

# A new method of «geochemical logging» for studying Domanic deposits

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**Abstract.** Based on the study of the rocks of the Semiluksky horizon from the northwestern slope of the South Tatar arch (Tatarstan Republic), new data on the ratio of scattered organic matter, carbonate and siliceous components in domanicite rocks were obtained. Based on the results of geochemical studies of the bitumoids of these rocks, new information was obtained on the distribution patterns of aromatic biomarkers in rocks of various lithological composition. Peculiarities of distribution of paleorenieratane and isorenieratane in such rocks are revealed. Due to the use of aromatic biomarkers, a number of new geochemical coefficients have been developed, which make it possible to characterize not only Domanic strata along the sediment section, but also the processes of their transformation, starting from the stage of biota formation. The substantiation of the use of these geochemical coefficients when carrying out geochemical logging along the well column to establish the boundaries of the Domanic strata formation and productive intervals in them, as well as to assess the facies conditions of their formation, is given. At the same time, the patterns established by these coefficients correlate well with other geochemical and geological parameters. The studies performed have shown that at least two types of organic matter are present in the domanicite sequence: migrational, more mature and thermocatalytically transformed, and syngenetic, less mature with a low degree of thermocatalytic transformation. The application of the developed geochemical coefficients determines a new approach to the use of «geochemical logging» in the complex of express logging while drilling. When studying cuttings, these coefficients make it possible to identify reservoir intervals, zones of fracturing and decompression, containing traces of migrational hydrocarbon fluids, moved hydrocarbons, which may indicate the presence of oil deposits. The integration of geochemical studies of cuttings with its rapid study by pyrolysis and X-ray analysis methods can significantly increase the accuracy of identifying interlayers with a high content of organic matter in the section of domanicite rocks, as well as potential reservoirs with moved migrational hydrocarbons.

**Keywords:** Domanic, domanikites, aromatic hydrocarbons, geochemical coefficients, geochemical logging, migrational bitumoids

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## Introduction

At present, much attention is paid to the study of Domanik deposits. Evaluation of the prospects for the production of shale oil from high-carbon strata of the Semiluksko-Rechitsky complex initiated the beginning of more detailed work on their study, including geochemical studies. A new stage in the study of the Semiluksko-Rechitsky high-carbon rocks (Ostroukhov et al., 2015; Plotnikova et al., 2017a, b) clearly showed that at the present stage more detailed knowledge is needed about the conditions of their formation and distribution in the depths. To do this, it is necessary to

expand the previously created and used today complex of geochemical studies, since the isolation of high-carbon strata in the section only by the amount of organic matter (OM) content in the rocks with an assessment of its catagenetic maturity is insufficient and does not fully characterize the geological history of OM formation and its distribution along the section of the sedimentary cover. In addition, the problem of identifying promising oil-saturated intervals in the section of Domanik deposits by well logging methods has not been fully resolved, and the complex of geological and technical studies used needs to be supplemented with mobile express methods of pyrolysis, X-ray studies of the rock matrix and geochemical study of dispersed organic matter and mobile hydrocarbons. The use of new geochemical coefficients will make it possible to differentiate the section of Domanik deposits by the nature of the saturating fluid and to identify areas with

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the predominant development of immobile syngenetic organic matter in dense carbonate-siliceous rocks and mobile migratory bitumoids, which are responsible for the formation of commercial accumulations.

Deposits of the Semiluksko-Rechitsky age on the territory of the Republic of Tatarstan are referred to the so-called “Domanik type” deposits. They stand out among the higher and lower bedding rocks with a certain mineralogical composition and a high content of scattered organic matter (total organic carbon, Total Organic Carbon, TOC, varies from 5 to 20% and above), which gives grounds to class them as oil shale. The standard set of geochemical studies used at the present stage does not always allow a full assessment of their features, the nature of distribution and the conditions of formation. This necessitates the creation and application of new approaches to geochemical studies of organic matter, which will expand their practical significance both at the stage of prospecting and exploration, and during the development of identified deposits.

### Materials and research methods

In this work, the object of study was the rocks of the Semiluksky horizon of the Frasnian stage of the Upper Devonian, exposed in the interval 1775–1800 m by well No. 5055 at the Tavel'skoye oil field in the Republic of Tatarstan. It should be noted that these deposits are lithologically heterogeneous and are represented by alternation of limestones, dolomitized limestones, siliceous-carbonate, carbonate-siliceous and predominantly siliceous rocks. To study them, studies were carried out by the method of X-ray phase analysis (12 samples), pyrolytic studies (16 samples), geochemical studies of bitumoids (25 samples) extracted from rocks that most fully characterize the specified interval of the section. Due to the high lithological heterogeneity of the studied interval of the section, work was carried out to identify and study interlayers of various lithological types, which contributed to obtaining more complete information for these deposits.

The studies carried out are mainly focused on the geochemical study at the molecular level of the bitumoids of rocks of the Domanik facies, the characteristic compounds of these bitumoids in rocks of various lithological composition. For these purposes, new geochemical coefficients were used, which make it possible to differentiate bitumoids according to the conditions of formation, according to the degree of thermocatalytic transformation, as well as according to their confinement to certain types of rocks of the studied section.

To study the OM of the sedimentary rocks, at the first stage, a standard complex of geochemical studies was used, including sample preparation using hot chloroform extraction, determination of the bitumen

content, followed by its division into groups by liquid column chromatography.

Oil fractions of OM of rocks were analyzed on a gas chromatography-mass spectrometer “Thermo Fisher Scientific” (USA), using computer data processing in the SCAN mode. Separation of hydrocarbons (HC) was carried out on a capillary column 30 m long, 0.32 mm in diameter with a PE-XLB phase. Chromatography was carried out in the linear programming mode from 100°C to 300°C, in the temperature range from 100°C to 150°C, the rate of temperature rise was 12.5°C per minute and 3°C per minute in the range from 150°C to 300°C. The isothermal regime at the initial temperature lasted 2 minutes, at the final (300°C) – 14 minutes. Evaporator temperature is 300°C. The carrier gas is helium, the flow rate is 2 ml/min. Under these chromatographic conditions, special attention was paid to the analysis of isorenieratane, a high-molecular aromatic compound of the composition C<sub>40</sub>. Oil fractions of OM of rocks were analyzed on a gas chromatography-mass spectrometer «Thermo Fisher Scientific» (USA), using computer data processing in the SCAN mode. Separation of hydrocarbons (HC) was carried out on a capillary column 30 m long, 0.32 mm in diameter with a PE-XLB phase.

To compare the data of gas chromatography-mass spectrometry (CMS), pyrolysis of rock samples was carried out using a HAWK Resource Workstation (Wildcat Technologies, USA) in the BulkRock mode before and after extraction, as well as X-ray studies of rock samples.

### Results

The studied area of the geological section of the well in the depth interval of 1775–1800 m is characterized by high lithological heterogeneity and is represented by alternating layers of gray or light gray limestones, dark gray siliceous limestones, as well as carbonate-siliceous, carbonate-siliceous-carbonaceous and mainly siliceous-carbonaceous rocks of black color. The thickness of the alternating layers varies from the first millimeters to 10-15 centimeters.

In the series limestone → siliceous limestone → carbonate – siliceous rock → carbonate – siliceous – carbonaceous rock → siliceous – carbonaceous rock (Figure 1), there is a decrease in the content of the carbonate component (from 100 to 11%, hereinafter, wt% is used), an increase silica content (from 0 to 80%) and an increase in TOC content (from 0.7 to 23.6%).

The content of TOC and a wide range of its values are associated with the lithotype of rocks (Figure 2). The lowest OM content, not exceeding 0.7%, is typical for limestones (Figure 3, A). An abnormally high TOC value of 23.6% was recorded in one sample of siliceous rock without carbonate interlayers (Figure 3, D). The main OM content, ranging from 3.5 to 6.5%, is associated

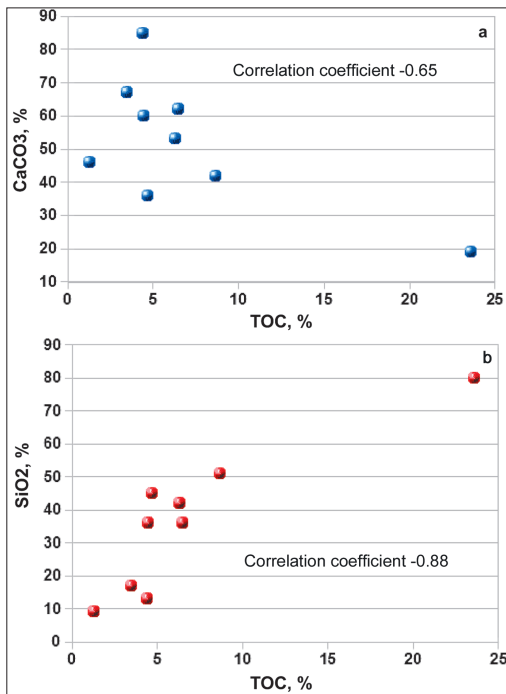


Fig. 1. Dependence of the content of total organic carbon (TOC) on the content of carbonate (a) and siliceous (b) components in the rock

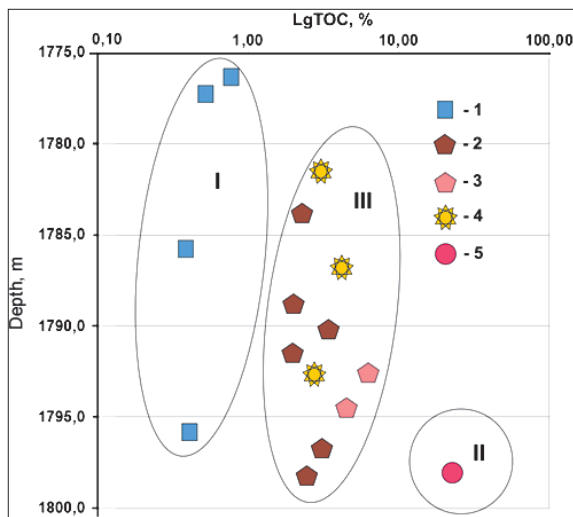


Fig. 2. TOC values in rock samples from the interval 1775–1800 m. 1 – limestones, 2 – siliceous-carbonate rocks, 3 – carbonate-siliceous rocks, 4 – fine alternation of siliceous-carbonate, carbonate-siliceous, siliceous rocks and limestone interlayers, 5 – siliceous rock (silicite).

with siliceous-carbonate and carbonate-siliceous rocks with limestone interlayers (Figure 3, B, C).

Figure 4 shows the dependence of the content of free mobile hydrocarbons S1 on the TOC of the rocks of the considered interval of the studied section. The main part of the values on it is grouped in a rather narrow range, which evenly increases with increasing TOC (blue dots), which is quite natural. However, some of the samples (red dots) indicate the presence of an increased content of mobile (allochthonous) HC in a number of samples,

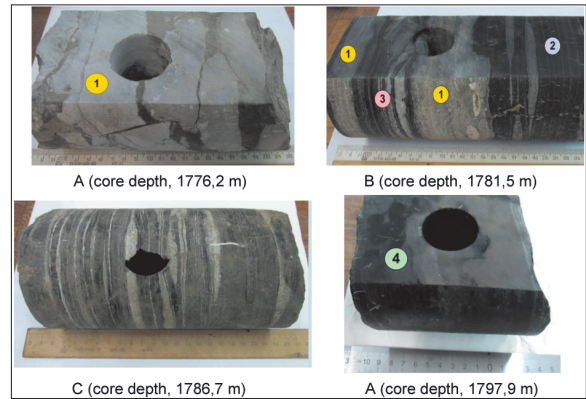


Fig. 3. Examples of rock samples from the Semiluksky horizon. A – limestone; B, C – alternation of interlayers of carbonate-siliceous and siliceous-carbonate rocks with interlayers of light limestone; D – carbonate-siliceous rock without limestone interlayers; 1 – limestone, 2 – thin interbedding of carbonate-siliceous and siliceous-carbonate rocks, 3 – thin layering of limestones and carbonate-siliceous rocks, 4 – siliceous rock (SiO<sub>2</sub> – 80%).

which may indicate different types of HC in the samples under study.

According to the results of group analysis, the composition of chloroform bitumen A (CBA) of rocks is dominated by resins with a content – from 24.31% to 64.47%, and asphaltenes – from 14.08% to 72.62%. This is mainly typical for limestone interlayers. The content of oils varies from 5 to 34% and is directly related to the OM content in the rock.

The complexity of the geological section of the Semiluksky horizon and the need to create new solutions in the search and exploration of industrial oil deposits confined to it determines the relevance of creating new geochemical approaches to the development of an effective complex of methods for finding oil in domanikites based on previously created and actively used criteria and geochemical coefficients (Petrov, 1984; Peters et al., 2005).

Expanded geochemical studies of the hydrocarbon composition of OM in the rocks of the Semiluksky horizon made it possible to identify a group of compounds characteristic of these deposits. They are monocyclic aromatic compounds of the C<sub>10</sub>-C<sub>30</sub> composition with an isoprenoid alkyl chain of irregular structure (Ostroukhov et al., 1982), which are derivatives of the natural aromatic carotenoid (AC) of the C<sub>40</sub> composition (isorenieratane). Isorenieratane (ISR) is widely represented in wildlife since the age of the Earth of 1.6 billion years (Paleoproterozoic) (Brocks et al., 2005, 2008) to the present. Moreover, its content in the natural environment has not been constant over the entire geological time. At certain periods, the content of isorenieratane (a diagenetic product of ISR) in wildlife, and then in sediments, either increased significantly or practically disappeared (French et al., 2015). One of

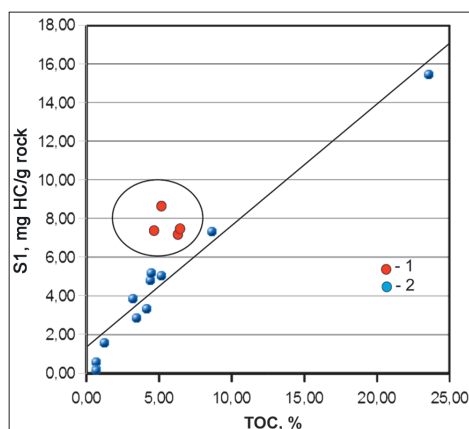


Fig. 4. The nature of the dependence of S1 (according to pyrolysis data) on TOC. 1 – S1 values indicating the presence of HC migration; 2 – S1 values, presumably not associated with migratory HC.

the periods with an increased content of isorenieratane includes the Frasco-Famennian deposits of the Late Devonian.

ISR refers to isoprenoid pigments produced by photosynthesized brown and green sulfur bacteria (Chlorobiaceae) (Maresca et al., 2008a). Since the metabolism of bacteria requires simultaneous access to both light and  $H_2S$  in their aquatic habitat, the discovery of their diagenetic and catagenetic products in the OM of rocks or oils is considered as evidence of the existence of the sulfide euxinic zone of the paleobasin (Summons, Powell, 1987; Rocks et al., 2005; Connock et al., 2018). This allows, when conducting geochemical logging, to identify similar areas in the studied sediments with the determination of their boundary values.

For the first time on the territory of the Republic of Tatarstan, isorenieratane, its diagenetic and catalytic products were found in the sediments of the Semiluki age in 2013–2014. and are described in (Ostroukhov et al., 2015). Similar compounds are observed in the rocks of the Domanik facies and in the adjacent territories of Tatarstan, which indicates the scale of the manifestation of common geological and facies conditions of sedimentation, which contribute to the periodic active development of the biota.

The mass fragmentogram scanned for ions  $m/z$  133+134 (Figure 5A) shows a group of aromatic carotenoids of the composition C14–C22 (hydrocarbons of this series are denoted by the symbol  $\Delta$ ) with methyl substitution of the benzene ring at position 2,3,6-ratio of the alkyl chain and individual compound II (isorenieratane) with methyl substitution of two benzene rings at position 2,3,6-/2,3,6- (Koopmans et al., 1996b), which are derivatives of the natural ISR of composition C40 (Figure 6).

Mass fragmentograms (Figure 5) also show the presence of a second homologous series (on the mass fragmentograms, hydrocarbons of this series

are indicated by  $\nabla$ ) and individual compound I (paleorenieratane) in composition and distribution in a series similar to compounds of the  $\Delta$  series and compound II. The structure of the compounds of this series was adopted on the basis of the studies described in the works (Hartgers et al., 1993, 1994; Clifford et al., 1998), according to which the compounds designated by  $\nabla$ , have a methyl substitution of the benzene ring at position 3,4,5- and compound I (paleorenieratane) with methyl substitution of benzene rings at position 3,4,5-/2,3,6- (Fig. 7).

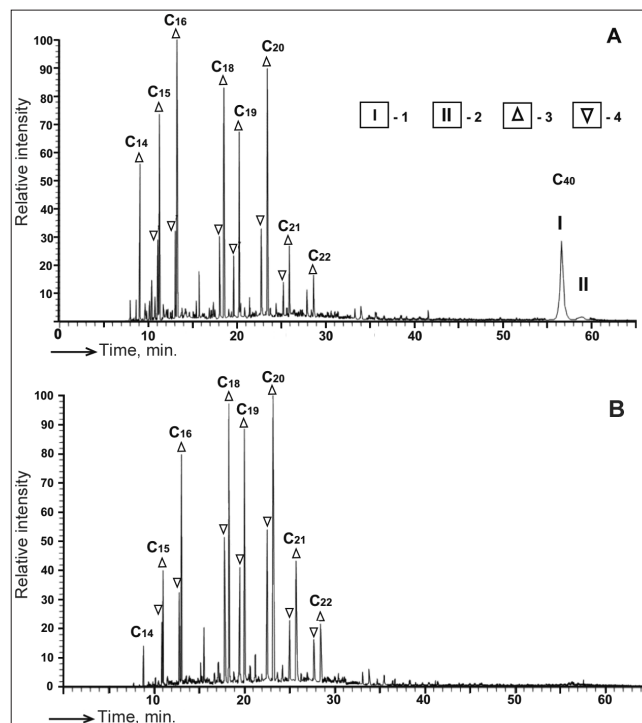


Fig. 5. Composition of aromatic carotenoids in the OM of rocks of the Semiluksky horizon, borehole 5055. A – depth 1781.0 m; B – depth 1790.5 m. 1 – 3,4,5-/2,3,6-paleorenieratane; 2 – 2,3,6-/2,3,6-isorenieratane; 3 – 2,3,6-trimethyl-1-isoalkylbenzenes; 4 – 3,4,5-trimethyl-1-isoalkylbenzenes ( $m/z$  133+134).

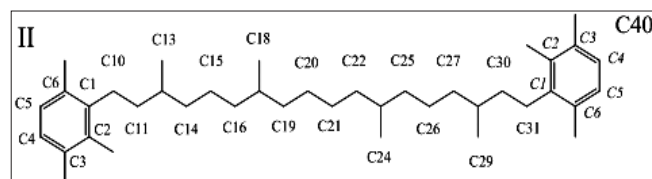


Fig. 6. The structure of isorenieratane with methyl substitution of two benzene rings at position 2,3,6-/2,3,6-, which are derived from the natural ISR of the composition C40

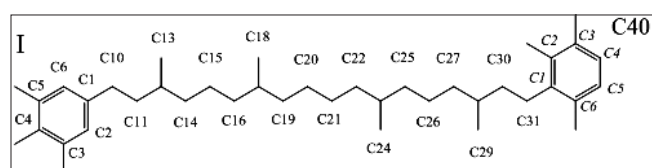


Fig. 7. The structure of paleorenieratane with methyl substitution of benzene rings at position 3,4,5-/2,3,6-

The presence of paleorenieratane (I) is noted in the OM of all rocks along the section of the Semiluksky horizon. It should be noted that its content is always higher than that of isorenieratane (II). The high representativeness of compound I implies its widespread use in the complex of geochemical studies of Domanik deposits. But this requires an understanding of the conditions for its formation and transformation in the natural environment. However, at present, there is a problem associated with the impossibility of establishing its natural analogue. In the composition of more than 700 identified natural compounds, no carotenoid compounds with methyl substitution 3,4,5-/2,3,6- in the ring have been identified (Maresca et al., 2008a). At the same time, a significant amount of compound I is present in the Late Devonian sediments (French et al., 2015). This arouses a certain interest both in its origin and in its association with Domanik type deposits.

In the natural environment, the end product of the biochemical process of transformation of carotenoids in the structure of green sulfur bacteria Chlorobiaceae under the conditions of a euxinic environment is isorenieratane (ISR) (Koopmans et al., 1996a, b). This occurs as a result of the action of the crtU genome, leading to the destruction of the geminal methyl groups of cyclohexene rings during their aromatization with the preservation of the number of methyl substituents in it with 2,3,6-/2,3,6- substitution with respect to the alkyl chain (Maresca et al., 2008b). In paleorenieratane, in contrast to isorenieratane, the methyl substitution of one of the rings is 3,4,5-.

Thermocatalytic effect on cyclic compounds with dimethyl geminal substitution in the process of aromatization leads to the destruction of the methyl group. As a result, one of the methyl groups is displaced to form two possible compounds with methyl substitution 2,3,6- and 2,4,6- (Ostroukhov et al., 1982). The formation of compounds with methyl substitution 3,4,5- was not established. Of the reaction products, only one compound with 2,3,6- substitution corresponded to oil, while compounds with 2,4,6- substitution were not found in the OM of rocks and oil. It should be added that the main product of thermocatalysis is trisubstituted alkylbenzenes with methyl substitution 2,6-, also not found in the composition of oil and OM of rocks.

The isomerization of one of the benzene rings of renieratane can be considered as one of the options for the formation of paleorenieratane (Figure 8).

Renieratane is a derivative of the naturally occurring compound renieratene (RNR) classified as a carotenoid (Schaechae et al., 1977, 1997). Renieratane is present in the OM of rocks and oils (Connock et al., 2018; Wanglu et al., 2007) of a certain age and conditions of formation of the oil source material. Isomerization of high-molecular-weight alkylbenzenes occurs mainly due to a change in

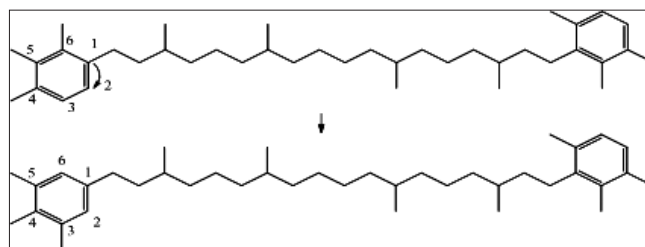


Fig. 8. Scheme of the formation of paleorenieratane as a result of isomerization of one of the benzene rings of renieratane

the position of the alkyl chain in the benzene ring. In this embodiment, the migration of the alkyl chain along the ring from position 1 to position 2 is assumed to form the most stable isomer with methyl substitution 3,4,5-. But there is some discrepancy in this, due to the fact that the methyl substitution of the isoprenoid chain, in contrast to its regular structure, blocks the migration process during thermocatalysis. In this regard, the possibility of isomerization of the benzene ring of natural RNR as a result of a biological process occurring at an early stage of the transformation of dispersed organic matter is not excluded.

At present, due to the absence of an established initial natural compound for paleorenieratane, pseudo paleorenieratane (PAR) can be taken as its precursor, by analogy with the compounds isorenieratane and renieratane. This makes it possible to fully use it for solving geochemical problems with the participation of paleorenieratane.

The representativeness and informational content of the oil series AC makes it possible to use them in a complex of geochemical studies. First of all, this concerns the features of the molecular weight distribution (MWD) of members of their homologous series. Earlier in the work (Schwark, Frimmel, 2004), the AIR coefficient (aryl isoprenoid ratio) was proposed, which reflects the ratio between the compositions C13-C17 and C18-C22 of AC in order to assess the variability and stability of the photic zone of the paleobasin under conditions of an anoxic environment. This coefficient has a narrow focus and is not capable of solving other geochemical problems. In this regard, in this work, a number of geochemical coefficients have been proposed that make it possible, through the composition of the AC, to characterize some of the processes associated with the formation and transformation of the initial OM in the composition of Domanik rocks.

One of the main indicators in the complex of geochemical studies is the thermocatalytic transformation of organic matter. This characteristic can be obtained based on the transformation of a number of AC compounds, expressed by the coefficient:

$$Kac1 = [\sum C10 / (\sum C10 + CI + CII)],$$

where  $\sum C10$  is the sum of prenitol and isodurool; CI – content of paleorenieratane (I); CII is the content of isorenieratane (II).

The coefficient is based on the ratio of the contents of compounds I and II and alkylbenzenes of composition C10 with methyl substitution of the benzene ring at positions 1,2,3,4- (prenitol) and 1,2,3,5- (isodurool), shown in Figure 9. The choice of these compounds is based on the fact that alkylbenzenes of composition C10 are the main products of thermal destruction of individual compounds I and II. This process has been confirmed by laboratory studies on rock samples with a high content of compounds I and II. In all products of flash pyrolysis up to 650°C of the studied rocks, a high content of two newly formed target compounds of composition C10 and a complete absence of starting compounds I and II were observed (Figure 10A, B). In this case, the preservation of the initial compounds of AC with the composition C16-C22 was also observed, which indicates a high thermocatalytic stability of these compounds and the absence of their effect on the formation of C10. This is also indicated by their dominance in the composition of pyrolysis products, in contrast to extracts.

It should be especially noted that the pyrolysis products do not contain low-molecular AC compounds with the composition C11-C15. It is known that the composition of the OM pyrolysis products is mainly represented by low-molecular aliphatic and cyclic compounds formed due to the destruction of high-molecular compounds. The absence of low molecular weight AC indicates the impossibility of high molecular weight analogs under these conditions to form compounds other than C10. At the same time, their presence in the composition of oils arouses interest in the process that contributes to their formation. Most likely, it is realized at an early stage of transformation of the initial oil source material.

The value of the coefficient Kac1 reflects the degree of transformation (destruction) of compounds I and

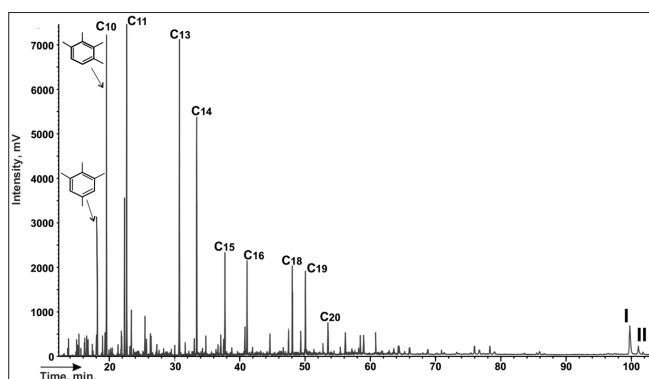


Fig. 9. Composition of aromatic carotenoids in oil ( $m/z$  133+134). C10-C20 is the number of carbon atoms in the molecule; I – 3,4,5-/2,3,6-paleorenieratane; II – 2,3,6-/2,3,6-isorenieratane.

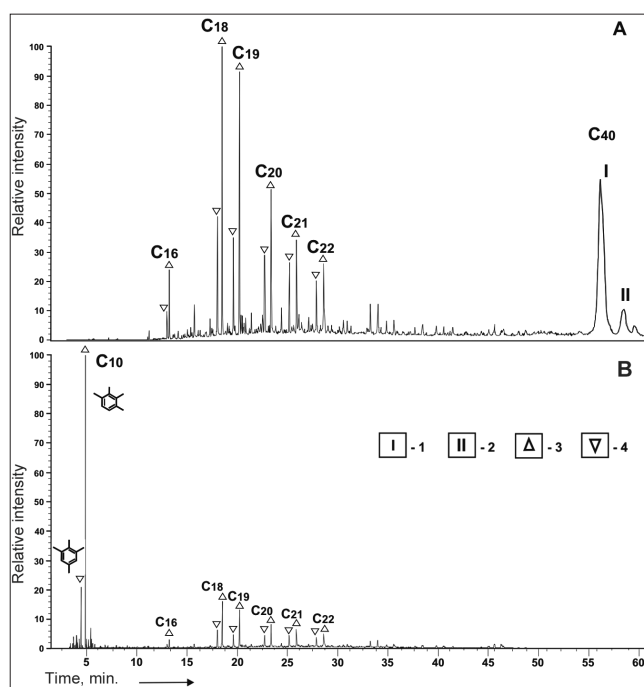


Fig. 10. Composition of aromatic carotenoids in the extract of the original sample (A), and in the product of its flash pyrolysis (B). 1 – 3,4,5-/2,3,6-paleorenieratane; 2 – 2,3,6-/2,3,6-isorenieratane; 3 – 2,3,6-trimethyl-1-isoalkylbenzenes; 4 – 3,4,5-trimethyl-1-isoalkylbenzenes ( $m/z$  133+134).

II. The maximum value of Kac1 is associated with the complete absence of compounds I and II in the oil composition. The Kac1 values for oils from the Semiluksky horizon in Tatarstan range from 0.7 to 1.0. That is, in a number of the studied oils, compounds I and II are practically absent.

The use of this coefficient to estimate the OM of rocks in most cases is difficult due to the absence in the homologous series of compounds with a composition up to C14, including alkylbenzenes C10 (Figure 5A, B). Despite this, rock samples that do not contain compounds I and II (Figure 6B) can be classified as highly transformed. These, in the considered depth interval, include all OM samples from limestone deposits that do not contain or contain compounds I and II at the background level (Figure 5B).

The organic matter of all carbonate-siliceous-carbonaceous rocks contains a sufficiently large amount of compound I with an insignificant content of compound II (Figure 5A). Unfortunately, the absence of C10 alkylbenzene in the composition of the samples does not allow us to determine the degree of their transformation, but the presence of compounds I and II indicates that it is much lower than for limestone deposits.

The composition of homologous series  $\nabla$  and  $\Delta$ AC of organic matter of rocks of the Domanik facies is represented by compounds C14-C22 of different intensities, in contrast to unfractionated oils, in which the composition of the homologous series starts from

C10. But the fact that low-molecular-weight C10-C13 compounds could be in their composition is beyond doubt, since they are an integral part of homologous series in the composition of oils in Domanik deposits, representing full-fledged products of a single process of destruction of the initial natural compounds ISR and PAR.

When considering the composition of homologous series, the absence of members of the series above C23-C30 is observed. In the presence of a high content of C10-C19 compounds formed as a result of chain destruction of ISR and PAR compounds of C40 composition, it is logical to expect the presence, respectively, of fragments of the C21-C30 composition with the same content. Nevertheless, they are practically absent or present in small quantities in the OM of rocks. This fact requires additional research. But such a distribution is possible due to the destruction of natural C40 compounds Chlorobactene (Maresca et al., 2008b), which have one benzene ring in their structure.

Despite the above-mentioned features of AC formation, the molecular weight distribution of members of their homologous series is highly informative and can be successfully used in the study of OM in Domanik deposits. Compounds of homologous series  $\nabla$  and  $\Delta$  have their own regularities, reflecting a wide range of natural processes associated with the formation of hydrocarbon deposits. This should include the genetic relationship between the compounds of the series  $\Delta$  and I, since they, presumably, are products of the natural compound PAR containing one of two benzene rings with methyl substitution 3,4,5-. In turn, the members of the  $\Delta$  series are represented by the sum of the degradation products of the initial natural compounds PAR and ISR containing benzene rings with methyl substitution 2,3,6-.

Since in the composition of oils and organic matter of rocks there is a significant dominance of compound I over II, it is interesting to follow this pattern for low-molecular compounds of the same composition. The predominance of one or another natural compound (PAR or ISR) in the formation of the composition of the  $\Delta$  and  $\nabla$  series can be estimated based on the following coefficient:

$$Kac2 = PAR / (PAR + ISR) = 2\sum C\nabla / (2\sum C\nabla + \sum C\Delta),$$

where  $2\sum C\nabla$  characterizes the contribution of PAR to the formation of members of the homologous series  $\nabla$ ,  $\sum C\nabla$  is the sum of the heights H or the area S of chromatographic peaks C15-C22.

The  $\sum C\Delta$  value characterizes the share of ISR in the composition of the  $\Delta$  series members. Their number is determined as a result of deducting from the total content of the member of the series the share of  $C\nabla$ .

Due to the fact that in most cases the ratio between the peaks of the same composition in the series  $\Delta$  and  $\nabla$  remains practically unchanged, then in the calculation of this coefficient, the values of AC C18 can be used.

In the OM of carbonate-siliceous-carbonaceous rocks, the Kac2 coefficient is 0.40, which indicates the predominance of ISR over PAR during the formation of compounds of the  $\nabla$  and  $\Delta$  series. In the OM of limestones, the prevalence of ISR is also observed, as indicated by the value of the considered coefficient, which is 0.45. The difference between them sufficiently indicates the absence of a direct genetic link. The OM values of rocks with interlayers fall into the intermediate region with an interval of 0.41–0.44. Moreover, depending on the predominance and nature of the interlayer, they tend to one or another area of its location.

Comparison of the results obtained in order to establish the effect of natural compounds ISR and PAR on the composition of members of the homologous series  $\nabla$  and  $\Delta$  and compounds I and II revealed a certain pattern. One might expect that during the formation of the composition of oil or OM of rocks, both for low-molecular hydrocarbons and for high-molecular compounds I and II of composition C40 one type of initial substance should prevail, but this is not the case. In practice, it is revealed that for the Domanik deposits of Tatarstan, in the composition of the homologous series  $AC\nabla$  and  $\Delta$ , there is a predominance of ISR products over PAR, as indicated by the values of  $K = 0.35–0.49$ . At the same time, for the same deposits among compounds I and II, the PAR product always prevails over ISR in a ratio of 2 to 10 times. From this it follows that ISR is almost completely converted into low molecular weight compounds, while PAR is more preserved and is represented in high molecular weight compound I. This indicates a rather complex nature of the transformation of the initial natural substances of the carotenoid type in the interior.

For the complex characterization of OM of Domanik deposits, the coefficient  $Kac3 = (C\Delta + C\nabla) / (C\Delta + C\nabla + C_I + C_{II})$  was also used, developed on the basis of compounds I and II and members of the series  $\nabla$  and  $\Delta$  of composition C20. The members of the indicated series are accepted on the basis of their location in the representative area of the sample composition. This is especially true for the OM of rocks subject to the greatest changes. The Kac3 coefficient supplements the information obtained by using the Kac1 and Kac2 coefficients on the processes associated with the formation and change in the composition of this group of compounds. Kac3 is based on the ratio of compounds I and II to the degradation products of the initial biological substance. The main changes in the values of the coefficient in a single geological object are associated with the content of  $C_I$  and  $C_{II}$ , which is significantly influenced by both thermal impact and migration through porous media. Clarification of the dominance of one of these processes, if necessary, is carried out according to the results of comparison with other specialized methods of analysis.

For the considered Domanik sediments, opened within the Republic of Tatarstan, due to the absence or extremely low content of compound II ( $C_{II}$ ) in the OM of rocks, a coefficient with a simplified set of parameters was used:

$$Kac3 = 2C_{\nabla} / (2C_{\nabla} + C_I).$$

Figure 11 shows the change in the value of this coefficient ( $Kac3$ ) with the depth of the rocks in the section of the interval under consideration. Its values vary in a fairly wide range from 0.3 to 1.0. At the same time, low  $Kac3$  values are associated with a high content of compound I in the composition of the OM of rocks, while high values are associated with its decrease.

Comparison of the  $Kac3$  values with the lithological type of rocks reveals a certain relationship between them. For example, it was found that its lowest values (up to 0.55) are characteristic of the OM composition of carbonate-siliceous-carbonaceous rocks, which is associated with the high content of compound I. Its highest values (over 0.8) are characteristic of OM in interlayers light gray limestone. It is necessary to pay attention to the range of values of the coefficient  $Kac3$  in the range of 0.55–0.8. These values are typical for rock samples from the transitional region between carbonate-siliceous-carbonaceous varieties containing paleorenieratane and light gray limestones not containing paleorenieratane. The lithology of these rocks has a more complex composition and is represented by thin interlayers that are difficult to separate during sample preparation. This affects the values of the coefficient characterizing the total OM composition of these interlayers.

For a comparative assessment of the transformation of the OM composition in the rocks, the C27 hopane isomers with the Ts and Tm configurations, traditionally used in the complex of geochemical studies, were used. The use of hopanes is associated with a high bacterial activity (Kannenberget al., 1999) in the anaerobic sulfide euxinic environment of the considered paleobasin.

Thermocatalytic action on saturated polycyclic compounds leads to their isomerization with the accumulation of more thermodynamically stable isomers in the mixture. The required thermal energy in the interior increases with the depth of OM, thus activating isomerization in the composition of hopane of the composition C27 with the Tm configuration in Ts. To assess this process in practice, the coefficient  $Kg = Ts / (Ts + Tm)$  is widely used, the values of which are in the range 0–1. The maximum  $Kg$  value indicates the complete transformation of hopane with the Tm configuration into Ts and, accordingly, a high degree of the thermocatalytic process.

The values of the coefficient  $Kg$  for the investigated samples vary in the range from 0.1 to 0.4 and indicate a low degree of thermocatalytic conversion. Figure 11 shows the distribution of values with the depth of the

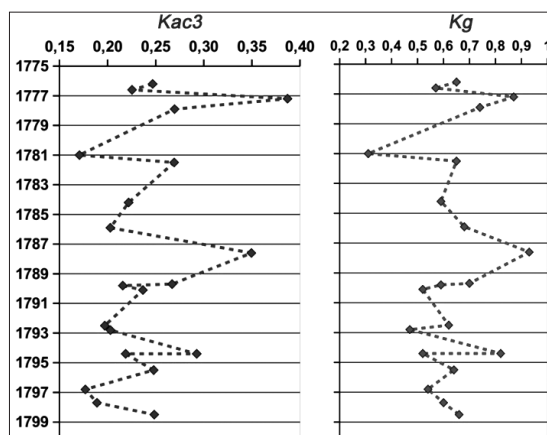


Fig. 11. Distribution of the values of the coefficients  $Kac3$  and  $Kg$  in the depth interval 1775–1800 m.

samples. It is quite natural that due to the small thickness of the studied interval, this distribution does not reveal any definite relationship with the depth of the samples. However, there is a dependence of the values of the coefficient  $Kg$  on the lithology of rocks. The lowest  $Kg$  values (up to 0.15) are characteristic of OM-enriched carbonate-siliceous-carbonaceous rocks with the highest content of compound I.  $Kg$  values above 0.27 are characteristic of the OM of limestones or siliceous-carbonate rocks with a low silica content, which are depleted of OM. Paleorenieratane is absent or is at the background level.

The  $Kg$  values equal to 0.15 and 0.27 characterize the transition region associated with the heterogeneity of the rock due to the presence in it of thin interbedding of limestones and carbonate-siliceous-carbonaceous varieties. The dominance of one or another interlayer in the sample brings its value closer either to the group of limestones or to the group of carbonate-siliceous rocks enriched in OM.

In a small interval of depths, the wide scatter of the values of the coefficient  $Kr$ , which reflects the activity of the isomerization process, requires a special explanation, which cannot be linked with the difference in the catalytic activity of rocks with practically the same thermal effect on the formation. The catagenic transformation of OM in pure limestones, based on the values of the coefficient, is 2 times higher than that for carbonate-siliceous and siliceous rocks. At the same time, attention is drawn to the clear separation of OM according to the values of transformation at the boundaries of the interlayers. This indicates the absence of a genetic relationship between the OM of limestones and the OM of carbonate-siliceous interlayers.

Comparative analysis of the values of the coefficients  $Kac2$  and  $Kg$  from the depths of occurrence showed a certain relationship between them. The following basic patterns are noted:

- in sediments with low isomerization of hopane C27, a high content of paleorenieratane is observed;



- in sediments with high isomerization of hopane C27, the absence of paleorenieratane is observed;
- in layered rocks, the transformation of hopan and paleorenieratane changes synchronously depending on the composition of the rock.

The correlation relationship between the values of  $K_{ac3}$  and  $K_g$  is well illustrated in Figure 11. A decrease and an increase in the values of these coefficients is observed synchronously in a narrow interval of depths, which indicates that hydrocarbons with a high degree of catagenetic transformation are mainly associated with interlayers filled with pure limestone (in which, according to according to pyrolysis data, the presence of syngenetic OM is minimal). Thus, in a narrow interval with a thickness of 15 m, hydrocarbons formed under different catagenetic conditions are simultaneously present. Considering that the temperature difference during the entire geological evolution of the studied section interval (15 m) did not exceed 2°C, the presence of hydrocarbons formed at higher temperatures in this interval unambiguously indicates the presence of at least two HC-systems in the studied part of the section – syngenetic scattered OM, the catagenetic degree of transformation of which is small, and migratory hydrocarbons that migrated into fractured limestone layers from another source and have a different genesis. The issue of the presence of migratory bitumoids in the Domanik strata and in other overlying horizons of the sedimentary cover was considered earlier (Plotnikova et al., 2017a, b).

Consequently, the observed regularities in the change in the composition of the OM of rocks indicate the influence on it of the migration process of hydrocarbons that entered the studied rocks from another source of their formation.

In our case, the higher isomerization of hopane and the absence of compounds I and II in the bitumoids from the interlayers of pure limestone indicate a higher thermocatalytic transformation of these hydrocarbons in comparison with the original syngenetic matter of the siliceous-carbonaceous-carbonate interlayers of the Semiluksky horizon.

Taking into account the practical absence of syngenetic organic matter in limestone interlayers and their low catalytic activity, as well as the conditions of their formation, which do not contribute to a high transformation of syngenetic organic matter, the following can be assumed. One of the reasons for the presence of hydrocarbons in a narrow interval of the geological section, significantly differing in the degree of catagenetic transformation, is that hydrocarbons characterized by high thermocatalytic transformation are migratory, that is, they migrated into the studied rocks of the Semiluksky horizon from another source of generation associated with high-temperature formation conditions hydrocarbons. At the same time,

carbonate interlayers, which have increased porosity and permeability in comparison with dense siliceous-carbonaceous ones, have more favorable conditions for the migration of mobile hydrocarbons along them. It was also established that the source of the formation of these migratory bitumoids is not related to the syngenetic OM of the siliceous-carbonaceous rocks of the Semiluksky horizon in the study area, but is probably of a deep nature.

### Conclusions

The studies carried out have shown that at least two types of bitumoids are present in the Domanikite sequence – migratory, more mature and thermocatalytically transformed, and syngenetic, less mature with a low degree of thermocatalytic transformation (autochthonous and allochthonous bitumoids, as it was commonly called earlier). This conclusion fully confirms the previously obtained results (Ostroukhov et al., 2017; Plotnikova et al., 2017a, b), which indicate the presence of migratory bitumoids in the rocks of the sedimentary cover and in the Semiluksky horizon, which are not related by their genesis to the scattered organic matter of the Domanik complex rocks within the study area. The use of new geochemical coefficients based on aromatic carotenoids characteristic of Domanik deposits allows, at a new level, in the “geochemical logging” mode, to assess the presence of “mobile” migratory and “stationary” syngenetic hydrocarbons in the rocks. This will make it possible to differentiate the section of the Semiluksky horizon and reveal dense interlayers with a high content of syngenetic OM, reservoir intervals and fracture zones.

It is logical to assume that migratory hydrocarbons are mainly associated with more permeable and fractured rocks, which include interlayers of limestones and siliceous-carbonate rocks. Carbonate-siliceous-carbonaceous and siliceous rocks enriched with OM, due to their lower permeability, seem to accept less “mobile” migratory hydrocarbons, while maintaining the composition of syngenetic organic matter and indicators of a low degree of its transformation.

The developed geochemical coefficients are the basis for a new approach to the use of “geochemical logging” in the general complex of express geological and technological research in the process of drilling wells. This approach can be very effective in determining OM concentrations in high-carbon strata, complementing gamma ray data, since there is a positive correlation between OM and uranium content. These new coefficients can be successfully applied in the study of cuttings to determine the reservoir intervals, fracture and decompaction zones, in which there are traces of hydrocarbon fluid migration, mobile HC, which may indicate the presence of oil deposits.

The integration of geochemical studies of cuttings with its rapid study by pyrolysis and X-ray analysis methods will significantly increase the accuracy of identifying interlayers with a high OM content in the Semilukski horizon, as well as potential reservoirs with mobile hydrocarbons.

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