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Geochemical Characterization of Paleozoic Source Rocks in Nerutinskaya-3 Well, Timan-Pechora Petroleum Province

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ABSTRACT

This article presents the results of geochemical studies of core samples from Nerutynskaya-3 well, located in Timan-Pechora petroleum province in the northern part of European Russia. The study aims to assess the hydrocarbon generation potential of the Silurian and Upper Devonian sections. The source rocks of Nerutynskaya-3 well, spanning the Carboniferous, Devonian, and Silurian periods, were characterized. Pyrolytic chromatography revealed that the studied intervals, based on total organic carbon (TOC) content, belong to sub-Domanikoid and Domanikoid formations, with Type II kerogen. The sources of organic matter were differentiated throughout the section, and distinct hydrocarbon generation zones were identified. Using Tmax values, the thermal maturity stages of the organic matter were determined, while S1 and S2 parameters were applied to evaluate the generation potential. Biomarker analysis helped identify the depositional environment of the organic matter and confirmed its kerogen typing. Key elements of the petroleum system were indicated. Based on these findings, a basin modeling study was conducted to reconstruct the evolution of the Paleozoic sedimentary complex. The burial history was restored. The stages of catagenetic maturity of organic matter were determined and activation energy calculations were performed.

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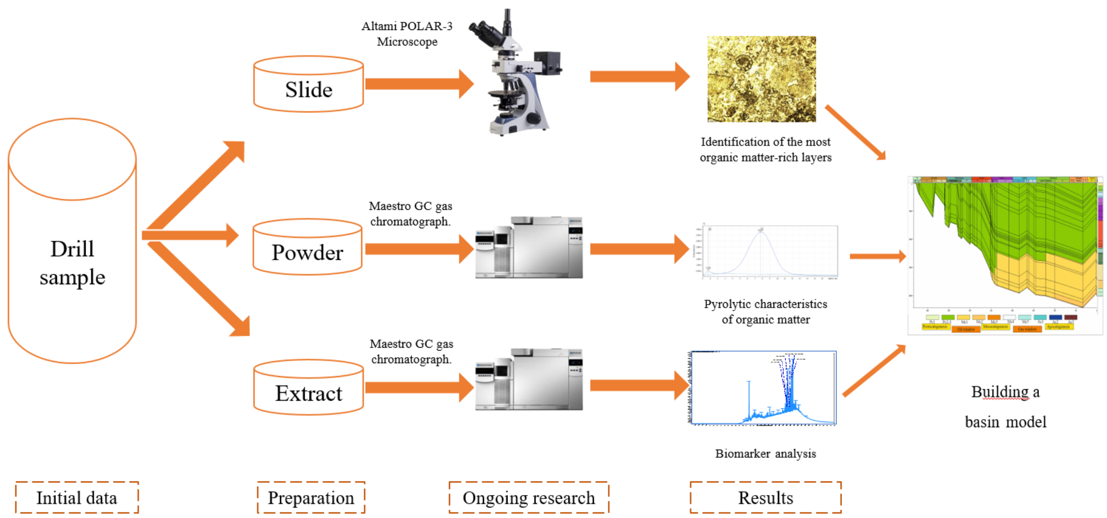
Graphical Abstract



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1. INTRODUCTION

Given the significant depletion of conventional oil reserves in intensively exploited regions, the strategic focus for sustaining and expanding the hydrocarbon resource base has shifted to complex geological formations. These include deep-seated targets and reservoirs that require capital-intensive exploration and development technologies (1, 2). Prime examples are low-permeability, heterogeneous carbonate, clay, and carbonate-clay-siliceous deposits formed in relatively deep marine environments, characterized by challenging filtration and storage properties (3, 4).

The efficient development of such reservoirs demands a thorough analysis and assessment of their hydrocarbon potential due to the high geological and technological risks involved (5). One of the most effective decision-support tools for oil and gas companies is basin analysis, which integrates comprehensive geochemical studies (including bituminological analysis, Rock-Eval pyrolysis, and biomarker analysis). This approach enables the reconstruction of original organic matter concentrations in source rocks, burial and thermal history modeling, identification of peak hydrocarbon generation phases, and evaluation of migration pathways and trap formation timing relative to hydrocarbon expulsion (6, 7).

Data obtained from core and fluid laboratory analyses are combined with seismic interpretation results to build a basin model, providing insights into the hydrocarbon potential of the study area. This methodology helps prioritize the most prospective zones for exploration, optimizing costs—a critical factor given declining investments in exploration and economic constraints driven by competition with green energy projects and sanction-related challenges (8, 9).

Thus, the study of Lower Paleozoic geochemical characteristics in a depression at the margin of the ancient Timan-Pechora sedimentary basin aims to identify potential source rocks of carbonate and carbonate-clay composition. These formations, intersected by wells alongside organic-rich limestones and dolomites with extremely low total organic carbon (TOC), allow for modeling hydrocarbon generation processes, defining petroleum system elements, and assessing hydrocarbon prospects (10).

2. GEOLOGICAL SETTING AND BURIAL HISTORY OF THE PLATFORM MARGIN

The study area is located in the Timan-Pechora petroleum province, at the junction of the Khoreyver Depression and Chernyshev Ridge (Figure 1). The region has been explored since the 1960s using geological and geophysical methods and deep drilling. Between the 1970s and 1990s, several wells confirmed oil-bearing potential in Upper Devonian reefal and Silurian-Lower Devonian carbonate deposits. In 2006–2007, the Nerutynskaya-3 exploration well (which discovered the Nerutynskoye field) yielded commercial oil flows from Famennian (Upper Devonian) and Lower Carboniferous formations (11).

In 2008, reserves of the Nerutynskoye field were estimated, and prospective reefal formations were identified on the Khosedayu-Neruysk uplift, including a two-level (Upper Frasnian and Lower Famennian) organogenic atoll-type structure in the vicinity of well HS-NER6 (12). To date, six exploration and appraisal wells have been drilled in the area, confirming the atoll-like nature of the reefal structure and its hydrocarbon potential associated with the realization of zonal hydrocarbon potential in the Lower Paleozoic section. The penetrated interval spans from Riphean-Vendian basement formations to Quaternary deposits (Figure 2).

The Ordovician System is represented by carbonate-terrigenous deposits, their thickness increasing eastward. The Silurian System includes Lower Silurian dolomites and limestones and Upper Silurian deposits. The Upper Silurian is represented by the Herdian Horizon (Ludlow Stage), composed of interbedded dolomites, clayey limestones and marls. In the area of Khosedayu-Neruysk structure its thickness is reduced due to pre-Devonian erosion (13, 14).

The Devonian System is represented by Lower Devonian carbonates and Upper Devonian deposits. The Upper Devonian includes the Domanik Horizon (Middle Frasnian Stage), consisting of bituminous limestones and argillites, as well as the Zelenetsky and Nyumylgsky Horizons (Upper Famennian) - shallow-water and reefal limestones yielding commercial oil flows.

The Carboniferous System is composed of Visean and Serpukhovian carbonates. The Lower Serpukhovian Horizon (Tarusa and Steshev beds) is represented by dolomites and anhydrites, serving as a regional fluid seal.

Figure 1. Map showing the four continuous assessment units (AUs) in the Timan-Pechora Basin Province of Russia

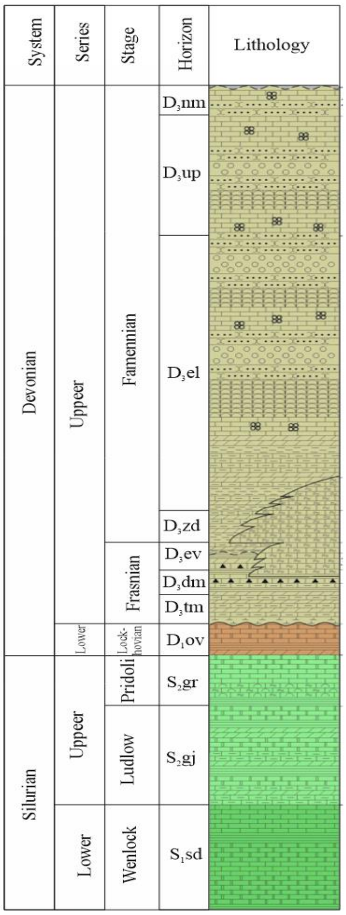

Figure 2. Lithostratigraphic Section Interval

The Permian System is represented by Lower Permian carbonate deposits (Asselian-Sakmarian, Artinskian, Kungurian) and Upper Permian terrigenous deposits (Ufimian, Kazanian-Tatarian).

Triassic deposits are not ubiquitous. The Jurassic System consists of interbedded clays, siltstones and sandstones, preserved fragmentarily after erosional events. The Cretaceous System is represented by sandy-clayey deposits pinching out at Chernyshev Ridge. The Quaternary System is composed of thin clays, loams and pebble beds.

According to the tectonic scheme of the Timan-Pechora Province (TPP), the study area is located in the southeastern part of the Khoreyver Depression, which represents a northwest-trending monocline (Figure 1), complicated by local structures, one of which is the Tsilegorsk Depression - a narrow linear structure of northeast trend (15).

The main hydrocarbon potential of the area is associated with four commercial hydrocarbon-bearing complexes: Middle Ordovician-Lower Devonian carbonate, Middle Frasnian-Tournaisian carbonate, Middle Visean-Lower Permian carbonate and Lower Permian terrigenous (Figure 2) (16).

3. MATERIALS AND METHODS

Material for the study consisted of core samples from the Nerutinskaya-3 well, drilled within the Khoreyver Depression of the Timan-Pechora petroleum province (Figure 3). Paleozoic deposits in the interval of 2300-3970 m, represented by carbonate rocks, were investigated.

The preparation of thin sections from the studied core samples and their microscopic petrographic description using optical microscopy were performed at the Saint Petersburg Mining University (Empress Catherine II) at the Department of Petroleum Geology. Based on lithological analysis of rock composition, the most organic-rich layers were identified as potential source rocks, which were subsequently studied using pyrolytic methods.

Geochemical analysis of samples was conducted using the BulkRock pyrolysis method with an EGA/PY-3030D pyrolytic cell. Pyrolytic studies involve the thermal decomposition of organic matter (OM) in source rocks. The OM analysis was performed using an analytical system comprising a Frontier Lab EGA/PY-3030D pyrolytic cell and a Maestro-MS gas chromatograph-mass spectrometer (GC-MS).

A finely ground rock powder (0.20-0.25 mm particle size, 300-500 µg mass) was placed in a crucible and subjected to helium-flow heating using a Rock-Eval (BulkRock)-like methodology, involving a two-stage heating process: Stage I - isothermal heating at 300°C for 3.43 min; Stage II - linear temperature increase from 300 to 650°C at 30°C/min for 15.09 min.

A standard reference material, "IFP 160000" (source rock standard), was used for instrument calibration. The pyrolytic system is not equipped with a chromatographic column; instead, a metal capillary is placed in the thermostat. The capillary prevents the separation of both free and bound hydrocarbons into individual compounds, allowing for clear and symmetrical S1 and S2 peaks.

Figure 3. Photograph of the core of the Nerutynskaya-3 well

Pyrolysis results were analyzed using Maestro-Analyst software. The pyrolysis methodology on the described equipment is certified in accordance with GOST R 8.563-2009 ("State System for Ensuring the Uniformity of Measurements. Measurement Procedures"). The certification was issued by the All-Russian Research Institute of Metrological Service (Moscow).

Compositional analysis of saturated and aromatic hydrocarbons, including biomarkers and their parameters in oils and bitumoids, was performed on the same analytical system by replacing the capillary with an Agilent DB-5MS Ultra Inert capillary column (internal diameter: 0.25 mm; length: 30 m). This method involves separating the maltene fraction into saturated and aromatic components using a capillary column with a nonpolar stationary liquid phase.

Biomarker analysis was conducted using the following temperature program: stepwise heating from 100 to 300°C at 600°C/min, followed by heating from 300 to 650°C at 30°C/min. After chromatographic separation, hydrocarbon compounds were detected by mass spectrometry. Biomarker parameters were determined based on mass-to-charge ratios (m/z) for characteristic fragment ions including phenanthrenes (178), dibenzothiophenes (184), tricyclic and pentacyclic terpanes/triterpanes (191), methylphenanthrenes (192), methyldibenzothiophenes (198), sternanes (217), isosternanes (218), diasteranes (259), triaromatic steroids (231), and monoaromatic steroids (253).

The obtained spectra were processed using specialized software, enabling the identification of individual compounds and quantitative assessment of their concentrations (17-19).

4. RESULTS AND DISCUSSING

4. 1. Geochemical Characteristics of Organic Matter. Pyrolytic Studies of the Substance The studied interval of core samples from the Nerutinskaya-3 well (2300-3970 m) penetrated carbonate deposits of Carboniferous, Devonian and Silurian age (C1s1-S2gj). Based on the realized potential values (S1), the section is differentiated into zones of source rocks with medium (0.5-1.0 mg HC/g rock), good (1.0-2.0 mg HC/g rock) and excellent potential (>2 mg HC/g rock). The residual potential values (S2) are assessed as medium (2.5-6.0 HC/g rock) (Figure 4) (20, 21).

The organic carbon content in this section ranges from 0.15 to 4.17%, characterizing the deposits as sub-Domanik (<0.5%) and Domanik-type (<5%) (22-24).

The level of catagenetic transformation corresponds to PC1-MK1 gradation (Tmax=360-434°C). A trend of increasing Tmax with depth is observed.

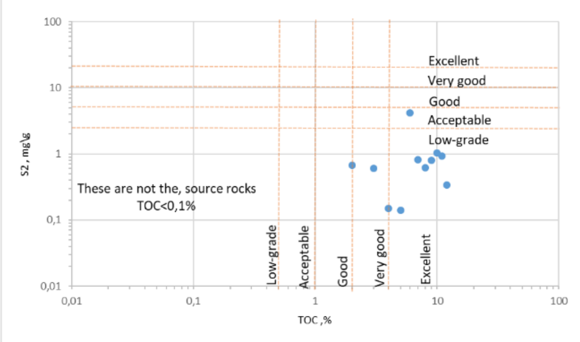

Figure 4. Generation potential of samples from Nerutinskaya-3 well

Based on hydrogen index values, the rocks possess medium (100-300 mg HC/g TOC) and good (300-600 mg HC/g TOC) generation potential (Figure 5) (25).

4. 2. Molecular Composition of Dispersed Organic Matter. Biomarker Analysis The composition of n-alkanes in oils and bitumoids directly reflects the nature of the original organic matter (OM). This parameter is widely used in geochemical studies to reconstruct sedimentation conditions and identify facies types of source rocks. Marine deposits, whose organic matter is formed primarily by plankton, are characterized by the predominance of low-molecular-weight n-alkanes (C_{15}–C_{17}). In continental deposits with contributions from higher plants, high-molecular-weight compounds (C_{27}–C_{31}) dominate (Figure 6).

HA reliable diagnostic criterion is the ratio of n-alkanes $C_{17}/C_{27}>1$, which indicates marine genesis of OM with a predominance of algal and bacterial components, while a ratio of $C_{17}/C_{27}<1$ suggests a significant contribution of terrestrial humic material. The distribution of n-alkanes in dispersed organic matter indicates its mixed genesis (Figure 7).

Among isoprenoid aliphatic hydrocarbons, the most common compounds are pristane (Pr) and phytane (Ph). The ratio of these biomarkers is used as an indicator of redox conditions during sedimentation. The predominance of pristane is characteristic of terrestrial OM from higher plants, while the dominance of phytane indicates marine hydrocarbon genesis. The geochemical characteristics of aliphatic hydrocarbons allow for the assessment of both similarities and specific features in the composition and transformation level of dispersed organic matter in the studied formations (Figure 8) (26).

Tetracyclic saturated hydrocarbons - steranes represent an important class of biomarkers formed during diagenetic transformation of sterols present in eukaryotic cell membranes. These compounds, widely distributed in fossil organic matter, oils, and natural bitumens, carry

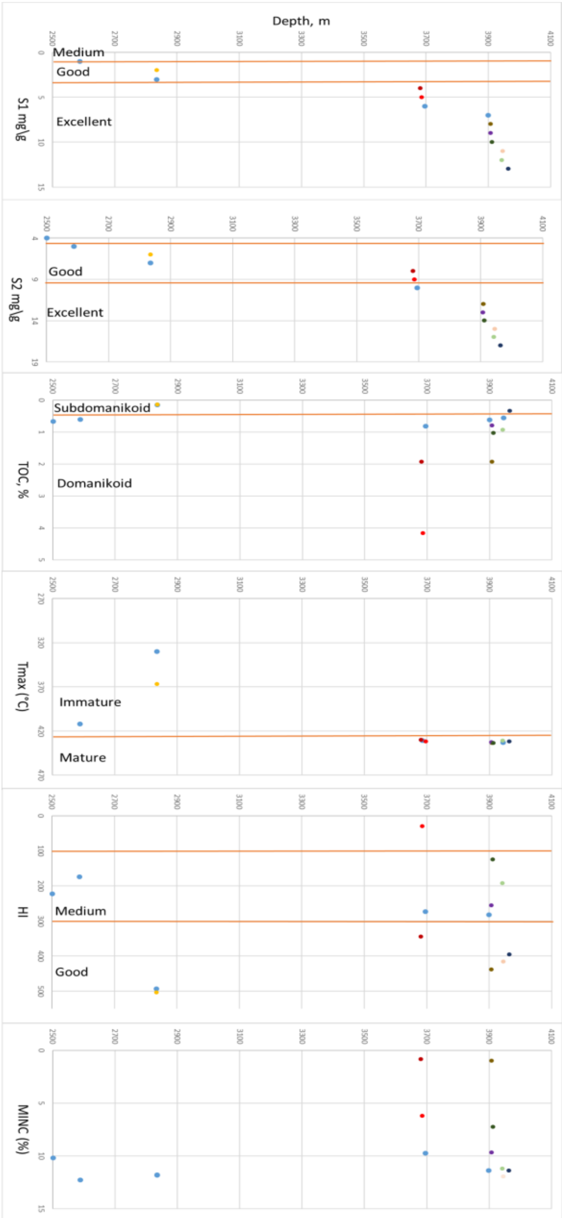

Figure 5. Geochemical Section of Potential Source Rocks in the Nerutinskaya-3 Well

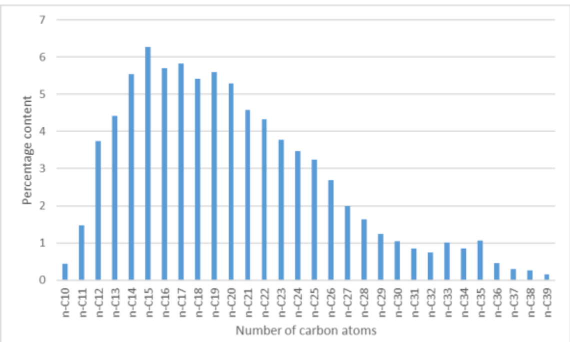

Figure 6. Distribution of n-alkanes in the Nerutinskaya-3 well

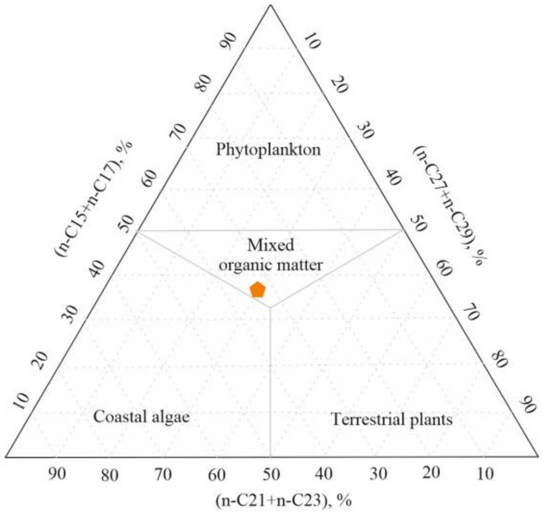

Figure 7. Genetic characteristics of dispersed organic matter (based on n-alkane composition)

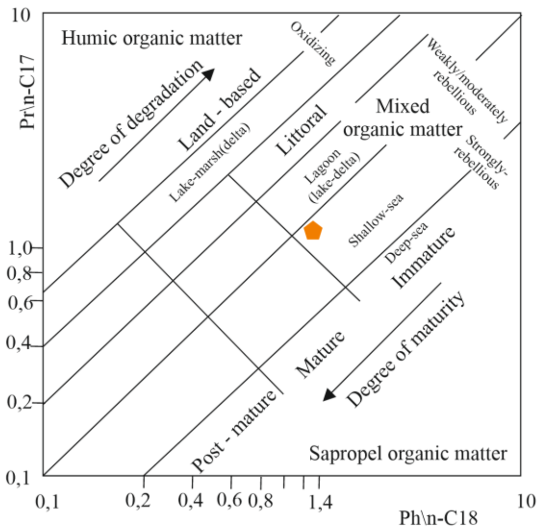

Figure 8. Characteristics of the genetic type and facies sedimentation conditions of dispersed organic matter (Cannon-Cassow diagram)

valuable information about several aspects of petroleum formation: the composition of the original biological material, sedimentation and diagenesis conditions, and post-sedimentary transformations. Additionally, the distribution patterns of steranes are successfully used as indicators of hydrocarbon migration and biodegradation processes (27, 28).

The diagnostic value of steranes is based on the specific distribution of their homologs: cholestane (C27) is a marker of microalgal organic matter, methylcholestane (C28) indicates contributions from zooplankton or lagoon algae, while ethylcholestane (C29) unequivocally points to the participation of higher terrestrial plants in the formation of the original organic matter. Analysis of the relative content of these compounds allows not only for determining the origin of organic matter but also for reconstructing paleoecological sedimentation conditions, which is fundamentally important for assessing the petroleum potential of sedimentary basins (Figure 9) (29).

The results of biomarker analysis enabled not only the identification of paleofacies environments but also the differentiation of hydrocarbon generation zones. By plotting the research results on a spider diagram, two potential oil generation zones were identified in the deposits of the Domanik and Herdian horizons. The diagram was constructed using n-alkanes and isoprenoids, steranes, phenanthrenes, as well as terpanes. This approach allowed for the diagnostic coverage of the widest possible range of compounds with different fragment ion masses for studying the oil generation process (Figure 10) (30, 31).

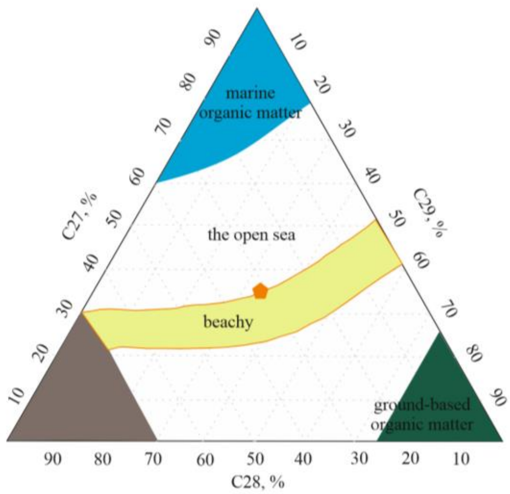

Figure 9. Facies-genetic characteristics of sedimentary rocks in the well (based on regular steranes)

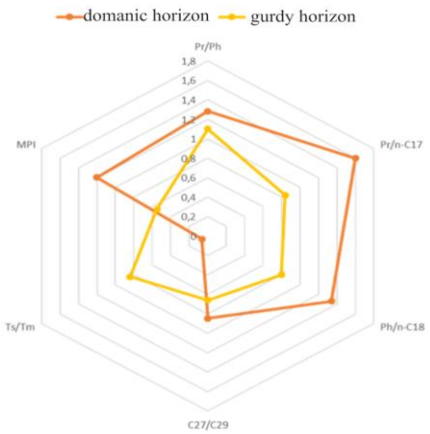

Figure 10. Spider diagram of Potential Source Rocks in the Nerutinskaya-3 Well

4. 3. Basin Modeling Historical-geological modeling represents a comprehensive method for reconstructing the evolution of sedimentary basins, based on reproducing geological processes at geological timescales. The essence of the method lies in step-by-step basin modeling from the formation of the oldest deposits to the present state, taking into account the sequential accumulation of all stratigraphic units (32, 33).

At each time interval, key geological processes are simulated: sedimentogenesis and lithogenesis (sedimentation, rock compaction, changes in petrophysical properties), thermodynamic processes (evolution of heat flow, calculation of paleotemperatures considering latent heat of fusion for crustal and mantle rocks), as well as petroleum generation processes (catagenetic transformation of organic matter, hydrocarbon generation, fluid phase transformations, hydrocarbon migration and accumulation) (34).

The modeling was performed using the specialized software complex "TemisFlow" at the Department of Arctic and World Ocean Petroleum Potential (VNIIOkeangeologia). Model verification was carried out by comparing calculated and actual temperature profiles.

This approach provided a comprehensive reconstruction of paleo-conditions and allowed assessment of the thermobaric evolution of the section, dynamics of catagenetic transformations, temporal and spatial patterns of petroleum generation, as well as hydrocarbon potential prospects of the studied deposits.

Detailed subdivision of the geological section was performed using an integrated method combining well logging data (GIS) with lithological analysis of core material, cuttings samples, and petrographic studies of thin sections. As a result of the analysis, 21 lithotypes were identified in the well interval, with the following parameters established for each: age attribution, absolute top and base depths, thickness, and detailed lithological characteristics. The obtained data formed the basis for subsequent geological modeling and interpretation of sedimentation conditions (Figure 11).

For parameterization of the geological model, a specialized lithological variability library was developed, containing detailed characteristics of rock composition. Each lithological variety was assigned quantitative indicators of the content of main rock-forming components (in percentage terms), as well as the type of mineral component distribution (homogeneous or stratified). This library ensures accurate assignment of lithological characteristics during geological modeling, considering both qualitative rock composition and features of spatial component distribution throughout the section.

Based on comprehensive analysis of the lithostratigraphic column and study of the historical-geological concept of basin development, sedimentary

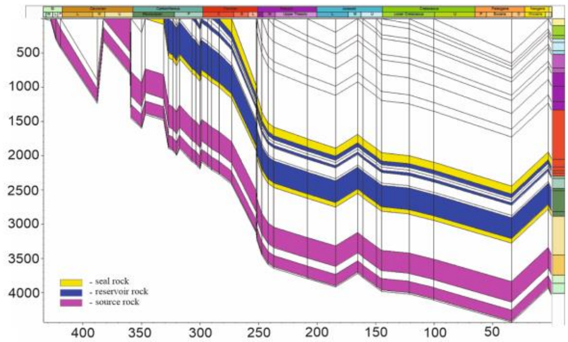

Figure 11. Subsidence of hydrocarbon system elements during the geological history of the sedimentary section penetrated by the Nerutinskaya-3 well

TABLE 1. Contents of the lithological library for the Nerutinskaya-3 well

Lithotype index	Composition of rocks
1	100% Sandstone
2	80% Sandstone + 20% Siltstone
3	60% Sandstone + 30% Siltstone +10% Mudstone
4	70% Sandstone + 30% Mudstone
5	100% Mudstone
6	80% Mudstone + 20% Siltstone
7	80% Mudstone + 20% Sandstone
8	70% Mudstone + 20% Siltstone + 10% Sandstone
9	50% Mudstone + 30% Siltstone + 20% Sandstone
10	40% Siltstone + 30% Mudstone +30% Sandstone
11	100% Mudstone (source rock)
12	100% Sandstone (reservoir rock)
13	100% Limestone (reservoir rock)
14	100% grainstone
15	100% dolostone
16	100% limestone
17	100% boundstone
18	boundstone 80%+20 % limestone
19	limestone 80%+20% boundstone
20	dolostone 80%+marl 20%
21	dolostone 80%+ boundstone 20%

hiatuses were identified and erosion thicknesses estimated. Six significant sedimentation breaks were established in the studied section: Early-Middle Devonian, Early Carboniferous (Visean), Late Carboniferous, Late Permian, Late Triassic, and Upper Cretaceous-Neogene. The obtained data on denudated formation thicknesses were systematized in the input lithostratigraphic parameters table.

Source rock identification and generation potential assessment were performed using pyrolytic studies. Analysis revealed relatively low organic matter content in the well penetrations. Potential hydrocarbon-generating units were identified as clayey formations of the following stratigraphic subdivisions: Frasnian Stage of Upper Devonian (Domanik Horizon) and Ludlow Stage of Upper Silurian (Herdian Horizon). Data on geochemical characteristics and source rock distribution within the section enable assessment of hydrocarbon potential in the study region and identification of priority targets for further investigation.

Geothermal gradient values were obtained from well temperature measurements (Figure 12).

The distribution of heat flows throughout the geological history of the sedimentary section is characterized by low values of 40-45 mW/m², which established stable thermal conditions (Figure 13).

The transformation ratio (TR) indicates source rock maturity achieved considering specific kinetic features of organic matter conversion to hydrocarbons. TR shows the proportion of kerogen already converted to hydrocarbons through chemical reactions (TR of 100% means complete kerogen exhaustion, with no future generation potential) (Figure 14).

Mesozoic, Permian and Carboniferous formations lie outside the active oil generation window (PC1-3). Upper Devonian Frasnian Stage organic matter (Domanik Horizon) is predominantly mixed Type II, currently in hydrocarbon generation zone MK1. Upper Silurian Ludlow Stage organic matter (Herdian Horizon) is also mixed Type II, in active generation zone MK2 (Figure 15).

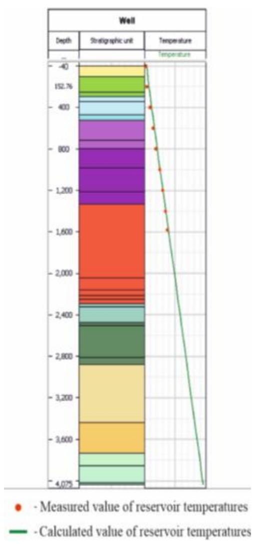

Figure 12. Model calibration results based on well temperature data

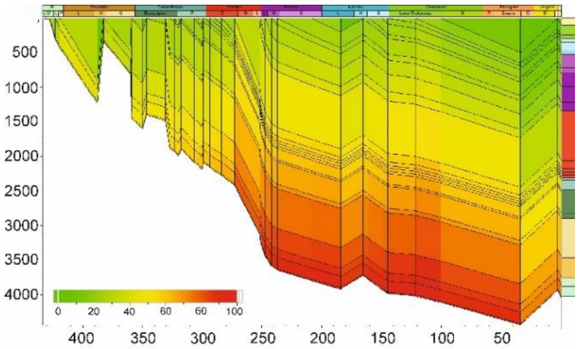

Figure 13. Formation temperature distribution through geological history of the sedimentary section penetrated by Nerutinskaya-3 well (According to the authors' data)

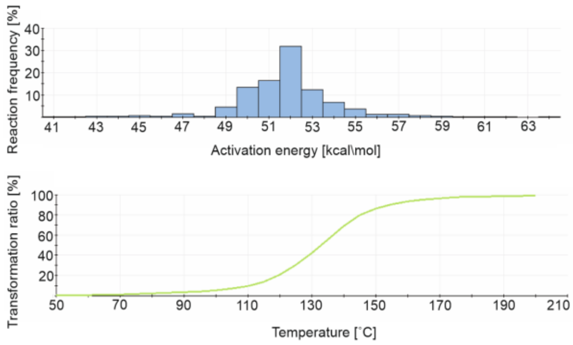

Figure 14. Distribution of transformation ratio and activation energy in samples from Nerutinskaya-3 well (According to the authors' data)

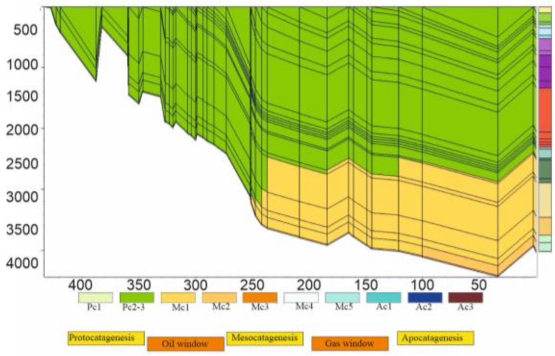

Figure 15. Catagenetic maturity of organic matter (EasyRo model) and hydrocarbon generation zones in the sedimentary section penetrated by Nerutinskaya-3 well

5. CONCLUSIONS

The comprehensive study of hydrocarbon potential in sedimentary formations of the third Nerutinskaya well in Timan-Pechora petroleum province, incorporating modern geochemical methods (pyrolytic chromatography mimicking Rock-Eval technique and biomarker analysis) coupled with 1D basin modeling, has updated understanding of hydrocarbon generation potential in Tsilegorsk Depression.

The research created a petrological thin section collection primarily from lowstand systems tracts. Organic-rich layers with source rock potential were identified through lithological analysis. Pyrolytic chromatography showed TOC content ranging 0.17-4.17%, characteristic of sub-Domanik (0.1-0.5%) and Domanik (0.5-5.0%) formations, with predominantly Type II organic matter. Residual, realized and generation potentials were characterized.

Tmax values determined organic matter maturity stages (immature/early mature), enabling assessment of transformation degree and hydrocarbon generation readiness. Biomarker analysis identified depositional environments (shallow marine facies) and organic matter type (mixed), while differentiating source inputs and distinguishing hydrocarbon generation kitchens.

Integration into 1D basin modeling enabled reconstruction of hydrocarbon system element subsidence through geological history, determination of organic matter catagenetic maturity (MK1-MK2), and calculation of activation energy (52 kcal/mol).

6. FINANCING

The article was prepared within the framework of the state task FSRW-2024-0008 "Investigation of thermodynamic processes of the Earth from the perspective of the genesis of hydrocarbons at great depths".

Authors' contributions:

Prischepa O.M. – Research conceptualization, formulation of the main hypothesis, writing the abstract and introduction sections.

Nefedov Yu.V. – Methodology development and study design.

Loginov A.V. – execution of experiments, data analysis, and results interpretation.

Tokarev I.V. – conclusions formulation and manuscript editing.

Zharkov A.M., Yashmolkin A.M. and Vostrikov N.N.– proofreading, reference formatting, and figure preparation.

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Persian Abstract

چکیده

این مقاله نتایج مطالعات ژئوشیمیایی نمونه‌های مغزه از چاه Nerutynskaya-3، واقع در استان نفتی Timan-Pechora در بخش شمالی روسیه اروپایی را ارائه می‌دهد. هدف از این مطالعه ارزیابی پتانسیل تولید هیدروکربن در بخش‌های سیلورین و دونین بالایی است. سنگ‌های منشأ چاه Nerutynskaya-3، که دوره‌های کربنیفر، دونین و سیلورین را در بر می‌گیرند، مشخص شدند. کروماتوگرافی پیرولیتیک نشان داد که فواصل مورد مطالعه، بر اساس محتوای کل کربن آلی (TOC)، متعلق به سازندهای زیر–دومانیکوئیدی و دومانیکوئیدی با کروژن نوع II هستند. منابع مواد آلی در سراسر برش متمایز شدند و مناطق متمایز تولید هیدروکربن شناسایی شدند. با استفاده از مقادیر Tmax، مراحل بلوغ حرارتی ماده آلی تعیین شد، در حالی که پارامترهای S1 و S2 برای ارزیابی پتانسیل تولید هیدروکربن اعمال شدند. تجزیه و تحلیل نشانگرهای زیستی به شناسایی محیط رسوبی ماده آلی کمک کرد و نوع کروژن آن را تأیید کرد. عناصر کلیدی سیستم نفتی مشخص شدند. بر اساس این یافته‌ها، یک مطالعه مدل‌سازی حوضه برای بازسازی تکامل مجموعه رسوبی پالئوزوئیک انجام شد. تاریخچه تدفین بازیابی شد. مراحل بلوغ کاتاژنتیکی مواد آلی تعیین و محاسبات انرژی فعال‌سازی انجام شد.