The hydrocarbon compounds sources in surface sediments of the Laptev Sea shelf

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Abstract: Rapid warming of the Arctic provokes large-scale degradation of permafrost on land terrestrial and in submarines. A vast amount of remobilized organic matter (OM) is involved in the modern biogeochemical cycle. Understanding of the fate of terrestrial OM moving from the land to the Arctic shelf is essential for predicting the potential feedback of Arctic ecosystems. In our research, an attempt was made to characterize the modern OM stored in the surface sediments of the Laptev Sea to estimate its composition variability and to identify the OM sources along with the "coastline - outer shelf" profile. Here we discuss the OM features revealed by Rock-Eval pyrolysis (RE) and the distribution of nalkanes in combination with sediment grain-size analysis. The GC/MS records are directly comparable with RE data tracing the terrestrial OM along with the entire studied profile. However, we observe both a significant decline of terrestrial input and the rise of hydrobiont in the outer shelf zone. We assume that different OM sources may produce different ranges of RE values.

1 Introduction

Increasing global warming in the Arctic leads to a significant rate of terrestrial and submarine permafrost degradation [1,2]. The thermal state of the permafrost reaches the critical destabilization point, which, in its turn, triggers the remobilization of the huge amounts of previously frozen organic carbon (OC) and its involvement in the modern biogeochemical cycle. Moreover, the Arctic ecosystem has a low regenerative capacity or resilience due to the prevailing year-round negative temperature and scarce biota, which aren't capable to reduce the stress connected with climate change [3,4]. It was shown that an increased supply of remobilized ("old") OC may lead to severe acidification [5] of the Arctic waters and significantly contribute to the greenhouse effect as a result of the OC to CO2 transformation [6]. According to preliminary estimates, about 44 ± 10 Mt [7] of terrestrial OC is exported to the East Siberian Arctic shelf by coastal erosion only. Reliable identification of both OM sources and the mechanisms of its transformation within the "land – shelf" system is an important step towards a comprehensive understanding of the modern Arctic carbon cycle. We can observe that the most vulnerable region is the most severe recipient of climate change, and this situation requires a detailed complex study.

In recent years, OM stored in the surface sediments of the Arctic seas has been a subject of growing interest, and many complex studies performed with molecular and isotopic tools

have been published [8-12]. In this work, we use a special, adapted Rock-Eval (RE) pyrolysis program to get new insights into the OM composition of surface sediments across the vast area of the Laptev Sea shelf. RE data for the East Siberian Arctic shelf are extremely limited. The Rock-Eval pyrolytic analysis is a traditional method in petroleum geology used to assess the oil generation potential of sedimentary rocks. Nevertheless, at present, the Rock-Eval method is increasingly used to study the organic components of soils and modern sediments. It was shown that pyrolytic analysis of immature organic material can provide valuable information about the sedimentary OM genesis and the degree of its diagenetic transformation. The Rock-Eval pyrolysis can serve as an additional tool that effectively complements the traditional geochemical methods for elemental, molecular, and isotopic composition identification.

2 Materials and methods

2.1 Study Area

The East Siberian Arctic Shelf (ESAS), represented by the Laptev Sea, the East Siberian Sea, and the Russian part of the Chukchi Sea, is unique because it occupies a huge area (>2*10⁶ km²) and has a shallow average depth (~50 m). Moreover, the ESAS contains more than 80% of the world's subsea permafrost which is believed to store permafrost-related and continental slope methane hydrates [13-15].

This research focuses on the transect of the Laptev Sea, the shallowest sea in the Arctic. More than half of the seabed (53%) is occupied by a slightly sloping shallow continental shelf with depths of up to 50 m. Up to $76^{\circ}N_{\perp}$ the depth does not exceed 25 m. In the northern part, the bottom drops abruptly to the ocean floor with depths of ~ 1 km (22% of the sea area).

The Laptev Sea is an Arctic sea dominated by terrestrial OMthat receives a substantial contribution from both coastal erosion and Lena river runoff [16,17]. It was previously shown that accelerating coastal erosion acts as the main contributor to the terrestrial OM pool exported to the Laptev Sea [7]. About 25% of the Laptev Sea coastline is composed of ice-rich permafrost deposit [1] known as the Yedoma Ice Complex which is highly susceptible to erosion. The retreat rate of the permafrost-dominated coast has been steadily increasing due to the combined action of thermal and mechanical forces [1]. The total input of the intense coastal erosion to the Laptev Sea and the East Siberian Sea is estimated at 4.0 – $22.0 \pm 8.0 \, \text{Tg/year}$ (the submarine permafrost degradation is included) [7,18]. Besides, the Lena River exports large volumes of the fresh water discharged to the Laptev Sea, being the main fluvial sediment source for the ESAS [19]. During the land-to-shelf transport, exported organic matter undergoes aerobic biochemical decomposition, which can be remineralized to CO₂ or delivered to the deep-water part of the Arctic Ocean [8].

The Laptev Sea has a significant petroleum potential. It is considered an analogue of the North Sea Petroleum Basin, and a number of their common features have been identified. [20]. At the moment, no wells have been drilled offshore except for the Khatanga license area (Tsentralno-Olginskaya-1 well). Sampling points indicated in this manuscript are located within the Ust-Lenskiy license area owned by Rosneft.

Oil likely played a significant role in the phase composition of naphtides. Its formation in the land and coastal shelf zone was stipulated by the presence of high-quality oil source rocks in the Riphean–Phanerozoic cover of the Siberian Craton. In the rest the shelf, where the Aptian–Cenozoic rift system is widespread, oil can also be present in pools, since these rocks probably contain not only gas source rocks but also oil-and-gas bearing rocks of deltaic and prodeltaic age, which are located in the main oil formation zone. The above

properties are specific features of the study region, and its hydrocarbon potential will be steadily increasing with the shelf development [21]. According to the results of the audit by DeGolyer and MacNaughton, as of 01.01.2019, the recoverable hydrocarbons reserves on the shelf of the Eastern Arctic amount to more than 13.7 bln toe net.

2.2 Sample collection and preparation

We analyzed 14 surface sediment samples (horizon 0 - 2 cm) collected across the Laptev Sea shelf during the Arctic expedition onboard the Russian R/V Academician M. Keldysh during fall 2018 (Figure 1). A box corer was used to collect sediment samples. The sediment samples were immediately transferred to plastic bags after collection and then stored in a refrigerator at $-20\,^{\circ}$ C.

The sample preparationand analytical part of the research were carried out in the International Research Laboratory for Arctic Seas Carbon of the Tomsk Polytechnic University. The samples were thawed at room temperature for 24 h,then brought to constant weight in a drying oven at 45°C,and then homogenized. After this step, part of the samples was transmitted to the Rock-Eval pyrolysis and Laser Diffraction to determine the particle size distribution. The rest of the surface sediment samples were subjected to further lipid biomarker analysis.

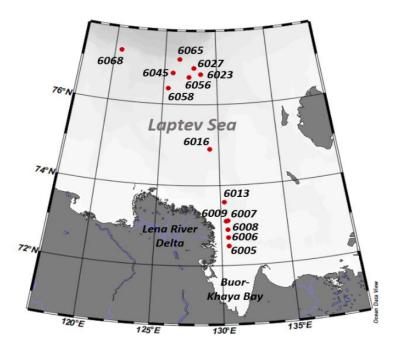


Fig. 1. Sample stations.

2.3 Analytical methods

2.3.1 Rock-Eval Pyrolysis

Pyrolytic analysis was performed on a Rock Eval 6 Turbo by Vinci Technologies. To provide relevant data for the modern OM an adapted Rock-Eval temperature program

"Reservoir" was applied (start of sample heating at +180°C, holding for 10 minutes, then heating up to +650°C at a rate of 25°C/min).

The peculiarity of the "Reservoir" program is the low initial pyrolysis temperature. A sample of about 40 mg is kept under 180°C for 10 minutes. During this time, the released hydrocarbons are transported into the flame ionization detector by an inert gas stream, and thus the S_{1r} peak (mg HC/g) is formed. Further heating from 180 to 650°C allows obtaining a double peak of S_{2a} (mg HC/g) and S_{2b} (mg HC/g). The S_{1r} peak corresponds to the lightest fractions detected during the temperature plateau at 180°C , whereas the S_{2a} peak detects hydrocarbon compounds between 180 and 325°C [22]. The S_{2b} peak is assigned to the cracking of geopolymers. The temperature of the highest hydrocarbon yield rate (during the formation of the S_{2b} peak) is denoted as T_{peak} (°C).

In addition to the pyrolysis oven, the Rock-Eval 6 Turbo is equipped with an oxidation oven and two infrared cells for registering CO and CO_2 gases emitted during pyrolysis and oxidation. The registration of CO and CO_2 provides information on the OM oxidation degree (S_3 peak, mg CO_2 /g).

Based on the determined pyrolysis parameters (S_{1r} , S_{2a} , etc.), the amount of pyrolyzed organic carbon (PC, wt%) is calculated.

An additional oxidation stage allows to calculate the hydrogen (HI, mg HC/g C_{org}) and oxygen (OI, mg CO₂/g C_{org}) indices, residual organic carbon (RC, wt%), total organic (TOC, wt%), and mineral carbon (MinC, wt%) in the rock samples.

To make our data consistent with previously published studies [22,23], the following equations are applied: $S_1 = S_{1r} + S_{2a}$ and $S_2 = S_{2b}$.

2.3.2 Laser Diffraction

The particle size distribution was determined by the laser diffraction SALD-7101 Shimadzu. A weighed part of the test sample was placed in a mixer bath with distilled water and dispersed using an ultrasonic setup (40 W, 40 kHz). Measurements were performed in a flow-through cell. Shepard's "sand-silt-clay" classification was applied: sand (> 63 μ m), silt (from 2 to 63 μ m), and clay (< 2 μ m).

2.3.3 Gas Chromatography-Mass Spectrometry

Dried and homogenized samples were extracted using Soxhlet extraction with chloroform for 16 hours. The total lipid extracts (TLE) were concentrated using a rotary evaporatot. Sodium sulfate and activated copper powder were added to remove water and elemental sulfur, respectively. Then, ~ 10 mg of internal standard (d50-tetracosane) was added. The extracts were analyzed by a GC-MS (Agilent 7890B (GC) – Agilent Q-TOF 7200 (MS)). Quantification was performed using a five-point calibration curve with commercially available standards.

3 Results

3.1 Rock-Eval Pyrolysis

According to the pyrolysis data, total organic carbon (TOC) varies from 0.4 to 2.71 wt%, which is consistent with previous studies in the region [24]. Free hydrocarbons and low molecular weight OM, considered as lipid fraction (S_1), range from 0.11 to 0.73 mg HC/g (Table 1) [23,25,26]. The predominantly higher TOC and S_1 values are found in the coastal zone (> 1 wt% and > 0.4 mg HC/g, respectively) (Figure 2).

n

6045

6053

6056

6058

6065

6068

0.33

0.34

0.19

0.11

0.11

0.19

1.22

1.52

1

0.87

0.67

0.92

1.86

3.32

1.75

1.3

1.18

2

TO Min Tpea PC RC OI S_1 S_2 S_3 HI C Statio C mg HC/g HC/g wt wt wt mg mg mg mg °C wt% % % % HC/g HC/g HC/g Corg Corg 0.2 1.1 1.4 6005 0.37 1.78 125 213 0.2 3.02 461 8 4 2 2.2 2.7 6006 0.65 2.92 5.74 462 0.5 108 212 0.4 1 1 0.6 2.0 2.6 6007 0.73 2.74 5.32 462 103 201 0.4 4 5 1 0.4 1.7 2.2 6008 0.71 2.61 462 115 212 0.3 4.82 9 7 0.3 1.5 1.9 6009 0.53 1.98 3.84 461 103 199 0.3 5 8 3 0.2 0.9 0.7 6013 0.28 1.12 1.92 464 118 202 0.2 5 1 4 0.3 1.0 1.3 6016 0.39 110 1.52 3.38 459 245 0.2 7 8 1 0.1 0.4 0.6 6027 0.17 1.01 1.98 453 158 309 0.2 7 7 4

0.5

9

0.9

0.5

8

4

0.3

5

0.2

9

0.5

3

0.2

0.2

8

0.1

6

0.1

3

0.1

1 0.1

380

390

382

459

392

395

0.7

9

1.2

6

0.7

0.4

8

0.4

0.6

154

121

143

181

168

133

0.2

0.2

0.2

0.1

0.1

0.2

235

263

250

271

295

290

Table 1. Rock-Eval parameters for Laptev Sea surface sediments.

Parameters T_{peak}, S₁, S₂, S₃, PC, RC, TOC, HI, OI, MinC are explained in the text (Section 2.3.1).

The contents of relatively thermo-labile hydrogen-rich OM or biopolymers (S₂) and CO/CO₂ released by oxygen-containing OM or geopolymers (S₃), correspond to 0.67 – 2.92 mg HC/g and to 1.18 – 5.4 mg HC/g, respectively (Table 1) [23,25,26]. Consequently, the fraction of the lipid extractable component in the total OM yield is, on average, 13 times less than the fraction of biogeopolymers stored in the sediments $(S_2 + S_3)$.

The fraction of mineral carbon (MinC) is significantly less than the TOC and varies from 0.09 to 0.38 wt%, with the correlation between the TOC and MinC arrays close to 1.

The sediment distribution suggests a relatively low HI (hydrogen index) and a higher OI (oxygen index). The hydrogen index of all samples is higher than 100 mg HC/g $C_{\rm org}$ and ranges from 103 to 181 mg HC/g $C_{\rm org}$, which indicates the presence of a hydrobiont component in the OM. The maximum HI values are recorded in the samples taken from the outer shelf. Consequently, they are characterized by a hypoxic or anoxic sedimentation environment, in contrast to the coastal samples, where intensive resuspension may induce oxidation of the sedimentary OM.

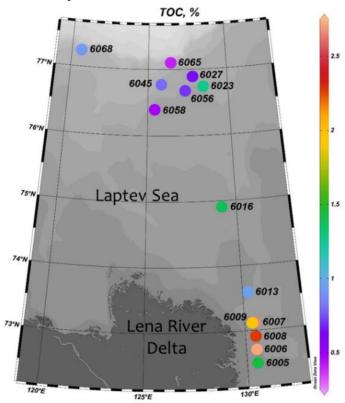


Fig. 2. Total Organic Carbon (TOC), w% values of surface sediments across the Laptev Sea shelf.

The OI ranges from 199 to 309 mg HC/g $C_{\rm org}$. The OI can reflect both the export of already oxidized OM with river runoff and coastal erosion and the subsequent degradation of allochthonous and autochthonous OM in the water column, as far as it is buried in sediments; therefore, it is important to separate these two processes.

 T_{peak} varies from 380 to 464°C, which is 64% higher than the T_{peak} boundary for modern sediments (<425°C) [27]. The studied samples can be divided into two clusters according to the T_{peak} ranges: 1) 380 – 395°C and 2) 453 – 464°C. The first range corresponds to the temperatures of destruction of polysaccharides and lignin (terrigenous OM), the second temperature window indicates the dominance of humic and fulvic acids in the OM composition [23].

A classical presentation of RE data is in the form of a pseudo-Van Krevelen diagram, which plots the OI and HI against each other in a manner analogous to the atomic O/C and H/C ratios used to classify kerogens [23,28]. The ratio diagram of hydrogen and oxygen indices (HI/OI) is shown in Figure 3.

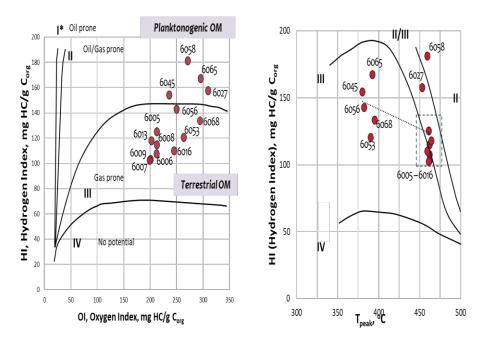


Fig. 3. Left: Modified Van Krevelen-type diagram of surface sediments across the Laptev Sea shelf.

Right: HI, mg HC/g C_{org} as a function of T_{peak}, °C.

Ratio HI/OI < 1 may be compared to a mix of "Type 2" and "Type 3" kerogens for matured OM determining planktonogenic and terrestrial origin, respectively. The samples taken from the coastal part show the dominant terrestrial origin of OM. However, the contribution of autochthonous OM is clearly traced for the outer shelf samples. The T_{peak} / HI ratio, shown in Figure 3, also confirms these statements [17].

The RE parameters reflect the genesis of OM (of marine or terrigenous origin), as well as the degree of dia- and catagenesis OM transformation. For surface sediments, S_1 , S_2 , S_3 , RC, and T_{peak} are the most informative. Relatively high values of S_1 and S_2 characterize the marine primary production, while high S_3 and residual carbon (RC) correspond to terrestrial organic material. These features are due to the marine OM composition: a low concentration or absence of lignin (an oxygen-containing polymer, which has terrestrial origin) and a high lipid content.

During the process of sediment transportation and resuspension coupled with OM oxidation (degradation), the proportion of oxygen-containing compounds increases, while the content of hydrogen decreases. It is directly reflected in the HI and OI indexes corresponding to the degree of OM transformation [23]. Thus, the "fresh" OM of modern sediments is characterized by high values of the HI/OI parameter (> 2); whereas the HI/OI values decrease for degraded OM.

3.2 Grain-Size distribution

The lithological type of sediments was based on the Shepard's "sand-silt-clay" rations [29]. According to the grain size analysis, sediments are dominated by clay ($< 2 \mu m$) and silt ($2 - 63 \mu m$) fractions. The sand fraction ($> 63 \mu m$) is almost absent (Table 2).

Sampling station	Latitude	Longitude	Depth	Sand (>63µm)	Silt (2 – 63 μm)	Clay (<2 µm)	Lithological type
			m	w%	$W^{0}/_{0}$	w%	
6005	72.5000	130.4990	14.5	0.2	38.1	61.7	Silty clay
6006	72.7070	130.4990	18.5	0.1	69.3	30.6	Clayey silt
6007	73.1230	130.5000	24.3	0	79.3	20.7	Silt
6008	72.9110	130.5000	22	0	73.2	26.8	Silt
6009	73.1150	130.3740	24	0	71.5	28.5	Silt
6013	73.5930	130.2760	23.5	0	44.9	55.1	Silty clay
6016	74.9080	129.1890	40	0.1	76.8	23.1	Silt
6027	76.8920	127.7970	64	0.1	43.5	56.4	Silty clay
6045	76.7750	125.8290	72	0	55.9	44.1	Clayey silt
6053	76.7390	128.4530	65	0	69.4	30.6	Clayey silt
6056	76.6790	127.3170	62	0	59.3	40.7	Clayey silt
6058	76.3960	125.4190	52	0	41.9	58.1	Silty clay
6065	77.1030	126.4240	251	0.1	9.3	90.6	Clay
6068	77.2460	120.6140	185	0	73.4	26.6	Silt

Table 2. Grain-size characteristics of surface sediments.

The positive correlation between HI and clay content (r = 0.71) is higher than the connection between OI and clay fraction (r = 0.42) (Figure 4).

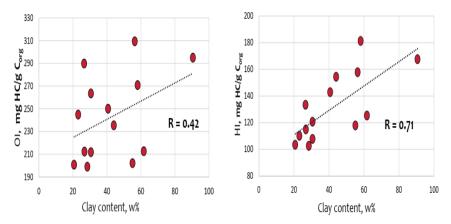


Fig. 4. OI, mg HC/g C_{org} and HI, mg HC/g C_{org} as a function of clay content, w%.

It suggests that clay particles may create a favorable depositional environment, and, therefore, partly preserve the mineral-associated OM from oxidation. Nevertheless, we would not mention the mineral matrix as a first-order control factor for OM preservation.

3.3 GC-MS records

3.3.1 Qualitative interpretation of n-alkanes distribution

Currently, the study focuses on the qualitative interpretation of n-alkanes (neutral non-polar fraction) and isoprenoids (pristane and phytane) distribution. Obviously, terrestrial input is a main contributor to the OM of the studied sediments. Overall dominance of the high molecular weight (HMW) odd C_{25} – C_{31} n-alkanes indicates a significant portion of

terrestrial OM exported with river discharge and thermo abrasion material [7,30]. However, for many outer shelf samples both the hydrobiont markers of the autochthonous nature (C_{15} - C_{19} n-alkanes) and the terrestrial markers mentioned before are contrastingly expressed.

Such classic geochemical indices were calculated based on the peak exit areas on received chromatograms: CPI (Carbon Preference Index), OEP₁₇,OEP₁₉(Odd Even Predominance) indexes, K_i, TAR (terrigenious to aquatic ratio), Paq, and Pr/Phy ratio (Table 3).

Sample	CPI*	Ki	OEP ₁₇	OEP ₁₉	TAR	Paq	Pr/Phy
6005	-**	0.37	1.23	1.24	18.87	0.37	1.42
6006	7.25	0.34	1.19	1.37	33.45	0.36	1.82
6008	7.75	0.34	2.05	1.60	37.64	0.34	2.27
6009	7.25	0.43	1.73	1.40	36.29	0.32	1.30
6013	5.33	0.61	-	1.07	-	0.30	1.10
6016	-	0.48	-	1.24	-	0.31	1.13
6027	-	0.54	1.12	1.32	6.25	0.28	2.88
6045	-	0.62	1.14	1.13	10.27	0.30	1.69

1.08

1.03

1.12

1.72

10.70

11.85

0.95

5.31

0.27

0.24

0.26

0.35

0.29

1.96

2.23

1.78

1.03

Table 3. Geochemical Indexes based on GC-MS records.

5.31

5.09

3.77

6053

6056

6058

6065

6068

0.39

0.67

0.13

0.63

0.86

1.10

0.90

1.33

The predominance of odd-number carbon atoms n-alkanes over their even homologues was evaluated by the CPI and OEP indices. K_i demonstrates the degree of diagenetic transformation and increases with maturity. The TAR determines the genesis of the initial OM, and Paq index reflects the contribution of aquatic macrophytes. The paramount ratio of pristane to phytane gives information about the redox potential of the sedimentation environment.

 ^{*}CPI = 0.5 * [(nC₂₅ + nC₂₇ + nC₂₉ + nC₃₁ + nC₃₁) / (nC₂₄ + nC₂₆ + nC₂₈ + nC₃₀ + nC₃₂) + (nC₂₅ + nC₂₇ + nC₂₉ + nC₃₁ + nC₃₃) / (nC₂₆ + nC₂₈ + nC₃₀ + nC₃₂ + nC₃₄)].

 $Ki = (Pr + Phy)/(nC_{17} + nC_{18}).$

 $OEP_{17} = (nC_{15} + 6 * nC_{17} + nC_{19}) / (4 * nC_{16} + 4 * nC_{18}).$

 $OEP_{19} = (nC_{17} + 6 * nC_{19} + nC_{21}) / (4 * nC_{18} + 4 * nC_{20}).$

 $TAR = (nC_{27} + nC_{29} + nC_{31})/(nC_{15} + nC_{17} + nC_{19}).$

Paq = $(nC_{23} + nC_{25}) / (C_{23} + C_{25} + C_{29} + C_{31}).$

^{** - (}there is no way to calculate the index from the obtained n-alkanes distribution).

High values of the CPI (>> 3) indicate a prevalence of vascular land plants as a source of OM and low microbial degradation state. The average Ki (0.46) and OEP (1.28) indexes also confirm low diagenetic transformation of OM. The TAR traces an increasing supply of autochtonous OM with increasing distance from the coast. In the zone of coastal sediments, the terrestrial component is clearly pronounced (TAR = 31.6), while for the outer shelf sediments, the index is 4 times lower (TAR = 7.6) (Figure 5). The Paq index points out a low contribution of macrophytes (Paq = 0.31) with increasing values in the coastal part. The Pr/Phy ratio confirms the suboxidative environment revealed by the pyrolysis data (HI/OI ratio).

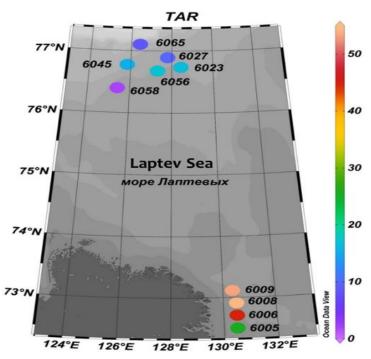


Fig.5.TAR(terrigenous to aquatic ratio) index values of surface sediments across the Laptev Sea shelf.

4 Conclusions

The content of TOC in the studied samples varies from 0.40 to 2.73%, while the PC in the total volume of TOC is 20 to 30%. The lipid (S_1) fraction in the total OM yield is on average 13 times less than the sum of biogeopolymers $(S_2 + S_3)$.

Surface sediments correspond to clay, silt, and their mixed fractions. A significant positive correlation was established between the clay content and the hydrogen index (HI). It suggests that clay particles may create a favorable depositional environment, and, therefore, partly preserve the mineral-associated OM from oxidation.

The OM of surface sediments is divided into two types: the coastal OM predominantly has a terrestrial source; the outer shelf OM is characterized as a mixed allochthonous-autochthonous type. Overall, the decisive contribution to the OM composition is provided by terrestrial sources: river runoff and coastal erosion.

In general, the GC-MS records are directly comparable to the Rock-Eval data. Along the studied profile, the contribution of the terrestrial OM in the outer shelf surface sediments is clearly traced despite the great distance from the coastal zone. This is a distinctive feature of the Laptev Sea biogeochemical regime, which was previously noted

by other researchers [8,9]. Our results confirm and enhance their findings with new geochemical data providing an additional piece towards a deeper understanding of the modern biogeochemical carbon cycle in the Arctic.

With regard to the applied aspect, we plan to identify compounds of naphthydogenic nature, which are markers of the hydrocarbon depth migration, in the key of geochemical prospecting methods. These anomalies can be used to identify areas with the potential presence of hydrocarbon deposits.

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