

Transformation of Terrestrial Organic Matter during Mesocatagenesis and Apocatagenesis

A.E. Kontorovich , K.V. Dolzhenko, A.N. Fomin

Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences,
prosp. Akademika Koptyuga 3, Novosibirsk, 630090, Russia

Novosibirsk State University, ul. Pirogova 1, Novosibirsk, 630090, Russia

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Abstract—A combination of modern analytical methods was used to study terrestrial organic matter from upper Paleozoic rocks in the central part of the Vilyui hemisyncline (East Siberia) sampled from the depth interval 3370–6458 m penetrated in the Srednevelyuiskaya-27 superdeep well. In this study, we used 71 core samples to trace depth variations in the geochemical characteristics of organic-matter during middle–late mesocatagenesis and apocatagenesis: organic carbon content (C_{org}), Rock-Eval pyrolysis parameters (HI, T_{max}), carbon isotope composition, thermal maturity (R_{vt}^o , %), hydrocarbon type composition (hydrocarbons, resins, and asphaltenes), distributions of *n*-alkanes (TIC), steranes (m/z 217), and terpanes (m/z 191), and standard biomarker indices with increasing degree of thermal maturity. It is shown that during late mesocatagenesis and apocatagenesis, the pyrolysis parameters and biomarker indicators are no longer effective as indicators of organic-matter maturity and genesis.

Keywords: Vilyui hemisyncline, upper Paleozoic deposits, terrestrial organic matter, pyrolysis, hydrocarbon type composition, biomarker hydrocarbons, catagenesis

INTRODUCTION

The term “terrestrial” organic matter (OM) implying that it is developed on dry land (from Latin “terra” – Earth, land, ground) was proposed by A.E. Kontorovich as a substitute for the term “humic” OM, which has been widely used in Russian language scientific literature in the 1950–1970’s (Kontorovich, 1976). When choosing the term, the author also took into account the semantic closeness of the words in the original term used in the English language scientific literature terrestrial organic carbon, terrestrial organic matter. Arguments for abandoning the term “humic” were first proposed by N.B. Vassoevich (Vyshemirskii et al., 1986). Terrestrial organic matter originates from higher land plants.

The thermal maturity of terrestrial OM and, especially, its bituminous components at higher grades of catagenesis, beyond the oil window is not well understood. One of the first such attempts to study this problem was analysis of coals from different regions of Siberia (Kontorovich et al., 1973a,b; Danilova et al., 1974; Kontorovich et al., 1974).

The impetus for much of these theoretical developments on the catagenesis of terrestrial organic matter at great depths has been supplied in 1982–1984 by drilling of the Srednevelyuiskaya-27 superdeep well on the Khapchagai

swell in the Vilyui hemisyncline (A.M. Zoteev, V.E. Bakin) (Fig. 1). The core samples taken from the upper Paleozoic sedimentary complex in the Srednevelyuiskaya-27 well were used to study the gradual change in terrestrial OM at depths from 3.0 to 6.5 km during mesocatagenesis and apocatagenesis. These core samples were analyzed in previous studies (Perozio et al., 1981; Kontorovich et al., 1988).

This historic core was resampled from the Srednevelyuiskaya-27 at the initiative of A.N. Fomin in 2015–2019 and was used for further analysis (Kashirtsev et al., 2016, 2017; Dolzhenko et al., 2019). This study is a continuation of previous research.

MATERIALS AND METHODS

In this study, we used 71 core samples from the historic core taken from the Srednevelyuiskaya-27 well for a detailed geochemical analysis using the procedure developed in Trofimuk Institute of Petroleum Geology and Geochemistry, Siberian Branch, Russian Academy of Sciences. Based on the analysis of core samples from depths of 3370–6458 m, the following data were obtained: the level of organic maturity (R_{vt}^o , %), Rock-Eval pyrolysis parameters (HI, T_{max}), hydrocarbon type composition (hydrocarbons, resins, asphaltenes), organic carbon content (C_{org}) per rock, carbon isotope composition ($\delta^{13}C$), and distributions of the indivi-

 Corresponding author.

E-mail address: KontorovichAE@ipgg.sbras.ru (A.E. Kontorovich)

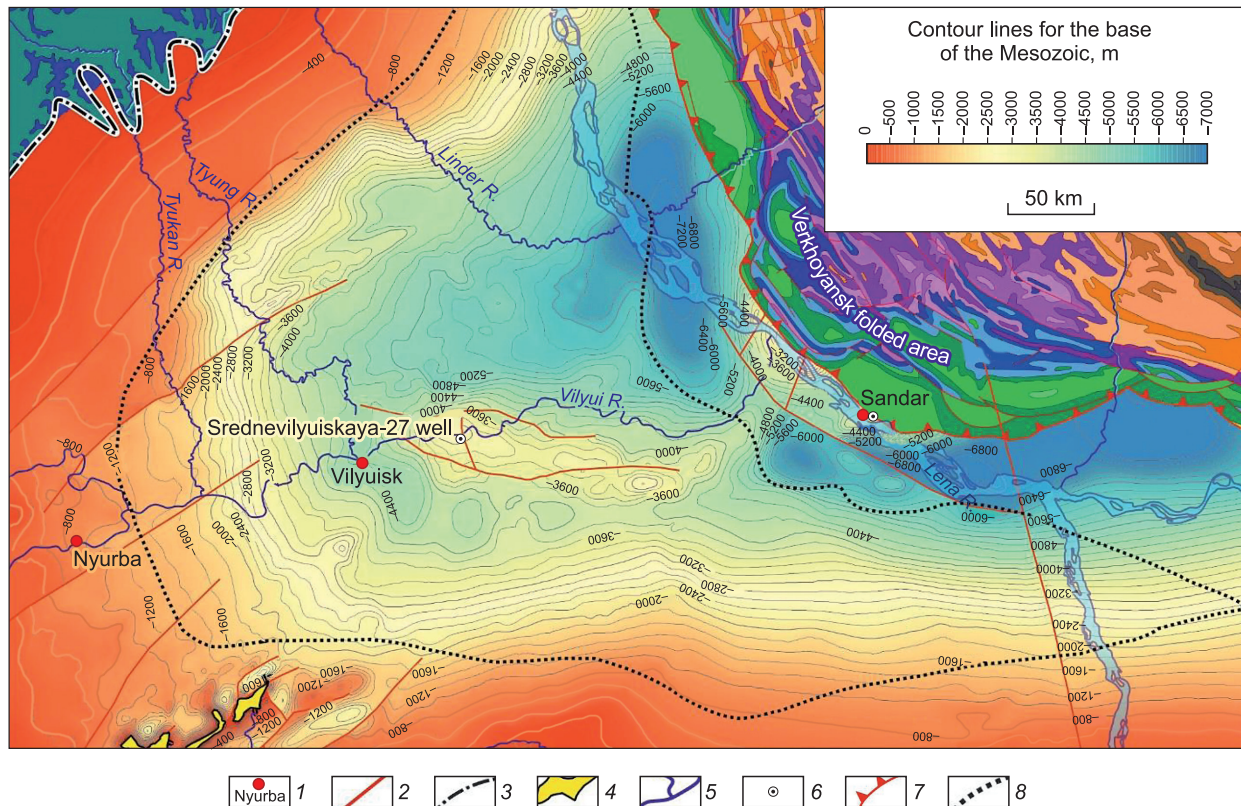


Fig. 1. Structural map for the base of the Mesozoic (after I.A. Gubin). Legend: 1, settlements; 2, faults; 3, boundary of Cambrian outcrops; 4, outcrops of the Devonian, Carboniferous and Permian within the Kempendyai faults; 5, rivers; 6, location of Srednevelyuiskaya-27 well; 7, the outer boundary of the thrust zone from the side of the Verkhoyansk folded area; 8, the boundary of the Vilyui petroleum area.

dual biomarker hydrocarbons. Organic matter was extracted from sedimentary rock samples with chloroform and asphaltene were precipitated with petroleum ether. Maltenes were further separated into fractions by column chromatography. The saturated and aromatic fractions were analyzed by chromatography-mass spectrometry using the Agilent 6890 gas chromatograph with the 5973N mass-selective detector. Vitrinite reflectance measurements were performed on a MSFP-2 microscope spectrophotometer. Quantification of organic matter was performed by Rock-Eval pyrolysis in the absence of oxygen, by double analysis of each sample. The total organic carbon content of rocks was determined on an AN-7529 carbon analyzer. The carbon isotope composition was measured on a MI 1201B mass spectrometer.

RESULTS

Geology of the study area. Geochemical characteristics of organic matter from upper Paleozoic sediments of the Vilyui hemisyncline. The Carboniferous-Permian and Permian section of the Vilyui hemisyncline is represented by lacustrine-boggy and alluvial, deltaic, coal-bearing deposits, as well as by shelf and marginal marine deposits in the easternmost part of the Verkhoyansk trough (Kontorovich, 1994;

Parfenov and Kuzmin, 2001). The upper Paleozoic strata penetrated in the Srednevelyuiskaya-27 well are composed of alternate layers of sandstones, siltstones and mudstones with carbon-rich organic material and thin coal seams.

The lithologic and stratigraphic characteristics of the upper Paleozoic section of the Vilyui hemisyncline were given using data from previous studies (Golubeva et al., 1980; Grausman et al., 1986). The top of the Permian coal-bearing complex is traced in the Outer belt of the Vilyui hemisyncline at depths of 0–600 m in the northwest, 0–1000 m in the west, 400–1200 m in the southwest, and 600–2000 m in the south (Fig. 1). In the inner region of the Vilyui hemisyncline, the top of the Permian section is mapped at depths of 2900–4200 m on the Khapchagai swell, 2600–4400 m on the Loglor swell, 4200–6200 m in the Linde depression, and 4200–7200 m in the Lunkha depression. The thickness of the Permian section varies from 0 to 300 m in the Outer Belt and increases to 3000–3400 m in the Linde and Lunkha depressions in the inner region.

In the Srednevelyuiskaya-27 well, the top and base of the Permian section are at depths of 2922 and 6073 m, respectively. The presence of upper Carboniferous plant remains (Golubeva et al., 1980; Grausman et al., 1986) in the underlying beds (6073–6519 m) suggests a late-middle Carbonif-

Table 1. Depths of the top and base of the Permian and Carboniferous formations penetrated in the Srednevelyuskaya-27 ultradeep well (after Golubeva et al. (1980), Grausman et al. (1986))

| Stratigraphy | | | Top, m | Base, m | Thickness, m |
|------------------|--------------|------------|--------|---------|--------------|
| System | Division | Formation | | | |
| Triassic, T | Lower | Taganzhin | 2465 | 2868 | 403 |
| | | Nedzhelin | 2868 | 2922 | 54 |
| Permian, P | Upper | Taragai | 2922 | 3226 | 304 |
| | | Kyundei | 3226 | 3480 | 254 |
| | | Kharyya | 3480 | 3887 | 407 |
| | Lower | Khomustakh | 3887 | 4305 | 418 |
| | | Kubalangda | 4305 | 4696 | 391 |
| | | Kharbalakh | 4696 | 5143 | 447 |
| | | Chochos | 5143 | 5663 | 520 |
| | Yyunkyur | 5663 | 6073 | 410 | |
| Carboniferous, C | Middle-upper | Yuren | 6073 | 6519 | 446 |

erous age. The thickness of the penetrated Permian section exceeds 3 km. Sediment core samples collected from the interval 3370–6519 m characterize the following formations (Table 1): Kyundei, kn (3226–3480 m); Kharyya, hr (3480–3887 m); Khomustakh, hm (3887–4305 m); Kubalangda, kb (4305–4696 m); Kharbalakh, hrb (4696–5143 m); Chochos, cc (5143–5663 m); Yunkur, jn (5663–6073 m); Yuren, jr (6073–6519 m). Throughout this depth interval, organic matter has a terrigenous, coal-bearing and sub-coal-bearing nature. This type of OM is confirmed by petrographic characterization, and chemical analysis of dispersed organic matter and coals.

In this study, the palynological analysis indicates that the Permian flora was dominated by gymnosperms (cordaites, ginkgos, cypresses) and grassy vascular ferns (Mikhailova et al., 2011). The presence of higher land plants as the main source of organic matter in Permian deposits is also confirmed by the carbon isotope composition (Kontorovich et al., 1985a,b) (Table 2). The core analysis shows that the carbon isotope composition of coals and kerogen from Permian and Carboniferous deposits of the Vilyui hemisyncline varies from –26.9‰ to –21.8‰, being most often between –25.0‰ and –23.0‰ (Fig. 2).

In most upper Paleozoic samples collected from the Srednevelyuskaya-27 well, the total content of organic carbon (C_{org}) varies from 0.11 to 0.45% (mean 0.22%) for sandstones, from 0.58 to 1.92% (mean 1.17%) for siltstones, and from 1.06 to 2.76% (mean 1.81%) for mudstones (Table 3). Due to the presence of layers of carbonaceous material, the highest concentrations of organic carbon are detected in carbonaceous siltstones (2.27–3.90%, mean 3.01%).

The catagenesis of organic matter was studied in the depth intervals of 890 to 6458 m (Fig. 3). This figure has been published previously (Kashirtsev et al., 2017) to consider the effect of the levels of thermal maturity on biomarker indices, but it was not discussed with respect to the influence of geological processes on thermal maturation of organic matter and source rocks. Thermal maturity of organic matter was studied in wells drilled in the depth range of 890–2744 m on the northwestern side of the Vilyui hemisyncline, in the depth range of 2336–2854 m on the southern side (additional two core samples taken from depths of 908 m and 3839 m), 2572–3936 m on the Loglor swell (one additional core samples taken at a depth of 1402 m) and 2840–6458 m on the Khapchagai megaswell (one sample from a depth of 1681 m). Vitrinite reflectance measurements

Table 2. Carbon isotope composition of rocks of the upper Paleozoic formations penetrated in the Srednevelyuskaya-27 ultradeep well

| System | Formation | $\delta^{13}C$, ‰ | | | Number of samples |
|---------------|------------|--------------------|-------|-------|-------------------|
| | | min | max | mean | |
| Permian | Kyundei | –23.1 | –22.5 | –22.9 | 4 |
| | Kharyya | –25.9 | –22.8 | –24.2 | 16 |
| | Khomustakh | –23.5 | –23.4 | –23.5 | 3 |
| | Kubalangda | –24.2 | –24.1 | –24.2 | 2 |
| | Kharbalakh | –26.9 | –23.5 | –24.7 | 12 |
| | Chochos | –26.7 | –21.8 | –24.4 | 13 |
| | Yyunkyur | –25.8 | –23.8 | –24.7 | 8 |
| Carboniferous | Yuren | –25.9 | –23.9 | –24.8 | 4 |

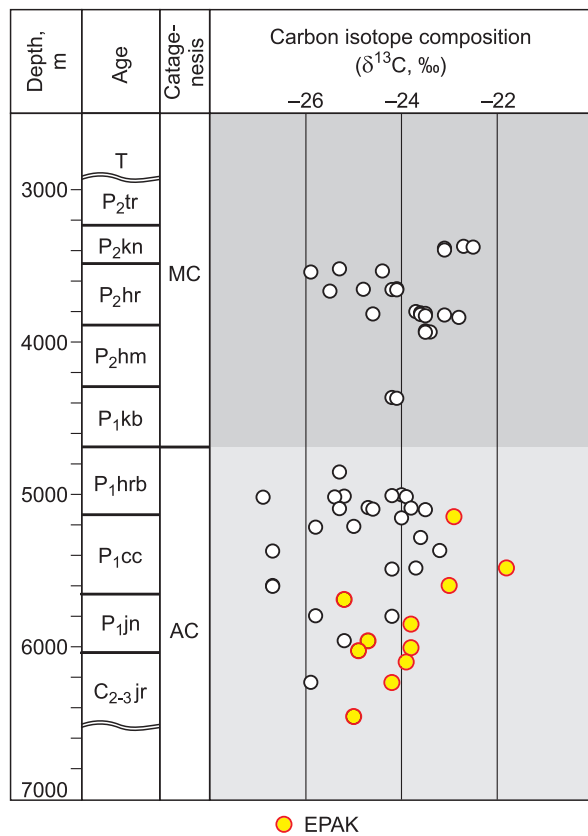


Fig. 2. Distribution of organic carbon isotopes ($\delta^{13}\text{C}$) in the upper Paleozoic section penetrated in the Srednevelyuiskaya-27 well. EPAK, Epiaspaltenic kerogen.

were conducted in the Srednevelyuiskaya-27 well in the depth interval of 3370–6458 m.

Below we consider the depth variation in the catagenesis grades (Fig. 3; Table 4). In the depth range of 680–1800 m, the values of vitrinite reflectance in oil (R_{Vt}^{o}) remain almost the same and ranges from 0.45 to 0.60% ($\text{PC}_3\text{--MC}_1^1$ grades), then gradually increasing down the section from 0.55–0.65% (MC_1^1) at 2300–2700 m to 0.65–0.85% (MC_2^1) at 3400–3700 m. In the Srednevelyuiskaya-27 well, an abrupt increase in the vitrinite reflectance to 1.00–1.15–1.40% ($\text{MC}_2\text{--MC}_3^1$) is recorded in the depth interval of 3300–3900 m. At 5000–6458 m, the vitrinite reflectance increases steadily from 2.90 to 4.80% ($\text{AC}_2\text{--AC}_3$). Rapid changes in vitrinite reflectance values (R_{Vt}^{o}) in the depth intervals of 3300–3900 m (Kharyya Formation–top of the Khomustakh Formation) and 5200–5500 m (Chochos Formation) are probably associated with the presence of dolerite dikes near the wellbore. This assumption is supported by the presence of layers of tuff sandstones and tuffites at the top of the Kyundeï Formation (Grausman et al., 1986). In some cases, variations in vitrinite reflectance with depth (Fig. 3) can also be explained by postcatagenetic vertical tectonic movements.

In the Srednevelyuiskaya-27 well, organic matter in the upper part of the Permian section above the Kharbalakh For-

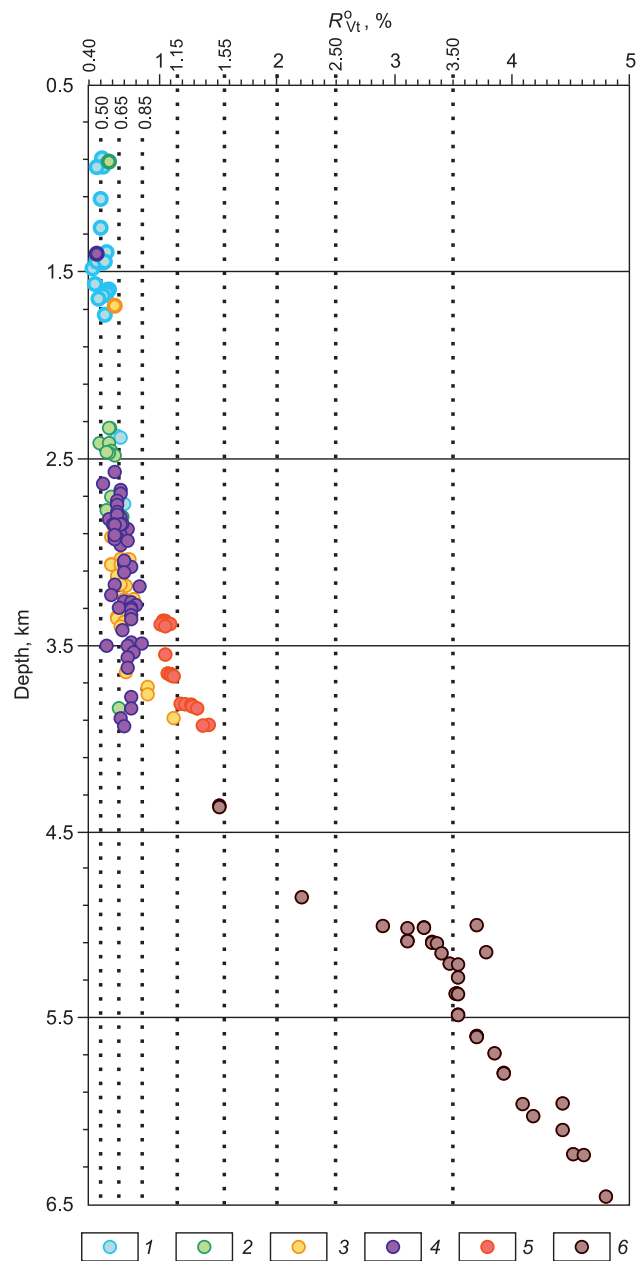


Fig. 3. Variations in vitrinite reflectance values (R_{Vt}^{o}) for the upper Paleozoic section of the Vilyui hemisyncline (Kashirtsev et al., 2017). Upper Permian (P_2) deposits: 1, Northwestern flank. Prospects: S. Sagitaiskaya, Tyukyan-Tyungskaya, W. Tyungskaya, Khorgochumskaya, N. Lindenskaya; 2, Southern flank. Prospects: Kumakhskaya, Baiskaya, Chebydinskaya, Byrakanskaya, Khailakhskaya; 3, Khapchagai megaswell. Prospects: Sobolokhskaya, Nedzhelinskaya, Mastakhskaya, Tolonskaya, Srednevelyuiskaya, Badaranskaya; 4, Loglor swell. Prospects: Srednetyungskaya, Verkhnelindenskaya, Tysakytkskaya, Andylakhskaya. In Srednevelyuiskaya-27 well ($\text{P}_2\text{--C}_{2-3}$): 5, P_2 ; 6, $\text{P}_1\text{--C}_{2-3}$.

mation corresponds to substages of the middle and late mesocatagenesis and to apocatagenesis further in the section.

Transformations of bitumen extracted from terrestrial organic matter during meso- and apocatagenesis. In the 1960s, it was shown that the catagenesis of organic matter

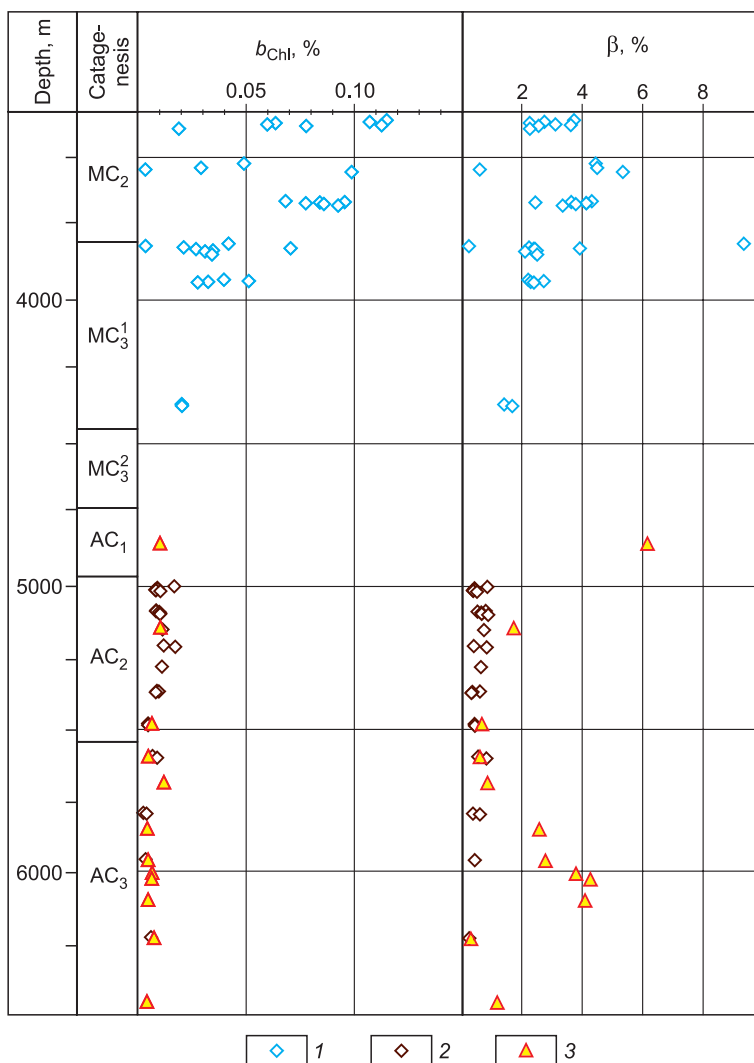


Fig. 4. Variations in the yield of chloroform-extracted bitumen (b_{ChI}) and bitumen coefficient (β) with increasing maturity in the Srednevyuiskaya-27 well. Samples collected from: 1, the mesocatagenesis zone; 2, the apocatagenesis zone; 3, EPAK.

controls the change in the content and composition of bitumen extracts (Vassoevich, 1967; Neruchev, 1973; Kontorovich and Trofimuk, 1976; Kontorovich, 1976). During protocatagenesis, early and middle mesocatagenesis, the concentration of bitumens usually increases, reaching its maximum at substages MC₁¹ and MC₂ and then decreases. These grades correspond to the oil window.

In the section of the Srednevyuiskaya-27 well, the concentration of bitumen extracts in the rock samples representing mesocatagenesis (MC₂, MC₃¹) gradually decreases from 0.12–0.10 to 0.02% per rock (Fig. 4). During apocatagenesis, the concentration of bitumens in rocks does not exceed 0.02% throughout the studied interval. At the same time, the bitumen coefficient decreases from 2–6 to 1.0–2.0% during middle and late mesocatagenesis and to 0.05–1.0% during apocatagenesis. The analysis of core samples from the Srednevyuiskaya-27 well revealed the variation trends in the bitumen concentration and bitumen coefficient as the rock passes through the oil window.

Generally, a high positive correlation ($R = 0.82$) is seen between the bitumen concentrations and C_{org} in rocks during middle and late mesocatagenesis (Fig. 5). However, such a correlation is not observed during apocatagenesis, at the end of generation of bitumens and hydrocarbons (Fig. 5). During middle and late mesocatagenesis, the bitumen coefficient varies from 2 to 5–6% and shows no correlation with C_{org} (Fig. 6). The bitumen coefficient values decrease during apocatagenesis; they do not exceed 1.0% and show no correlation with C_{org} (Fig. 6), except for the core samples with C_{org} less than 0.5%. These are mostly sandstones with low bitumen concentrations and relatively high values of the bitumen coefficient (up to 6.0%). Most likely, these bitumens are of allochthonous or para-autochthonous origin.

In the studied part of the section, the bitumen content of rocks and organic matter changes, as well as the composition of bitumens vary depending on different thermal maturity levels (Fig. 7): at a depth greater than 4–5 km, the resin content begins to increase with decreasing asphaltene con-

Table 3. Distribution of organic carbon in the rocks of the upper Paleozoic section penetrated in the Srednevelyuskaya-27 well

| Upper Paleozoic rocks | | | | |
|--|---------------------|------|------|-------------------|
| Rock | C _{org.} % | | | Number of samples |
| | min | max | mean | |
| Sandstone | 0.11 | 0.45 | 0.22 | 8 |
| Siltstone | 0.58 | 1.92 | 1.17 | 25 |
| Carb. siltstone | 2.27 | 3.90 | 3.01 | 10 |
| Mudstone | 1.06 | 2.76 | 1.81 | 26 |
| Upper-lower Permian (P _{1,2}) | | | | |
| Sandstone | – | – | 0.45 | 1 |
| Siltstone | 0.58 | 1.92 | 1.34 | 15 |
| Carb. siltstone | 2.27 | 3.90 | 3.01 | 9 |
| Mudstone | 1.15 | 1.88 | 1.56 | 4 |
| Middle-upper Carboniferous (C _{2,3}) | | | | |
| Sandstone | 0.11 | 0.35 | 0.18 | 7 |
| Siltstone | 0.60 | 1.40 | 0.92 | 10 |
| Carb. siltstone | – | – | 3.02 | 1 |
| Mudstone | 1.06 | 2.76 | 1.86 | 22 |

centration. Below a depth of 5300 m, the disappearance of asphaltenes from bitumen extracts results in the formation of liquid and gaseous, mostly saturated compounds at the expense of the labile components and condensation of high molecular weight compounds, and their further structural complication and transition into an insoluble phase, i.e. kerogen. This feature of the catagenesis of terrestrial OM was first noted by Kontorovich et al. (1988) and later discussed by Dolzhenko et al. (2019).

The composition of bitumen extracts does not remain unchanged (Fig. 7). During mesocatagenesis, the ratio of saturated to aromatic compounds varies from 1 to 2–3. The apocatagenesis grade is characterized by a sharp increase in the content of the saturated compounds, while the ratio of the saturated to aromatic hydrocarbons increases to 4–5 and

even to 5–10. Variations in the composition of saturated and aromatic hydrocarbons in terrestrial OM will be discussed in more detail below.

Rock-Eval pyrolysis parameters generally support the results of chemical analysis of the organic carbon and bitumen content of Permian rock samples collected in the Srednevelyuskaya-27 well. A strong positive correlation ($R = 0.88$) exists between S_2 and C_{org} of rocks within the mesocatagenesis grade (Fig. 8). A different situation is observed during apocatagenesis. In this zone, the S_2 peak values are very low in all analyzed samples and show no correlation with the total organic carbon content of rocks. We studied the dependence of the S_1 peak on the content of chloroform-extracted bitumens of the rock. These values show a strong positive correlation ($R = 0.91$) for the mesocatagenesis grade (Fig. 9).

Table 4. Catagenesis grades used in the Russian literature

| Stages | Substages | Catagenesis grades | | Coal ranks | R_{Vr}^o , % |
|--------------|-----------|--------------------|------------------------------|----------------|------------------|
| Lithogenesis | | Vassoevich, 1977 | Kontorovich, 1976 | GOST-12113–94 | Onset of a grade |
| Catagenesis | Proto- | PC ₁ | PC ₁ | B ₁ | 0.25 |
| | | PC ₂ | PC ₂ | B ₂ | 0.3 |
| | | PC ₃ | PC ₃ | B ₃ | 0.4 |
| | Meso- | MC ₁ | MC ₁ ¹ | D | 0.5 |
| | | MC ₂ | MC ₁ ² | G | 0.65 |
| | | MC ₃ | MC ₂ | J | 0.85 |
| | | MC ₄ | MC ₃ ¹ | K | 1.15 |
| | | MC ₅ | MC ₃ ² | OS | 1.55 |
| | Apo- | AC ₁ | AC ₁ | T | 2 |
| | | AC ₂ | AC ₂ | PA | 2.5 |
| | | AC ₃ | AC ₃ | A | 3.5 |
| | | AC ₄ | AC ₄ | | 5 |

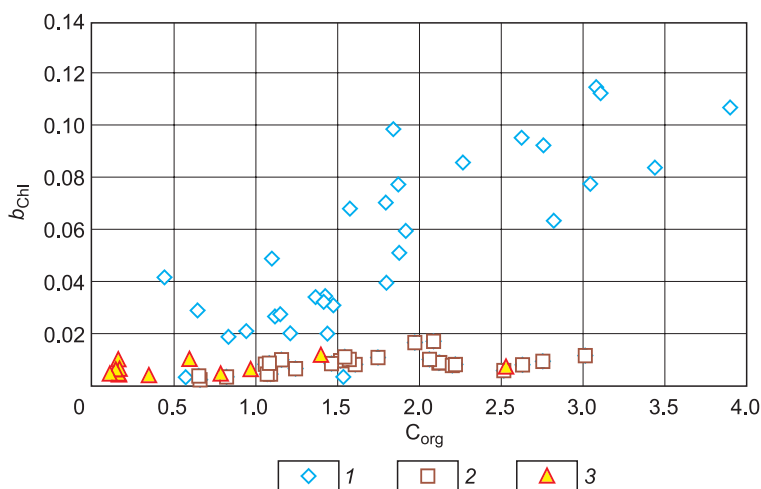


Fig. 5. Dependence of the concentration of chloroform-extracted bitumen (b_{Chl} , %) on the organic carbon content (C_{org}) of the rock. 1, mesocatagenesis; 2, apocatagenesis; 3, EPAK.

As shown above, the rocks within the apocatagenesis grade are characterized by very low concentrations of bitumen extracts and, correspondingly, the lowest S_1 values.

The analysis of the dependence of the temperature of maximum hydrocarbon yield (T_{max}) at pyrolysis (Table 4) on sampling depth and vitrinite reflectance data (Fig. 10) shows interesting and somewhat unexpected results. The majority of samples show that the T_{max} values increase to 570–580 °C to a depth of about 5 km ($R_{\text{vt}}^0 \sim 2.5\%$), and they remain constant deeper. This suggests that T_{max} values can be reliable indicators of maturity only before the onset of apocatagenesis and below temperatures of 570–580 °C. For organic matter during apocatagenesis, this indicator may only indicate that organic matter has reached the apocatagenesis grade, but cannot be used effectively as a proxy for a particular substage of apocatagenesis (Table 4).

Figure 10 presents an example of another unexpected and rather paradoxical result. It can be seen that all studied samples representing apocatagenesis can be divided into two groups. As shown above, Group I is characterized by

the highest T_{max} values. Group II shows lower T_{max} values between 450 and 380 °C and below. However, two points should be noted. First, in the above set of samples, asphaltenes were precipitated into an insoluble phase, i.e., kerogen. As shown above, following to the Uspenskii-Vassoevich relationship, the bitumens extracted from such samples (sandstones and siltstones) can be classified as allochthonous ones (Fig. 6). The authors suggest that the kerogen in these samples is the products formed from the fraction of asphaltenes that were converted to an insoluble phase during apocatagenesis. Therefore, kerogens formed during apocatagenesis are less mature than those underwent normal evolution during catagenesis. We propose to call such kerogens epi-asphaltenic. The proposed explanation of this phenomenon also supports the dependence of the hydrogen index HI (residual hydrocarbon generative potential) on the thermal maturity of terrestrial organic matter (Fig. 11). Figure 11 shows that HI of terrestrial organic matter in Group I samples (except for epi-asphaltenic kerogens, EPAKs) decreases

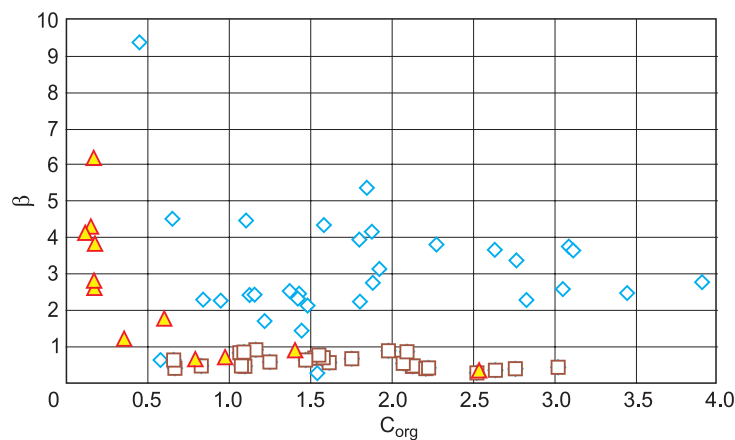


Fig. 6. The dependence of the bitumen coefficient (β) on the organic carbon content (C_{org}) of the rock. For notation see Fig. 5.

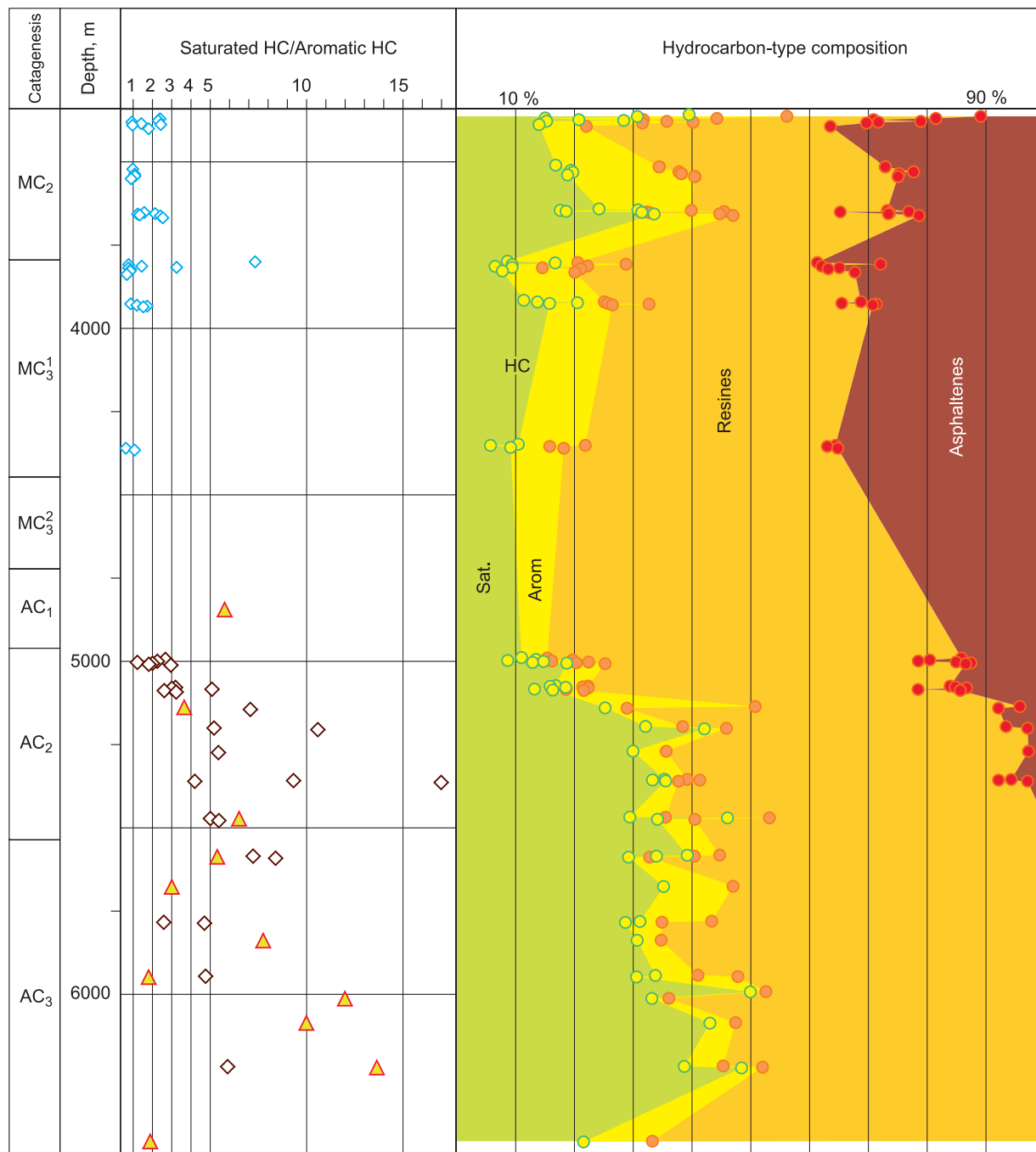


Fig. 7. Variations in the saturated/aromatic ratio and hydrocarbon type composition of bitumen with increasing maturity in the Sredneviluyiskaya-27 well. For notation see Fig. 4.

from 123–200 to 0–10 mg HC/g C_{org} with increasing depth and vitrinite reflectance from mid- (MC_2) to deep mesocatagenesis (MC_3^{1-2}) and especially apocatagenesis (AC).

Group II samples (EPAKs) within the apocatagenesis grade have HI between 60 and 0 mg HC/g C_{org} .

It was shown that the hydrocarbon type composition of bitumens undergoes significant changes. At the same time, some trends in the composition of saturated biomarker hydrocarbons, as well as composition and concentration of indi-

vidual hydrocarbons with depth during mesocatagenesis and apocatagenesis are recorded. During catagenesis, the rocks are characterized by an increase in the relative concentrations of low molecular weight *n*-alkanes ($C_{19}+C_{20}+C_{21}$) and a sharp decrease in the relative concentrations of high molecular weight *n*-alkanes ($C_{27}+C_{28}+C_{29}$), as indicated by a stochastic increase in the $(C_{19}+C_{20}+C_{21})/(C_{27}+C_{28}+C_{29})$ ratio with increasing maturity (R_{vt}^0) (Fig. 12). Note that in the hydrocarbon fraction of epi-asphaltenic kerogens, catagenetic

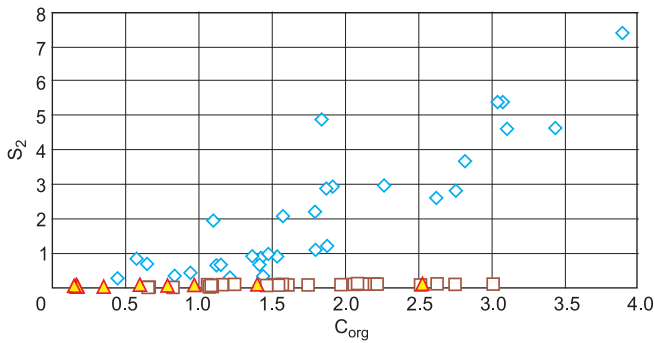


Fig. 8. Variations in S_2 (mgHC/gC_{org}) as a function of organic carbon content (C_{org}) of rocks from the Srednevelyuskaya-27 well. For notation see Fig. 5.

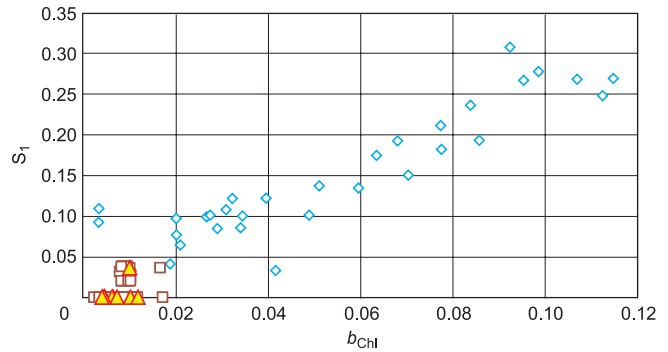


Fig. 9. Variations in S_1 (mgHC/gC_{org}) as a function of the yield of chloroform-extracted bitumen (b_{ChI}) in rocks from the Srednevelyuskaya-27 well. For notation see Fig. 5.

transformations occur more slowly, without a gradient increase in the low molecular weight *n*-alkanes.

Isoprenoid alkanes show a complex behavior (Fig. 13). During middle mesocatagenesis, the pristane to phytane (Pr/Ph) ratio exceeds 1 and varies from 2 to 3, reaching >4 in some samples. This ratio decreases from 2 to 1 during late mesocatagenesis and further to <1 varying from 0.3 to 1.0 during apocatagenesis, which is typical of aquatic organic matter during protocatagenesis, early and middle mesocatagenesis (Petrov, 1984; Kontorovich et al., 1991; Peters et al., 1993, 2004). The phytane (Ph) to *n*-C₁₈ alkane ratio is generally <0.50, ranging from 0.30 to 0.80 during mesocatage-

nesis, but it increases gradually from 0.50 to 1.0–1.5 during apocatagenesis. For the Pr/*n*-C₁₈ ratio, the situation is reversed; it decreases from 1.0–1.5 to 0.5 from middle to late mesocatagenesis and gradually increases to 1.0 during apocatagenesis.

The composition of steranes does not remain unchanged with increasing maturity (Fig. 14). During mesocatagenesis, the pregnane to sterane ratio is 0.08–0.35, varying between 0.3–0.9 in most samples during apocatagenesis. Therefore, the pregnane/sterane ratio increases substantially with increasing maturity, except for epi-asphaltenic kerogens, where it does not generally exceed 0.4.

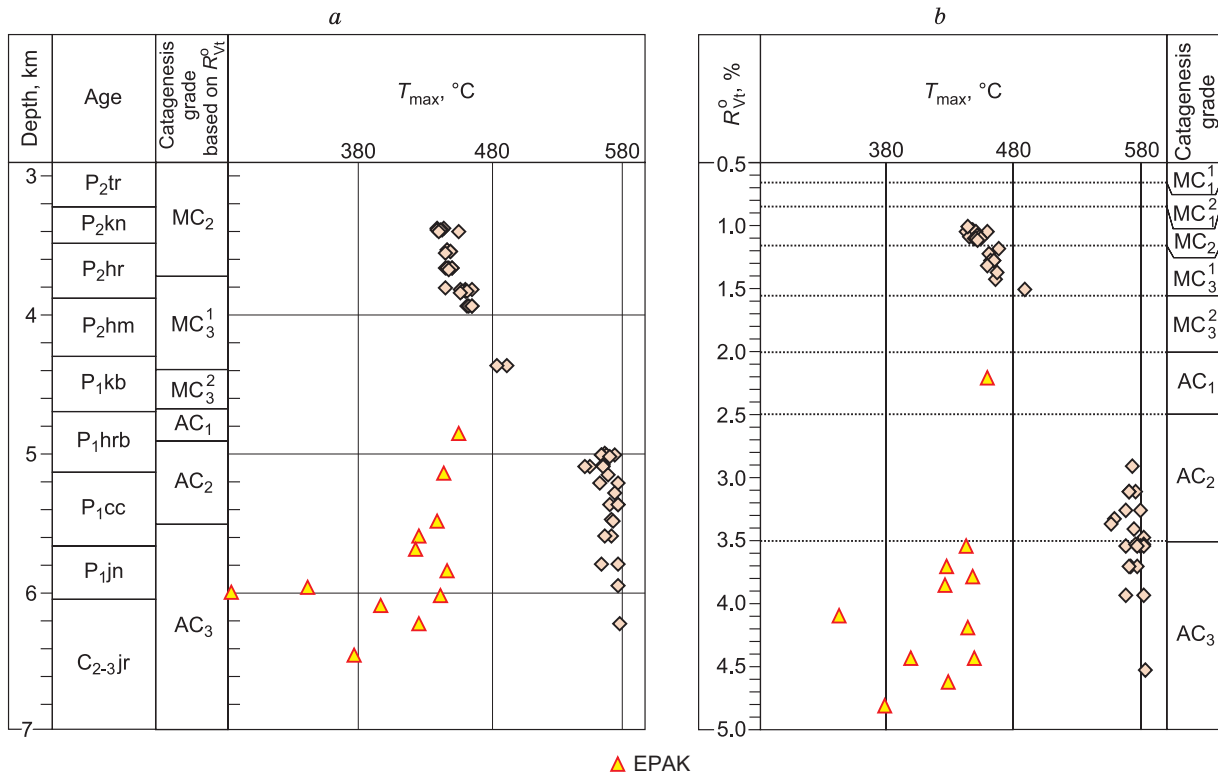


Fig. 10. Variations in temperature of maximum hydrocarbon yield (T_{max}) with increasing depth (a) and vitrinite reflectance (R_{vt}^0) (b) in the Srednevelyuskaya-27 well.

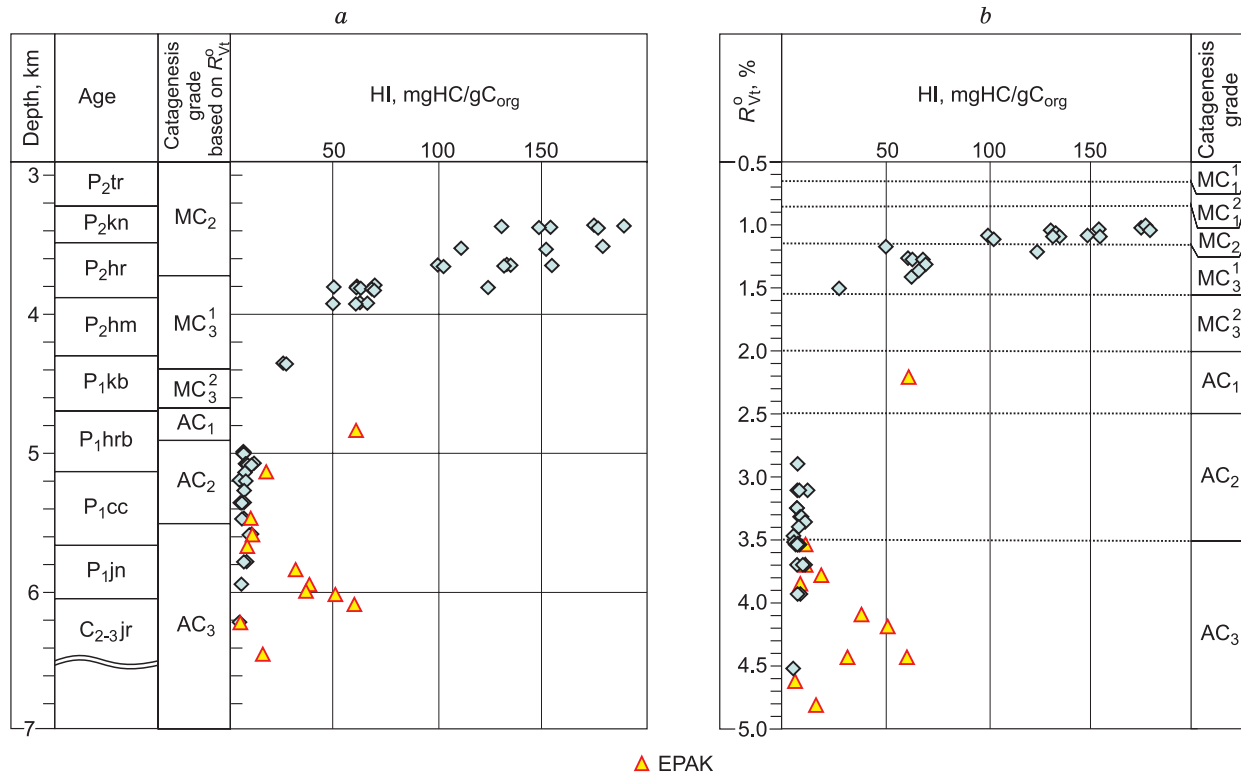


Fig. 11. Variations in residual HI with increasing depth (a) and vitrinite reflectance ($R_{V_t}^0$) (b) in the Srednevilyskaya-27 well.

During meso- and apocatagenesis, the sterane distribution in bitumens from terrestrial organic matter also changes; it is generally dominated ethyl cholestane (C_{29}) during mesocatagenesis, which is indicative of terrestrial organic matter (Fig. 15a). During late mesocatagenesis and apocatagenesis, the sum of C_{27} – C_{29} steranes is characterized by an increase in the relative concentrations of cholestanes (C_{27}) and methylcholestanes (C_{28}) and a decrease in the concentration of ethylcholestanes (C_{29}). As a result, on the C_{27} – C_{28} – C_{29} sterane ternary diagram, all terrestrial organic matter samples within late meso- and apocatagenesis are shifted

toward the field of aquatic organic matter within proto- and early-middle mesocatagenesis (Petrov, 1984; Kontorovich et al., 1991; Peters et al., 1993, 2004). The steranes of epiasphaltenic kerogens are also plotted in the same field (Fig. 15b).

The ratio of tricyclane hydrocarbons

$$I_{TC} = 2 \times \frac{\sum C_{19-20}}{\sum C_{23-26}}$$

was first identified and termed the tricyclane index I_{TC} in the earlier works of Kontorovich et al. (1991, 1996). It is used

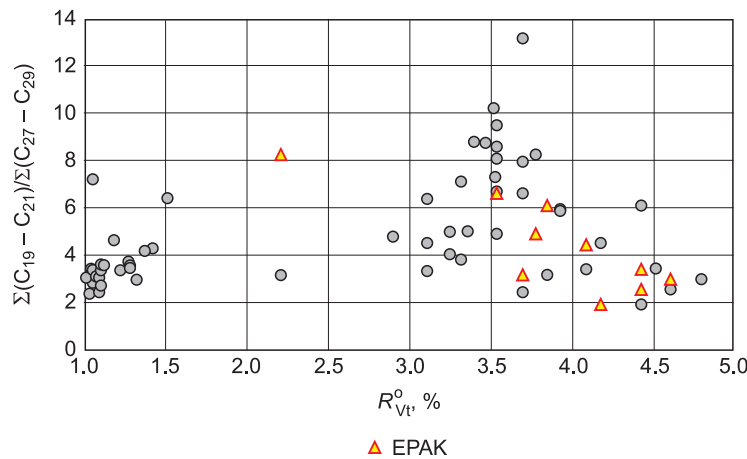


Fig. 12. The ratio of high to low molecular weight n -alkanes as a function on vitrinite reflectance ($R_{V_t}^0$) in the Srednevilyskaya-27 well.

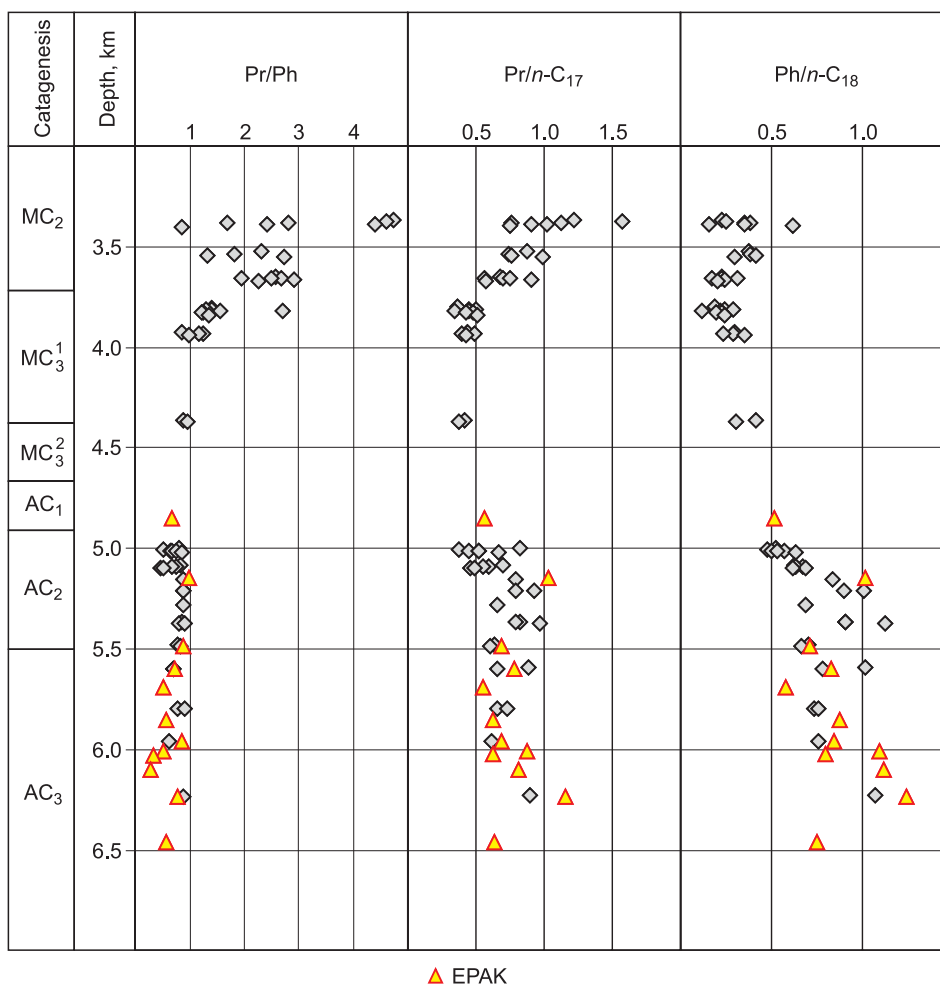


Fig. 13. Variations in the normal to isoprenoid alkane ratio with increasing depth in the Srednevelyuiskaya-27 well.

to discriminate between different types of organic matter. During protocatagenesis, early and middle mesocatagenesis, the tricyclane index is <1 in aquatic organic matter and >1 in terrestrial organic matter. The majority of core samples (Figs. 16 and 17) collected from depths corresponding to mesocatagenesis show the tricyclane index greater than 1, with the highest values ranging between 2 and 4. During late

mesocatagenesis and apocatagenesis, the tricyclane index of bitumens is <1 or equal to 1 in some samples. All epi-asphaltenic kerogens fall into the same group.

In conclusion, we discuss variations in the C₂₇ Ts/Tm trisnorhopane ratio in the zone of catagenesis. In organic geochemistry, this ratio is used to determine the level of thermal maturity of the organic matter and crude oils

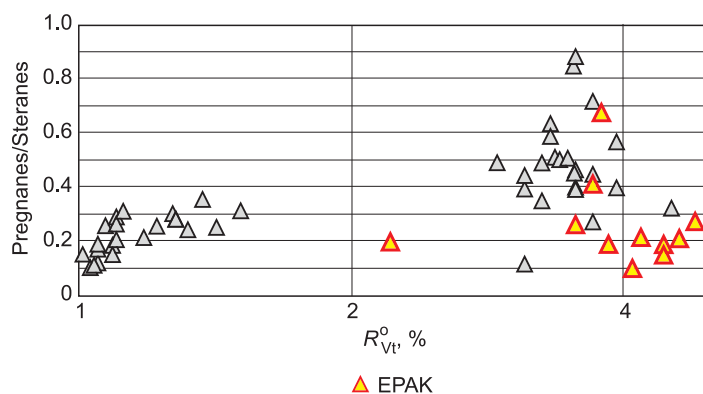


Fig. 14. Variations in the pregnane to sterane ratio with maturity in the Srednevelyuiskaya-27 well.

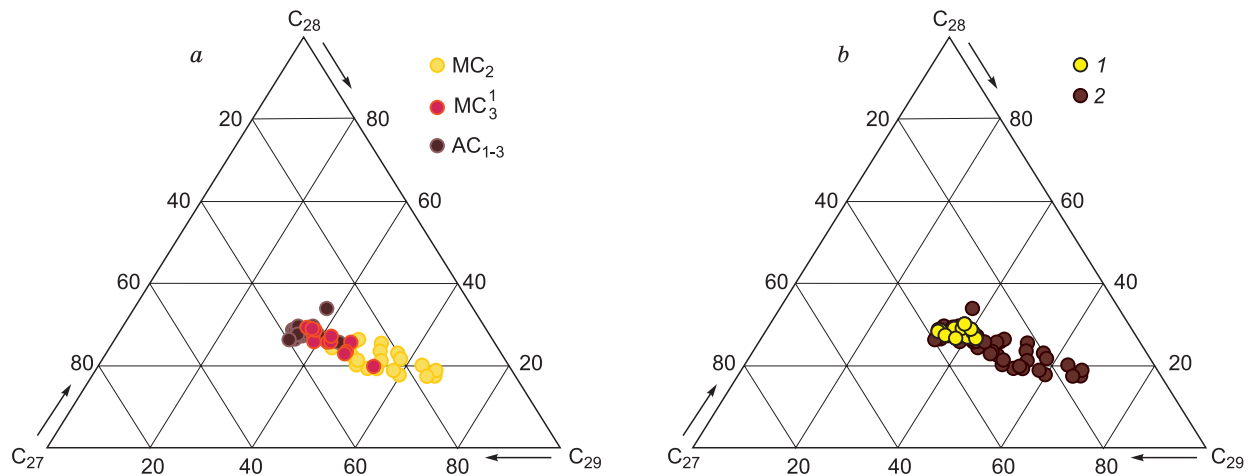


Fig. 15. C_{27} – C_{28} – C_{29} sterane ternary diagram for rocks from the Srednevelyuiskaya-27 well during meso- and apocatagenesis. *a*, Without EPAK; *b*, 1, EPAK; 2, remaining samples.

(Petrov, 1984; Peters et al., 2004). It is known that during protocatagenesis and early mesocatagenesis, the Ts/Tm ratio increases from 0.5–0.6 to 1.0. During middle mesocatagen-

esis (MC_2) and the beginning of late mesocatagenesis, the analyzed core samples have Ts/Tm between 1.0 and 3–4 (Figs. 18 and 19). The situation differs considerably at the end of late mesocatagenesis ($R_{Vt}^0 > 1.15$), whereas during apocatagenesis Ts concentration decreases relative to that of Tm and the Ts/Tm ratio increases from 0.8 to 1.5. In the same depth interval, the Ts/Tm ratio of epi-asphaltenic kerogens does not remain unaltered.

Our results support the previous conclusion that for late mesocatagenesis and apocatagenesis, the biomarker indicators are no longer effective as maturity indicators (Kashirtsev et al., 2017). As shown above, the biomarker indices and the type of organic matter can also be no longer considered diagnostic.

A detailed study of aromatic hydrocarbons from terrestrial organic matter undergoing meso- and apocatagenetic transformations was performed earlier using on core samples collected from the Permian sediments penetrated by the Srednevelyuiskaya-27 well (Kontorovich et al., 1988). It was shown that the composition of aromatic hydrocarbons at these stages of catagenetic transformation does not remain unaltered. Based on UV spectrometry data (analyst L.F. Lipnitskaya), bi- (naphthalene), tri- (phenanthrene and anthracene) and tetracyclic (chrysene, pyrene) aromatic hydrocarbons account for 40–50% of the naphthenic aromatic fraction during middle mesocatagenesis, which corresponds to the oil window. Over half of these are hydrocarbons with phenanthrene aromatic nuclei. During early apocatagenesis, their total concentration gradually decreases to 10–12% of the mass naphthenic aromatic fraction, being 7–10% with increasing thermal maturity. Moreover, the ratio naphthalene/phenanthrene ratio during mesocatagenesis is <1 , gradually increasing to 2–5–10 during apocatagenesis. The concentration of anthracene during middle and late mesocatagenesis is 1–2% of the mass naphthenic aromatic fraction and decreases to zero during apocatagenesis.

Low-temperature luminescence (according to E.V. Shpol'skii) of the naphthenic aromatic fractions of the studied

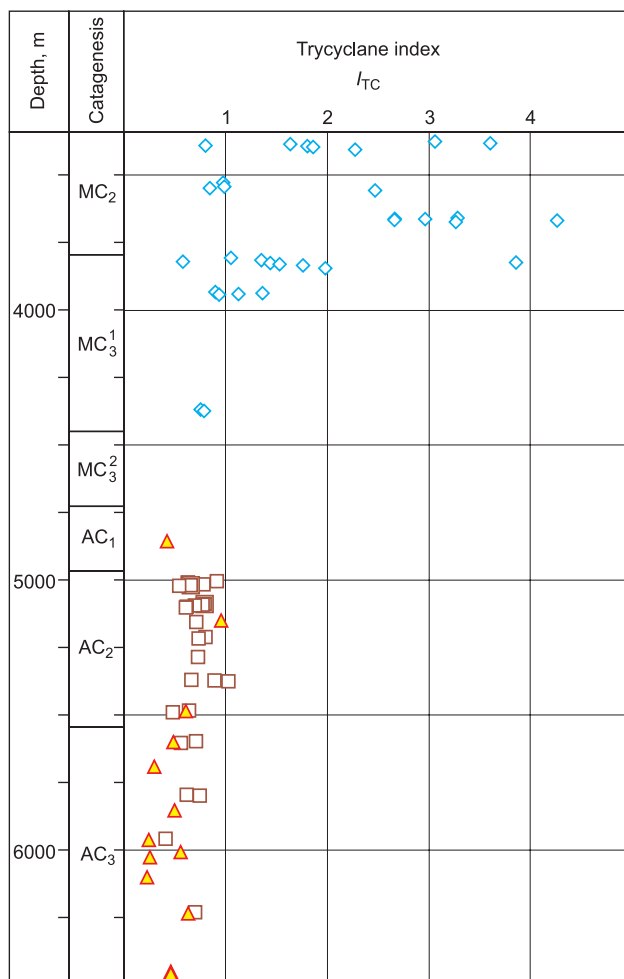


Fig. 16. Variations in the tricyclane index (I_{TC}) with depth in the Srednevelyuiskaya-27 well. For notation see Fig. 6.

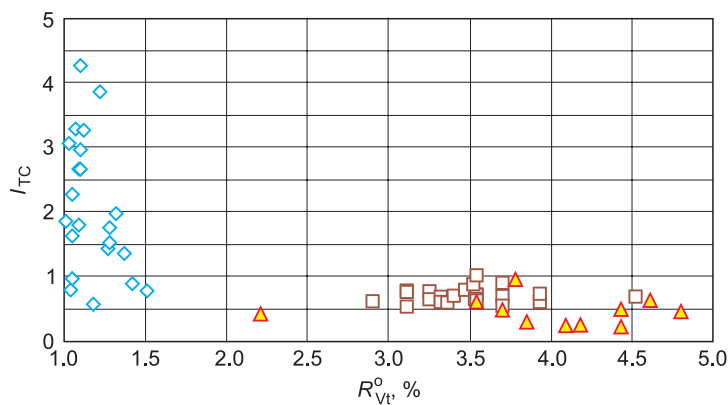


Fig. 17. Variations in the tricyclane index (I_{TC}) as a function of vitrinite reflectance (R_{Vt}^0) in the Srednevelyuskaya-27 well. For notation see Fig. 6.

samples (analyst N.M. Babina) showed that during meso-catagenesis, as is the case with the terrestrial organic matter, they contain a wide spectrum of polynuclear aromatic hydrocarbons, such as benzopyrene and its homologues, i.e., perylene, benzoperylene, and coronene. During apocatage-

nesis, these compounds are not detected in the naphthenic aromatic fraction.

Recent studies of Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch, Russian Academy of Sciences showed that aromatic hydrocarbons from Permian

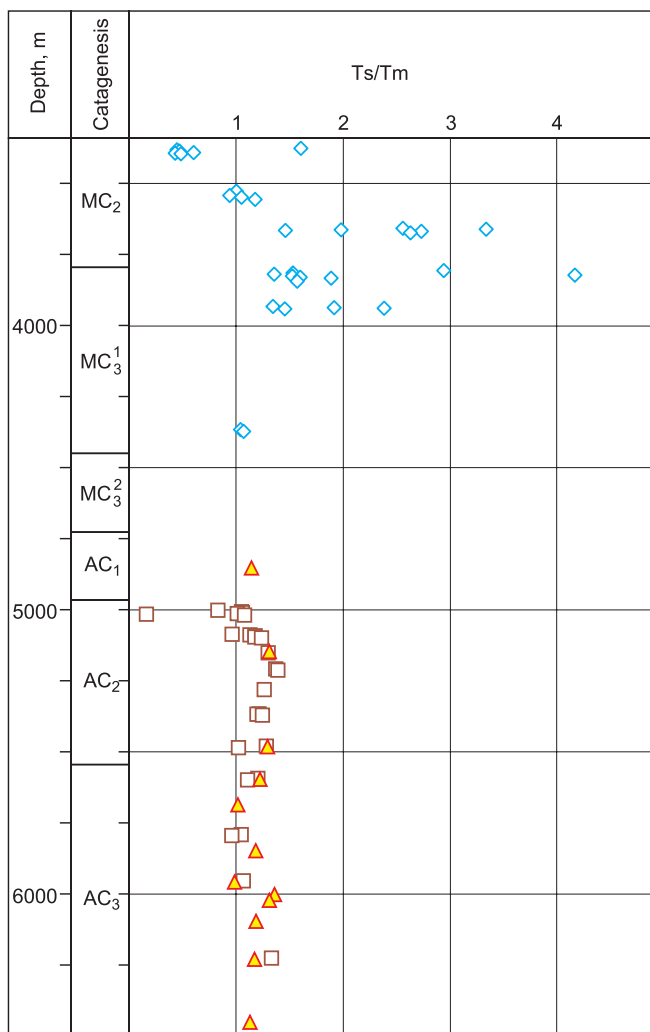


Fig. 18. Variations in the Ts/Tm terpane ratio with depth in the Srednevelyuskaya-27 well. Ts/Tm is the ratio between 18 α (H)-22,29,30-trisnorhopane (Ts) and 17 α (H)-22,29,30-trisnorhopane. For notation see Fig. 6.

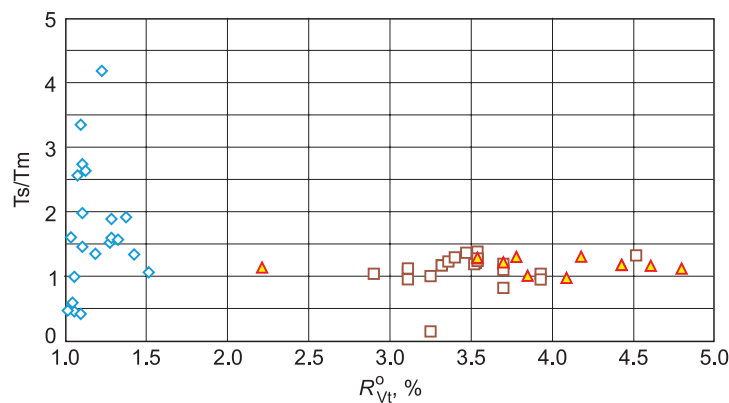


Fig. 19. Ts/Tm terpane ratio as a function of vitrinite reflectance (R_{Vt}^o) in the Srednevelyuiskaya-27 well. For notation see Fig. 6.

rocks of the Vilyui hemisyncline contain four diastereoisomers of monoaromatic steranes of unknown structure in the zone of apocatagenesis (Kashirtsev et al., 2016, 2017). Based on the results of mass spectrometric investigation, these compounds were determined as a new type of 17-desmethyl-23-methylmono-aromatic steroids C_{27} . The presence of these compounds in the bitumens can be used as an indicator of strong catagenetic transformation of sedimentary rocks and organic matter. It is important to note that these new compounds are not related to the above-mentioned epi-asphaltenic kerogens. These four diastereoisomers of 17-desmethyl-23-methylmonoaromatic steroid C_{27} is most likely associated with earlier compounds that have been formed in bitumens due to the opening of initial closed pores of asphaltenes.

The main regularities that control the transformation of terrestrial organic matter during mesocatagenesis and apocatagenesis are described in the above discussion.

CONCLUSIONS

A combination of modern analytical methods was used to study terrestrial organic matter in the zones of middle and late mesocatagenesis and apocatagenesis. The four diastereoisomers of 17-desmethyl-23-methylmonoaromatic steroid C_{27} cannot be related to newly-formed compounds, called epi-asphaltenic kerogens. These new compounds seem to have been formed earlier in bitumens due to the opening of initial closed pores of asphaltenes during apocatagenesis. This is the first detailed study of terrestrial organic matter, which is extremely important for the theory of petroleum generation.

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REFERENCES

- Danilova, V.P., Kontorovich, A.E., Fomichev, A.S., 1974. Change in the content of bitumens in organic matter in the catagenesis zone, in: Organic Geochemistry of Mesozoic Oil-Bearing Deposits of Siberia [in Russian]. Nedra, Moscow, pp. 73–75.
- Dolzhenko, K.V., Fomin, A.N., Melenevskiy, V.N., 2019. Geochemical characteristics of terrestrial organic matter in the Upper Paleozoic complex of the Vilyui syncline and some features of its transformation under thermobaric conditions at great depths. *Georesursy* (Georesources), 21 (4), 77–84.
- Golubeva, I.I., Grausman, V.V., Meyen, S.V., Petrova, E.K., 1980. The stratigraphic division of Permian gas-bearing deposits in the central part of the Vilyui syncline, in: Stratigrafiya Neftegazonosnykh Otolozhenii Yakutii [in Russian]. YaF SO AN SSSR, Yakutsk, pp. 36–45.
- Grausman, V.V., Zhernovskii, V.P., Meien, S.V., 1986. The study of sections of deep wells, their subdivision and correlation as a stratigraphic basis for oil exploration in the YaASSR, in: Funds of PGO Lenaneftegazgeologiya [in Russian]. Yakutsk.
- Kashirtsev, V.A., Fomin, A.N., Shevchenko, N.P., Dolzhenko, K.V., 2016. New monoaromatic steroids in organic matter of the apocatagenesis zone. *Dokl. Earth Sci.* 469 (4), 815–818.
- Kashirtsev, V.A., Dolzhenko, K.V., Fomin, A.N., Kontorovich, A.E., Shevchenko, N.P., 2017. Hydrocarbon composition of bitumen from deeply buried terrestrial organic matter (apocatagenesis zone). *Russian Geology and Geophysics (Geologiya i Geofizika)* 58 (6), 702–710 (869–879).
- Kontorovich, A.E., 1976. Geochemical methods for the quantitative prediction of oil and gas potential. *Trans. SNIIGGiMS* [in Russian]. Nedra, Moscow, Issue 229.
- Kontorovich, A.E., Trofimuk, A.A., 1976. Lithogenesis and oil and gas formation, in: Fossil Fuels. Problems of Geology and Geochemistry of Naphthides and Bituminous Rocks [in Russian]. Nauka, Moscow, pp. 19–36.
- Kontorovich, A.E., Babina, N.M., Danilova, V.P., Zueva, T.V., Melnikova, V.M., 1973a. Polynuclear aromatic hydrocarbons of dispersed organic matter. *Geologiya i Geofizika* 9, 84–91.

- Kontorovich, A.E., Danilova, V.P., Dindoin, V.M., 1973b. Changes in the chemical composition of humic organic matter and its paramagnetic properties in the catagenesis zone. *Dokl. AN SSSR*, 209 (6), 1431–1434.
- Kontorovich, A.E., Bogorodskaya, L.I., Danilova, V.P., 1974. Patterns of changes in the chemical composition and paramagnetic properties of the debituminized organic matter (kerogen) in the catagenesis zone, in: *Organic Geochemistry of the Mesozoic Oil-Bearing Sediments of Siberia* [in Russian]. Nedra, Moscow, pp. 66–73.
- Kontorovich, A.E., Bogorodskaya, L.I., Golyshev, S.I., 1985a. Principles of fractionation of carbon isotopes in sediments. *Geologiya i Geofizika (Soviet Geology and Geophysics)* 26 (9), 31–40.
- Kontorovich, A.E., Bogorodskaya, L.I., Golyshev, S.I., 1985b. Distribution of stable carbon isotopes in sediments of different genetic nature. *Geologiya i Geofizika (Soviet Geology and Geophysics)* (26) 7, 1–8.
- Kontorovich, A.E., Polyakova, I.D., Kolganova, M.M., Soboleva, E.I., 1988. Transformations of organic matter in meso- and apocatagenesis. *Sovetskaya Geologiya* 7, 26–36.
- Kontorovich, A.E., Peters, K.E., Moldowan, J.M., Andrusevich, V.E., Demaison, G.I., Stasova, O.F., Huizinga, B.J., 1991. Biomarker hydrocarbons in the oils from the Middle Ob region (West Siberia). *Soviet Geology and Geophysics (Geologiya i Geofizika)* 32 (10), 1–27.
- Kontorovich, A.E. (Ed.), 1994. *Petroleum Basin and Regions of Siberia: Lena-Vilyui Basin* [in Russian]. UIGGM SB RAS, Novosibirsk. Issue 4.
- Kontorovich, A.E., Izosimova, A.N., Kontorovich, A.A., Khabarov, E.M., Timoshina, I.D., 1996. Geological structure and conditions of the formation of the giant Yurubchen-Tokhomo zone of oil and gas accumulation in the Upper Proterozoic of the Siberian Platform. *Russian Geology and Geophysics (Geologiya i Geofizika)* 37 (8), 156–185.
- Mikhailova, T.E., Fartunatova, L.M., Sandakova, L.G., 2011. Stratigraphy and correlation of the Upper Permian deposits of the Vilyui hemisyncline based on palynological data. *Bull. Ammosov North-east. Fed. Univer.*, 8 (1), 48–54.
- Neruchev, S.G., 1973. Study of the main phase of oil generation, in: Khain, V.E. (Ed.), *Contemporary Problems of Geology and Geochemistry of Fossil Fuels* [in Russian]. Nauka, Moscow, pp. 43–48.
- Parfenov, L.M., Kuzmin, M.I. (Eds.), 2001. *Tectonics, Geodynamics and Metallogeny of the Republic of Sakha (Yakutia)* [in Russian]. MAIK Nauka/Interperiodika, Moscow.
- Perozio, G.N., Polyakova, I.D., Bogorodskaya, L.I., Soboleva, E.I., 1981. Laws governing the catagenesis of organic matter and the rocks containing it. *Soviet Geology and Geophysics (Geologiya i Geofizika)* 22 (9), 8–12.
- Peters, K.E., Kontorovich, A.E., Moldowan, J.M., Andrusevich, V.E., Huizinga, B.J., Demaison, G.I., Stasova, O.F., 1993. *Geochemistry of selected oils and rocks from the central portion of the West Siberian basin, Russia*. AAPG Bull. 77 (5), 863–887.
- Peters, K.E., Walters, C.C., Moldowan, J.M., 2004. *The Biomarker Guide. Biomarkers and Isotopes in Petroleum Exploration and Earth History*. UK Cambridge University Press, Cambridge.
- Petrov, A.A., 1984. *Hydrocarbons of Crude Oils* [in Russian]. Nauka, Moscow.
- Vassoevich, N.B., 1967. Theory of sedimentary-migratory origin of oil [in Russian]. *Izv. AN SSSR, Geol. Ser.*, No. 11, 137–142.
- Vassoevich, N.B., 1977. Clarification of concepts and terms related to sedimentation cycles, stages of lithogenesis and oil generation, in: Trofimuk, A.A., Mirchink, M.F., Karogodin, Yu.N. (Eds.), *Main Theoretical Questions of the Sedimentogenesis Cyclicality* [in Russian]. Nauka, Moscow, pp. 34–58.
- Vyshemirskii, V.S., Kontorovich, A.E., Neruchev, S.G., Trofimuk, A.A., 1986. Contribution of N.B. Vassoevich's doctrine of source rocks and methods for their diagnostics, in: *Modern Geochemical Methods for the Diagnostics of Source Rocks* [in Russian]. Nauka, Moscow, pp. 5–18.

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