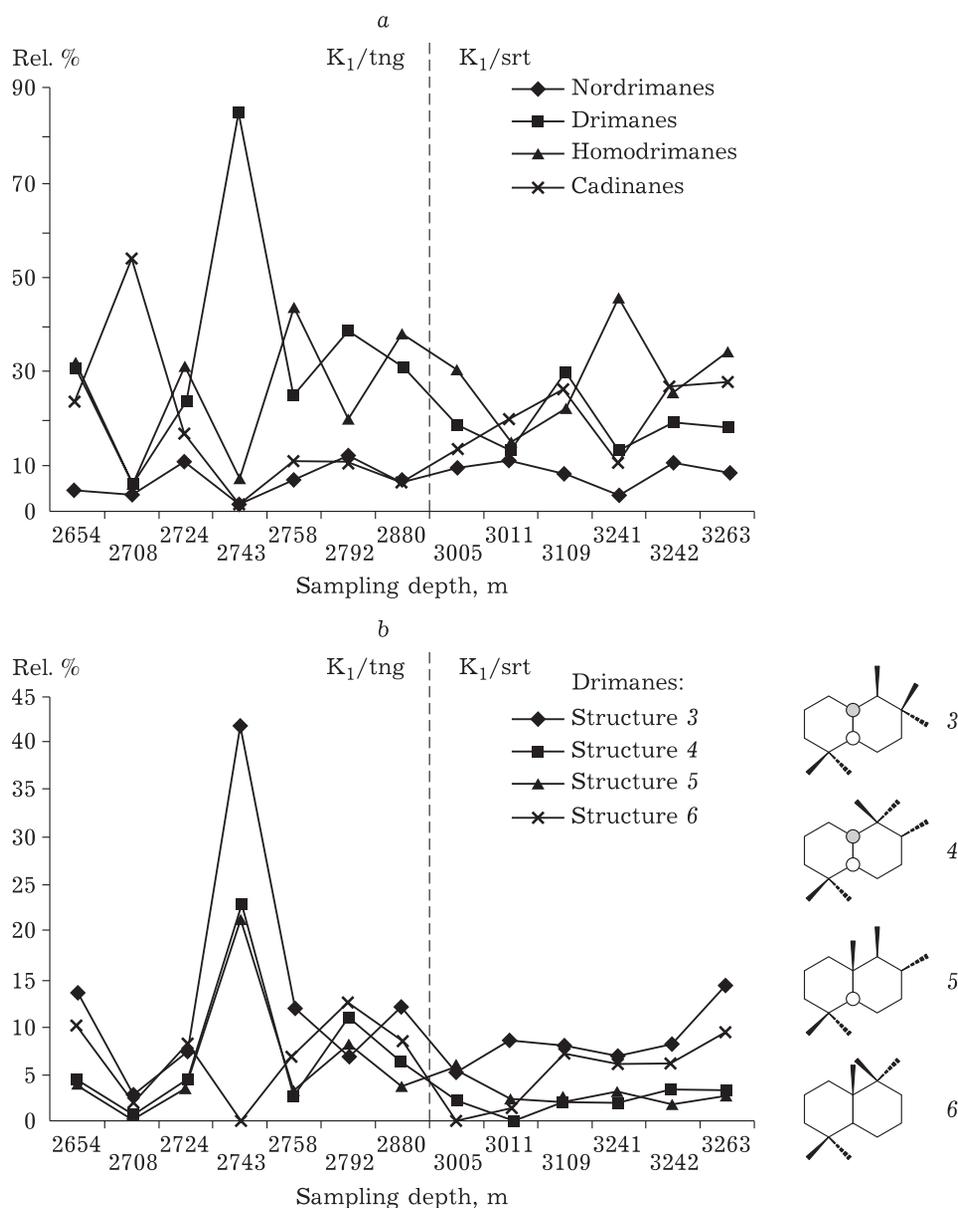


Fig. 4. The group composition of sesquiterpanes (a) and the distribution of drimanes (b) over the section of lower Cretaceous sediments.

the composition of hopanes and steranes suggest that sedimentation conditions were boundary between coastal marine and lacustrine.

According to the index depicting hydrocarbon oddness, CPI (Carbon Preference Index), all the studied samples from the north-western zone (except sample 14, well 621) are characterized as mature. However, the relations between isoprenoid and normal alkanes, as well as the parameters of sterane and hopane composition, point to not very high thermal transformation of the OM, and R_c value in the majority of samples corresponds to catagenesis stage MK₁.

So, the OM disseminated in the rocks of the southern zone is characterized by transformation corresponding to the major zone of oil formation (catagenesis stage from MK₁ to the middle of MK₂), while lower thermal maturity is detected for the rocks of the north-western zone (from PK₃ to early MK₁). The maximum of the molecular mass distribution of *n*-alkanes falling on the low-molecular region (C₁₅–C₁₇) in almost all samples points to phytoplankton as the major source of the organic material, while the value of Pr/Ph ratio points to mainly sub-oxidative conditions that were existing in sedimentation basin.

Analysis of the composition of hydrocarbons in the OM disseminated in rocks reveals prevalence of saturated structures (except sample 12), among which, in addition to alkanes, the identified compounds include steranes, hopanes, bicyclic sesquiterpanes (drimanes and cadinanes) [1]. Aromatic compounds are represented by the series of bi-, tri-, tetra- and pentacyclic homologues among which biarenes dominate, while tetra- and pentacyclic compounds were detected in minor amounts [1]. AN indicator of the substantial contribution of terrestrial plants is an increased relative content of retene and especially cadalene (see Fig. 1), as well as simonellite which is present in almost all the samples of the southern zone: it is partially aromatized derivative of abietinic acid [2].

Hopane C₃₀ (H) dominates among the hopanes of C₂₇–C₃₄ composition (see Fig. 3) in the majority of the studied samples. The deposits of the north-western part of the Tangal formation are characterized by the close content of hopanes C₂₉ and C₃₀ (see Table 2, Fig. 3). The continental genesis of the OM of Tangal and Sortym formations in the studied region of the northern territories of West Siberia is confirmed by the composition of steranes (St) and their decreased amount with respect to hopanes (C₂₉St/C₃₀H).

Tricyclic terpanes represented by C₂₃ and C₂₄ homologues are present only in sample 8. Tetracyclic terpane C₂₄ was detected in that sample, too. Tri- and tetracyclic terpanes were not detected in other samples.

Among terpanes detected in the disseminated OM in rocks, the most representative class is sesquiterpanes (61–99 %). Only in sample 6 hopanes dominate among cyclanes, and the content of sesquiterpanes decreases to 32 %. The group composition of sesquiterpanes in the studied rocks is represented by the isomers of nordrimane, drimane and homodrimane, a and by bicyclic cadinanes (Fig. 4, a). The distribution of drimanes over the lower Cretaceous section (the Tabgal and Sortym formations) is represented in Fig. 4, b). For the Tangal formation, the sample from the depth of 2743 m differing from other rocks in lithological composition (marl) is characterized by the absence of drimane 6. This structure was not detected also in the sample from the depth of 3005 m from the top part of the Sortym formation, which is a rock of complicated lithology: alternation of sandstone and grey siltstone with coaly detritus.

In general, substantial variations of the conditions of sediment accumulation and the source that had supplied the OM to the sediments are observed in the section of Cretaceous sediments.

CONCLUSION

The data on the distribution and features of the composition of disseminated organic matter in the section of Cretaceous sediments over four exploratory wells at the oil mining areas of the Yamal-Nenets autonomous area provide evidence of the prevailing sub-oxidative sedimentation conditions that existed in sedimentation basin. The most probable major bioproducers for the initial organic matter were phytoplankton and terrestrial vegetation, which were accumulated near the coast line of the sea or in coastal water reservoir occasionally flooded by the sea. The continental genesis of the organic matter is evidenced by the composition of steranes and their decreased amount with respect to hopanes. An increase in the degree of thermal transformation of the organic matter from the north (from PK3 to early MK1) to the south (from MK1 to middle MK2) was detected.

The work was carried out within the State Assignment for the IPC SB RAS (Project V.46.2.3)

financed by the Ministry of Science and Higher Education of the Russian Federation.

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