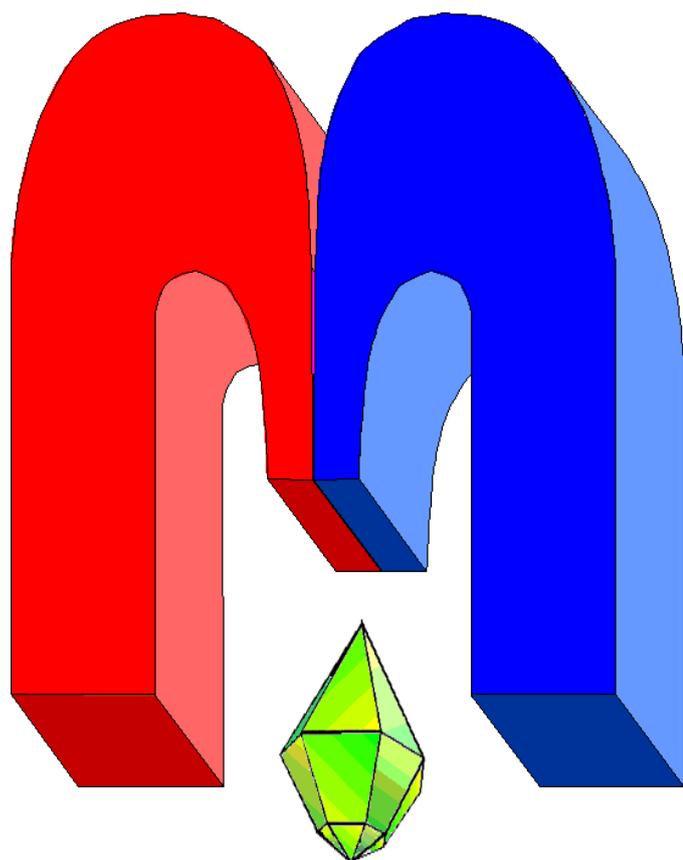


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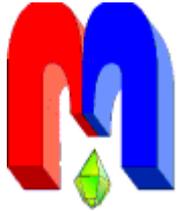
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In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

# EPR study of hydrocarbon generation potential of organic-rich domanik rocks

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The objects of investigation were samples of domanik formation rocks of Bereзовskaya area of Romashkinskoye oil field. Content of Mn<sup>2+</sup>, SO<sub>3</sub><sup>-</sup>, SO<sub>2</sub><sup>-</sup> ions, vanadyl-ions and free radicals has been estimated with the X-band (9.43 GHz) electron paramagnetic resonance (EPR) spectroscopy. Composition of rock and extracted from it bitumen has been studied with methods of thermal analysis, X-ray-structural analysis and gas chromatography. Significant differences in mineralogical composition and content of organic matter were revealed in samples taken from adjacent intervals. Pyrolytic experiments have been conducted to simulate kerogen maturation and petroleum generation. The increasing number of free radicals was registered in all samples after pyrolysis in a hydrogen atmosphere at 350°C. A new organic free radical C<sub>350</sub> was registered after pyrolysis. It is suggested that domanik source rocks have not fully realized their hydrocarbon generation potential.

**PACS:** 76.30.-v.

**Keywords:** EPR spectroscopy, generation potential, kerogen, pyrolysis, domanik rocks.

## 1. Introduction

Domanik sediments are widespread in the Volga-Ural Basin and stratigraphically confined to the Upper Devonian Frasnian stage [1-12]. Domanik sediments thickness in Tatarstan do not exceed several tens of meters [13]. Domanik sediments are composed of bituminous siliceous-carbonate rocks with a small argillaceous admixture (5.9-13.6 %). The rocks are black and dark brown due to the high organic matter content (18-20 %) [8-11]. Certain structural features, such as fissibility, strong pyritization and specific complex of organic remains characterize domanik sediments [12]. According to many researchers [8, 12, 14-20], accumulation of domanik sediments in Volga-Ural region was carried under conditions of tectonic and volcanic activation. According to Neruchev S.G. [17], the reason of the sharp extinction of many species living in this time was increasing concentrations of uranium and other radioactive elements, entering the sedimentation basin because of hydrothermal activity.

Semiluki (domanik) sediments are analogous to oil shales. The increasing interest to them in recent years is explained by the possibility of shale oil extraction [1-4, 20, 21]. A distinctive feature is that rocks along with light oil contain the organic matter as a component of rock, called kerogen [3, 22-27].

There are different methods of studying domanik rocks to assess the prospects of the liquid hydrocarbons generation depending on the composition of organic matter in rocks and its thermal stability [28, 29]. The special place among these methods takes the electron paramagnetic resonance (EPR) [30-36]. The essence of the EPR phenomenon is the resonance absorption of electromagnetic radiation by unpaired electrons. One of the traditional objects of EPR researches are stable free radicals, these are particles containing one or more unpaired electrons, so-called paramagnetic centers [32]. Free radicals are reliable diagnostic criterion in the reconstruction of sedimentary environments, as well as in layering and correlation of sections of sedimentary rocks. Free radicals reflect the composition of carbonate components, show presence of organic matter, indicate ferruginization and other features of rocks composition [35, 36].

The aim of the work was to study the characteristics of the composition and structure of the mineral matrix, bitumen and kerogen, as well as the conversion of kerogen and rocks in the pyrolytic laboratory experiments using EPR spectroscopy.

## 2. Materials and methods

The objects of investigations were core materials, selected from the domanik sediments of Berezovskaya area of Romashkinskoye field from 1712.5-1718.5 m and 1718.5-1724.5 m depth intervals.

Rock samples were extracted on Soxhlet apparatus with a solvent mixture containing chloroform, benzene and isopropyl alcohol in equal proportions to extract soluble hydrocarbons.

Samples before and after extraction were investigated with methods of thermal, X-ray structural analysis and with EPR spectroscopy.

The content of organic matter and the presence of thermal effects were identified on the instrument of simultaneous thermal analysis STA 443 F3 Jupiter (Netzsch, Germany). Measurement conditions: oxidizing atmosphere (air), heating rate was 10 °C/min. Temperature range was 20-1000 °C. Sample mass was 30-50 mg. Processing of TG-DSC curves (thermogravimetric curve and differential scanning calorimetry) was performed on a computer using the Netzsch Proteus Thermal Analysis software.

Mineral composition of the rocks was studied with X-ray structural analysis. Diffraction spectra registration was conducted on the automatic powder diffractometer Shimadzu XRD-7000S, on CuK $\alpha$  radiation with wavelength  $\lambda = 1.54060$  nm, using a nickel monochromator with diffracted beam with step 0.0008 Å<sup>-1</sup> and single exposition at point 3 seconds. Processing of diffraction spectra and diagnosis of present crystalline phases were carried by the original EVA interactive computer system, version 4.0.

For pyrolysis the rock samples were placed into quartz tube of flow-through cell (CDS 1500, Valved interface), located inside of platinum wire spiral in an electric furnace SUOL (MR 0.15 2/12 180 B; 950 W). Investigations were conducted in hydrogen atmosphere, which was provided into the reaction chamber through a gas supply line connected with hydrogen generator TsvetKhrom-16 (ColorChrome-16). Pyrolysis of samples was carried out at temperatures 350 and 600 °C for 30 minutes for each one. The first temperature is the transition point between the release of free and adsorbed hydrocarbons mode and kerogen destruction mode [25, 26, 28, 29]. The second temperature corresponding to the completion of thermal destruction process is due to C-C and C-H bonds breaking because of the large thermal energy (thermal decomposition of kerogen). The process is accompanied by the formation of new free hydrocarbon radicals [22, 28-30, 35, 36].

Registration of the EPR spectra of the initial rock samples and thermally activated in the pyrolysis process was conducted on CMS-8400 X-band spectrometer at frequency of 9.43 GHz. Samples previously were triturated, weighed and loaded into polyethylene ampoules.

EPR spectra were recorded at room temperature with a magnetic field sweep 360 mT (from 40 to 400) for the registration of Fe<sup>3+</sup> ions, 140 mT (from 263 to 403) for the registration Mn<sup>2+</sup> ions and vanadyl complexes (VO<sup>2+</sup>) and 10 mT (from 329.3 to 339.3) for registration vanadyl complexes (most intense line), sulfate ions (SO<sub>3</sub><sup>-</sup>, SO<sub>2</sub><sup>-</sup>) and stable organic free radicals (R<sup>\*</sup>, C<sub>350</sub>). The content of stable free radicals and ions was measured in arbitrary units (the amplitude of EPR signal corrected for line width, obtained values were correlated to the weight of samples).

The bitumen was separated into four fractions (asphaltenes, saturated hydrocarbons, aromatics and resins) according to all-Union State Standard 32269-2013, which is analogous to widely used abroad SARA analysis. Asphaltenes were precipitated in a 40-fold amount of hexane. Malthenes were separated by liquid-solid chromatography on alumina calcined at 425 °C into saturated hydrocarbons, aromatics and resins by elution from the adsorbent with hexane, toluene and solvent mixture containing toluene and isopropyl alcohol in equal proportions respectively. The analysis of the saturated hydrocarbons composition was performed on a gas chromatograph "Kristall 2000M" (Crystal 2000M) in the temperature-programming mode from 100 °C to 300 °C: at range from 100 to 150 °C heating rate in furnace was 10 °C per minute, at the range from 150 to 300 °C heating rate was 3 °C per minute. Helium was used as carrier gas. Temperature of injector's evaporator is 310 °C, temperature of detector is 250 °C.

### 3. Results and discussion

According to X-ray structural and thermal analysis samples have different mineral composition and various organic matter content in the rocks.

As it follows from the published data [5, 6, 14-18], domanik rocks feature high content of silica, which was confirmed by the results of X-ray diffraction and thermal analysis. For example, the sample 1 consists of 88.87 % quartz, sample 2 contains a total of 26.8 % quartz (Table 1),

which is associated with low levels of silica input during the formation of sediment. On the other hand, the high content of microcline, muscovite and albite (allothigenous minerals) in sample 2 indicates the presence of the clastic materials source area. Pyrite in rocks was formed at the diagenesis stage as a result of sulfate reduction processes. The content of the carbonate material was identified by diffraction patterns and by results of thermal analysis (endothermic effects in the temperature range 650-800 °C). In sample 1 content of the carbonate material is 4 times less than in sample 2, which may indicate the variability of sedimentary processes [8].

The differences between the samples also appear in the content of organic matter. According to thermal analysis results (Table 2), samples have different mass losses in the specific temperature ranges from 20 to 1000 °C, consequently samples have different content of organic matter and form of organic matter department in the rocks [37]. The content of organic matter in the sample 1 is 35.48 %, and in the second sample is 13.36 %. Thermal analysis allows to evaluate the chemical and physical changes that occur in rocks in the conditions of temperature change [37, 38]. The amount of organic matter in the samples was evaluated by mass loss in the temperature range 200-600 °C. The mass loss at temperatures above 600 °C was associated with thermal decomposition of carbonate rocks. The mass loss at temperatures from 20 to 200 °C may be associated with removal of adsorbed water [39].

Thermal analysis was conducted with the original and extracted samples (Fig. 1). Qualitative changes in the DSC and TG curves after organic matter extraction have not been observed. The different mass losses are mainly due to the heterogeneity of the samples. It was confirmed that the extraction almost does not change the content of organic matter in the domanik rocks, because it is mainly represented by insoluble in organic solvents kerogen. Therefore, samples mass loss and exothermic effects in the temperature range 300-600 °C are associated with kerogen destruction.

Data of group composition of obtained extracts are given in Table 3. The yield of extracts is 0.38 wt% and 0.25 wt% for samples 1 and 2 respectively, which is not enough for the usual type of sandstone reservoirs, but for compact varieties, like domanik rocks, such values are normal. It only shows the presence in domanik sediments insoluble organic matter such as kerogen.

**Table 1.** The mineral composition of the domanik rock samples of Berezovskaya area of Romashkinskoye field.

Minerals	Sample 1	Sample 2
Quartz (silica)	88.87	26.80
Calcite	11.13	46.45
Microcline (potash feldspar)	-	14.13
Muscovite	-	9.40
Albite (sodium feldspar)	-	2.71
Pyrite	-	0.50

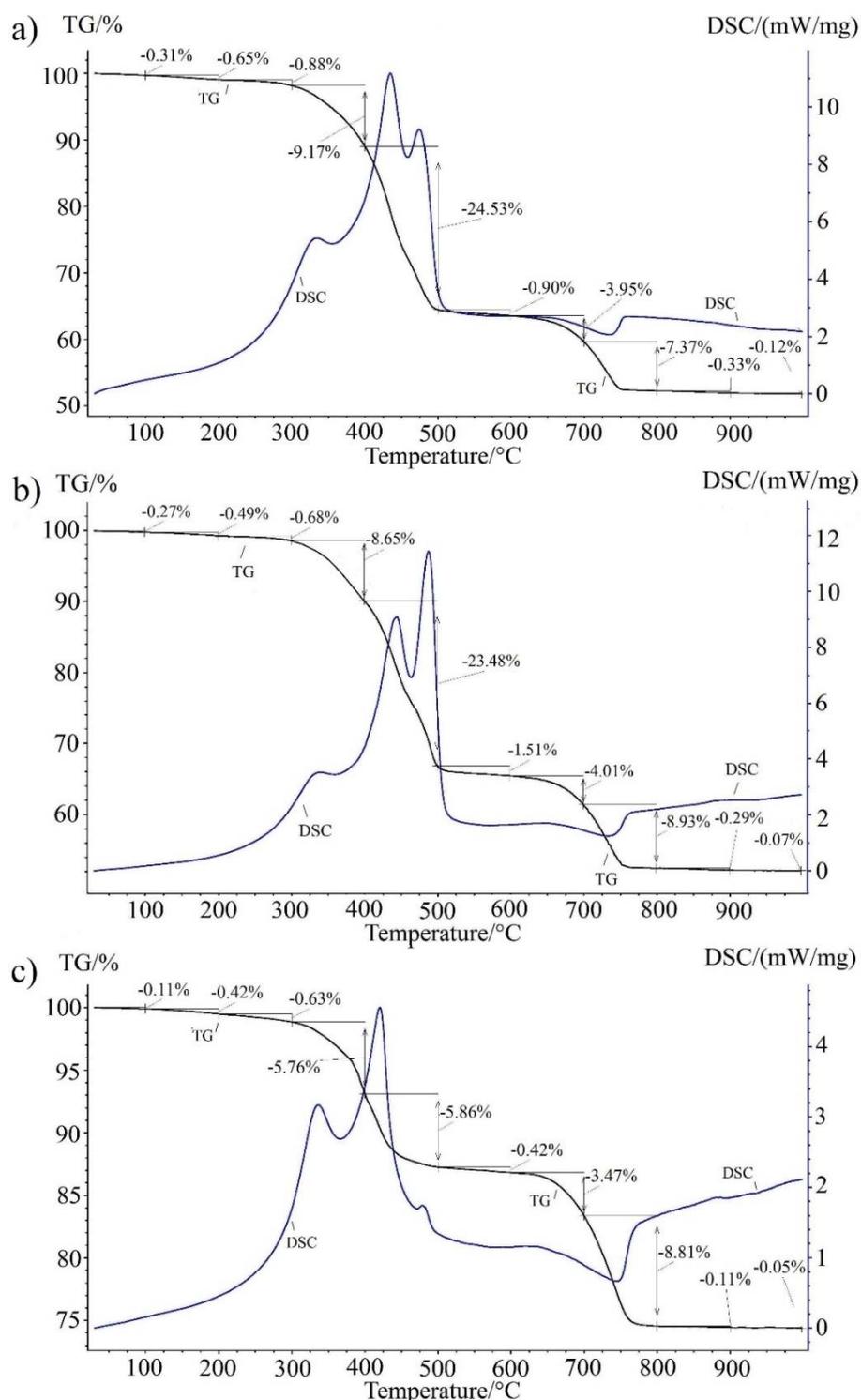
**Table 2.** Thermal analysis results of domanik rock samples of Berezovskaya area of Romashkinskoye field.

Sample number	Mass loss (wt%) at temperature range from 20 to 1000 °C					
	20-200	200-400	400-600	600-800	800-1000	∑ organic matter (200-600 °C)
1	0.96	10.05	25.43	11.32	0.45	35.48
1ex*	0.76	9.33	24.99	12.94	0.36	34.32
2	0.53	7.02	6.28	12.82	0.16	13.30

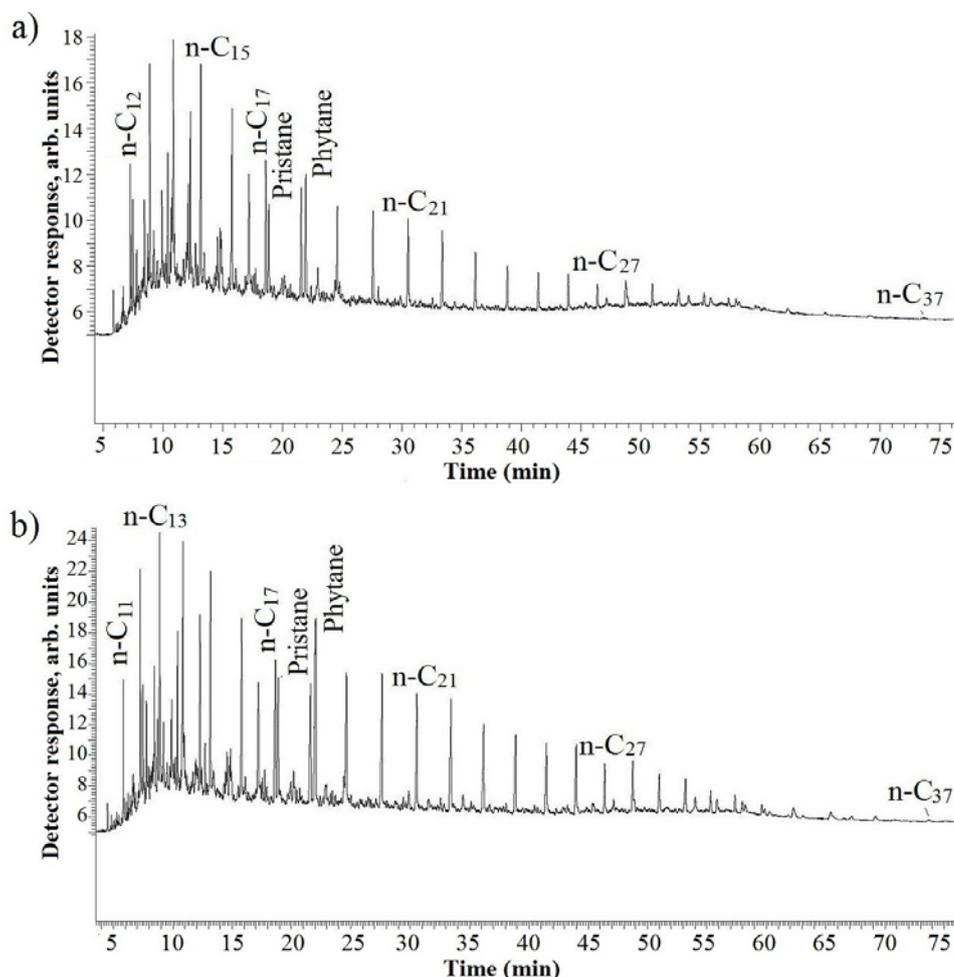
\*Sample 1 after organic matter extraction.

**Table 3.** Results of hydrocarbon group analysis of extracts from the domanik rocks of Berezovskaya area of Romashkinskoye field.

Sample number	Extraction yield, wt%	Composition, wt%			
		Satur.	Arom.	Resins	Asph.
1	0.38	18.58	38.94	28.32	14.16
2	0.25	18.18	22.73	43.18	15.91



**Figure 1.** DSC (blue) and TG (black) curves for domanik rock samples of Berezovskaya area of Romashkinskoye field: (a) sample 1 of the coring interval 1712.5-1718.5 m, (b) sample 1 after soluble OM extraction, (c) sample 2 of the coring interval 1718.5-1724.5 m.



**Figure 2.** The chromatograms of extracts from the domonik rocks of Berezovskaya area of Romashkinskoye field: (a) sample 1 of coring interval 1712.5-1718.5 m; (b) sample 2 of coring interval 1718.5-1724.5 m.

The extract from sample 1 contains more aromatics, but the extract from sample 2 contains more resinous substances. In both extracts content of saturated hydrocarbons and asphaltenes is nearly the same. As follows from the chromatograms (Fig. 2) molecular mass distribution of saturated hydrocarbons from extracts includes C<sub>11</sub>-C<sub>37</sub> normal alkanes (n-alkanes), among which n-alkanes C<sub>14</sub> have the maximum concentration. The content of the low-molecular compounds up to n-C<sub>17</sub> is 61 % for sample 1 and 54 % for sample 2. Whereas, in contrast, the high molecular part (from n-C<sub>27</sub> to n-C<sub>37</sub>) accounted for 7 % and 10.5 %, respectively. This points at predominant contribution of sapropel type of organic matter [40].

Table 4 shows the chromatographic indicators for the studied extracts. Even n-alkanes predominance (CPI < 1) in n-C<sub>24</sub> to n-C<sub>34</sub> range indicates a predominantly reducing conditions of organic matter accumulation. This can also be a sign of insufficient maturity of

**Table 4.** Values of chromatographic indicators.

Ratios	Sample 1	Sample 2
Pristane/phytane	0.75	0.69
Pristane / n-C <sub>17</sub>	0.70	0.87
Phytane / n-C <sub>18</sub>	1.12	1.51
$\Sigma(n-C_{27}-n-C_{31})/\Sigma(n-C_{15}-n-C_{19})$	0.15	0.26
$2n-C_{29}/n-C_{28} + n-C_{30}$	1.03	0.91
CPI (n-C <sub>24</sub> -n-C <sub>34</sub> )	0.93	0.89
Odd/Even	0.97	0.99
$\Sigma i\text{-Alkanes} / \Sigma n\text{-Alkanes}$	0.43	0.38
$\Sigma (n-C_{11}-n-C_{17})/\Sigma (n-C_{11}-n-C_{37})$	0.61	0.54
$\Sigma (n-C_{27}-n-C_{37})/\Sigma (n-C_{11}-n-C_{37})$	0.07	0.11

**Table 5.** Results of EPR spectroscopy of domanik rock samples of Berezovskaya area of Romashkinskoye field before and after pyrolysis at different temperatures.

Sample number	Content of paramagnetic centers, arb. units						
	Free organic (hydrocarbon) radical			Inorganic radicals and ions			
	23 °C	350 °C	600 °C	SO <sub>2</sub> <sup>-</sup>	SO <sub>3</sub> <sup>-</sup>	VO <sup>2+</sup>	Mn <sup>2+</sup>
Coring interval 1712.5-1718.5 m							
1	613.2	5860.9	437.3	322.2	472.4	720.9	2375.2
1ex	1057.2	2690.7	412.6	295.2	916.0	979.6	2708.6
Coring interval 1718.5-1724.5 m							
2	164.0	817.4	341.6	304.1	150.2	141.7	2082.2
2ex	367.8	753.3	311.9	156.7	120.9	441.7	844.8

organic matter and an evidence of carbonate-rich source rocks. Saturated hydrocarbons contain alkanes with isoprenoid structure (isoalkanes), but in much smaller quantities than n-alkanes (ratio of isoalkanes to n-alkanes is 0.43 and 0.38 for samples 1 and 2 respectively), which may also point to the low thermal maturity of organic matter. The ratio of pristane to phytane for the investigated extracts, which is an important genetic trait, varied from 0.69 to 0.75, which confirms mainly sapropel type of organic matter. According to the distribution of pristane/C<sub>17</sub> and phytane/C<sub>18</sub> ratios bitumen of sample 2 is less mature. In general, according to gas chromatography results, the extracts from the rocks are typical for Tatarstan [41].

This study focuses on domanik rocks research using EPR spectroscopy. Four samples of rocks were taken: initial samples (1 and 2), and the same samples after soluble organic extraction (1ex and 2ex).

Comparative analysis of the EPR spectra of the initial and extracted samples showed that in the extracted rocks there are the vanadyl-ions (VO<sup>2+</sup>) and the free radicals R\*, which belong to a bitumen part of rock. Moreover, extraction increases their concentration per unit weight of sample. Vanadium can be found in a mobile state in oil and bitumen and in immobile state in kerogen. Increasing concentration of vanadyl porphyrins in rocks after organic matter extraction gives a reason to believe that the vanadium enters to the structure of kerogen. In addition, this may serve as a criteria to include the studied rocks to the group of shales, containing kerogen in its composition.

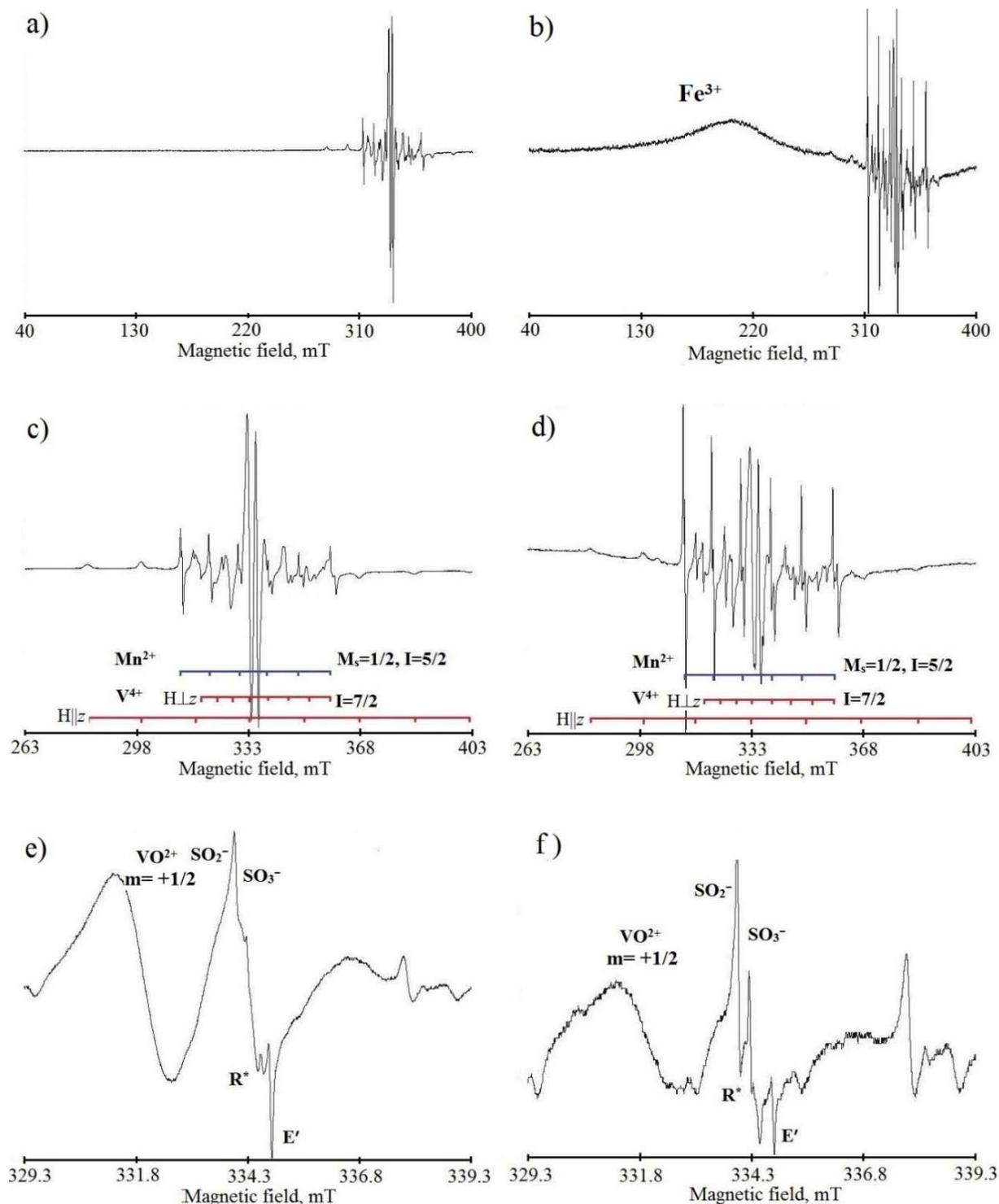
Results of subjected to preliminary thermal treatment in a hydrogen atmosphere at 350 and 600 °C samples study are of particular interest. EPR spectroscopy results for all samples are presented in Table 5.

Fe<sup>3+</sup> ions, SO<sub>3</sub><sup>-</sup> and SO<sub>2</sub><sup>-</sup> ions in CO<sub>3</sub><sup>2-</sup> position in the structure of calcite, Mn<sup>2+</sup> ions in the position of calcium and the presence of silicium due to radiation E' centers were identified by EPR spectra (Fig. 3). Mn<sup>2+</sup> ions indicate the presence of deep-water facies formed in conditions of oxygen insufficiency [42, 43].

Distribution details of SO<sub>3</sub><sup>-</sup> and SO<sub>2</sub><sup>-</sup> ions in carbonate minerals are especially interesting for analysis as they are indicators of eodiagenesis (early diagenesis) of carbonate silts with the participation of syngenetic organic matter [33, 34]. The inequation SO<sub>3</sub><sup>-</sup> / SO<sub>2</sub><sup>-</sup> > 0.5 indicates that the carbonate formation occurred in oxidizing environment of sedimentation. Alternatively, the inequation SO<sub>3</sub><sup>-</sup> / SO<sub>2</sub><sup>-</sup> < 0.5 shows that the carbonate formation occurred in reducing environment of sedimentation.

It should be noted that the pyrolysis of samples was conducted with preliminary exposure of hydrochloric acid for calcite dissolving which enable to avoid the overlay of crystal matrix spectra on organic free radical signal.

The number of paramagnetic centers, belonging to organic matter, significantly increased after pyrolysis. In addition to quantitative changes, qualitative changes were registered as well. Organic matter undergoes thermal conversion, which is evident because of the formation of new organic radical  $C_{350}$  after heating at  $350\text{ }^{\circ}\text{C}$  in a hydrogen atmosphere.  $C_{350}$  radical signatures differ in shape, not merely in intensity from the radicals  $R^*$  registered in the initial sample (Fig. 4). New radical indicates the appearance of newly formed free hydrocarbons. The research results give good reason to believe that



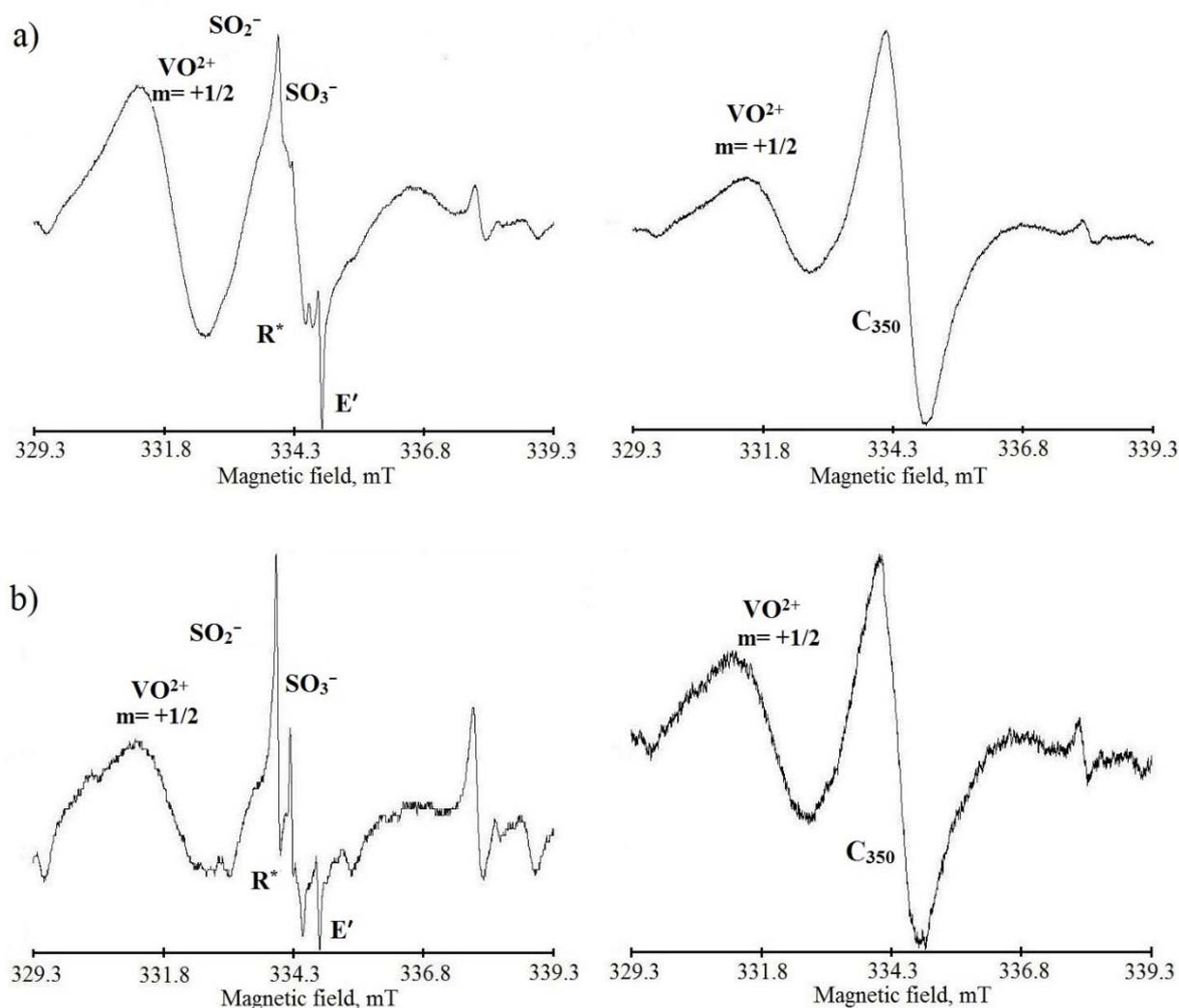
**Figure 3.** EPR spectra: the area of  $Fe^{3+}$  ion (absent in the first sample) for sample 1 (a) and for sample 2 (b), the area of  $Mn^{2+}$  and  $VO^{2+}$  ions for sample 1 (c) and for sample 2 (d), the area of the organic radical, most intense ion signal  $VO^{2+}$ , and  $E'$ ,  $SO_3^-$ ,  $SO_2^-$  for sample 1 (e) and for sample 2 (f).

the process of pyrolysis, to some extent, simulates the natural conditions of organic matter maturation, because content of paramagnetic centers in the organic matter increases with increasing degree of thermal maturation and sediments depth [44-46].

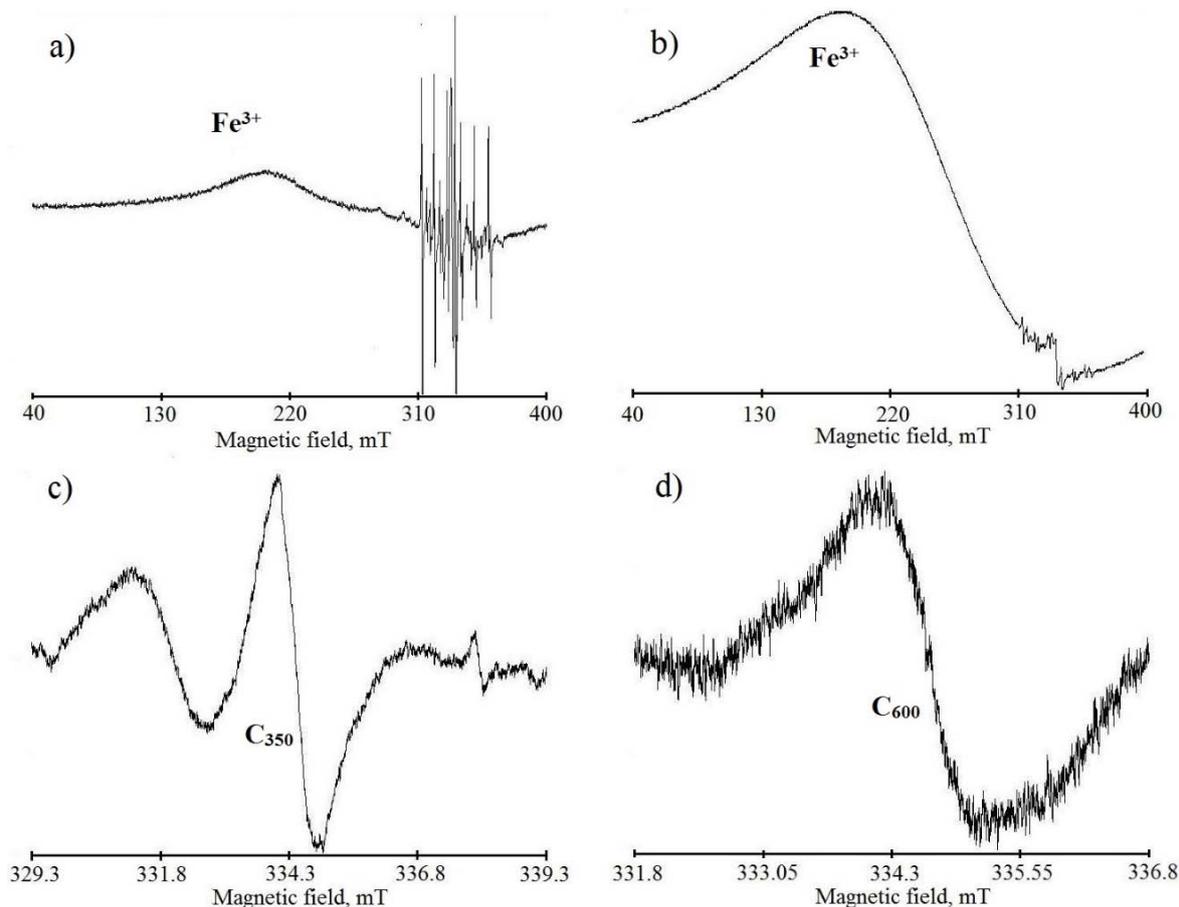
Kerogen destruction processes are associated with increasing temperature, resulting in decomposition of polymeric polycondensed compounds to less complex compounds including hydrocarbons. It happens because the kerogen loses aliphatic chains while aromatic structural fragments redistributed in its matrix [35].

Pyrolysis at 600 °C is accompanied by intensive detachment of ferric iron from the structure of siliceous minerals. A new free hydrocarbon radical  $C_{600}$  forms as well. In  $C_{600}$  radical area, multiple overlapping signals are observed. Newly formed free hydrocarbon radical  $C_{600}$  distinguishes from  $C_{350}$  radical by smaller intensity. The absence of divalent manganese after pyrolysis at 600 °C is due to the processes of carbonate minerals destruction (Fig. 5).

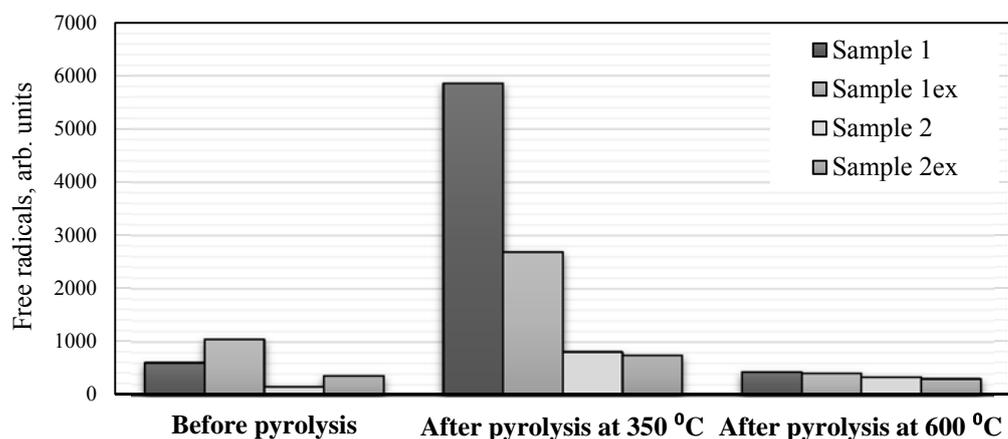
The diagram (Fig. 6) reflects the concentration of hydrocarbon free radicals. It may be noted that the sample 1 has a much larger oil generating potential. There is a growing number of free radicals in all samples after pyrolysis at 350 °C. Inverse trend is observed for pyrolysis at 600 °C (number of free radicals for all samples after pyrolysis at 600 °C is lower than after pyrolysis at 350 °C), which probably can be explained by the exhaustion of the kerogen generation potential and the subsequent destruction of newly formed compounds at high temperatures.



**Figure 4.** Differences in the EPR spectra in organic radicals area before (left) and after (right) pyrolysis at 350 °C: (a) sample 1, (b) sample 2.



**Figure 5.** EPR spectra: (a) the area of  $\text{Fe}^{3+}$  ion before pyrolysis at 600 °C, (b) area of  $\text{Fe}^{3+}$  ion after pyrolysis at 600 °C, (c) the area of organic radical after pyrolysis of 350 °C, (d) the area of organic radical after pyrolysis at 600 °C. For d spectrum sweep of the magnetic field is 5 mT.



**Figure 6.** Diagram of free radicals content in organic matter (in arbitrary units).

#### 4. Summary

Comprehensive analysis of the samples revealed the following features of domanik sediments:

1. The high heterogeneity through the section, which is manifested in the mineral composition of rocks and in the content of organic matter.
2. High content of kerogen.
3. Extracted bitumen composition is generally similar, except the content of aromatics and resins.

The calculated values of geochemical ratios suggest a mainly sapropel type of initial organic matter, buried in the reducing and subaqueous conditions and low thermal maturity of organic matter.

4. The increasing number of free radicals, belonging to organic matter, was registered in all samples after pyrolysis in a hydrogen atmosphere at 350°C. A new organic free radical C<sub>350</sub> was registered after pyrolysis. This indicates the appearance of free newly formed hydrocarbons.

Based on the values of geochemical ratios, results of thermal analysis and interpretation of the EPR spectra, it can be assumed that domanik sediments have not fully realized their oil generation potential.

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## **References**

1. Speight J.G. *Deep Shale Oil and Gas*, Golf Professional Publishing, Cambridge (2017)
2. Gordon D. *Understanding Unconventional Oil (Carnegie's Energy and Climate Program)*, Carnegie Endowment for International Peace, Washington, D.C. (2012)
3. Muslimov R.Kh., Plotnikova I.N. *Neftyanoe Khozyaistvo [Oil Industry]* **1**, 12 (2014) (*in Russian*)
4. Muslimov R.Kh., Plotnikova I.N. *Evaluation of the Resource Potential of Shale Hydrocarbons on the Territory Tatarstan Republic (Volga-Ural Oil and Gas Province)*, EGU General Assembly: Geophysical Research Abstracts, Vienna, (2015)
5. Khusainov R.F., Nazimov N.A., Gumarov N.F., Ganiev B.G., Shvydenko M.V., Absalyamov R.Sh. *Georesursy [Georesources]* No. 4(63), Vol. 2, 14 (2015) (*in Russian*)
6. Ulmishek G.F., Klemme H.D. *Depositional Control, Distribution and Effectiveness of World's Petroleum Source Rocks*, U.S. Government Printing Office, Denver, (1990)
7. Ostrouhov S.B., Plotnikova I.N., Nosova F.F., Pronin N.V. *Georesursy [Georesources]* No. 3(62), Vol. 1, 42 (2015) (*in Russian*)
8. Maksimova S.V. *Ecological and Facial Features and Forming Conditions of Domanik Sediments*, Nauka, Moscow (1970) (*in Russian*)
9. McMillan N.J., Embry A.F., Glass D.J. (eds.) *Devonian of the World, Volume I – Regional Syntheses*, Calgary, Canadian Society Of Petroleum Geologists (1988)
10. Fadeeva N.P., Kozlova E.V., Poludetkina E.N., Shardanova T.A., Pronina N.V., Stupakova A.V., Kalmykov G.A., Khomyak A.N. *Moscow University Geology Bulletin* **71**, 41 (2016)
11. Michele L.W. Tuttle, Paul G.L., Jerry L.C. *Molecular Stratigraphy of the Devonian Domanik Formation, Timan-Pechora Basin, Russia*, Geological Survey Open-File Report 99-379 (1999)
12. Fadeeva N.P., Shardanova T.A., Smirnov M.B., Poludetkina E.N., Molenkova A.A. *Peculiarities of Domanik Formation Organic Matter within the South-Tatar Arch*, 27<sup>th</sup> International Meeting on Organic Geochemistry: Book of Abstracts, Prague (2015)
13. Burov B.V. *Tatarstan Geology: Stratigraphy and Tectonics*, GEOS, Moscow (2003) (*in Russian*)
14. Gottih R.P., Pisockiy B.I. *Georesursy [Georesources]* 4, 6 (2006) (*in Russian*)
15. MacLeod N. *Russian Geology and Geophysics* **9**, 979 (2005)
16. MacLeod N. *The Great Extinction: What Causes Them and How They Shape Life*, The Natural History Museum, London (2013)
17. Neruchev S.G. *Uranium and Life in Earth History*, Nedra, Saint-Petersburg (1982) (*in Russian*)
18. Afanasieva M.S., Mikhailova M.V. *Stratigraphy and Geological Correlation* **9** (5), 419 (2001)
19. Lindquist S.J. *The Timan-Pechora Basin Province of Northwest Arctic Russia: Domanik–Paleozoic Total Petroleum System*, U.S. Geological Survey Open-File Report 99–50–G, (1999)

20. Zaidelson M.I., Surovnikov E.Ya., Kazmin L.L., Vaynbaum, S.Ya., Semenova, E.G. *Geologiya Nefti i Gaza [Oil and Gas Geology]* **6**, 2 (1990) (in Russian)
21. Anan'ev V.V., Smelkov V.M., Pronin N.V. *Geologiya Nefti i Gaza [Oil and Gas Geology]* **1**, 32 (2007) (in Russian)
22. Vandenbroucke M. *Oil & Gas Science and Technology – Revue de l'Institut de Français du Pétrole* **58**, 243 (2003)
23. Tissot B.P., Welte D.H. *Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration*, Springer-Verlag, Berlin (1978)
24. McCarthy K., Rojas K., Niemann M., Palmowski D., Peters K., Stankiewicz A. *Oilfield Review* **23**, 32 (2011)
25. Solli H., BJORoy M., Leplat P., Hall K. *Journal of Analytical and Applied Pyrolysis* **7**, 101 (1984)
26. Behar F., Vandenbroucke M. *Organic Geochemistry* **13**, 927 (1988)
27. Kayukova G.P., Kiyamova A.M., Mikhailova A.N., Kosachev I.P., Petrov S.M., Romanov G.V., Sitdikova L.M., Plotnikova I.N., Vakhin A.V. *Chemistry and Technology of Fuels and Oils* **52**, 149 (2016)
28. Tagiev M.F., Zejnalov G.A. *Trudy NIPI «Neftegaz» SOCAR [NIPI «Neftegaz» SOCAR works]* **2**, 16 (2010) (in Russian)
29. Kök M.V., Şengüler I. *Journal of Thermal Analysis and Calorimetry* **116**, 367 (2014)
30. Bulka G.R., Nizamutdinov N.M., Mukhutdinova N.G., Khasanova N.M., Galeev A.A., Vinokurov V.M. *Applied Magnetic Resonance* **2**, 107 (1991)
31. Eaton G.R., Eaton S.S., Salikhov K.M. *Foundations of Modern EPR*, World Scientific Publishing (1998)
32. Gilinskaya L.G. *Journal of Structural Chemistry* **49**, 245 (2008)
33. Kai A., Miki T. *International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry* **40**, 469 (1992)
34. Barabas M. *International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements* **20**, 453 (1992)
35. Bushnev D.A., Burdel'naya N.S. *Petroleum Chemistry* **53**, 145 (2013)
36. Burdel'naya N.S., Bushnev D.A., Mokeev M.V. *Vestnik IG Komi NC UrO RAN* **6**, 33 (2015) (in Russian)
37. Kök M.V. *Journal of Thermal Analysis and Calorimetry* **91**, 763 (2008)
38. Labus M. *Journal of Thermal Analysis and Calorimetry* (2017) DOI: [10.1007/s10973-017-6259-7](https://doi.org/10.1007/s10973-017-6259-7)
39. Vakhin A.V., Morozov V.P., Sitnov S.A., Eskin A.A., Petrovnina M.S., Nurgaliev D.K., Kayukova G.P., Romanov G.V., Yusupova T.N. *Chemistry and Technology of Fuels and Oils* **50**, 569 (2015)
40. Peters K.E., Walters C.C., Moldowan J.M. *The Biomarker Guide: Volume 2, Biomarkers and Isotopes in Petroleum Systems and Earth History*, Cambridge University Press (2007)
41. Nosova F.F., Pronin N.V. *Organic Geochemical Study of Domanik Deposits, Tatarstan Republic*, EGU General Assembly: Geophysical Research Abstracts, Vienna (2010)
42. Babakhani A., Yang X. *EPR Systems for Flow Assurance and Logging*, United States patent application 2016/0223478
43. Díaz M., Aldana M., Jiménez S.M., Sequera P., Costanzo-Álvarez V. *Revista Mexicana de Física* **52** (3), 65 (2006)
44. Chilingarian G.V., Buryakovskiy L.A., Eremenko N.A., Gorfunkel M.V. *Geology and Geochemistry of Oil and Gas*, Elsevier (2005)
45. Bakr M.Y., Akiyama M., Sanada Y. *Organic Geochemistry* **15** (6), 595 (1990)
46. Bakr M., Akiyama M., Sanada Y., Yokono T. *Organic Geochemistry* **12** (1), 29 (1988)