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Oil genesis in the Kaliningrad region: Physicochemical analysis of oil from offshore and continental fields

Genèse du pétrole dans la région de Kaliningrad : Analyse physico-chimique du pétrole des gisements offshore et continentaux

Yakov Andreyevich Masyutin[1], Anna Vladislavovna Vatagina[1], Pavel Sergeyevich Shcherban[2]

1. *Baltic Federal University of Immanuel Kant, BSC "Institute of medicine and life sciences", Kaliningrad, Russian Federation, ORCID: 0000-0003-4347-3425*
2. *Baltic Federal University of Immanuel Kant, BSC "Institute of High technologies", Kaliningrad, Russian Federation, ORCID: 0000-0001-5106-7852*

Résumé. Le développement de la production pétrolière sur le territoire des États baltes du sud a une longue histoire. Dès les années 1920, le gouvernement allemand a mené plusieurs études géologiques en Prusse-Orientale afin de rechercher des gisements d'hydrocarbures. La découverte de gisements pétroliers dans cette région remonte à l'époque soviétique. Ainsi, en 1973-1974, le gisement de Krasnoborskoe a été découvert, devenant ainsi le premier gisement exploité sur le territoire de la région de Kaliningrad. À ce jour, une quarantaine de gisements ont été découverts dans la région, la plupart avec de faibles réserves pétrolières. Au cours des cinquante années d'exploitation, d'importants matériaux géologiques et géochimiques ont été collectés, lesquels se sont considérablement enrichis ces dernières années grâce au développement de la production pétrolière offshore. L'exploitation intensive du plateau continental de la Baltique a permis de mener une étude comparative des particularités géochimiques de l'origine pétrolière des gisements d'hydrocarbures offshore et continentaux de la région de Kaliningrad. En conséquence, un certain nombre d'échantillons de pétrole ont été prélevés afin de réaliser une analyse physique et chimique complète et d'établir la source de la genèse du pétrole dans la partie centrale de la synéclise baltique.

Mots clés : pétroléogenèse, hydrocarbures, chromatographie, catagenèse, bioproducteurs, Kaliningrad (Féderation russe).

Abstract. The oil production development on the territory of the southern Baltic states has a long history. Back in the 1920s, the German government carried out a number of geological studies in East Prussia in order to search for hydrocarbon deposits. The discovery of oil fields in this region is dated to the period of the Soviet Union. Thus, in 1973-1974 the Krasnoborskoe field was discovered, which became the first developed oil field on the territory of the Kaliningrad region. By the present time about 40 fields have been found in the region, mostly with small oil reserves. For fifty years of their exploitation significant geological and geochemical material has been collected, which in recent years has been significantly enriched due to the development of offshore oil production. Extensive development of the Baltic shelf has created an opportunity to conduct a comparative study of the geochemical peculiarities of oil origin of offshore and continental hydrocarbon fields in the Kaliningrad region. As a result, a number of oil samples were taken in order to carry out a comprehensive physical and chemical analysis and to establish the source of oil genesis in the central part of the Baltic syneclise.

Keywords: petroleogenesis, hydrocarbons, chromatography, catagenesis, bioproducers, Kaliningrad (Russian Federation).

INTRODUCTION

The issue of oil origin in the Baltic oil and gas producing province is little studied. Studies on offshore oil fields are particularly poorly covered, they refer mainly only to the D6 field. There are no comparative analyses between onshore and offshore fields of the region for the last ten years (including at the same time gas chromatographic and mass spectrometric studies) in scientific periodicals. This paper presents the results of a comprehensive comparative study of oil from two onshore fields (Ladushkinskoe and Krasnoborskoe) and two offshore fields (D6 and D33) in the Kaliningrad region (Fig. 1). Based on the results of the study, a number of assumptions on the specifics of oil formation process in the territory of the central part of the Baltic syneclise were put forward.

It should be noted that the study of oil genesis in the Kaliningrad region plays an important role from the point of view of not only fundamental but also applied character. Today, based on the indicators of prospecting and exploration works and development of discovered fields, the Kaliningrad region belongs to the "old" regions, which are at the final stage of development of the resource base for classical hydrocarbons: the reserves of the majority of onshore fields are more than 80-90% depleted. At the same time, there is a strong trend towards the development of offshore oil reserves, and additional exploration works are being carried out (Mukhametshin *et al.* 2006). It should be noted that the subsoil of the Vistula and Curonian Bays of the Baltic Sea remains poorly explored for potential hydrocarbon reserves, as well as the issue of shale oil and gas deposits in the region is open. A comparative study of the characteristics of hydrocarbons on the shelf and onshore of the Kaliningrad region can significantly expand the understanding of potential reserves and help their development.

The purpose of this study is to establish the common nature of the oil genesis process in the shelf and continental zones of the center of the Baltic syneclise on the basis of a comparative analysis of the physical and chemical characteristics of oil from two offshore and two continental fields in the Kaliningrad region. To assess the specifics of hydrocarbon migration from the primary oil-maternal strata, the possibility of their accumulation in underexplored traps or in the form of scattered accumulations. The objectives of the study were: (i) studying fields and predicting the oil-bearing capacity of new nearby structures, (which allows oil companies to optimize the process of exploration and development of fields); (ii) to develop an understanding of the chemical composition and properties of oil in the Kaliningrad region, which determine the quality and type of oil (as well as important for the development of methods of its extraction) and (iii) analyzing geological processes and Earth history, which provides an opportunity to improve geological models of oil genesis.

GEOLOGIC OBJECTS OF THE STUDY

Most of the deposits in the Baltic oil and gas province belong to the Kurshsky oil-bearing region, in its boundaries the terrigenous formations of the Deimen Formation of the Middle Cambrian are the most productive for oil, to which all known oil fields are related (Zumberge 1987). The productive section of the Formation is represented by a stratum of interbedded sandstones and siltstones, with a subordinate amount of argillite and clay interbeds. Oil deposits are associated with local anticlinal uplifts, silt-sand reservoirs of the Deimansuprahorizon, confined to the upper part of the Middle Cambrian sediments (Zhamoida *et al.* 1998). This horizon lies at a depth of 1450-2550 m and, depending on the depth, is characterized by normal hydrostatic reservoir pressures (14.9 - 25.1 MPa) and temperatures (44-84°C). The area of oil deposits in open fields ranges from 0.1 km^2 to 23 km^2. With the height of deposits from 2 to 50-70 m, their effective oil saturated thickness is from 1.3-1.5 m to 16-17 m. Oil fields of Kaliningrad region have the following average parameters: average area of a structural trap controlling one field - 3.5 km^2; average trap height - 33 m; average deposit area - 2.4 km^2; average trap fill factor – 0.67. The oils of the Kaliningrad region, except for the Druzhba field, are light, low-sulfur, low-viscosity (less than 30 mPa·s), paraffinic, and belong to the methanonaphthene type by their chemical composition. Formation oils of the main part of the fields are described by low gas content (up to 53.6 m^3/t) and gas saturation pressure (0.58-5.43 MPa).

An exception is the Ladushkinskoye field, the major part of which deposit is located under the water area of the Kaliningrad Gulf and contains gas saturated (290 m^3/t) oil of “transition state” with density of 614 kg/m^3 (Zdanaviciute *et al.* 1998). The authors have previously conducted studies of the main physical and chemical properties of the investigated oils of the Kaliningrad region and it was found that they belong to the type of especially light oils, to the class of low-sulfur oils, contain a small amount of water, resinous-asphaltene compounds and mechanical impurities, are flammable liquids, the fractional composition indicates a significant content of fuel oil in the investigated oils, but the predominant fractions of light oil products (Shcherban *et al.* 2022).

It should be noted that the development of Kravtsovskoye field (D6), which is an offshore field, is of crucial importance for the entire oil production industry of the country, as its recoverable reserves are estimated at 9.1 million tons. Another offshore field, D33, is of even greater interest, with recoverable reserves estimated at 21.2 million tons. Explored reserves onshore are close to 85%, offshore reserves are 30%. Depletion of explored reserves of oil fields has reached 90%, offshore – 40% (Shcherban *et al.* 2022).

The objects of the study are oil samples from 2 onshore fields - Ladushkinskoye and Krasnoborskoye and 2 offshore fields - D6 and D33 - of the Baltic oil and gas province (Fig. 1). A total of 1000 ml of oil was sampled for each of the fields for the study. Sampling, their transportation and transfer to the laboratory for research was carried out in accordance with the current regulatory and technical requirements. Then the whole standard complex of physical and chemical analyses was carried out including density, kinematic viscosity, sulfur content, salts, mechanical impurities, water, fractional composition. After that, the samples were analyzed using isotope mass spectrometric and chromatography.

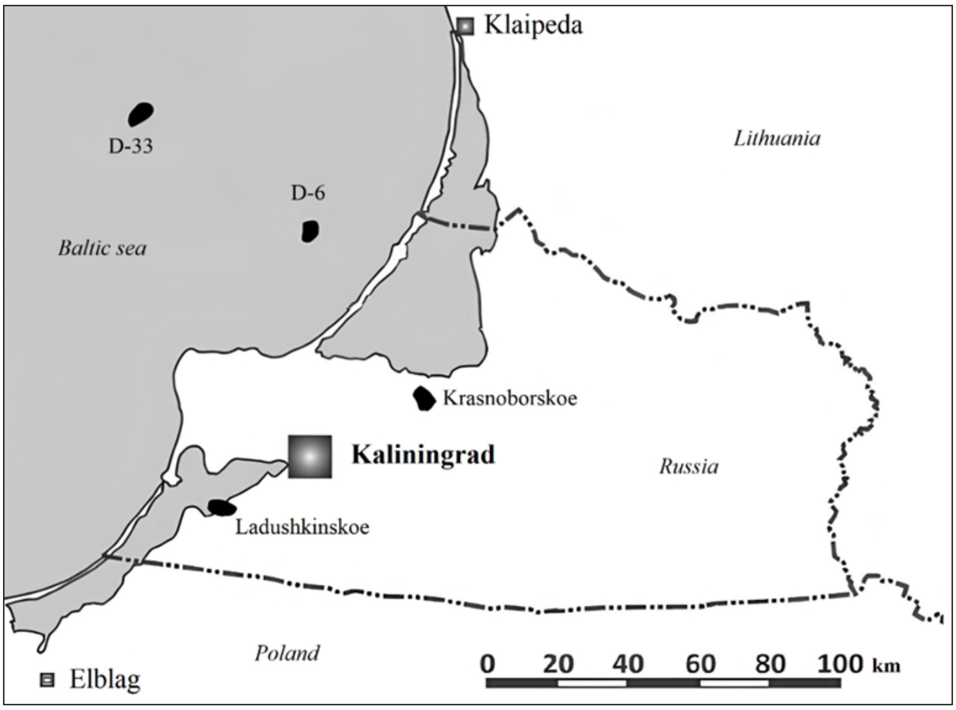

Figure 1. Localisation des gisements dans la partie centrale de la synéclise baltique sur lesquels les études ont été menées.
Figure 1. Location of deposits in the central part of the Baltic Syneclise on which the studies were conducted.

SAMPLE PREPARATION. ISOTOPE MASS SPECTROMETRIC ANALYSIS OF OILS AND FRACTIONS

SARA analysis (S - saturates, A - aromatics, R - resins, A - asphaltenes) was used for sample preparation. The design of the experiment is shown in (Fig. 2). This method is based on the separation of oil into saturated hydrocarbons, aromatic compounds, resins and asphaltenes based on their solubility and polarity. In this method, asphaltenes are separated from other hydrocarbon components by adding, for example, n-heptane or propane. The solvent-to-suspension ratio should be 1:40 by weight. The nature of asphaltenes separated from oil depends on the nature of the solvent-precipitant (Seitkhaziev 2021). Currently, in this stage of SARA analysis, petroleum ether with boiling points of 40-700 °C or n-hexane is used as a precipitant for asphaltenes in most cases. The remaining components, called maltene, are then separated by passing their mixture through a chromatographic column with an adsorbent. The application of SARA analysis to characterize petroleum dispersion systems allows us to: describe the petroleum dispersion system and its components, describe the change in asphaltene content as pressure drops, determine the amount of asphaltenes precipitated and establish the upper and lower boundary of the asphaltene precipitation region. Another advantage of this method is the direct separation of asphaltenes from the mixture, which allows further study of them by mass spectroscopy, molecular diffusion methods.

To carry out mass-spectrometric study it is necessary to put the weight of oil or separated fractions (from 0.1 to 3 mg) into a capsule from tin foil, which with the help of tweezers tightly packed to get a ball. The sealed capsules with samples should be placed in the automatic sample introduction device (autosampler) with which the elemental analyzer is equipped. In the experiment under consideration, this was the Flash 2000. The autosampler, according to a preset program, discharged samples into a redox reactor heated to a temperature of 1020 °C, where their combustion took place in a constant flow of helium (90 ml/min) with a short-term oxygen supply. At the outlet of the reactor, which is sequentially filled with chromium oxide (Cr_2O_3), reduced copper (Cu) silvered cobalt oxide (Co_3O_4) pellets, the oxidation and reduction processes produced pure N_2 and CO_2. Since in the process of combustion of samples besides carbon dioxide and nitrogen water is formed, which has an interfering effect in determining the carbon isotopic composition, a trap with magnesium perchlorate is installed at the outlet of the redox reactor (Behar 2001). After the trap, a metal packed column is installed where nitrogen and carbon dioxide are separated at 45°C. After the elemental analyzer, the nitrogen and carbon dioxide are sequentially transferred to the ConFlo IV universal interface, where they are diluted with helium to obtain the desired signal intensity, after which they are sent directly to the isotope mass spectrometer for analysis. The isotope ratio mass spectrometry method does not involve absolute measurements. Comparison with calibrated standards must be used in determining isotopic ratios. Due to the need to minimize instrumental errors, it is recommended to measure the gas-standard immediately before or after measuring the sample gas peak.

The oils and the obtained fractions of saturated hydrocarbons and aromatic fraction were analyzed by gas chromatography-mass spectrometry (GC/MS) using a Hewlett Packard 6890/5973 instrument with HP-1-MS column (30 m, 0.25 mm) in linear temperature programming mode (3 min 45 °C, from 45 °C to 310 °C heating rate 3 °C/min, thermostatization time at 310 °C - 20 min).

The analysis was performed in the individual mass scanning mode (SIM - specific ion monitoring) with ion detection: m/z 57 (alkanes), m/z 91 (alkylbenzenes), m/z 142 (methylnaphthalenes), m/z 156 (dimethylnaphthalenes), m/z 178 (phenanthrene), m/z 191 (cheylantanes, gopanes) m/z 192 (methylphenanthrenes), m/z 184 (dibenzothiophene), m/z 198 (methyldibenzothiophenes), m/z 217/218 (steranes), m/z 231 (triaromatic steroids). Data were collected and processed using ChemStation software. Sample preparation was carried out prior to the experimental procedures themselves.

ANALYSIS OF CARBON ISOTOPIC COMPOSITION OF CARBON IN OIL

The study of the isotopic composition of hydrocarbons can provide a great deal of information about the process of oil genesis. In recent years, extensive studies of carbon, hydrogen and sulfur isotopes in oils and gases of different areas have been carried out worldwide, both by regional dip of layers and by section. In most cases, fractionation of the isotopic composition of oils and gases along the direction of migration was found, with oils and gases enriched in light isotopes and losing heavy ones, although in some cases contradictory data were obtained and the picture turned out to be more complicated.

Some regularities characterize the age dependence of the isotopic composition of oils, in particular, the isotopic composition of carbon and sulfur in oils. Thus, with increasing geologic age, the content of lighter carbon isotope increases steadily (if the Triassic is excluded) in oils. The older the horizon, the more 34S isotope the oils contain, the deviation is observed only for Cretaceous oils. Changes in the isotopic composition with geologic age are also observed for hydrogen, which is a component of oil components. Carbon and hydrogen are the main chemical elements that make up oil and natural gases. Carbon exists both in the Free State and as part of organic compounds and minerals. Three isotopes of carbon are found in natural compounds: ^{12}C, ^{13}C, ^{14}C. The ^{12}C isotope is sharply predominant (Seitkhaziev 2021). Isotopic composition (R) refers to the ratio of isotope concentrations in a particular sample. At the same time, in isotope geochemistry it is customary to use not absolute but relative isotopic composition, i.e., relative deviation of the isotopic composition of a given sample from some standard isotopic composition. In the course of numerous experiments, it was established that carbon of different origins differs in isotopic composition, which is characterized by the ratio $^{13}C/^{12}C$ and the value of compaction $\delta^{13}C$, % or ‰.

$$\delta^{13}\mathrm{C} = \left[\frac{(^{13}C/^{12}C)}{(^{13}C/^{12}C)_{st}} - 1\right] * 1000 \quad \mathbf{(1)}$$

Where: $(^{13}C/^{12}C)st$ is the ratio of carbon isotopes in Belemnitella americana belemnites of the Cretaceous period (PDB).

Such samples are intended to verify the accuracy of mass spectroscopy methods. In case of excess of ^{13}C isotope in the studied samples compared to PDB the value of compaction is positive, in case of deficiency - negative. It should be noted that the current accuracy of $\delta^{13}C$ determination is ±0.01-0.05 % (Behar 2001). In the presented study, only determination of carbon isotopic composition was carried out for each of the samples by fields. For a long time, it was believed that continental organic substance was characterized by a lighter carbon isotopic composition. However, the ambiguity of the chosen criterion was subsequently revealed. Works began to appear in which enrichment of oils with light carbon isotope was considered as the influence of a marine source. In reality, the carbon isotopic composition of organic matter depends not only on the type of bioproducers, but also on its diagenetic evolution. Thus, marine kerogen can be both lighter than continental kerogen in the case of the sapropelic type and heavier (aquahumus type), this greatly complicates interpretation. In this connection, it is impossible to speak unambiguously about the source of oil origin based on the results of isotopic analysis alone. This requires a more comprehensive approach, conjugation with isotopic analysis of other components (sulfur, hydrogen), assessment of geomorphological processes in the studied region, analysis of biomarkers.

OIL BIOMARKER ANALYSIS

The transformation of hydrocarbons, which occurs in reservoir conditions, during migration with formation water, during ingress into soils, during diffusion and filtration of oils, etc., also plays an important role in the study of genesis. Oxidation of various hydrocarbon components of oils is due to the activity of bacteria, which first of all absorb C_{10}-C_{20} n-alkanes. After microorganisms decompose branched alkanes including isoprenoid alkanes. The most informative isoprenoid alkanes in terms of geochemistry are pristane $C_{19}H_{40}$ and phytane $C_{20}H_{42}$.The precursor of isoprenanes - pristane (Pr) iso-C_{19} and phytane (Ph) iso-C_{20} - is phytol, which is converted to pristane in oxidizing environment and to phytane in reducing environment (Figures 3 and 4). The Pr/Ph ratio characterizes the redox potential of oil and gas bearing basins:

- Pr/Ph < 1.0 - highly reductive environment;
- Pr/Ph = 1.0-1.5 - reductive environment;
- Pr/Ph = 1.5-2.0 - sub-oxidizing environment;
- Pr/Ph > 2.0 - oxidizing environment.

Another important quantitative characteristic is the isoprenoid coefficient Ki - the ratio of the content of the sum of the isoprenoids pristan and phytane to the sum of n-C_{17} and n-C_{18} (Pr+Ph)/(n-C_{17}+n-C_{18}). This parameter helps to classify oils according to Al. A. Petrov (Tab. 1).

The numerator shows the measurement limits of the parameters, while the denominator shows the most frequently occurring values. (Behar 2001).

Tableau 1. Caractérisation chromatographique des huiles de différents types chimiques.

Table 1. Chromatographic characterization of oils of different chemical types.

Type of oil	Ki
A^1	$\frac{0.05-2.5}{0.2-1.0}$
A^2	$\frac{2.5-100}{5-50}$
B^2	-
B^1	-

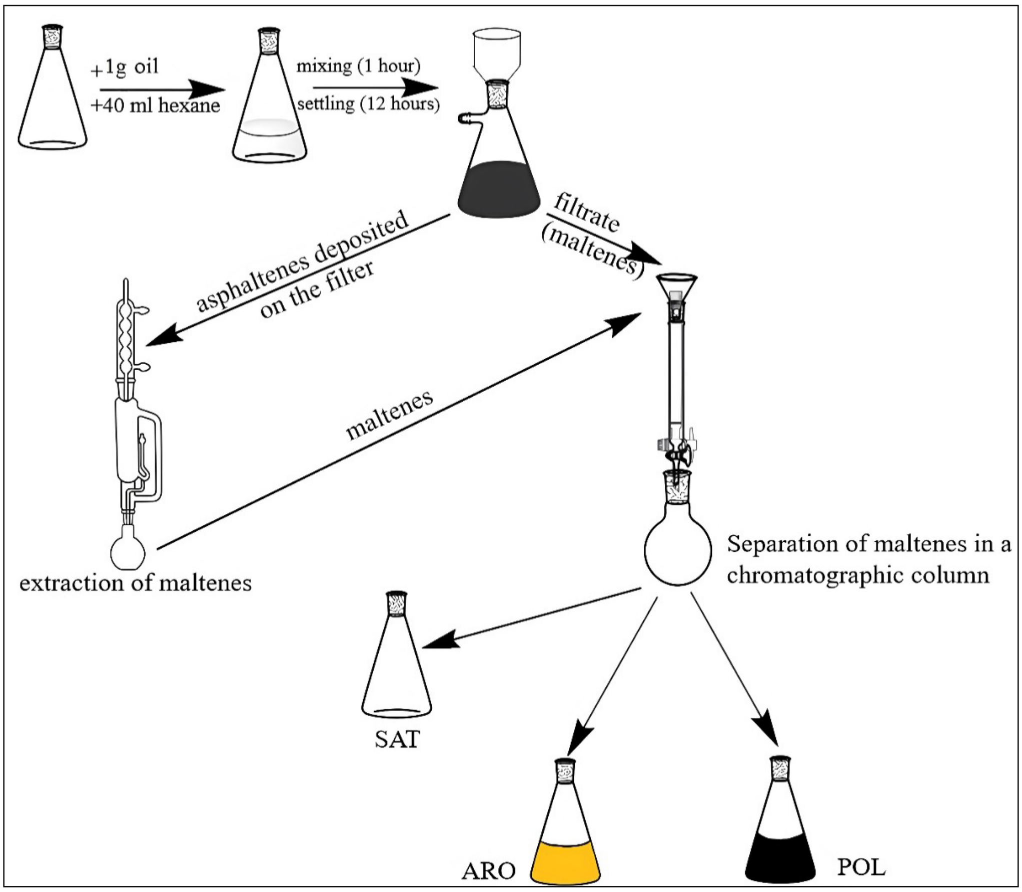

Figure 2. Conception de l'expérience de préparation d'échantillons d'huile.

Figure 2. Design of the oil sample preparation experiment.

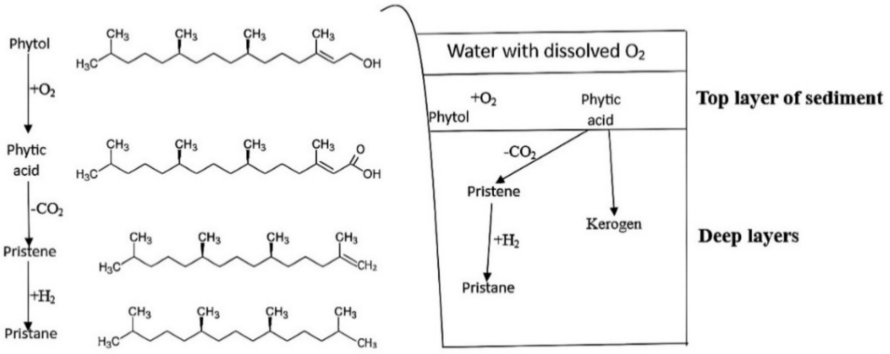

Figure 3. Schéma de formation du pristan.
Figure 3: Scheme of pristan formation.

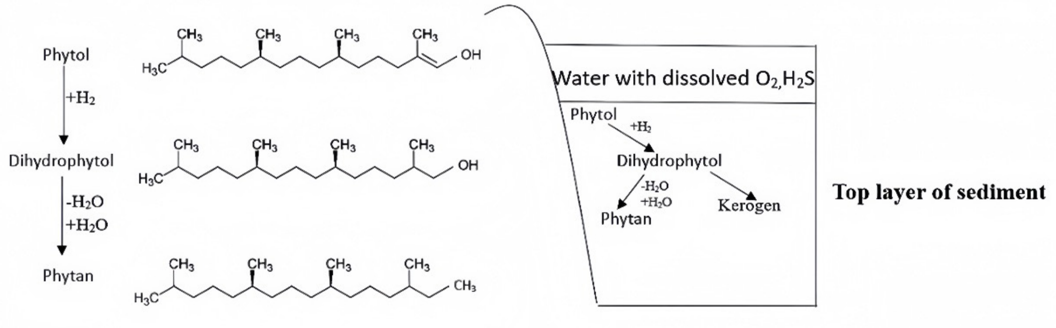

Figure 4. Schéma de formation du phytane.
Figure 4. Scheme of phytane formation.

In addition, there are a several characteristics that determine the thermal maturity of oil. They are based on the content of different classes of organic substances: tetracyclic triterpanes, bi- and tricyclic arenes, thiophenes (Seifert 1986). Tetracyclic triterpanes - steranes C_{27} - C_{29} - are a vast group of chemical compounds, derivatives of which are found in lipoids of all living organisms. However, steranes that have undergone stereochemical and structural transformations of natural precursors are found in petroleum. Sterane C_{27} is called α-cholestane, C_{28} - ergostane (α-24-methylcholestane), C_{29} - sitostane (α-24-ethylcholestane).

Due to the presence of several chiral centers, steranes are capable of forming epimers that determine the optical activity of the oil. According to the position of hydrogen in the chiral centers, one distinguishes: 5α,14α,17α,20R-configuration (ααα, biosteranes or α-steranes); 5α,14β,17β,20R- and 20S-epimers (αββ, isosteranes); 10α,13β,17α,20R- and 20S-epimers (αβα, diasteranes). During oil formation, epimerization processes of biosteranes into isosteranes occur, due to thermodynamic benefit by relieving the tension in the rings (Fig. 5). This reaction is a measure to assess the degree of catagenetic maturation of biomolecules to oil. The isosterane/α-sterane ratio (αββ 20R+20S / αααα 20R) is called the maturation ratio (Zhonghong *et al.* 2021).

The bicyclic hydrocarbons naphthalene and biphenyl and their homologs have long been detected in various oil samples. However, it is naphthalene homologs such as mono-, di- and trimethyl homologs that are more abundant (Yi. *et al.* 2020). Such a prevalence of this type of hydrocarbons is associated with the aggregate state (naphthalene is solid, its homologs are liquids) and with the structure of aromatization products of steroids and triterpenoids.

In geochemistry, bicyclic hydrocarbons are used to assess the maturity of oils and rock organic matter, more specifically dimethyl homologs of naphthalene: 2,6- , 2,7- and 1,5-dimethylnaphthalenes (Fig. 6). Among tricyclic arenes in oil, two types of benzene ring articulation are distinguished: methyl homologs of anthracene (with linear structure) and methyl homologs of phenanthrene (with angular structure). Monomethylphenanthrenes (MP) have a significant role in the genesis of hydrocarbons. It is important to note that C-1, C-2, C-3, C-4, and C-9 can have a methyl radical in these homologs, while none of the methylphenanthrenes found have a radical at C-4 and C-5. This is explained by the absence of methyl substituents at the corresponding carbon atoms in steroids, the precursors of hydrocarbons of the phenanthrene series (Mango 1997). The greater thermodynamic stability of 2- and 3-methylphenanthrenes than that of 1- and 9-methylphenanthrenes is used to determine the degree of catagenesis of organic matter (Fig. 7) (Y.-P. Wang *et al.* 2022). The degree of catagenesis of organic matter is determined by the content of phenanthrenes, which are used to calculate the methylphenanthrene index (MPI) (Radke 1988).

This group also includes 1-methyl-7-isopropylphenanthrene (retene), which belongs to relict hydrocarbons. Homologs of pyrene, perylene, fluorene, chrysenes, benzfluorenes are also present in oil.Heterocyclic sulfur compounds - thiophenes - are concentrated in tarry asphaltene substances of oil and are thiophene homologs. Mono-, di-, trimethylthiophenes, ethylthiophene and other thiophene homologs with long alkyl radicals are not identified in all oils. More often benzothiophenes, dibenzothiophenes and their methyl homologs are detected. The most representative compounds of this class in the

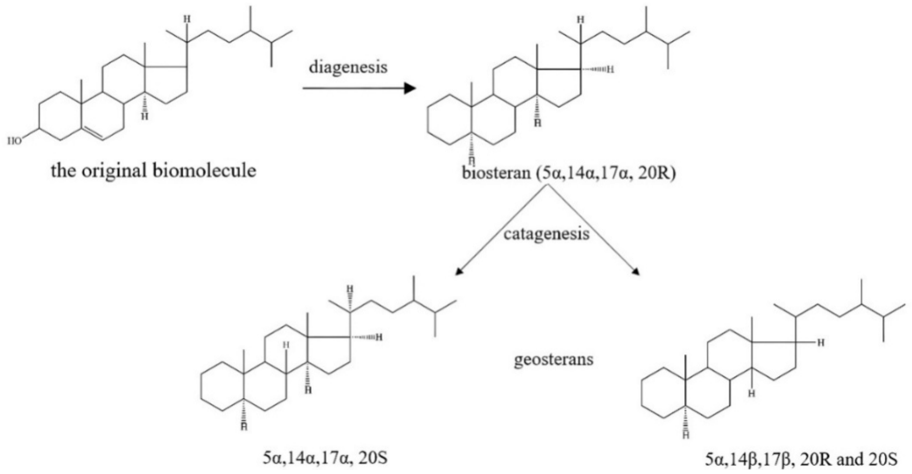

Figure 5. Schéma de conversion du sterane.
Figure 5. Scheme of sterane conversion.

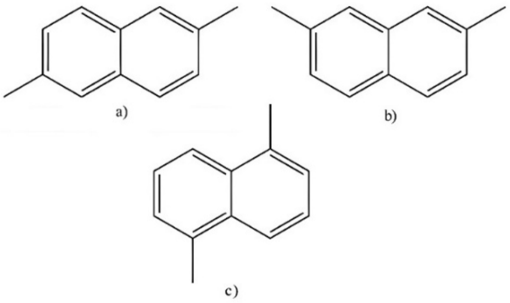

Figure 6 : Hydrocarbures bicycliques : a) 2,6-diméthylnaphtalène ; b) 2,7-diméthylnaphtalène ; c) 1,5-diméthylnaphtalène.
Figure 6: Bicyclic hydrocarbons: a) 2,6-dimethylnaphthalene; b) 2,7-dimethylnaphthalene; c) 1,5-dimethylnaphthalene.

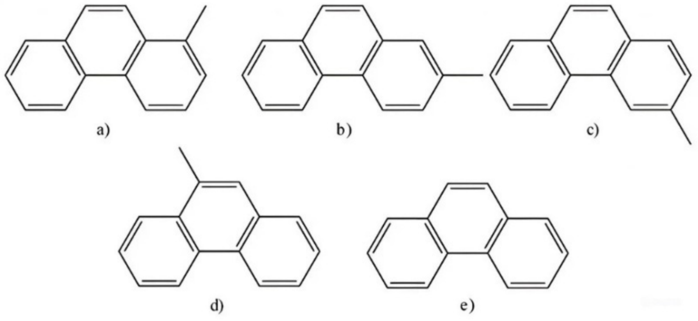

Figure 7. Formules des substances de la série des phénanthrènes : a) 1-méthylphénanthrène ; b) 2-méthylphénanthrène ; c) 3-méthylphénanthrène ; d) 9-méthylphénanthrène ; e) phénanthrène.
Figure 7. Formulas of substances of the phenanthrene series: a) 1-methylphenanthrene; b)2-methylphenanthrene; c) 3- methylphenanthrene; d) 9-methylphenanthrene; e) phenanthrene.

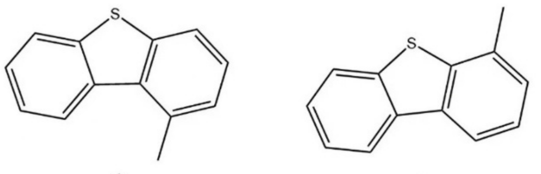

Figure 8. Formules des méthyldibenzothiophènes : a) 4-méthyldibenzothiophène ; b) 1-méthyldibenzothiophène.
Figure 8. Formulas of methyldibenzothiophenes: a) 4-methyldibenzothiophene; b) 1-methyldibenzothiophene.

question of the origin of hydrocarbons are isomers of methyldibenzothiophene (MDBT) (Fig. 8) (Seifert 1986).

In general, it is possible to establish a correlation between the type of primary oil-maternal strata and analyzed hydrocarbons by thiophenes. Thus, the ratio of 4-methyldibenzothiophene to phenanthrene can be used in determining the oil source rock. In particular, for hydrocarbons derived from carbonate rocks the ratio, MDBT will be between 4.2 and 8.3, for siliceous rocks 0.3-1.8, for clayey rocks not more than 0.38 (Curiale 1986). According to the presented research methods, gas chromatographic and mass spectrometric analysis of four samples was carried out for different deposits of Kaliningrad region. Let us proceed directly to the review and discussion of the obtained results.

DETERMINATION OF PARAMETERS OF ISOTOPIC COMPOSITION OF OILS AND FRACTIONS

Within planet Earth, the most stable are 2 carbon isotopes: light ^{12}C and heavy ^{13}C, which are involved in all biogenic processes. The ratio of heavy carbon to light carbon, or the compaction value δ^{13}C‰, allows us to determine the age of living or plant matter, the carbon composition of the biogenic and abiogenic complex, as well as the genesis of oil. It is important to mention that oil fractions differ in carbon isotopic composition, due to the presence of different types of bonds in the molecules of saturated HCs, aromatic compounds, resins and asphaltenes.

Crude oil is the most common fraction used for analysis. It is a mixture of different hydrocarbons and contains information about the processes that took place during its formation. Asphaltenes can also provide information about the conditions under which the oil was formed, such as temperature and pressure. Resins and paraffins are essential for analysis because they can indicate the maturity of the oil. Aromatic compounds contain more carbon than naphthenic and paraffinic hydrocarbons and their isotopic composition can indicate the processes that led to their formation (Kartsev 2023). By mass spectrometric analysis of samples from continental and shelf fields of Kaliningrad region the value of compaction δ^{13}C‰ was determined, and its correlation analysis was also carried out, relative to the indicator of Krasnoborsk field (Tab. 2 and 3).

As a result, it was found that both shelf and continental oils of the central part of the Baltic Syneclise (territories of the Kaliningrad region) are similar in their isotopic composition and, therefore, have a common oil-maternal rock. Taking into account the fact that the Devonian and Silurian traps in the region are practically empty and contain only traces of hydrocarbons, as well as the relatively high ability of the local Phanerozoic rock strata to drain upward along the section, it can be argued that the oil discovered in the Cambrian rocks was formed in the same period, and its migration took place mainly horizontally along the formation, with partial dispersion and loss. In addition, the available physical and chemical characteristics also indicate that the oil of these fields is Cambrian (about 520 million years old) (Kharin 2014).Taking into account the paleogeographic peculiarities of the location of the territory of the Kaliningrad region in the Cambrian period (location in the southern hemisphere between Laurentia and Gondwana), as well as comparing the obtained values of isotopic composition with other hydrocarbon deposits in the world, it can be stated that oil from all four fields, regardless of their current location within the Baltic syneclise, is of oceanic origin. Samples for all oil deposits were converted into ionized form.

Ions were separated according to their mass-to-charge ratio. Such analysis provides important information for determining the molecular weight, molecular formula or elemental composition and structure of molecules. A number of chromatograms of unseparated oils were obtained (Fig. 9-10-11).

The chromatograms presented for the fields show a high similarity of the hydrocarbon mixture for all analyzed fields, but it is not enough just to compare the distribution and intensity of different compounds, it is of great importance to perform deep analysis of the results and determine the main molecular parameters. The section describes the organic

Tableau 2 - Valeur de compaction δ^{13}C‰ dans les échantillons d'huile.

Table 2 - Compaction value δ^{13}C‰ in oil samples.

Deposit	δ^{13}C‰				
	Oil	SAT	ARO	POL	ASP
Krasnoborskoye	-30.6	-31.0	-30.3	-30.2	-29.9
Ladushkinskoe	-30.6	-30.9	-30.1	-30.0	-30.1
D6	-30.6	-31.0	-30.2	-29.8	-30.2
D33	-30.5	-31.0	-30.5	-30.0	-30.2

Tableau 3 - Analyse de corrélation de la valeur de compactage δ^{13}C‰.

Table 3 - Correlation analysis of compaction value δ^{13}C‰.

Deposit	Krasnoborskoye	Ladushkinskoe	D6	D33
Krasnoborskoye	1	-	-	-
Ladushkinskoe	0.96	1	-	-
D6	0.86	0.96	1	-
D33	0.86	0.91	0.93	1

substances that determine the parameters characterizing oils (Okhotnikova *et al.* 2021). During chromatography, one can qualitatively and quantitatively separate oil fractions, determining the content of biomarkers and calculating the necessary coefficients for its classification by the degree of thermal maturity, the type of oil and gas basin. The content of Pristane and Phytane (Pr/Ph) was determined in the study for all four deposits. The value of isoprene ratio (contents of the sum of isoprenoids Pristan and Phytane and the sum of n-C_{17} and n-C_{18}) was determined. The methyldibenzotetophene ratio (4MDBT/1MDBT) and methylphinatetrate index (MPI-1) were determined. The results are summarized in (Tab. 4).

The spectra shown in the Figure 9 present the results of a study on four oil samples from various fields (Krasnoborskoe; Ladushkinskoe; D6; D33). The proximity of the parameter n-C_{17} and n-C_{18} values is further evidence that confirms the common origin in the whole, and especially in fields of the common type of bedding (offshore and onshore).

The figure 10 shows polycyclic aromatic hydrocarbons (phenanthrenes), whose distributions gradually evolve, indicating increasing maturation of petrogenic organic matter, accompanied by a decrease in phenanthrene and a relative increase in methyl-phenanthrenes.

These spectra of aromatic sulfur compounds in the figure 11 show a clear evolution in the structural distribution of substituted dibenzothiophenes, characterizing a progressive increase in thermal maturity and a relative decrease in heavier sulfur compounds between samples A and D.

The study further established carbon assimilation preference index (CPI) which is to capture the abundance of odd number of n-alkanes relative to even number of n-alkanes. The TA(I)/TA(I+II) maturity index was identified and the maturity of DNR-1 oils was evaluated. According to the characteristic ions, the maturation coefficients were calculated. For S/(S+R) St-C_{29}, the calculation was done according to 5α,14α,17α,20S C_{29}/ (5α,14α,17α,17α,20S C_{29}+ 5α,14α,17α,20R C_{29}) (m/z 217), and for ββ/(ααα+ββ)St-C_{29} used 5α,14β,17β,17β,20R+20S C_{29}/(5α,14α,17α,20R C_{29} + 5α,14β,17β,20R+20S C_{29}) (m/z 217). The results of these calculations for all four fields are summarized in (Tab.5). For a long time, it was believed that continental organic matter was characterized by a lighter carbon isotopic composition.

However, the ambiguity of the chosen criterion was subsequently revealed. The works in which enrichment of oils with light carbon isotope was considered as the influence of a marine source began to appear. In reality, the carbon isotopic composition of organic matter depends not only on the type of bioproducers, but also on its diagenetic evolution. Thus, marine kerogen can be both lighter than continental kerogen in the case of sapropel type and heavier (aquahumus type).

The studied oil samples have relatively high values of the Pr/Ph parameter. This ratio generally characterizes the type of OM and the conditions of its accumulation at the stages of sedimentogenesis and diagenesis. According to (Lewan 1985), low values of Pr/Ph (less than 2) indicate an aquatic environment of sedimentation, including marine, fresh and brackish waters (reducing conditions), intermediate values (2-4) indicate sedimentation in the river-marine environment and coastal marsh zone, while high values (up to 10) are associated with sedimentation in peat bogs (oxidizing conditions). In the considered case, the Pr/Ph parameter for oil samples is slightly higher than 2.0, which indicates the oxidizing nature of the oil and gas bearing basin environment and also confirms the marine composition of bioproducts. In general, taking into account the location of the territory of the Kaliningrad region during the period of oil formation, it can be stated that the main bioproducers of hydrocarbon masses

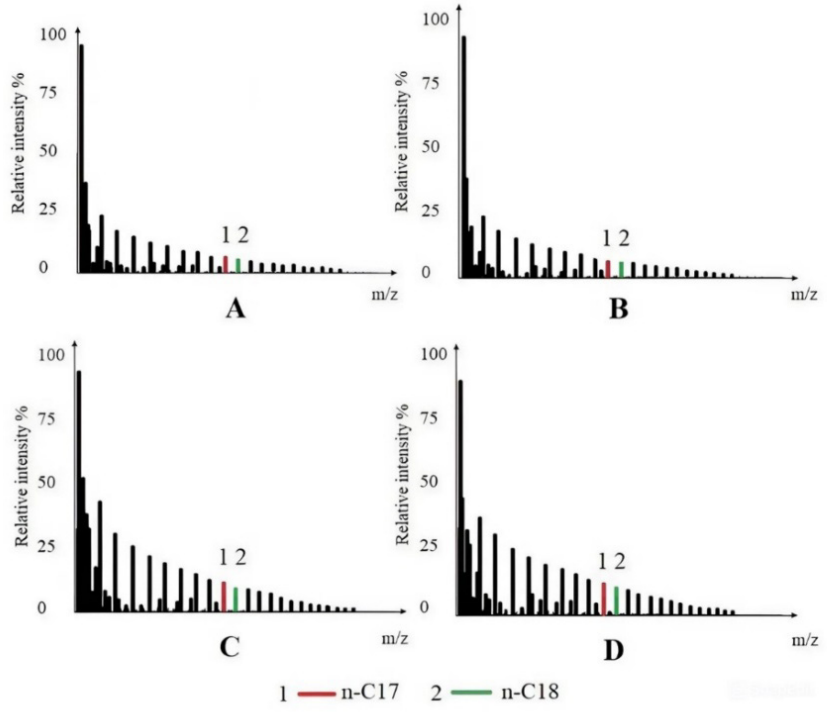

Figure 9. Chromatogrammes des huiles non divisées par m/z 57 : A - Krasnoborskoe ; B - Ladushkinskoe ; C - D6 ; D - D33.
Figure 9. Chromatogram of undivided oils by m/z 57: A - Krasnoborskoe; B - Ladushkinskoe; C - D6; D - D33.

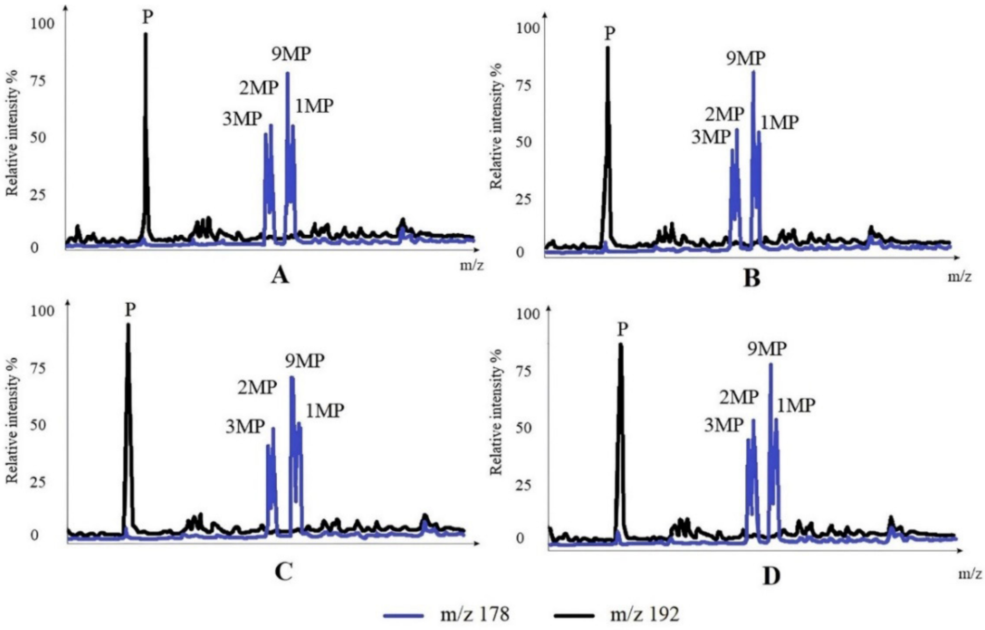

Figure 10. Chromatogrammesdes huiles non divisées de m/z 178 et 192 : A - Krasnoborskoe ; B - Ladushkinskoe ; C - D6 ; D -D-33.
Figure 10. Chromatogram of undivided oils by m/z 178 and 192: A - Krasnoborskoe; B - Ladushkinskoe; C - D6; D -D-33.

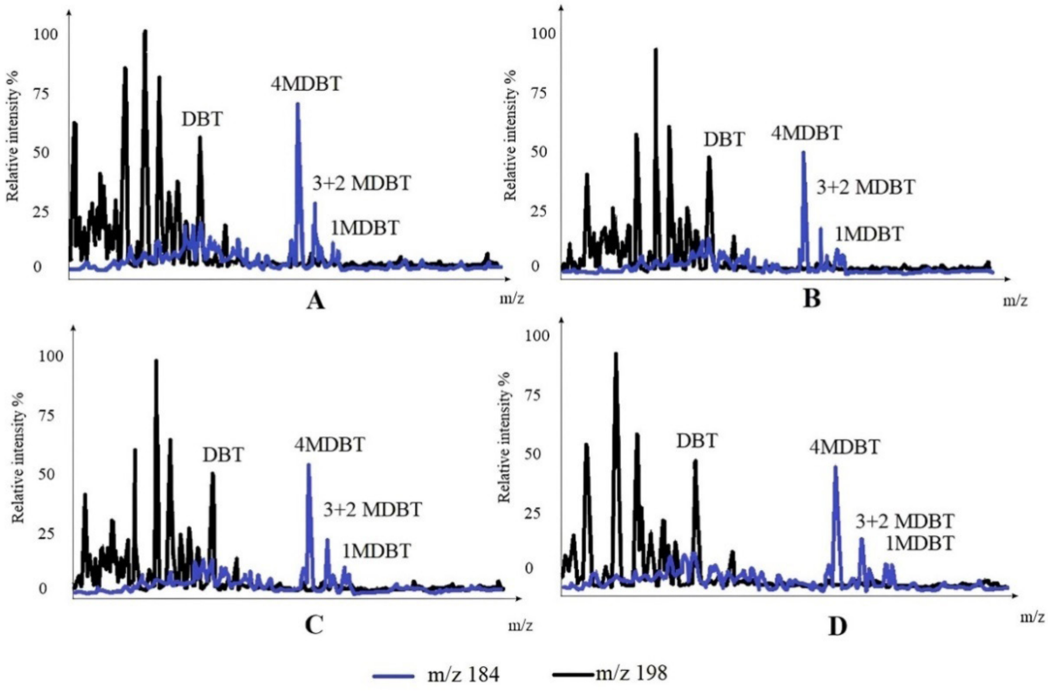

Figure 11. Chromatogrammes des huiles non divisées de m/z 184 et 198 : A - Krasnoborskoe ; B - Ladushkinskoe ; C - D6 ; D - D33.
Figure 11. Chromatogram of undivided oils by m/z 184 and 198: A - Krasnoborskoe; B - Ladushkinskoe; C - D6; D - D33.

Tableau 4 - Valeurs des paramètres moléculaires calculés pour les échantillons de pétrole brut.
Table 4 - Values of calculated molecular parameters for crude oil samples.

Deposit	Pr/Ph	Ki	CPI-1	4MDBT/1MDBT	MPI-1
Krasnoborskoye	2.27	0.45	1.03	7.62	0.76
Ladushkinskoe	2.35	0.50	1.01	6.65	0.75
D6	2.39	0.50	1.04	6.35	0.72
D33	2.39	0.53	1.04	6.07	0.76

were the coastal littoral biotope, shelf, between the Baltica and Laurentia.

According to the studies, thermally immature kerogen has been identified in the northern and eastern regions of Lithuania. Lower Paleozoic oil source rocks with the potential to generate hydrocarbons have been discovered at depths of 1,700–2,000 meters in the western part of Lithuania and in the Kaliningrad region. (Zdanavičiūte *et al.* 1998). In addition, oils accumulated in Middle Cambrian sandstones in the Polish sector of the Baltic region are characterized by a high degree of similarity of geochemical parameters with nearby regions. (Więcław D *et al*. 2010). It can be concluded from evaluating and comparing the oils of the entire Baltic Shield (Lithuania, Kaliningrad, Poland) that they have one genetic type of organic matter – they were formed from marine oil source rocks (clay shales containing kerogen of algal/bacterial origin) and are characterized by a relatively high degree of thermal maturity, with the exception of a number of deposits (for example, JuznoOlempijskoye and Deiminskoye fields (Kaliningrad), B3 and B4 (Poland). (Zdanaviciute *et al.*1998) (Fig. 12).

The most informative indicators of the degree of OM catagenesis are methyldibenzothiophene ratio, methylphenanthrene index and maturity index TA(I)/TA(I+II). The MDBT isomer ratio provides an indication of the thermal maturity of the oils, as the 1-MDBT isomer has lower thermal stability but higher biodegradation resistance than the 4-MDBT isomer. The values of methyl dibenzothiophene ratio of Kaliningrad oils fall within the range from 4.0 to 10.0, which allow classifying these samples as supermature. According to the methylphenanthrene index, which ranges from 0.3 to 1.65 for the studied samples, and the maturity index TA(I)/TA(I+II), the considered Kaliningrad oils are defined as ultra-mature, which makes these oils stable and preferable for production. Super-mature oils are characterized by a high content of light hydrocarbons and a low concentration of heavy, asphaltene-resinous components, as well as sulfur and metals.

This means that they have a lower viscosity and better fluidity, which simplifies their transportation and processing at oil refineries. Such oils do not require additional purification from salts, water by means of electric desalting units and heteroatomic compounds (O-, S-, N-containing) in hydroprocesses.

In addition, super-mature oils often have a higher resistance to overheating during processing and do not require to regenerate catalysts often. This property allows the use of higher temperatures and pressures that can lead to the production of more efficient and high-quality final products. Increased thermal stability also reduces the risk of coking compounds during the processing that leads to fewer expenses and increases the overall yield of light oil products. These judgments are also confirmed by less informative indicators such as CPI, whose values are as close as possible to 1.0: DNR-1; S/(S+R) and ββ/(ααα+ββ). In addition, due to the isoprenoid coefficient (Ki) determined by GC/MS method, the oils can be classified according to Al. A. Petrov. Samples from KrasnoborskyLadushkinskoe, D6 and D33 fields belong to class A1. Chemical typing of oils provides an understanding of the geochemical nature of oil, thus allowing to determine its origin and formation path. This knowledge is crucial for selecting the appropriate exploration and production technologies, since different types of oil require different approaches to managing production processes.

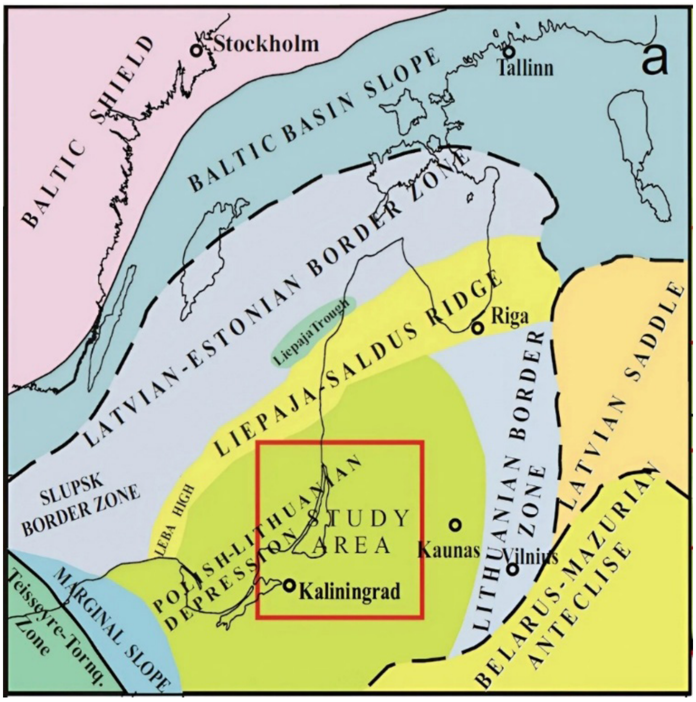

Figure 12. Carte régionale des principaux éléments tectoniques du bassin baltique (Zdanaviciute *et al.*1998).
Figure 12. Regional map of major tectonic elements in the Baltic Basin (Zdanaviciute et al. 1998).

Tableau 5 - Valeurs des paramètres moléculaires calculés pour les fractions d'huile saturées (SAT).

Table 5 - Values of calculated molecular parameters for saturated oil fractions (SAT).

Deposit	Pr/Ph	Ki	CPI-1	4MDBT/1MDBT	MPI-1	TA(I)/TA(I+II)	DNR-1	S/(S+R)	ββ/(αα+ββ)
Krasnoborskoye	2.14	0.43	1.07	6.06	0.80	0.26	1.20	0.50	0.53
Ladushkinskoe	2.12	0.48	1.04	5.71	0.75	0.29	1.06	0.52	0.55
D6	2.10	0.49	1.02	6.08	0.77	0.27	1.23	0.53	0.55
D33	2.14	0.50	1.02	5.87	0.76	0.28	1.07	0.50	0.55

CONCLUSION

As a result of this work, the peculiarities of geochemical parameters of oils from four fields of Kaliningrad region (two offshore fields – D6 and D33, and two onshore fields - Ladushkinskoe and Krasnoborskoe) were studied. According to the physical and chemical investigations previously carried out by the authors, these oils belong to the type of especially light oils, to the class of low-sulfur oils, which contain small amounts of water, resinous-asphaltene compounds and mechanical impurities, they are inflammable liquids; the fractional composition indicates a significant content of fuel oil in the studied oils, but light oil fractions prevail.

Valuable data on geochemical parameters of Kaliningrad region oil were obtained by isotope mass spectrometric analysis ($\delta^{13}C$‰) and GC/MS (Pr/Ph; Ki; 4MDBT/1MDBT; MPI-1; CPI; TA(I)/TA(I+II); DNR; S/(S+R) St-C_{29}; ββ/(ααα+ββ) St-C_{29}).

Based on the results, the studied oils have similar isotopic compositions, and the correlation analysis allows us to state that they all originated from the same petroleum parent rock. The results of the Pr/Ph ratio indicate oxidizing conditions of the medium. According to the values of methyldibenzothiophene ratio, methylphenanthrene index and TA(I)/TA(I+II) maturity index of Kaliningrad oils, they can be classified as super-mature.

It can be stated that all the studied hydrocarbons originated from the same petroleum source rock under oxidizing conditions from organic matter of littoral genesis, which indicates that samples from both offshore and onshore fields have a common origin despite their current geographical location. The hydrocarbon ages are on the order of 500-520 Ma.

If one pays attention at the entire Baltic region, including the oil fields of Poland and Lithuania, it can be noticed a correlation of physical and geochemical parameters. The fields studied have similar values of carbon isotope content and biomarkers to the values of the Lithuanian and Polish fields. Based on this, it should be concluded that these oils have a common source rock and a relatively high degree of maturation.

Obviously, sedimentation conditions allowed the formation of an oil-maternal stratum in the coastal zone of the Baltic continent at that time. Littoral sapropelic muds containing a large amount of organic material were gradually formed in relatively warm coastal conditions, possibly in a number of lagoons. Thereafter, during the northward drift of the Baltic, a series of transgressions and regressions were observed in the shelf zone. This led to overlapping of the formed oil-maternal strata and their subsequent subsidence. To start the catagenesis process (the first stage), temperatures of about 20-65°C are required (Zhen *et al*. 2020). Obviously, this process took place from the Cambrian to the Silurian. Thus, oil genesis occurred at shallow depths, about 0.5-0.7 km. At this time, Baltica drifted from the south towards the equator. This path took more than 200 million years. At the end of the Silurian and the beginning of the Devonian, a new continent, Laurentia, was formed at the equator as a result of the collision of Baltica, Avalonia and Laurentia. The territory of the Baltic countries appeared on an inland plain at the foot of the high CaledonidesMountains, which rose as a result of the collision between Laurentia and Baltica. It is known that the processes of orogenesis contribute to active destruction of primary oil-maternal strata (Civan 2023).

As a result, presumably at this time (about 440 million years ago), the destruction of the primary zones of oil accumulation and subsequent secondary migration of hydrocarbons into those traps, which are now identified as separate fields in the central part of the Baltic syneclise.

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