ISSN 2411-3336; e-ISSN 2541-9404

JOURNAL OF MINING INSTITUTE
Zapiski Gornogo instituta
Journal homepage: pmi.spmi.ru

Research article

Potential trace element markers of naphthogenesis processes: modeling and experimentation

Tatyana N. Aleksandrova, Valentin V. Kuznetsov✉, Nadezhda V. Nikolaeva
Empress Catherine II Saint Petersburg Mining University, Saint Petersburg, Russia

***How to cite this article*:** Aleksandrova T.N., Kuznetsov V.V., Nikolaeva N.V. Potential trace element markers of naphthogenesis processes: modeling and experimentation. Journal of Mining Institute. 2024. Vol. 269, p. 687-699.

Abstract. With the growing demand for hydrocarbon energy resources, there is a need to involve oil fields at deeper horizons in processing and increase the profitability of their development. Reduction of expenses on prospecting works is possible at revealing and substantiation of physicochemical markers of the naphthogenesis processes. One of the key markers is the transition metals content, which are both a measure of oil age and markers of potential associated processes in the migration and formation of hydrocarbons in the Earth's strata. The elemental composition of samples of oil and reservoir rocks of the Timan-Pechora field was studied. Based on the results of thermodynamic modeling, plausible processes of contact rock minerals transformation were proposed. Based on the results of molecular modeling the probable structure of vanadium and nickel host molecules in the heavy fraction of oils is proposed. The ratios of transition metal and sulfur contents were experimentally established, and assumptions about possible mechanisms of formation of deep hydrocarbon reservoirs were made. Analysis of the obtained ratios of transition metal contents in reservoir rocks and oil samples allowed to suggest possible processes of mantle fluids contact with the host rock and subsequent accumulation of hydrocarbons on sorption active rocks. According to the combined results of experimental and theoretical studies it was found that polymers of heavy fraction more selectively capture vanadium, which indicates the predominance of vanadium content in oil-bearing rocks in relation to the content of nickel. In this case, oil acts as a transport of transition metals, leaching them from the bedrock.

***Keywords*:** trace elements; naphthogenesis; thermodynamic modeling; molecular modeling; deep oil

***Funding*.** The work was carried out within the framework of the state assignment “Study of thermodynamic processes of the Earth from the position of hydrocarbon genesis at great depths” FSRW-2024-0008.

Received: 13.05.2024 ***Accepted: 05.09.2024*** ***Online: 26.09.2024*** ***Published: 12.11.2024***

Introduction. The gradual recovery of the global economy in 2021 has led to a significant increase in the consumption of liquid hydrocarbons. According to BP Statistical Review of World Energy, in 2021 the growth in relation to 2020 amounted to 6 % – from 88.7 to 94.1 mln barrels per day. The US (18.7 mb/day) and China (15.4 mb/day) remained the largest consumers of carbon raw materials, with their combined consumption amounting to 36.2 % of the world total. The largest consumers also included India (4.9 mb/day), Saudi Arabia (3.6 mb/day), Russia (3.4 mb/day), Japan (3.3 mb/day), South Korea (2.8 mb/day), and Brazil (2.3 mb/day); the combined share of these six countries in the global figure amounted to 21.6 %[1].

The growing demand for natural energy resources requires the involvement in processing of hydrocarbon deposits of deeper horizons and new technologies of their exploration and extraction [1-3]. Each deposit is characterized by unique chemical and fractional compositions of hydrocarbons and impurities due to the genesis of these deposits [4, 5]. The reservoir formation

[1] State report 2021. URL: https://www.rosnedra.gov.ru/article/15043.html (accessed 13.05.2024).

This is an open access article under the CC BY 4.0 license

features of various discovered deep fields can be used to identify hydrocarbon reservoir location markers [5-7].

Based on the existing theories of oil formation in the Earth's strata, naphtho-genesis is the sum result of many geological events: sedimentation and post-sedimentation diagenetic processes, metamorphic and metasomatic transformations of rocks, as well as hydrocarbon migration processes of both abiogenic and biogenic origin [8, 9]. All these geologic events are reflected in the mineralogeochemical and petrochemical properties of the rocks and the oil-bearing bodies formed in them [10-12]. The primary stages of forecasting and assessment of oil-bearing potential of such fields are possible on the basis of analysis of elemental, phase and mineralogical compositions of both the inorganic part of oils and collector rocks, which will allow designing technologies for their recovery, transportation and further processing [13-15].

Such features include the significant presence of noble metal particles, intermetallides of natural alloys, sulfides, carbides and silicides, both in the oil itself and in the collector rocks, which may indicate the participation of mantle processes in oil formation [16-18]. One of the potential opportunities for naphthogenesis is the interaction of mantle fluid flows of gas and hydrocarbons with the already formed sedimentary mantle. Higher temperatures at deep horizons cause significant amounts of methane to be present in the oils, which will migrate to higher horizons. In the temperature range from 200 to 400 °C methane has high chemical activity, which promotes the processes of reduction of metal compounds with variable valence (Fe, Mn, Cu, V, Ni, Co, Cr, Mo, etc.) [19]. During the migration of mantle hydrocarbon gases, they will be in contact with rocks, which, in turn, will lead to changes in the chemical form of mineral formations of these metals [20, 21]. During migration, saturated hydrocarbons may encounter layers of sorption-active rocks, which are capable of absorbing and accumulating transition metal compounds, which affects their technological properties from the application of processing technologies standpoint [22-24]. Contact with these rocks can be both a barrier to further migration of hydrocarbon fluids and a marker of their potential location.

When predicting the locations of such hydrocarbon accumulations, an important aspect is the approximate estimation of the age of hydrocarbon formation and migration of the forms of companion minerals of potential abiogenic formation. To assess the possibility of sedimentary rock-collectors to act as an accumulator of migrating abiogenic oil it is possible to use petrochemical modules – a number of ratios of chemical element contents, which are direct or indirect markers of ongoing processes [25].

The purpose of this work was to establish possible trace element markers of deep naphthogenesis processes based on the results of molecular and thermodynamic modeling, as well as the study of collector rock properties.

Materials and methods. The experiment was conducted in two stages. The first one was modeling of the associated naphthogenesis processes of transformation of minerals of contact rocks and modeling of stability of potential compounds of transition metal carriers. At the second stage, the elemental composition of reservoir rock samples was investigated.

The Gibbs free energy calculation module of the HSC Chemistry 6.0[2] program was used to model possible oil genesis processes. The main purpose of the module is to determine the change in thermodynamic functions during a chemical reaction. The essence of the approach is to estimate the overall probability of the potential reaction of hydrocarbon formation based on the value of the change in Gibbs energy

$$\Delta G = \Delta H - T\Delta S,$$

where ΔH – enthalpy change value, kJ/mol; ΔS – entropy change, kJ/(mol·K); T – absolute temperature, K.

[2] HSC Version 6.0. URL: https://www.scientific-computing.com/press-releases/hsc-version-60 (accessed 13.05.2024).

This is an open access article under the CC BY 4.0 license

A negative value of the Gibbs energy change means a high probability of the reaction proceeding in the forward direction, and a positive value means an extremely low probability of the reaction. The lower the value of the Gibbs energy change, the more probable the reaction is. Calculation of thermodynamic functions in the Gibbs free energy calculation module was performed based on the database of standard enthalpy and entropy values.

The stability of the molecular structure of carrier compounds was assessed using the Avogadro software package, a molecular editor and visualizer whose main purpose is cross-platform use in computational chemistry. The program used the UFF bond potential energy minimization method to find the most stable structure of the molecule. The UFF method belongs to a class of molecular mechanics methods that focus on finding the optimal geometric characteristics and energies of multi-atomic systems based on the equations of mechanics. The total energy of the molecule under study is the sum of the different type of energies: chemical interaction, valence angles, torsion interaction, van der Waals interaction, and electrostatic interaction[3].

Energy assessment algorithm:

• bond energy potential

$$U_b = 0.5K_r\left(l - l_{\text{p}}\right)^2,$$

where K_r – force field constant for calculating the bonding energy potential, K_r = 12,5 kJ·mol^{-1}/Å^2; l_{p} – accepted equilibrium distance between particles, l_{p} = 4,7 Å; l – interparticle distance, Å;

• valence angle potential

$$U_a = 0.5K_a\left(\cos Q - \cos Q_{\text{p}}\right)^2,$$

where K_a – force field constant for calculating the valence angles potential, K_a = 25 kJ·mol $^{-1}$/rad^2; Q_{p} – assumed equilibrium angle, Q_{p} = 120 rad; Q – valence angle between particles, rad;

• charged particle interaction potential

$$U_c = \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_l l},$$

where q_i, q_j – reduced particle charge, C/mol; ε_0 – vacuum dielectric constant, F/m; ε_l – relative medium permittivity;

• potential of van der Waals interactions as the Lennard – Jones potential,

$$U_W = 4\varepsilon_W\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right),$$

where ε_w – minimum energy barrier (potential pit); σ – the distance at which the interaction is minimal.

The objects of the study were samples of heavy oil of the Timan-Pechora province, as well as samples of its reservoir rocks.

The composition of oil samples was analyzed in two stages. At the first stage the heavy component of oil was separated according to the difference in solubility by SARA-analysis. The name of the method is the first letters of the fractions separated in the process of analysis – saturates (aliphatic hydrocarbons), aromatic (aromatic compounds), resin (rubbers), asphaltene (asphaltenes). The method is based on the solvent method of separation of compounds according to their polarity using extractants. The heavy oil fraction, consisting mainly of the asphaltene fraction, was separated from the maltene fraction by extraction using n-heptane. The separation was carried out in a centrifugal field to intensify extraction [26, 27]. The undissolved fraction was washed in toluene and then the residual solvent was evaporated at 110 °C.

[3] Auto Optimize Tool. URL: https://avogadro.cc/docs/tools/auto-optimize-tool/ (accessed 13.05.2024).

This is an open access article under the CC BY 4.0 license

At the second stage, X-ray fluorescence analysis of the undissolved fraction after washing with toluene was carried out. Microphotographs of rock particles were obtained using TESCAN – Vega3 scanning electron microscope.

In addition, experiments were conducted on the concentration of minerals with low magnetic susceptibility using a high-gradient magnetic separator Slon 100. For the experiments samples were prepared of collector rock samples of –0.2 mm in size and 100 g in weight. All experiments with the use of a high-gradient magnetic separator were conducted at the same magnetic induction of 1.1 Tesla, the size of the diameter of the matrix rods was 3 mm. The chemical composition of samples of host rocks, heavy oil fraction and magnetic concentration products were analyzed using EDX – 7000 X-ray fluorescence analysis device. This method belongs to the group of spectroscopic nondestructive methods of elemental analysis, based on exposure of the sample under study by X-ray radiation and registration of the spectrum of back radiation from the sample. It is based on the correlation of the intensity induced by irradiation of fluorescence with the content of a certain element in the sample. Each emission intensity value is correlated with a standard emission resulting from the emission of a photon from a certain energy level (K, L, M). The results are interpreted using the intensity values for alpha, beta and gamma emissions for each element.

Results and discussion. *Modeling results of potential associated processes of deep naphthogenesis and transition metal carrier molecules to substantiate potential elemental markers*. In works [28, 29] correlation of deep oil composition with the ratio of vanadium and nickel content, as well as potential participation of mantle gases in the process of hydrocarbon accumulation is presented. Correlation of oil composition with the ratio of nickel and vanadium content is associated with the mineral forms conditions of formation and transformation due to contact with ascending mantle gases, which can participate in the potential mechanism of low-molecular hydrocarbons synthesis due to sharp cooling of the gas mass and formation of condensate. Primary synthesis proceeds by interaction of fluid compounds H_2, CO_2 and H_2S. The most probable mechanism is the Fischer – Tropsch reaction, transition metal compounds such as vanadium and nickel can act as catalysts. Sulfur-containing components of mantle gases can participate in chemical reactions with mineral compounds of vanadium and nickel. Potential reactions of transformation of vanadium and nickel compounds as associated processes of naphthogenesis are presented in Table 1.

Table 1

Potential transformations of vanadium- and nickel-containing compounds

Reaction number	Potential transformation reactions of vanadium compounds	ΔG reaction, kJ/mol	Potential conversion reactions nickel compounds	ΔG reaction, kJ/mol
1	$VO + 0.5O_2 \rightarrow VO_2$	–13.357	$NiS + SO_2 \rightarrow O_2 + NiS_2$	15.461
2	$2VO + 0.5O_2 \rightarrow V_2O_3$	–17.555	$3NiS + O_2 \rightarrow SO_2 + Ni_3S_2$	–14.671
3	$2VO + 1.5O_2 \rightarrow V_2O_5$	–30.553	$3NiS + SO_2 \rightarrow O_2 + Ni_3S_4$	15.423
4	$VO + O_2 + SO_2 \rightarrow VOSO_4$	–19.953	$NiS + 2O_2 \rightarrow NiSO_4$	–32.221
5	$2VO_2 + 0.5O_2 \rightarrow V_2O_5$	–3.838	$3NiS_2 + 4O_2 \rightarrow 4SO_2 + Ni_3S_2$	–61.054
6	$VO_2 + 0.5O_2 + SO_2 \rightarrow VOSO_4$	–6.596	$3NiS_2 + 2O_2 \rightarrow 2SO_2 + Ni_3S_4$	–30.960
7	$VO_2 + SO_2 \rightarrow 2O_2 + VS$	42.108	$NiS_2 + 3O_2 \rightarrow SO_2 + NiSO_4$	–47.682
8	$2VO_2 + 3SO_2 \rightarrow 5O_2 + V_2S_3$	93.050	$Ni_3S_2 + 2SO_2 \rightarrow 2O_2 + Ni_3S_4$	30.095
9	$V_2O_3 + O_2 \rightarrow V_2O_5$	–12.997	$0.333Ni_3S_2 + 0.333SO_2 + 1.667O_2 \rightarrow NiSO_4$	–27.330
10	$0.5V_2O_3 + 0.75O_2 + SO_2 \rightarrow VOSO_4$	–11.176	$0.333Ni_3S_4 + 2.333O_2 \rightarrow 0.333SO_2 + NiSO_4$	–37.362
11	$0.5V_2O_3 + SO_2 \rightarrow 1.75O_2 + VS$	37.529	$0.111Ni_9S_8 + 0.111SO_2 + 1.889O_2 \rightarrow NiSO_4$	–31.294
12	$V_2O_3 + 3SO_2 \rightarrow 4.5O_2 + V_2S_3$	83.891	$NiS + H_2S(g) \rightarrow H_2(г) + NiS_2$	1.007
13	$0.5V_2O_5 + 0.25O_2 + SO_2 \rightarrow VOSO_4$	–4.677	$3NiS + H_2(г) \rightarrow H_2S(г) + Ni_3S_2$	–0.217
14	$0.5V_2O_5 + SO_2 \rightarrow 2.25O_2 + VS$	44.027	$3NiS + H_2S(г) \rightarrow H_2(г) + Ni_3S_4$	0.969

This is an open access article under the CC BY 4.0 license

End of Table 1

Reaction number	Potential transformation reactions of vanadium compounds	ΔG reaction, kJ/mol	Potential conversion reactions nickel compounds	ΔG reaction, kJ/mol
15	$V_2O_5 + 3SO_2 \rightarrow 5.5O_2 + V_2S_3$	96.889	$3NiS_2 + 4H_2(г) \rightarrow 4H_2S(г) + Ni_3S_2$	–3.237
16	$VOSO_4 \rightarrow 2.5O_2 + VS$	48.704	$3NiS_2 + 2\ H_2(г) \rightarrow 2H_2S(г) + Ni_3S_4$	–2.051
17	$2VOSO_4 + SO_2 \rightarrow 6O_2 + V_2S_3$	106.243	$Ni_3S_2 + 2H_2S(г) \rightarrow 2H_2(г) + Ni_3S_4$	1.186
18	$VS + 3SO_2 \rightarrow 3O_2 + VS_4$	48.718	–	–
19	$2VS + SO_2 \rightarrow O_2 + V_2S_3$	8.834	–	–

Based on the analysis of the values of the Gibbs energy change it was established that in the system under consideration for vanadium compounds the most probable reactions are oxidation reactions to its higher oxide with the subsequent transition to vanadyl sulfate (reactions 1-6, 9, 10, 13). For nickel compounds the formation of nickel sulfides and sulfates is more characteristic (reactions 2, 4-7, 9-11, 13, 15, 16).

The main polymeric structures of the heavy fraction of oils are various kerogen configurations [30]. Heterocyclic nitrogen compounds in them are represented by various forms of pyrrole compounds. Thus, after the transformation of paraffins into unsaturated hydrocarbons and nitrogen- and sulfur-containing compounds, the changing conditions should promote the formation of complex compounds based on porfins [31, 32].

For more stable existence of heavy oil molecules, sulfide bridges are formed due to contact with sulfur compounds in mantle fluids. The formation of polymer structures occurs due to the interaction of porphins with sulfur-containing compounds in mantle gases. The formation of sulfide bridges unites the molecules and allows to significantly reduce the required energy for bond formation.

Since the most stable form of vanadium compounds according to the results of thermodynamic modeling are vanadyl sulfates, it is most likely that the vanadyl ion VO^{2+} due to donor-acceptor interactions will be incorporated into the heterocyclic porphine molecule. In work [28] thermodynamic possibility of existence of various compounds of porphyrin and transition metals was analyzed. It was found that the potential energy of two molecules of vanadyl porphyrin complex is 211.25 kJ/mol more than that of the condensed form with one sulfide bridge, 68.16 kJ/mol more than that of the condensed form with two sulfide bridges, and 184.40 kJ/mol less than that of the condensed form with three sulfide bridges. Consequently, the existence of the form with one and two sulfide bridges connecting two different metalloporphyrin molecules is more probable than the existence of two separate complexes. The existence of the form with three sulfide bridges is thermodynamically unfavorable.

Modeling of potential vanadium carrier compounds based on vanadyl porphins due to the formation of one and two sulfide bridges has been carried out. To predict the thermodynamic possibility of existence of polymeric compounds, the criterion characterizing the ratio of the energy of formation of a molecule U to its molecular mass M was used:

$$E_M = U/M\,.$$

The transition from one configuration to another is most probable when the value of this criterion decreases. The results of the analysis of the structure of the proposed polymeric molecules-carriers of vanadium are presented in Fig.1, energy characteristics of the proposed compounds are given in Table 2.

Based on the analysis of the obtained results, it was found that a potential mechanism of condensation of polymeric molecules based on vanadyl porphyrins is thermodynamically possible. The formation of sulfide bridges between molecules leads to a decrease in the E_M criterion. The lowest value of the criterion was obtained for the molecule where the center is a vanadylporphyrin molecule, which, due to four sulfide bridges, forms an inner contour of porphyrin molecules connected by two sulfide bridges. The outer circuit is connected to the inner circuit by one sulfide bridge per two molecules. The ratio of vanadium to sulfur content for this configuration is 0.066.

This is an open access article under the CC BY 4.0 license

Journal of Mining Institute. 2024. Vol. 269. P. 687-699
© Tatyana N. Aleksandrova, Valentin V. Kuznetsov, Nadezhda V. Nikolaeva, 2024

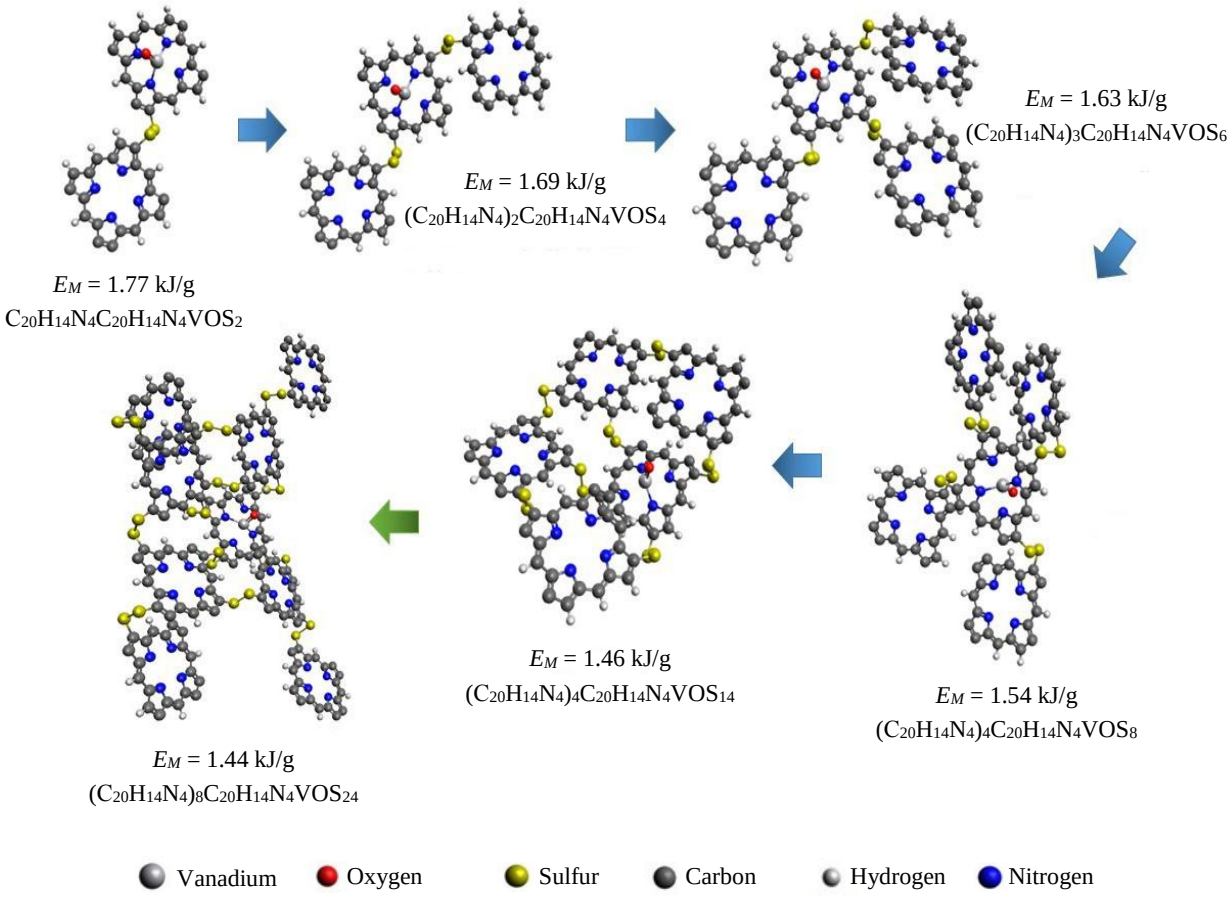


Fig.1. Potential structures of polymeric molecules-carriers of vanadium in heavy fraction of oil and their transitions to thermodynamically more favorable states

Table 2

Energetic characteristics of alleged vanadium compounds

Polymer molecular formula	Formation energy, kJ/mol	E_M, kJ/g
$C_{20}H_{14}N_4C_{20}H_{14}N_4VOS_2$	921.34	1.77
$(C_{20}H_{14}N_4)_2C_{20}H_{14}N_4VOS_4$	1903.23	1.69
$(C_{20}H_{14}N_4)_3C_{20}H_{14}N_4VOS_6$	2440.75	1.63
$(C_{20}H_{14}N_4)_4C_{20}H_{14}N_4VOS_8$	2882.55	1.54
$(C_{20}H_{14}N_4)_4C_{20}H_{14}N_4VOS_{14}$	3009.15	1.46
$(C_{20}H_{14}N_4)_8C_{20}H_{14}N_4VOS_{24}$	5215.57	1.44

The most stable form of nickel compounds according to the results of thermodynamic modeling are sulfides and sulfates, porphins due to donor-acceptor interactions form bidentate complex compounds with nickel atom in sulfides. Intermolecular coupling should occur due to the formation of sulfide bridges as extraligands [32]. The probable molecular structure of nickel carrier molecules in heavy fraction of oils is shown in Fig.2, energy characteristics of the proposed compounds are presented in Table 3.

Based on the analysis of the obtained results, it was found that the thermodynamic possibility of condensation is rather low due to the increasing value of E_M for more massive polymers. For the configuration of nickel carrier molecule with the lowest E_M value, the ratio of nickel to sulfur content is 0.92.

Results of studies of reservoir rock samples and oil samples of the Timan-Pechora province. Results of a series of experiments of centrifugal extraction of oil samples of the Timan-Pechora province in n-heptane are given in Table 4.

This is an open access article under the CC BY 4.0 license

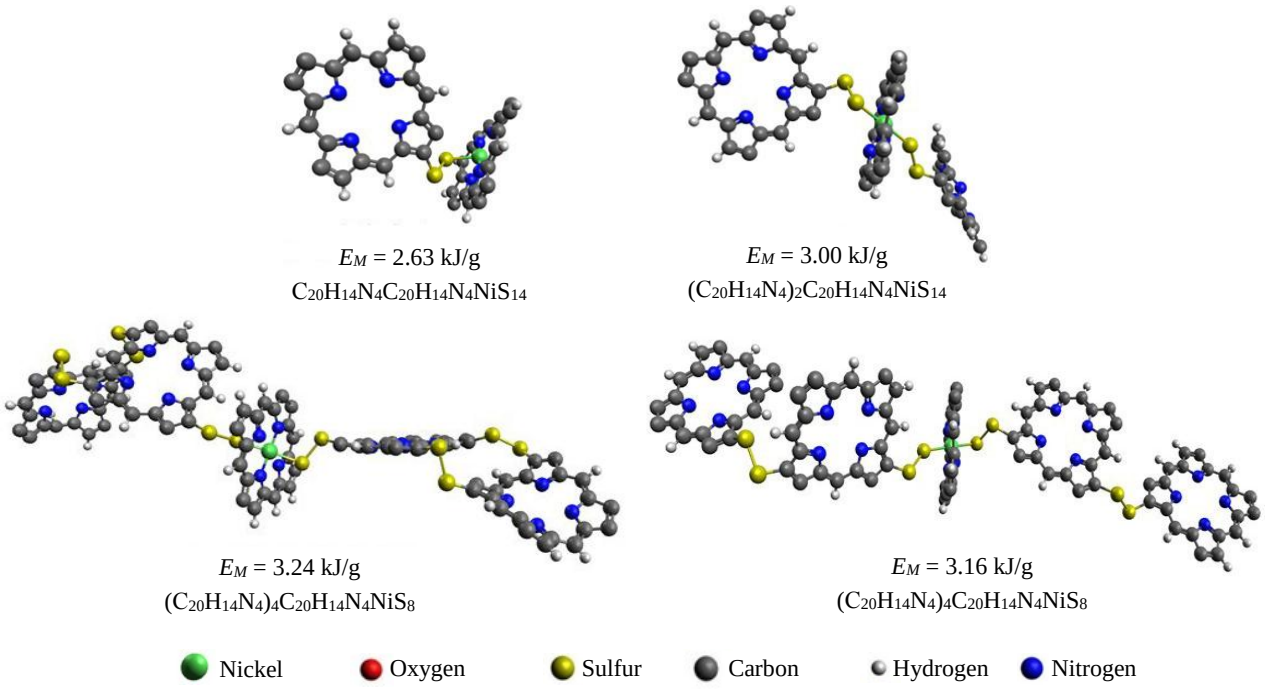


Fig.2. Potential structure of polymeric molecules-carriers of nickel in heavy fraction of oil

Table 3

Energetic characteristics of alleged nickel compounds

Polymer molecular formula	Formation energy, kJ/mol	E_M, kJ/g
$C_{20}H_{14}N_4C_{20}H_{14}N_4NiS_2$	1957.53	2.63
$(C_{20}H_{14}N_4)_2C_{20}H_{14}N_4$ NiS_4	3354.05	3.00
$(C_{20}H_{14}N_4)_4C_{20}H_{14}N_4$ NiS_8	4712.27	3.16
$(C_{20}H_{14}N_4)_4C_{20}H_{14}N_4$ NiS_8	6050.23	3.24

Table 4

Yield and content of centrifugal extraction products in n-heptane, %

Number of the experiment	Malten output	Yield of n-heptane insoluble fraction	Inorganic content
1	84.7	15.3	0.4
2	81.4	18.6	0.9
3	82.8	17.2	1.1
4	82.1	17.9	1.2
5	81.9	18.1	0.5
Mean values	82.58	17.42	0.82

On the basis of data analysis (Table 4) it is established that the average value of maltene yield in the studied oil samples is 82.58 %, the yield of heavy fraction is 17.42 %, and the content of inorganic part in heavy fraction is 0.82 %. The studied oil samples are characterized by relatively high content of the fraction insoluble in n-heptane.

According to the results of inorganic part elemental analysis for oil heavy fraction it was established that the dominant element of inorganic part is sulfur – 70.38 %; the content of other elements in the sample: Cl – 10.81, Si – 5.81, Ca – 4.85, Fe – 2.09, K – 1.96, V – 1.62, Ti – 0.77, Cu – 0.43, Cr – 0.43, Ni – 0.40, Zn – 0.32, Mn – 0.15 %. The high sulfur content is due to the presence in the oil of fine sulfide suspensions left behind after the oil has been exposed to the reservoir rocks, as well as

This is an open access article under the CC BY 4.0 license

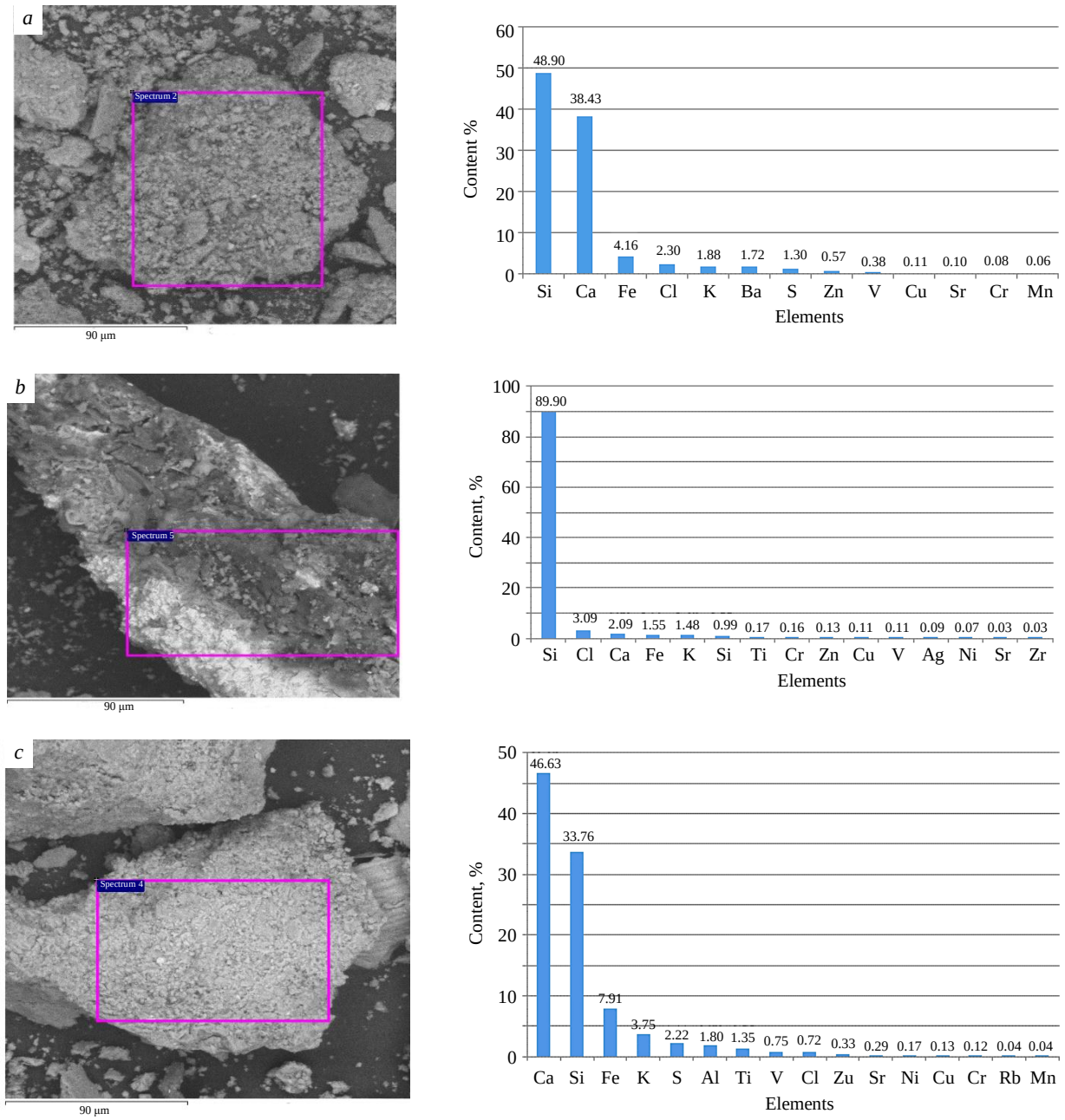


Fig.3. Samples of quartz sandstones and limestones of heavy oil sample reservoir rocks of the Timan-Pechora province:
a, *b* – quartz sandstones; *c* – limestones

residues of high molecular weight heterocyclic compounds. The presence of chlorine, silicon and calcium is also associated with the leaching of silicate minerals of the host rock such as quartz, sericite, and chlorite. The presence of transition metals such as vanadium, titanium, copper, chromium and nickel was also recorded.

In the samples of the host rock of oil samples of the Timan-Pechora province submitted for analysis three characteristic groups were identified: quartz sandstones (Fig.3 *a*, *b*), limestones (Fig.3, *c*) and thin-layered shales (Fig.4).

Based on the data analysis (see Fig.3), it was found that the main minerals of quartz sandstones composing the reservoir rocks are represented by quartz, sericite and chlorite. The presence of sulfur is noted, which is caused by the presence of sulfide mineralization (sphalerite, chalcopyrite). The highest content in the sample corresponds to silicon. The second most abundant element is calcium, which is due to the high content of calcite. Alkaline-earth metals are in the form of isomorphic impurities

This is an open access article under the CC BY 4.0 license

in calcite. Vanadium is also present in the sample (Fig.3, *a*). Analysis of the data of Fig.3, *b* showed that in this sample of quartz sandstones is dominated by siliceous minerals. The presence of titanium, chromium, zinc, copper, vanadium and nickel is associated with the leaching of their mineral associations from rocks of magmatic genesis and transfer to sandstones. Transition metals are predominantly associated with sulfides.

Based on the interpretation of the results of the elemental composition analysis, the dominant calcium content in the sample of limestone reservoir rocks was established (Fig.3, *c*). The presence of iron in the sample is associated with the presence of iron-bearing silicates and siderite. The presence of aluminum and chlorine indicates the presence of chlorite in the sample as a mineral of the host rock. The presence of titanium is due to the presence of thin grains of rutile and leucoxene. Of the studied reservoir rock samples, limestone contains the highest amount of vanadium.

The studied shale samples are characterized by the presence of carbonaceous matter in the form of bitumoids and kerogen. Thinly layered shale structure and multiple pores with potential for absorption of oil material were recorded (Fig.4). The presence of transition metals with high sulfur content was also detected in shale samples, which is caused by oil leaching of sulfides from the parent rock and its accumulation in adsorption-active carbonaceous rocks.

Analysis of the data in Table 5 showed that high-gradient magnetic separation provided extraction of vanadium- and nickel-containing mineral associations in the magnetic fraction above 95 %, while the extraction of sulfur with these forms amounted to only 16.47 %. The results of the magnetic fraction study using scanning electron microscopy are shown in Fig.5. High-gradient magnetic separation was carried out for recovery of transition metals mineral associations, having low magnetic susceptibility, from samples of host rocks, the average results of magnetic separation for vanadium, nickel and sulfur are presented in Table 5.

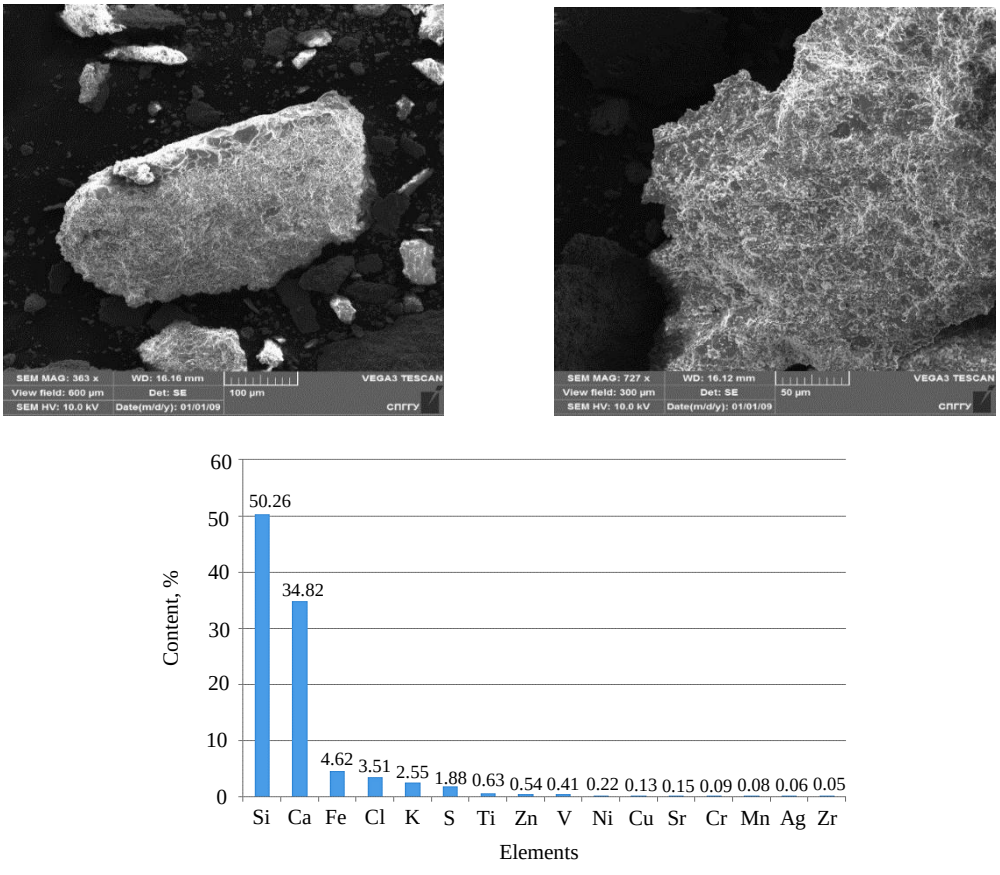


Fig.4. Samples of reservoir rocks shale for heavy oil sample of Timan-Pechora province

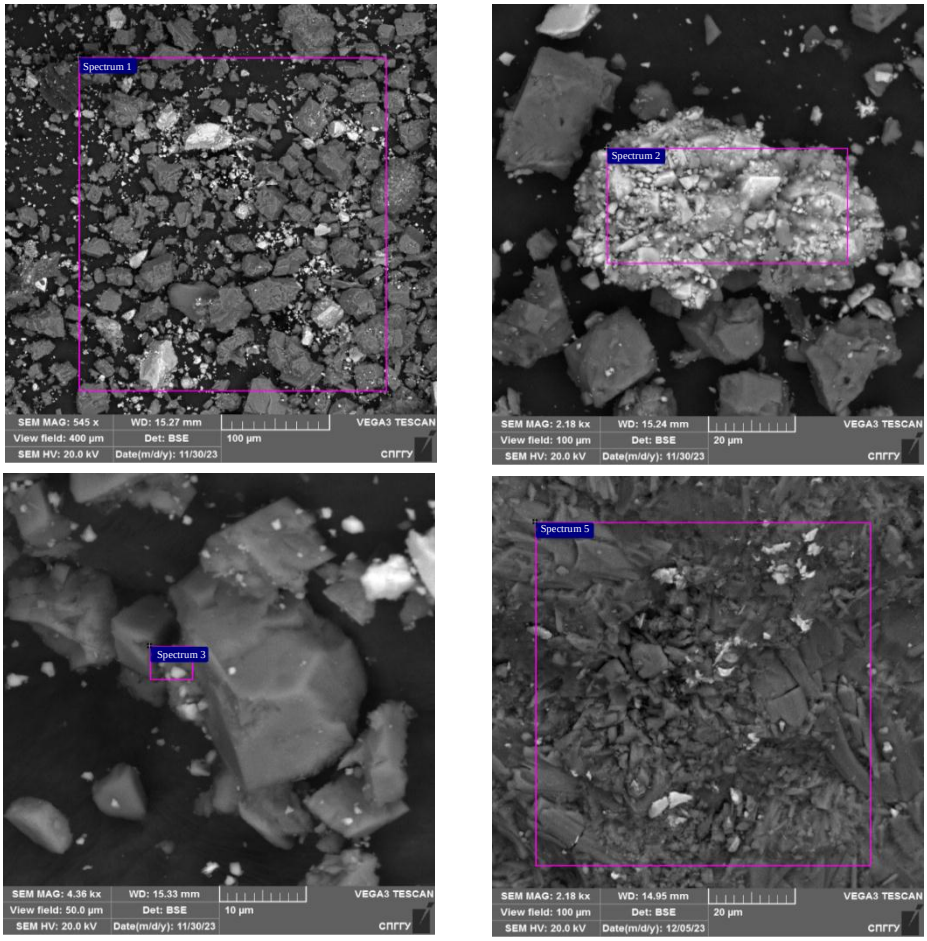
This is an open access article under the CC BY 4.0 license

Table 5

Results of experimental studies of magnetic separation of reservoir rocks

Product	Yield, %	Content			Recovery, %		
		S, %	V, ppm	Ni, ppm	S	V	Ni
Magnetic fraction	1.89	2.59	303.0	51.0	16.32	95.45	96.39
Nonmagnetic fraction	98.11	0.26	0.28*	0.04*	83.68	4.55	3.61
Feed	100	0.30	6.0	1.0	100	100	100

* Values determined from the results of mass-balance equations.



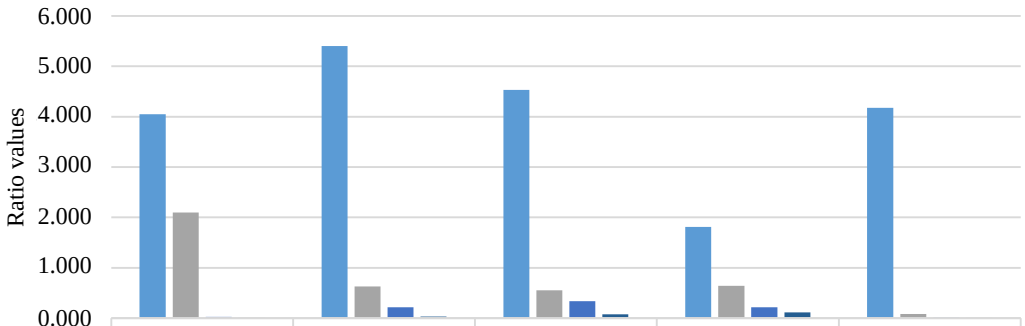
Spectre N	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	Ni	Cr	Zn	V	As	Sb
Spectre 1	42.21	0.33	1.02	7.12	10.74	19.34	2.39	0.41	0.45	15.78		0.12		0.08		
Spectre 2	19.53		1.48	1.04	1.82	16.88		2.39		53.98					0.96	1.92
Spectre 3	63.85		13.01	0.46	0.92	0.36	0.15	19.92		1.32						
Spectre 5	65.29		4.96	3.90	7.46	2.62	1.55	10.36	0.46	3.31	0.08					

Fig.5. Magnetic fraction of reservoir rocks of heavy oil sample of Timan-Pechora province

It was found that the magnetic product concentrates particles of sulfide and iron-bearing minerals with sizes from 2 to 54 microns. They can occur in the form of thin specks or form agglomerate. The presence of vanadium and nickel in scattered form is noted. Low coarseness of these mineral associations determines the possibility of their leaching and migration together with oil fluids.

Interpretation of the results of analysis of vanadium, nickel and sulfur ratios from the position of potential markers of associated naphthogenesis processes. The results of the analysis of transition metal and sulfur content ratios are presented in Fig.6.

This is an open access article under the CC BY 4.0 license



	Inorganic oil residue	Sandstones	Limestones	Shales	Magnetic fraction of reservoir rocks
V/Ni	4.050	5.400	4.530	1.810	4.174
V/Ti	2.100	0.630	0.550	0.640	0.081
V/S	0.023	0.214	0.338	0.218	0.012
Ni/S	0.006	0.031	0.077	0.117	0.003

Fig.6. Ratios of vanadium, nickel and titanium contents in oil and collector rock samples

It was found that the highest value of V/Ni corresponds to quartz sandstone samples, and the highest value of V/Ti – to inorganic oil residue (Fig.6). The general increase of the vanadium, nickel and titanium content in the inorganic oil residue in comparison with the samples of the host rock was established, associated with the interaction of oil compounds with transition metal carriers in the reservoir rocks and the formation of new compounds (metalporphyrins) and washing out of fine particles of transition metal carriers into the oil suspension.

It can be assumed that the decrease in the V/Ni ratio is due to the property of oil compounds capable of forming complex compounds with vanadium and nickel to form predominantly compounds with vanadium. This is confirmed by the results of molecular modeling – polymeric molecules-carriers of vanadium are more thermodynamically stable than the assumed carriers of nickel. At the same time, the V/S ratio in the potential polymeric molecule of vanadylporphyrin is 0.043 units higher than in the inorganic residue of the heavy fraction of oil, which is due to the presence of fine sulfide mineral particles in the oil suspension.

The increase of V/Ti ratio in oil samples taking into account lower reactivity of rutile and leucoxene in comparison with sulfides is caused by transport of fine particles of titanium carriers into oil suspension. The lower value of V/Ni for shale is due to the fact that absorption of complex compounds of vanadium and nickel in the pores of shale is less selective. The close value of V/Ti to the values for quartz sandstone and limestone samples also confirms the preferential character of leaching of fine particles of titanium-bearing minerals and the impossibility of their absorption by shale.

Based on the hypotheses put forward and studies of the elemental composition of oil samples and reservoir rocks, it can be assumed that the main role in the accumulation of hydrocarbons is played by the processes of migration of mantle gas fluids that undergo changes in their composition in contact with the host rocks.

Based on the totality of the presented research results, the following properties may be markers for searching for deep hydrocarbon deposits:

• developed fracture system and presence in the system of rocks with natural catalysts of hydrocarbon transformation processes in the form of transition metal sulfides;

• presence in the fracture system of rocks with natural hydrocarbon absorbers (shales);

• peculiarities of elemental composition – presence of transition metals and certain ratios of them.

Conclusion. The need to involve deep hydrocarbon deposits in processing requires improvement of prospecting methods based on complex ideas about the processes of oil clusters formation.

This is an open access article under the CC BY 4.0 license

On the basis of thermodynamic and molecular modeling the probable processes of transition metals mineral forms transformation accompanying naphthogenesis are substantiated. Based on molecular modeling the potential structures of molecules-carriers of vanadium and nickel based on porphine, which are the main component of heavy oils, were proposed.

The elemental compositions of samples of heavy oil and their reservoir rocks of the Timan-Pechora province have been studied. Based on the established ratios of transition metal contents, an assumption was made about possible processes of contact between mantle fluids and the host rock and subsequent accumulation of hydrocarbons on carbonaceous rocks. In process of experimental and theoretical studies, it was found that polymers of the heavy fraction more selectively capture vanadium, so a potential marker will be the predominance of vanadium content in oil-bearing rocks in relation to the content of nickel.

It is shown that oil potentially acts as a transport of transition metals, leaching them from the parent rocks. The increase in their content in younger rocks indicates the probable migration of oil through the fracture system to the upper horizons and accumulation on sorption-active rocks.

REFERENCES

1. Radoushinsky D., Gogolinskiy K., Dellal Y. et al. Actual Quality Changes in Natural Resource and Gas Grid Use in Prospective Hydrogen Technology Roll-Out in the World and Russia. *Sustainability*. 2023. Vol. 15. Iss. 20. N 15059. DOI: 10.3390/su152015059

2. Litvinenko V.S., Leitchenkov G.L., Vasiliev N.I. Anticipated sub-bottom geology of Lake Vostok and technological approaches considered for sampling. *Geochemistry*. 2020. Vol. 80. Iss. 3. N 125556. DOI:10.1016/j.chemer.2019.125556

3. Mingaleva T., Gorelik G., Egorov A., Gulin V. Correction of Depth-Velocity Models by Gravity Prospecting for Hard-to-Reach Areas of the Shelf Zone. *Mining Informational and Analytical Bulletin*. 2022. N 10-1, p. 77-86 (in Russian). DOI: 10.25018/0236_1493_2022_101_0_77

4. Jianzhong Li, Xiaowan Tao, Bin Bai et al. Geological conditions, reservoir evolution and favorable exploration directions of marine ultra-deep oil and gas in China. *Petroleum Exploration and Development*. 2021. Vol. 48. Iss. 1, p. 60-79. DOI: 10.1016/S1876-3804(21)60005-8

5. Haige Wang, Hongchun Huang, Wenxin Bi et al. Deep and ultra-deep oil and gas well drilling technologies: Progress and prospect. *Natural Gas Industry B*. 2022. Vol. 9. Iss. 2, p. 141-157. DOI: 10.1016/j.ngib.2021.08.019

6. Filimonova I.V., Nemov V.Yu., Provornaya I.V., Mishenin M.V. Regional features of production and refining of oil in Russia. *Burenie & neft*. 2020. N 10, p. 3-10 (in Russian).

7. Adeola A.O., Akingboye A.S., Ore O.T. et al. Crude oil exploration in Africa: socio-economic implications, environmental impacts, and mitigation strategies. *Environment Systems and Decisions*. 2022. Vol. 42. Iss. 1, p. 26-50. DOI: 10.1007/s10669-021-09827-x

8. Timurziev A. Myth of power hunger from Habbert and ways of the decision of the global power problem on base of "Deepoil" project realization. *Burenie & neft*. 2019. N 1, p. 12-21 (in Russian).

9. Chengzao Jia, Xiongqi Pang, Yan Song. The mechanism of unconventional hydrocarbon formation: Hydrocarbon self-sealing and intermolecular forces. *Petroleum Exploration and Development*. 2021. Vol. 48. Iss. 3, p. 507-526.

10. Sinitsa N.V., Prishchepa O.M. A conceptual model for the formation of oil and gas accumulation zone within the Paleozoic basement of the southeastern West Siberian basin. *Actual Problems of Oil and Gas*. 2023. Iss. 1 (40), p. 14-26 (in Russian). DOI: 10.29222/ipng.2078-5712.2023-40.art2

11. Ilyinov M.D., Petrov D.N., Karmanskiy D.A., Selikhov A.A. Physical simulation aspects of structural changes in rock samples under thermobaric conditions at great depths. *Mining Science and Technology (Russia)*. 2023. Vol. 8. N 4, p. 290-302. DOI: 10.17073/2500-0632-2023-09-150

12. Zhijun Jin, Rukai Zhu, Xinping Liang, Yunqi Shen. Several issues worthy of attention in current lacustrine shale oil exploration and development. *Petroleum Exploration and Development*. 2021. Vol. 48. Iss. 6, p. 1471-1484. DOI: 10.1016/S1876-3804(21)60303-8

13. Leusheva E.L., Alikhanov N.T., Brovkina N.N. Study on the rheological properties of barite-free drilling mud with high density. *Journal of Mining Institute*. 2022. Vol. 258, p. 976-985. DOI: 10.31897/PMI.2022.38

14. Palaev A.G., Shammazov I.A., Dzhemilev E.R. Research of the impact of ultrasonic and thermal effects on oil to reduce its viscosity. *Journal of Physics: Conference Series*. 2020. Vol. 1679. N 052073. DOI: 10.1088/1742-6596/1679/5/052073

15. Cherdantsev G.A., Zharkov A.M. Prospects for the oil and gas content of the Upper Permian deposits of the southwestern part of the Vilyui syneclise based on the analysis of sedimentary environments and geochemical conditions of oil and gas content. *Journal of Mining Institute*. 2021. Vol. 251, p. 698-711. DOI: 10.31897/PMI.2021.5.9

16. Nyakairu G.W.A., Kasule J., Ouma O., Bahati G. Origin and hydrogeochemical formation processes of geothermal fluids from the Kibiro area, Western Uganda. *Applied Geochemistry*. 2023. Vol. 152. N 105648. DOI: 10.1016/j.apgeochem.2023.105648

17. Xiaofeng Wang, Quanyou Liu, Wenhui Liu et al. Accumulation mechanism of mantle-derived helium resources in petroliferous basins, eastern China. *Science China Earth Sciences*. 2022. Vol. 65. Iss. 12, p. 2322-2334. DOI: 10.1007/s11430-022-9977-8

18. Serovaiskii A., Kutcherov V. Formation of complex hydrocarbon systems from methane at the upper mantle thermobaric conditions. *Scientific Reports*. 2020. Vol. 10. N 4559. DOI: 10.1038/s41598-020-61644-5

19. Lure M.A. Sources of hydrocarbons, heterocomponents, and trace elements of abiogenic oil: properties and composition of deep fluids. *Russian Oil and Gas Geology*. 2020. N 3, p. 43-49 (in Russian). DOI: 10.31087/0016-7894-2020-3-43-49

This is an open access article under the CC BY 4.0 license

20. Chacón-Patiño M.L., Nelson J., Rogel E. et al. Vanadium and nickel distributions in Pentane, In-between C5-C7 Asphaltenes, and heptane asphaltenes of heavy crude oils. *Fuel.* 2021. Vol. 292. N 120259. DOI: 10.1016/j.fuel.2021.120259

21. Chacón-Patiño M.L., Nelson J., Rogel E. et al. Vanadium and nickel distributions in selective-separated *n*-heptane asphaltenes of heavy crude oils. *Fuel*. 2022. Vol. 312. N 122939. DOI: 10.1016/j.fuel.2021.122939

22. Aleksandrova T., Nikolaeva N., Afanasova A. et al. Extraction of Low-Dimensional Structures of Noble and Rare Metals from Carbonaceous Ores Using Low-Temperature and Energy Impacts at Succeeding Stages of Raw Material Transformation. *Minerals*. 2023. Vol. 13. Iss. 1. N 84. DOI: 10.3390/min13010084

23. Afanasova A.V., Aburova V.A. Growth of low-dimensional structure noble metals in carbonaceous materials under microwave treatment. *Mining Informational and Analytical Bulletin.* 2024. N 1, p. 20-35 (in Russian). DOI: 10.25018/0236_1493_2024_1_0_20

24. Canhimbue L., Talovina I. Geochemical Distribution of Platinum Metals, Gold and Silver in Intrusive Rocks of the Norilsk Region. *Minerals*. Vol. 13. Iss. 6. N 719. DOI: 10.3390/min13060719

25. Yudovich Ya.E., Ketris M.P. Fundamentals of lithochemistry. Saint Petersburg: Nauka, 2000, p. 479.

26. Ruiying Xiong, Jixiang Guo, Kiyingi W. et al. Method for Judging the Stability of Asphaltenes in Crude Oil. *ACS Omega*. 2020. Vol. 5. Iss. 34, p. 21420-21427. DOI: 10.1021/acsomega.0c01779

27. El Nagy H.A., El Sayed H. El Tamany, Abbas O.A. et al. Rapid and Simple Method for Measuring Petroleum Asphaltenes by the Centrifugation Technique. *ACS Omega*. 2022. Vol. 7. Iss. 50, p. 47078-47083. DOI: 10.1021/acsomega.2c06225

28. Aleksandrova T., Nikolaeva N., Kuznetsov V. Thermodynamic and Experimental Substantiation of the Possibility of Formation and Extraction of Organometallic Compounds as Indicators of Deep Naphthogenesis. *Energies*. 2023. Vol. 16. Iss. 9. № 3862. DOI: 10.3390/en16093862

29. Punanova S.A. The microelement composition of caustobioliths and oil generation processes – from the D.I.Mendeleev's hypothesis to the present day. *Georesources.* 2020. Vol. 22. N 2, p. 45-55 (in Russian). DOI: 10.18599/grs.2020.2.45-55

30. Prischepa O.M., Kireev S.B., Nefedov Yu.V. et al. Theoretical and methodological approaches to identifying deep accumulations of oil and gas in oil and gas basins of the Russian Federation. *Frontiers in Earth Science*. 2023. Vol. 11. N 1192051. DOI: 10.3389/feart.2023.1192051

31. Yakubova S.G., Abilova G.R., Tazeeva E.G. et al. A Comparative Analysis of Vanadyl Porphyrins Isolated from Heavy Oil Asphaltenes with High and Low Vanadium Content. *Petroleum Chemistry.* 2022. Vol. 62. N 1, p. 83-93. DOI: 10.1134/S0965544122010030

32. Ivanova Y.B., Semeikin A.S., Pukhovskaya S.G., Mamardashvili N.Z. Synthesis and Spectral and Coordination Properties of *meso*-Tetraarylporphyrins. *Russian Journal of Organic Chemistry.* 2019. Vol. 55. N 12, p. 1878-1883. DOI: 10.1134/S107042801912011X

Authors: **Tatyana N. Aleksandrova,** *Doctor of Engineering Sciences, Corresponding Member of the RAS, Professor, https://orcid.org/0000-0002-3069-0001 (Empress Catherine II Saint Petersburg Mining University, Saint Petersburg, Russia),* **Valentin V. Kuznetsov,** *Candidate of Engineering Sciences, Assistant Lecturer, Kuznetsov_VV@pers.spmi.ru, https://orcid.org/0000-0001-6159-316X (Empress Catherine II Saint Petersburg Mining University, Saint Petersburg, Russia),* **Nadezhda V. Nikolaeva,** *Candidate of Engineering Sciences, Associate Professor, https://orcid.org/0000-0001-7492-1847 (Empress Catherine II Saint Petersburg Mining University, Saint Petersburg, Russia).*

The authors declare no conflict of interests.

This is an open access article under the CC BY 4.0 license