

Proof of Formation of Organic Matter in Upper Devonian Carbonate and Carbonate-Siliceous Sediments of the South-Tatar Uplift in Constant Photic Layer Anoxia¹

E. N. Poludetkina^{a, *}, M. B. Smirnov^{b, **}, N. P. Fadeeva^{a, ***}, and E. V. Kozlova^{c, ****}

^a*Faculty of Geology, Lomonosov Moscow State University, Moscow, 119991 Russia*

^b*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia*

^c*Skolkovo Institute of Science and Technology, Moscow, 143026 Russia*

**e-mail: poludetkinaelena@mail.ru*

***e-mail: m-smirnov@yandex.ru*

****e-mail: fadeeva_nataly@mail.ru*

*****e-mail: miliyakozlova@mail.ru*

Received July 5, 2016

Abstract—Samples of carbonate and siliceous-carbonate deposits of Semiluk—Sargaev horizons of the N—NE slope of the South Tatar uplift, Volga-Ural petroliferous basin, have been studied. Specific feature of the source rocks—high concentration of compounds—anoxia testifiers in the photic layer has been identified. That is, organic matter has been deposited under the conditions of the constant presence of anoxia in the photic layer of the sedimentation basin at sufficiently high thickness of the water column contaminated with hydrogen sulfide. Since by the composition of saturated hydrocarbons the studied samples are typical for deposits of the Semiluk horizon of the central part of the Volga-Ural basin, we can assume a fairly wide prevalence of such conditions within the South-Tatar arch. Changes in the concentrations of the components—anoxia markers—show cyclical changes in output layer contaminated with hydrogen sulfide or its bioproduction within the studied time.

Keywords: South-Tatar arch, biomarker composition analysis, source rocks, anoxia testifiers

DOI: 10.1134/S0016702917080079

INTRODUCTION

The first compounds—testifiers of anoxic conditions in the photic layer of sedimentation basin—have been discovered in the oil of Shakalyk-Astana field over 30 years ago (Ostroukhov et al., 1982). At the same time their structure has been proven via counter synthesis: 1,2,6-trimethyl-alkylbenzene with isoprenoid chain of irregular structure. However, geochemical significance of these alkyl-benzenes was found later. As a result of detailed composition and structure study of a huge number of components of aromatic fractions extracted from bitumen of a wide range of different age deposits, it was found that more than 100 compounds C₁₃–C₄₀ represent transformation products of two–three C₄₀-bicyclic aromatic carotenoids with polyene isoprenoid chain of irregular structure connecting two tri-methyl-substituted benzene cycles (Hartgers et al., 1994; Koopmans et al., 1996). Producers of these aromatic carotenoids are photosynthetic bacteria that exist only in the condi-

tions of hydrogen sulfide contamination. Produced by each type C₄₀-carotenoids differ in the position of methyl groups in one of the benzene rings. One type may exist up to the lower limit to the photic layer (Hartgers et al., 1994). Because of the very specific structure of the identified compounds, they are reliable markers of anoxic conditions in the photic layer of the sedimentation basin (Koopmans et al., 1996).

Estimation of such special conditions of organic matter formation is very important at least in terms of the possible ways and rate of conversion. Indeed, the polyene chains present in appreciable concentrations may by themselves through a system of coupled reactions affect the transformation processes of the buried dispersed organic matter (DOM). Further variants may occur if the hydrogen sulphide is present in the sediment (Koopmans et al., 1996). However, to date, with a few exceptions such as the global anoxic event 1, special study of spreading of such sedimentation conditions was not carried out. A small number of publications exist for Russia where on limited material, inter alia, presence of bitumen and oils of correspond-

¹ The article was translated by the authors.

ing compounds—anoxia markers—is singled out. Thus, their presence has been identified in the samples of Domanik strata of the Timan-Pechora petroliferous basin (Bushnev, 2002, Bushnev et al., 2016). Presence of anoxia in the Early Cretaceous basin of the Russian plate is fixed in the material out of the well in the Ulyanovsk region (Bushnev, 2005). Anoxia markers in the photic layer have been found in the oil of Devonian carbonate deposits of the same region (Bochkarev et al., 2010). Detection of these markers in the individual oils of Timan-Pechora, Volga-Ural and West Siberian petroliferous basin, as well as Sakhalin, was reported in (Pevneva et al., 2010).

It is fundamentally important that none of the works, except for (Hartgers et al., 1994; Koopmans et al., 1996), contains quantitative estimation of the total content of components—anoxia testifiers.

Lacking this information it is impossible to determine whether hydrogen sulfide contamination was permanent covering most of the water column, so that a substantial portion of the buried organic material was formed under these conditions, or—episodic, distributed to a limited water layer, when the proportion of such substance in the overall balance of dispersed organic matter (DOM) was small.

Therefore, the aim of this article is to prove high input of organic matter formed in anoxic conditions in the photic layer in the overall balance of Domanik and Sargaev deposits for the N–NE slope of the South-Tatar arch based on quantitative analysis of the widest possible set of compounds—biomarkers.

EXPERIMENTAL PART

Chloroform bitumen was extracted from the rock crashed to powder 0.25 mm in size by chloroform in the Soxhlet apparatus for at least 120 hours. After standard asphaltene precipitation by hexane, malthenes obtained were separated on silica gel (Merck), impregnated with AgNO_3 . When allocating saturates fraction used eluent was hexane, for aromatics fraction – toluene. Completeness of separation was confirmed by chromatomass-spectrometry (GCMS).

Mass spectral analysis was performed on GC-MS Thermo Focus DSQ II. Used capillary column—HP-5, length 15 m, internal diameter 0.25 mm, 0.25 mcm phase thickness, carrier gas—helium. Mode: injector temperature 300°C, initial temperature of the thermostat chromatograph—70°C, heating rate 2°C/min up to 310°C, then—isootherm for 20 minutes; operation of the mass spectrometer: ionization energy 70 eV, source temperature—250°C, scanning in the range of 10–Da at a rate of 1.0 scans/s, resolution around a single mass range.

RESULTS AND DISCUSSION

The objects of study are represented by the samples of the Devonian carbonate complex of the two wells located on the N–NE slope of the South Tatar arch (Tlyanchi-Tamaksky area, Volga-Ural petroliferous basin). Deposits of the carbonate complex were studied in the stratigraphic interval of Sargaev–Semiluk horizons in the depth interval 1626–1706 m.

Wells of the N–NE slope of the South Tatar arch structurally belong to the depression part and the slopes of the Semiluk trough which formation began in Sargaev time. The most elevated part of the depression was located within the southern part of the arch. From Rechitsk time it takes the form of a clearly defined depression of the Aktanysh-Chishminsky trough (part of the Kama-Kinel trough system), dated to the northern and northeastern parts of the arch (Fig. 1). The total thickness of the studied sediments is about 50–60 m.

The studied section is represented by limestones with varying quantity of clayey admixture and significant part of siliceous component (Table 1). Content of clay minerals is relatively increased (30% average) in the lower part of the section (Sargaev horizon), while the Semiluk part practically does not contain clay (6% on average). Low organic matter content (total organic carbon (TOC)—0.07–4.7%, “subdomanikoid” and “domanikoid” concentrations) refer to light carbonate rocks represented by bioclastic limestones, micritic, dolomites, phtanites and claystones of gray, greenish gray and brown colors. High concentrations of OM (5.97–49.4%, “domanik type”) are typical of the predominantly dark-colored mixed siliceous-carbonate rocks; they form rythmites of pure calcareous to pure siliceous composition, at that organic component plays alongside the rock-forming role.

Content of bitumen in rocks is characterized by a wide range of values ($\text{ChB} = 0.01\text{--}4.1\%$) and depends on the concentration of OM. Organic matter is syngenetic that is confirmed by the correlation between the quantity of OM and bitumen (Fig. 2).

Single samples of siliceous and bioclastic limestone migratory bitumen are observed fixed by high values of bitumen coefficient $\beta^{\text{ChB}} = 52\text{--}62\%$, while the background concentration is less than 20% (Fig. 3). Relatively increased bitumen content of OM located at the beginning catagenesis level ($T_{\text{max}} = 400\text{--}433^\circ\text{C}$) is due to increased lipid fractions in the initial OM.

The group bitumen composition is represented by dominating asphaltene components (an average of 70%), 30% of malthenes; in some samples its content increases to 50–60%.

A complete set of standard analyzes the composition of alkanes, steranes and triterpanes, based on which conclusions on the sedimentation conditions in Domanik and pre-Domanik time are drawn. The results are shown in Tables 2 and 3. The main conclusion that follows from these data—the composition of

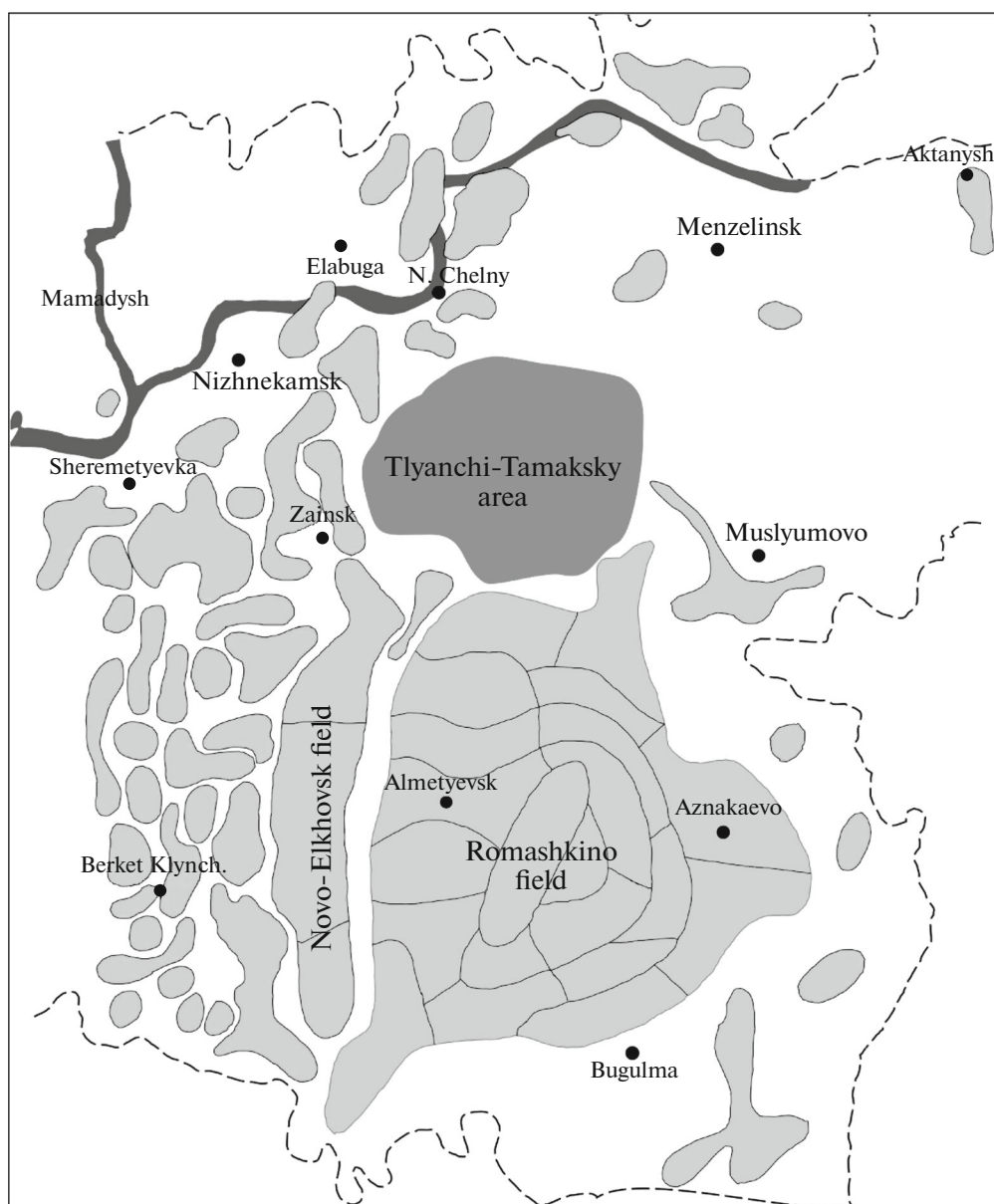


Fig. 1. Location of the study area.

saturated hydrocarbons of the studied samples is typical for DOM of the Semiluk horizon of the central part of the Volga-Ural region (Gordadze and Tikhomirov, 2005).

Alkanes composition is typical for reducing sedimentation conditions in the marine environment. Unimodal distribution of *n*-alkane HCs is observed. Chain length is C_{14} – C_{34} with maximum on n - C_{19-22} , that is characteristic for marine algal OM. $Pr/Ph < 0.9$ (smallest—0.3), $K_i = 1.1$ – 9.1 (2/3rd of the samples— from 2.0 to 4.5). No expressed evenness or oddness of *n*-alkanes is observed. Predominance of C_{27} among steranes $C_{27}:C_{28}:C_{29}$ is characteristic of shallow-marine depositional environment of the generating

strata with predominant phytoplankton, and the dominance of sterane C_{29} indicates the possible involvement of higher plants.

Under-Domanik deposits of Sargaev horizon are characterized by the presence of autochthonous OM accumulated in shallow-marine environments of predominantly carbonate sedimentation and reducing diagenetic conditions. Evidence of normal salinity in the pre-Domanik shallow basin is extremely low value of the ratio $G/H_{30} < 0.07$ and 0.03.

Sapropelic type of OM is proven by the data of macro- and micropetrography rock studies, ratios of iso-/*n*-alkanes, CPI. Organic matter is slightly transformed that is proven by the prevalence of R-configu-

Table 1. List of studied samples of Tlyanchi-Tamaksky area and its pyrolysis characteristics

Sample	Depth, m	Horizon	Mass content, %		Rock Eval pyrolysis					
			SiO ₂	carbonates	T _{max} , °C	TOC, %	S ₁	S ₂	PI	HI
							mg HCs/g rock			mg HCs/g TOC
well 300										
47	1675.3	D _{3dm}	98	2	419	24.28	9.01	152.6	0.06	629
41	1679.74	D _{3dm}	27	69	417	16.86	6.7	98.5	0.06	584
37	1682.29	D _{3dm}	39	61	411	29.69	9.71	180.9	0.05	609
33	1684.05	D _{3dm}	83	17	413	28.75	16.55	175.3	0.09	610
32	1684.48	D _{3dm}	1	99	421	0.4	0.06	0.98	0.06	245
27	1686.92	D _{3dm}	30	50	410	23.81	2.26	145.7	0.05	612
22	1689.05	D _{3dm}	26	71	413	49.37	13.78	284.8	0.05	577
9	1704.72	D _{3sr}	3	97	425	0.66	0.12	0.74	0.14	112
7	1705.51	D _{3sr}	Undef.	Undef.	413	21.61	11.71	121.8	0.09	564
well 859										
33	1626.2	D _{3dm}	3	97	420	1.87	0.99	8.15	0.11	436
29	1627.0	D _{3dm}	46	52	426	7.16	4.95	38.0	0.12	530
26	1628.05	D _{3dm}	84	14	423	8.79	8.25	51.2	0.14	582
25	1628.4	D _{3dm}	7	92	422	19.27	6.81	95.2	0.07	494
24	1629.0	D _{3dm}	2	92	423	2.98	1.83	15.3	0.11	514
19	1630.38	D _{3dm}	14	80	422	10.68	4.06	57.4	0.07	538

ration homohopanes over homohopanes with S-configuration ($22S/22R = 0.38$ and 0.97), low values of T_s/T_m ratio, prevalence of $\alpha\alpha$ -isomer of steranes over $\beta\beta$ -isomers, although the generation of “early” HC fluids has already started that is manifested in rela-

tively high degree of bituminization. This is also confirmed by maturity coefficients of polycyclic aromatic HCs: values $TAI/(TAI + TAI) = TA(I)/TA(II) = 4$ and 7% , DBT index $4\text{-Me-}/1\text{-Me-} = 0.45$ and 0.9 are consistent with the thermal indexes by steranes and

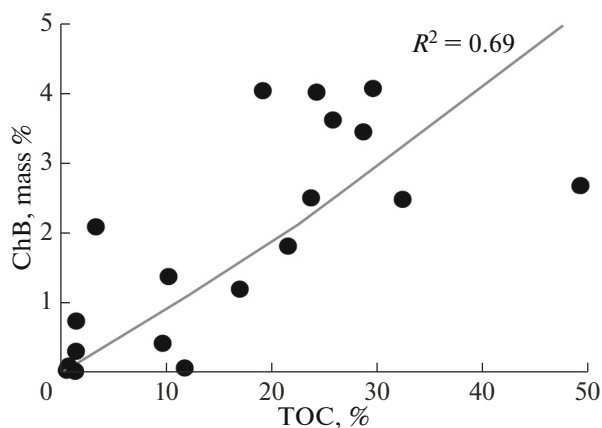


Fig. 2. Relation of TOC and chlorophorm bitumen concentrations in the rocks of carbonate complex of Tlyanchi-Tamaksky area.

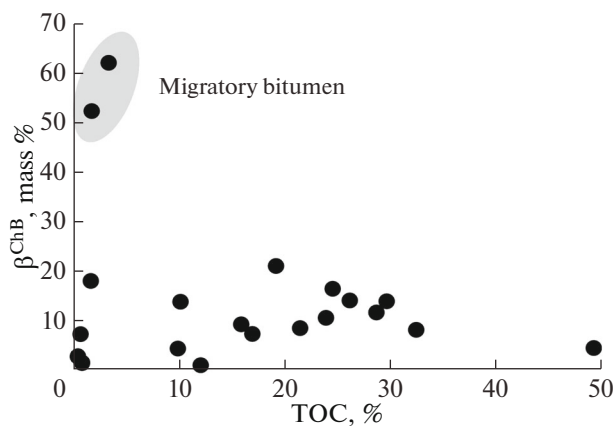


Fig. 3. Relation of OM concentrations and bitumen coefficient in the rocks of carbonate complex of Tlyanchi-Tamaksky area.

Table 2. Geochemical features of the samples by alkanes and steranes composition

Nº	Well	Sample	Age	Pr/Ph	Pr/ <i>n</i> -C ₁₇	Ph/ <i>n</i> -C ₁₈	<i>K_i</i>	$\alpha\alpha$ 20S/ 20(S + R)	$\beta\beta$ / ($\alpha\alpha + \beta\beta$)	dia-/ reg-	dia/ $\alpha\alpha$ -reg	C ₂₁ /ΣC ₂₉	C ₂₇ :C ₂₈ :C ₂₉
1	859	33	D _{3dm}	0.30	1.3	2.7	2.1	0.47	0.60	0.14	0.30	0.10	38:17:45
2	859	29	D _{3dm}	0.31	1.6	3.3	2.6	0.45	0.61	0.12	0.25	0.06	37:17:46
3	859	26	D _{3dm}	0.44	1.9	3.7	2.9	0.44	0.53	0.18	0.50	0.05	35:21:44
4	859	25	D _{3dm}	0.50	0.84	1.5	1.2	0.47	0.54	0.17	0.45	0.20	38:20:42
5	859	24	D _{3dm}	0.39	1.5	3.0	2.3	0.45	0.60	0.15	0.28	0.09	37:19:44
6	859	19	D _{3dm}	0.42	1.2	2.4	1.8	0.45	0.59	0.13	0.25	0.14	41:17:42
7	300	47	D _{3dm}	0.37	2.1	4.0	3.3	0.49	0.56	0.13	0.20	0.06	36:18:45
8	300	41	D _{3dm}	0.55	2.6	4.6	4.2	0.46	0.57	0.14	0.26	0.08	38:17:45
9	300	37	D _{3dm}	0.62	3.3	3.7	3.6	0.39	0.23	0.15	0.20	0.03	36:18:46
10	300	33	D _{3dm}	0.59	2.4	3.6	3.0	0.45	0.47	0.19	0.31	0.09	36:15:49
11	300	32	D _{3dm}	0.70	2.2	3.0	2.9	0.44	0.52	0.18	0.31	0.06	35:16:49
12	300	27	D _{3dm}	0.88	9.0	9.3	9.1	0.13	0.21	0.33	0.41	0.03	36:18:46
13	300	22	D _{3dm}	0.39	2.5	5.1	4.0	0.52	0.52	0.16	0.35	0.05	38:17:45
14	300	9	D _{3sr}	0.13	1.4	1.1	1.1	0.28	0.44	0.6	1.13	0.34	48:17:35
15	300	7	D _{3sr}	0.70	8.7	5.6	6.5	0.10	0.25	0.6	0.66	0.08	35:18:47

Dia-/reg- ratios are measured by steranes C₂₇.**Table 3.** Geochemical characteristics of the samples by triterpanes composition

Nº	Well	Sample	Age	T _s /T _m	H ₂₉ /H ₃₀	M ₃₀ /H ₃₀	Tri-/ Penta-	Tetra-/ Tri-	neo- H ₂₉ /H ₂₉	H ₃₅ /H ₃₄	Hopanes/ Steranes	G/H ₃₀
1	859	33	D _{3dm}	0.12	0.63	0.06	0.51	0.10	0.03	1.4	0.9	0.21
2	859	29	D _{3dm}	0.12	0.58	0.05	0.26	0.11	0.03	1.5	1.5	0.16
3	859	26	D _{3dm}	0.10	0.55	<0.03	0.44	<0.07	<0.05	1.4	0.5	0.94
4	859	25	D _{3dm}	0.11	0.64	0.09	0.57	0.08	0.07	undef.	0.6	0.76
5	859	24	D _{3dm}	0.12	0.60	0.06	0.37	0.11	0.02	2.2	1.3	0.16
6	859	19	D _{3dm}	0.13	0.66	0.05	0.52	0.11	0.02	1.5	1.3	0.17
7	300	47	D _{3dm}	0.11	0.55	0.04	0.18	0.18	0.05	1.4	0.6	0.27
8	300	41	D _{3dm}	0.11	0.45	0.07	0.11	0.22	0.03	1.4	1.1	0.29
9	300	37	D _{3dm}	0.07	0.81	0.17	0.19	0.25	0.03	0.9	0.5	0.56
10	300	33	D _{3dm}	0.11	0.53	0.08	0.13	0.25	0.04	1.3	0.8	0.24
11	300	32	D _{3dm}	0.16	0.49	0.07	0.09	0.27	0.02	1.2	0.8	0.23
12	300	27	D _{3dm}	0.10	0.63	0.30	0.09	0.63	0.04	0.6	0.4	0.38
13	300	22	D _{3dm}	0.11	0.55	0.06	0.14	0.22	0.03	1.3	0.7	0.29
14	300	9	D _{3sr}	0.19	0.66	0.27	0.42	0.39	0.25	0.8	1.3	0.03
15	300	7	D _{3sr}	0.14	0.35	0.31	0.07	0.35	0.13	1.0	0.6	<0.07

H—homohopanes, M—moretane, G—gammacerane, Tri-/Penta—tricyclane C₂₃/Hopane C₃₀, Tetra-/Tri—tetracyclane C₂₄/Tricyclane C₂₃.

hopanes and point on low thermal maturity of deposits (protocatagenesis—early stage of hydrocarbon generation).

Domanik deposits of Semiluk horizon contain autochthonous OM accumulated according to (Khisamov et al., 2015) in shelf conditions (depth 150–200 m) of predominantly carbonate sedimentation and reducing diagenetic conditions with low Eh values. Increasing of mineralization of the sea water in Semiluk time is stated from the value $G/H_{30} = 0.16–0.94$, at that three samples — 0.56, 0.76, 0.94, the rest — 0.16–0.38. Bitumen part of OM is mostly autochthonous, partially affected by migration (presence of para-autochthonous bitumen), represented mainly by the asphaltene fraction, which indicates low maturity of OM. Accumulation of the sediments occurred in the marine clastic-carbonate sedimentation conditions without significant input of humic OM. Initial OM was formed by marine phytoplankton and/or zooplankton. By the value of maturity coefficients OM is non-homogenous. Some samples are characterized by sharp prevalence of isoprenanes over n-alkanes, predominance of homohopanes of R-configuration over S-configuration, low values of T_s/T_m , predominance of $\alpha\alpha$ -isomers of steranes over $\beta\beta$ -isomers that indicates level of maturation of these deposits as late proto-catagenesis (PC_3). In the others composition of the cyclic biomarkers is typical of oils: S/R ratio for homohopane $C_{32} \sim 1.5$, $\beta\beta/(\alpha\alpha+\beta\beta)$ —in the range of 0.50 to 0.61, $20\alpha\alpha S/20\alpha\alpha(S+R)$ —0.41–0.47, that is taking into account T_{max} values and DBT index 4-Me-/1-Me- (0.9–2.1) indicates beginning of meso-catagenesis MC_1 .

An important feature of the aromatic fractions of the studied Domanik-Sargaev deposits is evidence of sharply reducing conditions in the sedimentation basin up to hydrogen sulfide contamination. Credible evidence of hydrogen sulphide contamination covering the photic layer of the paleobasin, is considered the presence of diagenetic derivatives of isorenieratene in organic matter of the sedimentary rocks. This is carotenoid synthesized by green sulfur photoautotrophic bacteria, genus Chlorobiaceae; necessary conditions of its existence are light and hydrogen sulfide dissolved in water (Hartgers et al., 1994; Koopmans et al., 1996). These components are distinguished by their isotopic composition: carbon is 10–15‰ heavier than the carbon of lipids of other photosynthetic organisms (Hartgers et al., 1994; Koopmans et al., 1996; Bushnev et al., 2016).

Trimethyl-alkylbenzenes of $C_{11}–C_{31}$ composition, bi-, tri-, and polycyclic aromatic structures with isoprenane substituents are identified in the aromatic fraction of bitumen (Fig. 4), indicating the existence of anoxia in the photic layer of the sedimentation basin, that is consistent with the reduced values of Pr/Ph and increasing concentrations of DBT and its derivatives.

Identification of compounds—anoxia testifiers in the photic layer of the sedimentation basin shown in Fig. 4 was carried out on the basis of GCMS, based on data on mass spectra and retention time of components, as well as those manifested in the chromatograms of the stereoisomers listed in (Hartgers et al., 1994; Koopmans et al., 1996; Clifford et al., 1998). Mass fragmentograms by characteristic ions with $m/z = 133, 134, 237, 287, 169, 183, 209, 223$ were analyzed, i.e. compounds those in accordance with (Hartgers et al., 1994; Koopmans et al., 1996) are the highest, and by listed in the same molecular ions hydrocarbons from $M = 546$ to $M = 148$. The peaks coinciding on mass fragmentograms by molecular and corresponding characteristic ions, were normalized to the total ion current. Samples where each identification component is present in highest concentrations were defined, and these samples were used for definition of a set of basic ions and their intensity in the mass spectrum of the compound compared with the data of (Hartgers et al., 1994; Koopmans et al., 1996).

Comparison took into account all the characteristic ions contained in the cited papers. Identification of peaks of biphenyls XXV is confirmed by the respective type of mass fragmentograms by ion $m/z = 237$ for a number of components $C_{19}–C_{22}$ shown in Fig. 1 in (Koopmans et al., 1996) (single peak C_{19} and couples of peaks $C_{20}–C_{22}$ with an intensity ratio 1:1 due to the presence of an asymmetric center in a substituent). To distinguish between the isomers with 2,3,6-Me₃- and 3,4,5-Me₃- benzene molecule fragments we used the ratio of peak intensities of ions with $m/z = 133$ and 134 (in compounds with 2,3,6-Me₃- fragment the ratio is much higher) (Hartgers et al., 1994; Koopmans et al., 1996). Structure XII is set according to (Clifford et al., 1998) based on the similarity of its mass spectrum and spectrum of analogue-2,3,6 Me₃- fragment (XIII) with typical at transition to isomers with 3,4,5-Me₃- fragment decreasing in the ratio of ion peak intensities with $m/z = 133$ and 134, and difference in retention time of chromatographic peaks XII and XIII, equal to that of I and II. Typical mass fragmentograms are shown in Fig. 5.

Strictly speaking, the data is insufficient for VII–X to establish a clear position of the methyl groups, so it is possible that some of these compounds have the structure not with assigned structure with 2,3,6-Me₃-, but with 3,4,5-Me₃-distribution of substituents. Because of their low content in all the samples it has no effect on the final conclusions. Components III and IV are located close on the chromatograms, so that their summary content was only measured. Regarding the number of compounds it was not possible to establish which of the isomers they correspond. There are three options for the structures XIX and XX (LVIIID–LIXD, R = Me and R = H, respectively, index “D” indicates the compound number in (Koopmans et al., 1996) and two—XXIV (LVD or LVID). In

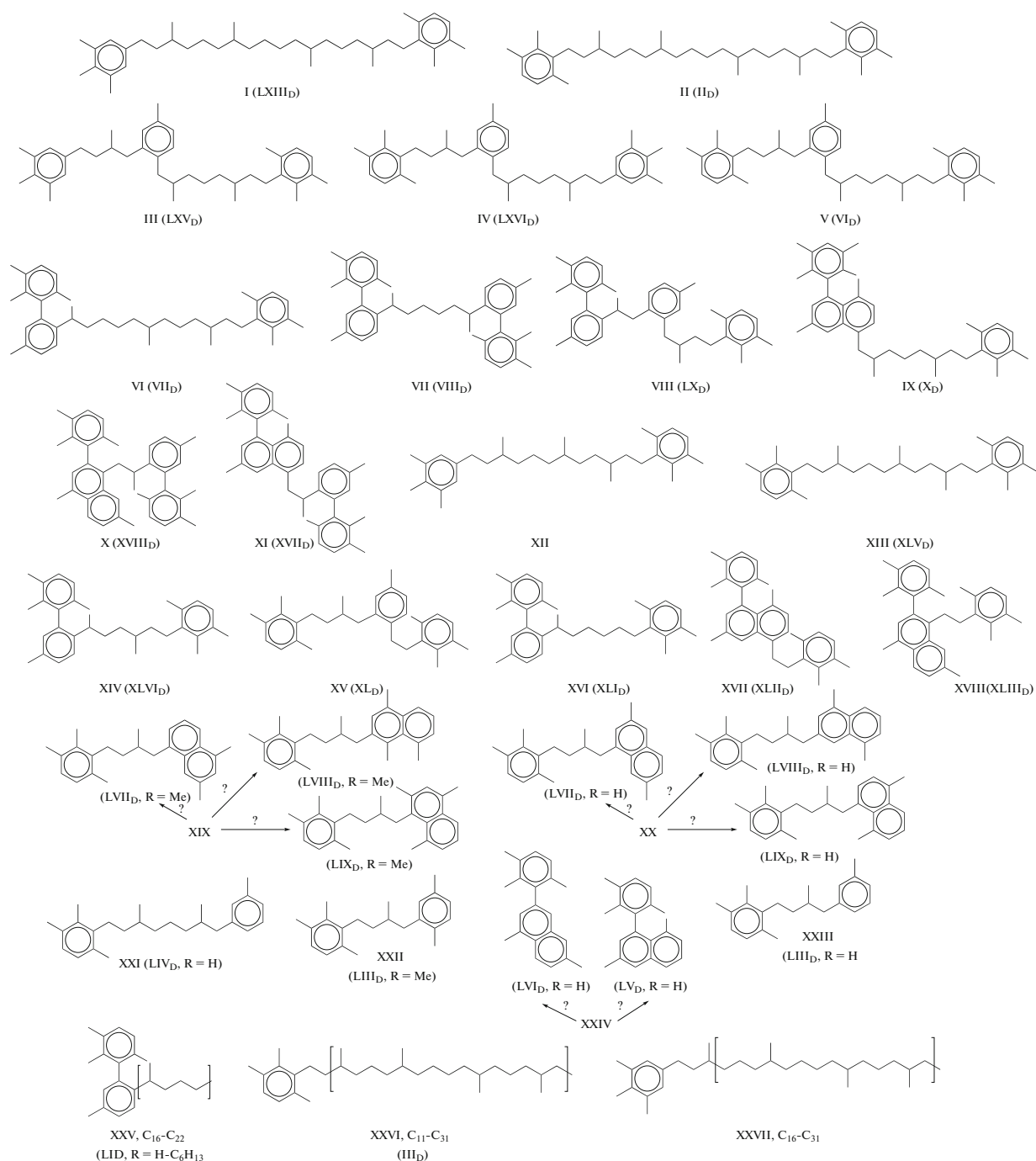


Fig. 4. Structure of the identified compounds—anoxia markers in the photic layer of the sedimentation basin. Question marks—cases when the structure is identified to the accuracy of the isomers stated in the figure.

Fig. 4 such cases are marked with question marks. The peaks of C₁₅ isomers of 2,3,6-Me₃- and 3,4,5-Me₃-substituted benzenes (C₁₅-XXVI and XXVII) are exactly coinciding, as follows from the dependences of the retention time of these two series of compounds by their molecular weight and an intermediate value of the ratio of intensities of the ions with $m/z = 133$ and 134.

According to the standard ratio $m_j = k_j \Sigma I_{\text{char}, i}$, where $I_{\text{char}, i}$ —integrated intensity of the sum of the characteristic ion peaks i (in the group j), m_j —weight % of the j -group, k_j —empirical coefficient for the j -th group (see below, summation of all the compounds of the group), quantitatively (mass % of the fractions of aromatic compounds) determined the content of the

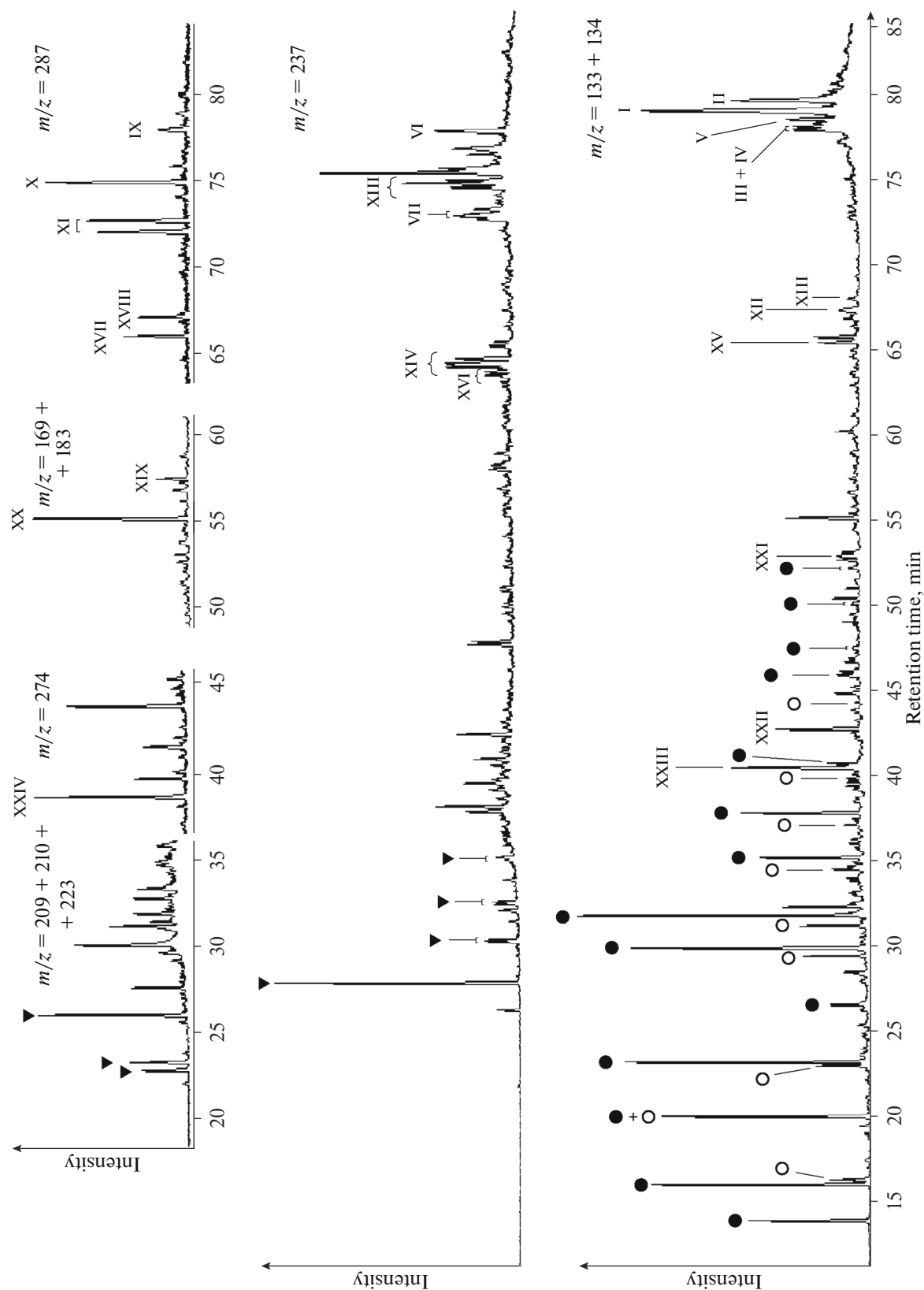


Fig. 5. Typical mass-fragmentograms for identification of compounds—anoxia markers in the photic layer of the sedimentation basin.

Table 4. Content of compounds—anoxia markers in the photic layer of the sedimentation basin in the aromatic fraction

No.	Well	Sample	Age	Content (mass %)	% of common content of compounds—anoxia markers						
					I + II	C ₄₀ , other	C ₃₂ , C ₃₃	C ₂₁ –C ₂₇	Σ XXV	Σ XXVI	Σ XXVII
1	859	19	D _{3dm}	5.1	7	1	1	4	3	65	19
2	859	24	D _{3dm}	5.6	26	2	2	3	2	48	17
3	859	25	D _{3dm}	>1.3	Undefined		0	5	14	58	23
4	859	26	D _{3dm}	>1.5	Undefined		3	5	13	58	21
5	859	29	D _{3dm}	5.5	46	1	1	3	2	32	15
6	859	33	D _{3dm}	4.5	31	2	2	4	2	41	19
7	300	22	D _{3dm}	4.3	14	2	2	4	6	51	20
8	300	27	D _{3dm}	4.2	17		2	25	5	38	13
9	300	32	D _{3dm}	6.1	61		3	3	2	18	12
10	300	33	D _{3dm}	7.6	6	1	1	4	5	60	23
11	300	37	D _{3dm}	1.5	18		3	9	5	44	21
12	300	41	D _{3dm}	3.1	30	6	6	9	3	31	15
13	300	47	D _{3dm}	2.5	15		2	5	8	52	19
14	300	7	D _{3sr}	5.5	15	8	3	10	14	39	11
15	300	9	D _{3sr}	1.2	44		3	12	0	28	12

following compounds and their groups: I + II, amount of other components C₄₀ (at low accuracy of their content estimation—all C₄₀ compounds cumulatively), C₃₂ and C₃₃, C₂₁–C₂₇, the sum of biphenyls row (XXV), 2,3,6-Me₃-substituted benzenes (XXVI), 3,4,5-Me₃-substituted benzenes (XXVII). Characteristic peaks are defined as sum of even and odd ions: m/z 133 + 134, 237 + 238, 287 + 288, 169 + 170, 183 + 184, 209 + 210, 223 + 224. For such sums k_j values within a set of such structures are less dependent on the structure and molecular weight of the individual compounds. In addition, we used molecular ion with m/z = 274 and m/z = 237.

Empirical coefficients k_j for the individual compounds in the first approximation, are equal to the ratio of the integrated intensity of the compound peak in the chromatogram obtained by total ion current to the integrated intensity of the peak of the same compound in the mass fragmentograms built on the corresponding ion or their sum, as the ionization cross sections, per unit mass, for all the aromatic fractions are close enough (Brodsky, 1985). Their measurement was conducted using the samples with proven corresponding peaks in the chromatograms by the ion current are not composite. Total coefficients for 10 compounds among the structures I–XXIV were measured, the biggest concentrations of which are highest for

4 members of the biphenyl row XXV (C₁₆ to C₁₉), 5 members of the row of 2,3,6-Me₃-substituted benzenes XXVI and 4 members of the row of 3,4,5-Me₃-substituted benzenes XXVII (in both rows—from C₁₄ to C₂₀).

Only four compounds were measured in one sample. For the rest, they were performed in two–three samples with further averaging. The measured coefficients for individual compounds were averaged by groups of components (see above) to obtain the average values k_j for the group. Except biphenyls XXV the greatest difference between the average value and the value determined for the individual compounds was less than 15 rel %. Biphenyls XXV obtain the coefficient for connection with methyl substituent that is about a half times less than the other. In all the samples studied in separate accounting of methyl substituted homologue and other members of the series compared with that obtained by using the group average coefficient difference of less than 5 rel %, that is acceptable. The compounds in that it was not possible to measure the empirical coefficients, according to the intensity of their peaks, amount a small fraction of each group, so that for any possible significance of these factors impact on their average value is negligible. The probable error of measurement the total concentration of the compounds—anoxia markers in the photic zone—is about 25 rel %.

The results are shown in Table 4. It should be noted that among the components C_{40} prevailing is I, concentration of II is three times less than that for component I. Elevated content of group $C_{21}-C_{27}$ are stipulated by sharply increased concentrations of XXI, XXII and, to a lesser extent, XIX.

From the stated data (Table 4) primarily it follows that in all studied samples content of anoxia markers in the photic zone is huge, ranging from about 1.2 to 7.6 wt % of the fraction, which occupies aromatic and part of saturated heteroatomic compounds (Smirnov et al., 2014). Calculating on the total malthene fraction their content lies in the same ranges as the content of a major group of alkanes—isoprenanes up to C_{20} inclusive. Smallest concentration fixed in appropriate DOM fractions and oils is about 100 times smaller—about 0.03%. Estimating the observed concentration it should be understood that all of the components — anoxia markers as a source have only 2–3 compounds which are not the basis of the lipid parts of the organisms, but pigments (see Introduction).

This concentration is not associated with any other parameter characterizing the content and composition of DOM (TOC, bitumen content, malthene fraction content, content of saturated hydrocarbons and aromatics, part of hydrogen in the aromatic ring of the total hydrogen of malthene fractions measured in (Smirnov et al., 2014) by PMR method. It does not depend on the maturity of DOM. Possible exception is the connection between the content of anoxia markers with water mineralization (parameter G/H_{30}). When considering Semiluk horizon deposits the Spearman correlation coefficient between the value of G/H_{30} and content of anoxia testifiers is -0.786 at the critical value of 0.801 for significance level 0.001 and 0.684 for significance level 0.01 (i.e., content of anoxia testifiers decreases with increasing of mineralization). However, inclusion of all the studied samples obtained correlation coefficient amounts -0.439 at the critical value 0.441 for the significance level of only 0.1 . At a low value of the ratio G/H_{30} both samples of Sargaev horizon content obtain different content of anoxia markers: in one of them—at the lower boundary of the values obtained, for the second— 5.5 wt %. Therefore, to address the issue of the relationship of water salinity and the content of compounds—anoxia testifiers in the photic layer large amount of additional data is required to attract.

CONCLUSIONS

Detailed geochemical study of carbonate and siliceous-carbonate source rocks of Semiluk–Sargaev complexes within the N–NE slope of the South Tatar uplift revealed a significant content of anoxia markers in the photic layer. For the first time total content of anoxia markers in fractions was calculated in the entire section. It is shown that they amount from 1.2

to 7.6 wt % in the fraction of aromatic compounds. Consequently, this substance was deposited under conditions of constant anoxia in the photic layer of the sedimentation basin at sufficiently high thickness of the water layer contaminated with hydrogen sulfide. Since by composition of saturated hydrocarbons the studied samples are typical for deposits of Semiluk horizon of the central part of the Volga–Ural basin, we can assume a fairly wide prevalence of such conditions within the South-Tatar arch. No relationship between the concentration of anoxia markers with any other parameter describing the content, structure or maturity of DOM has been defined. Changes in the concentrations of the components—anoxia markers—show cyclic changes of the thickness of the layer contaminated with hydrogen sulfide or bio-productivity within the studied time. Indeed, if the decrease in the concentration of the anoxia markers is stipulated by several-fold dilution by substance formed in the aerated area, it means that there has been several-fold increasing of the OM income into the sediment that has passed into the buried state. This should lead to increase of TOC and, ultimately, to negative correlation coefficient between the content of anoxia markers and TOC, which is not observed.

REFERENCES

- V. A. Bochkarev, S. B. Ostroukhov, and S. E. Sianisyan, "Concept of two-stage formation of hydrocarbon reservoirs in the western wall of the Caspian Basin," in *Success in Organic Geochemistry. Proceedings of All-Russian Conference, Novosibirsk, Russia, 2010* (Novosibirsk, 2010), pp. 64–69 (2010) [in Russian]. E. S. Brodskii, "Mass-spectrometric analysis of hydrocarbons and heteroatomic oil compounds," in *Methods of Study of Organic Compounds of Oil and Bitumens* (Nauka, Moscow, 1985), pp. 57–118 [in Russian]. D. A. Bushnev, "The composition of biomarkers in bitumen and pyrolysis products of kerogen from the Pechora-Basin Upper Devonian deposits," *Petrol. Chem.* **42** (5), 291–305 (2002).
- D. A. Bushnev, "Early Cretaceous anoxic basin of the Russian Plate: organic geochemistry," *Lithol. Miner. Resour.* **40** (1), 21–29 (2005).
- D. A. Bushnev, N. S. Burdel'naya, E. S. Ponomarenko, and T. A. Zubova (Kiryukhina), "Anoxia in the domanik basin of the Timan–Pechora Region," *Lithol. Miner. Resour.* **51** (4), 283–289 (2016).
- D. J. Clifford, J. L. Clayton, and J. S. S. Damste, "2,3,6-/3,4,5-Trimethyl substituted diaryl carotenoid derivatives (Chlorobiaceae) in petroleum in the Belorussian Pripyat River Basin," *Org. Geochem.* **29** (5–7), 1253–1267 (1998).
- G. N. Gordadze and V. I. Tikhomirov, "Geochemical characteristics of oils and dispersed organic matter from the rocks of the Central Volga–Ural Basin: hydrocarbon biomarker data," *Geochem. Int.* **43** (11), 1108–1123 (2005).
- W. A. Hartgers, J. S. S. Damste, A. G. Requejo, J. Allan, J. H. Hayes, Y. Ling, T.-M. Xie, J. Primack, and

- J. W. de Leeuw, "A molecular and carbon isotopic study towards the origin and diagenetic fate of diaromatic carotenoids," *Adv. Org. Geochem.* 1993. *Org. Geochem.* **22** (3–5), 703–725 (1994).
- R. S. Khisamov, T. A. Shardanova, A. V. Stupakova, N. P. Fadeeva, A. N. Khomyak, and V. L. Kosorukov, "Lithological–sedimentation model of the formation of highly carbonaceous complexes," in *Prospects for Increase of Resource Base of Developed Deposits, Including Domanik Sediments* (PAO Tatneft, Al'met'evsk, 2015), pp. 30–45 [in Russian].
- M. P. Koopmans, J. Koster, H. M. E. van-Kaam-Peters, F. Kenig, S. Schouten, W. A. Hartgers, J. W. de Leeuw, and J. S. S. Damste, "Diagenetic and catagenetic products of isorenieratene: molecular indicators for photic zone anoxia," *Geochim. Cosmochim. Acta*, **60** (22), 4467–4496 (1996).
- S. B. Ostroukhov, O. A. Aref'ev, V. M. Makushina, M. N. Zabrodina, and Al. A. Petrov, "Monocyclic aromatic hydrocarbons with isoprenoid chain," *Neftekhimiya* **22** (6), 723–728 (1982).
- G. S. Pevneva, A. K. Golovko, and E. A. Fursenko, "Distribution of alkylarenes in petroleums from sediments of different age," in *Success in Organic Geochemistry. Proceedings of All-Russian Conference, Novosibirsk, Russia, 2010* (Novosibirsk, 2010), pp. 269–272.
- Al. A. Petrov, *Petroleum Hydrocarbons* (Nauka, Moscow, 1984) [in Russian].
- M. B. Smirnov, E. N. Poludetkina, and N. A. Vanyukova, "Experience in application of NMR ^1H and ^{13}C spectroscopy for comparative analysis of composition of petroleums and petrolenes in source rocks by the example of the Volga–Ural PB," in *Conference of INKhS devoted to the 80th Anniversary of N.A. Plate, Moscow, Russia, 2014* (Moscow, 2014), p. 104 [in Russian].