Petroleum-related hydrocarbons in deep and subsurface sediments from South-Western Barents Sea

Stepan Boitsov[a][1], Vera Petrova[b], Henning K. B. Jensen[c], Anna Kursheva[b], Ivan Litvinenko[b], Yifeng Chen[c], Jarle Klungsøyr[a]

[a] - Institute of Marine Research (IMR), Bergen, Norway; [b] - Academician I.S. Gramberg All-Russia Research Institute for Geology and Mineral Resources of the World Ocean (VNIIO), St. Petersburg, Russia, [c] - Geological Survey of Norway (NGU), Trondheim, Norway.

Abstract

Subsurface sediments from a pockmark area in South-Western Barents Sea have been earlier found to contain elevated levels of petroleum-related polycyclic aromatic hydrocarbons. This work describes a comprehensive analysis of various biomarkers, including the highly source-specific hopanes, in a 4.5 m long gravity core from the same area, together with subsurface sediment samples from other areas in the region without pockmarks present ("background samples"). A clear difference between the pockmark gravity core and the background sediment cores was found, both with regard to genesis and the level of transformation of organic matter. A number of indicator parameters, such as methylphenanthrene index (MPI-1), point towards a significantly higher maturity of hydrocarbons in the pockmark core throughout its length as compared to the other sampled locations. Higher contents of microbial hopanoids (hopenes) may indicate the former presence of petroleum. These findings confirm the hypothesis of a natural hydrocarbon source in the deeper strata present in the studied location with pockmarks.

Keywords: Biomarkers, hopanes, sediments, pockmarks, PAH, alkanes, Barents Sea

1. Introduction

The Barents Sea continental shelf is rich in oil and gas resources. In the Norwegian sector, it may contain 1199 million standard cubic meters of oil equivalents (Sm^3 o.e.) according to the latest estimates made by Norwegian Oil Directorate (NPD 2010). Most of this, 910 million Sm^3 o.e., are undiscovered resources (*ibid.*) The ongoing MAREANO program, a long-term, multi-institutional Norwegian project aiming at extensive biological, geological and geochemical mapping of Norwegian continental shelf seabed, has recently provided detailed geological and geochemical data on the composition of seabed sediments in South-Western Barents Sea (MAREANO, 2010; Boitsov et al., 2009; Chand et al., 2009). The area of Ingøydjupet, located some 80 km North-West of the coast of Norway, was found to contain a pockmark field (depressions approximately 40–60 m in diameter and 6 m deep (Chand et al., 2009)). Pockmarks are geological formations which may signify former or recent seepages of hydrocarbon gas or fluids from formations below the sediment surface (e.g. Hovland and Judd, 1988). Levels of predominantly petrogenic polycyclic aromatic hydrocarbons (PAH) were found to increase in subsurface sediment layers (below 15 cm depth), also when corrected for total organic carbon (TOC) levels (Boitsov et al., 2009). A local natural petroleum source was suggested as a possible explanation (*ibid.*) This is not surprising in view of the proximity of the Goliat oil field (see Fig. 2). According to Juntilla et al. (2010), in

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[1] To whom the correspondence is to be addressed. Address: Institute of Marine Research, P.B. 1870 Nordnes, N-5817 Bergen, Norway. Tel.: +47-55236394, Fax: +47-55238555, email: stepan.boitsov@imr.no

other gravity cores of similar lengths taken within the area both Holocene and glaciomarine sediments are encountered.

A more detailed geochemical study was carried out to confirm the dominating source of hydrocarbons in sediments. A number of parameters have been used for this purpose, based either on the levels of source-specific compounds (e.g. a biogenic source in case of elevated levels of certain PAH compounds as perylene, retene, cadalene) or on the ratios and other relations between specific compounds (Venkatesan, 1988; Neff, 2002; Peters et al., 2004). One such useful ratio is methylphenanthrene index, MPI-1, providing an indication of the petrogenic input in the PAH levels. It is calculated according to the following formula:

MPI-1=1.89(2-MP+3-MP)/[P+1.26(1-MP+9-MP)]

where P is phenanthrene and MP is methylphenanthrene (Peters et al., 2004).

Aliphatic hydrocarbons (n-alkanes) may also serve as indicators of both genesis and thermal maturity of organic matter (Peters et al., 2004). These compounds tend to be less specific than PAH but several ratios can be useful, such as odd-to-even predominance index (OEP) and pristane/phytane ratio (summarised by Commendatore et al., 2000). OEP is used to determine maturity of organic matter, as odd-carbon-numbered alkanes dominate immature source rocks (OEP>>1 or OEP<<1)), while mature rocks have little or no carbon-number preference (OEP$\cong$1) (Peters et al., 2004). A high pristane/phytane ratio also indicates high thermal maturity and may further be used to determine redox conditions in the source rock, Pr/Ph<1 indicating anoxic and Pr/Ph>1 indicating oxic conditions (Peters et al., 2004). An additional parameter is isoprenoid/*n*-alkane ratio, which may be expressed as K_{iso}=(Pr+Ph)/(C_{17}+C_{18}), which decreases with thermal maturity as more *n*-alkanes are generated from kerogen (Peters et al., 2004).

Another, somewhat more reliable way of confirming petrogenic origin of hydrocarbons is to analyse geochemical biomarkers specific for petroleum, such as hopanes, in the same samples. Hopanes are aliphatic pentacyclic triterpanes formed in diagenetic processes and abundant in oil. Precursors of hopanes, bacteriohopanols, are a part of bacterial membranes, which is the reason for the ubiquitous nature of hopanoid-type compounds. They are found in all sediments and have been referred to as the most abundant natural products on Earth (Ourisson and Albrecht, 1992). Hopanes are strongly resistant to biodegradation and to weathering otherwise, and are therefore definitive markers of the presence of oil, former or current (Ourisson and Albrecht, 1992; Volkman et al., 1992; Prince et al., 1994; Peters et al., 2004). For the same reason, they have been used as "natural internal standards" to measure the degree of biodegradation (Prince et al., 1994). Stereoisomers of biological origin are maturity-sensitive, degrading under thermal and pressure influence. Various maturity parameters exist based on the relative abundances of two stereoisomers. One of them is T_s/T_m ratio ("terpane stable to terpane maturable", see Fig. 1), while another one is the ratio of the biogenic precursor of these two terpanes, T_e (Fig.1), to their sum, T_e/(T_s+T_m). These ratios may provide information on the degree of transformation of organic matter (Seifert and Moldowan, 1978; Farrimond et al., 1998). Another highly specific indicator
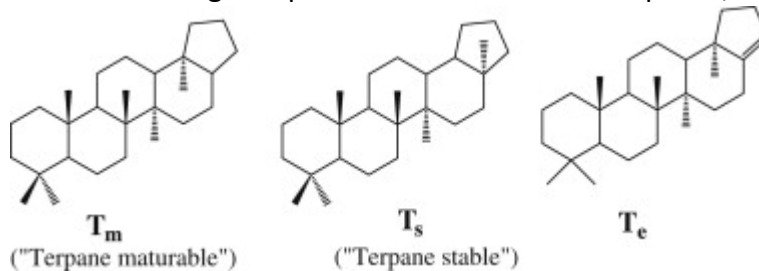

T_m
("Terpane maturable")

T_s
("Terpane stable")

T_e

Fig. 1. Chemical structures of 22,29,30-trisnor-17α-hopane (Tm), 22,29,30-trisnor-18α-hopane (Ts), and 22,29,30-trisnorhop-17(21)-ene (Te).

of immature to early oil generation is 22S/(22S+22R) isomerisation of homohopanes as C_{31}, giving characteristic doublets in m/z 191 mass chromatograms (hopanograms) (Peters et al., 2004). Similarly, the ratios of hopane C_{30} isomers, ($\alpha\beta/(\alpha\beta+\beta\alpha)$) C_{30} and $\beta\beta/(\alpha\beta+\beta\alpha)$ C_{30}, provide information on thermal maturity as $\beta\beta$-hopanes (biohopanes) convert readily to $\alpha\beta$- and $\beta\alpha$-configurations, and their high levels indicate low degree of maturity contrary to $\alpha\beta$-hopanes (Peters et al., 2004). A biomarker fingerprint (e.g. a hopanogram) may yield information on the particular source and has been used to determine specific oils (e.g. Boehm et al, 2001; Bartolomé et al., 2007; Saha et al., 2009). Due to a large number of isomers and low biomarker levels in more recent sediments, GC-MS analysis of biomarkers requires a fine-tuned analytical method and a thorough sample purification procedure. Several methods have been described (Boonyatumanond et al., 2006; Zakaria et al., 2001). Other less specific biomarkers, such as alkanes and PAH described above, may provide a confirmation of the conclusions drawn from hopane analysis, and a combined analysis of various types of biomarkers has been used to create an integrated approach to the study of the origin of hydrocarbons in sediments (e.g. Yunker et al., 1995).

2. Methods

2.1. Sampling (UiT-NGU, IMR).

This work is based on the analysis of two types of sediment samples. The first one is sediments from a 4.5 m long gravity core and the second type includes subsurface sediments from 3 shorter sediment cores, up to 0.5 m long, sampled either with a multicore sampler or a boxcore sampler. Both sampling tools are particularly useful in preserving the highly water-saturated top layer and therefore used for sampling for pollution studies. All the samples were analysed by the Geological Survey of Norway (NGU, Trondheim, Norway) for grain size, total sulphur, total carbon (TC) and total organic carbon (TOC) contents; extracted and cleaned up for hydrocarbon analyses at the Institute of Marine Research (IMR, Bergen, Norway); and analysed for various types of hydrocarbons at I.S. Gramberg All-Russia Research Institute for Geology and Mineral Resources of the World Ocean (VNIIO, St.Petersburg, Russia).

The gravity core was collected in 2006 by the University of Tromsø (UiT, Tromsø, Norway) in the pockmark area of Ingøydjupet in the southwest Barents Sea (see Table 1). The core was 4.58 m long, lithologically homogenous, with low carbonate values (total carbon contents <2%) and consisted of muddy sediments with high contents of silt and clay. Grain size was not determined in the whole core, but much shallower cores (approximately 30 cm) taken in the same area in the same year were comprised of between 86 and 95 % silt and clay (Jensen et al., 2007). The gravity core was frozen whole onboard and taken to the laboratory for analyses. Prior to analyses, it was sliced in 2 cm-thick samples, which were subsequently air-dried. A detailed description of the samples taken to geochemical analyses is given in Table 1, and the location of the sampling stations is shown in Fig. 2.

The shorter sediment cores were collected in 2009 by NGU and IMR during MAREANO cruises in other areas of southwest Barents Sea and northeast Norwegian Sea, from continental shelf (342 water depth) to the bottom of the continental slope (2220 m) (see Table 1). A multicorer was used to collect the samples at stations R406 and R488, whereas a boxcorer was used at station R422. The cores were between 30 and 42 cm long, lithologically homogenous, with low carbonate contents (Jensen et al., 2010; Jensen et al., 2011). The

cores were sliced onboard into 1 cm slices and kept frozen until the analyses. Prior to analyses, the samples were air-dried. A detailed description of the samples taken for geochemical analyses is given in Table 1, and the locations of the sampling stations are shown in Fig. 2.

Table 1. A description of the analysed sediment samples from 4 locations.

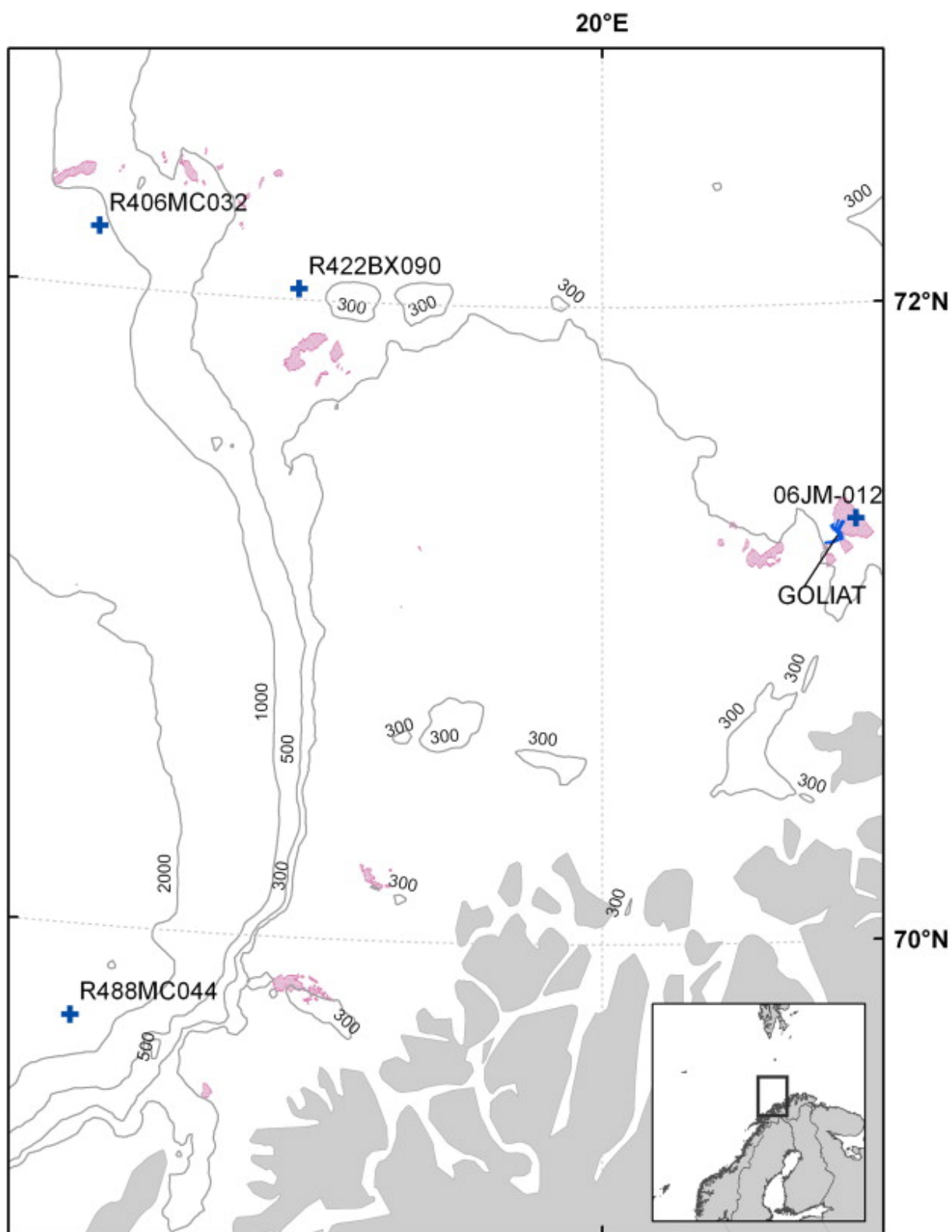| Station	Date	Latitude, N	Longitude, E	Water depth, m	Lithology	Core depth, cm	Sample dry weight, g
06JM-012	August 2006	71°19.38′	22°29.35′	432	silty clay	8-11	28
					silty clay	15-17	28
					silty clay	20-22	28
					silty clay	45-47	28
					silty clay	56.5-58.5	28
					silty clay	63-65	25
					silty clay	71-73	25
					silty clay	80-82	25
					silty clay	96-98	25
					silty clay	102-104	25
					silty clay	110-112	25
					silty clay	135-137	25
					silty clay	183-185	25
					silty clay	202-204	30
					silty clay	222-224	30
					silty clay	260-262	30
					clayey silt	270-272	30
					clayey silt	328-330	25
					clayey silt	419-421	30
R406 MC032	April 2009	72°11.38′	14°49.61′	1035	Sandy silt	19-20	20
					Sandy silt	24-25	20
					Sandy silt	29-30	20
						32-33	20
R422 BX090	April 2009	72°02.11′	16°54.74′	342	Silty sand	19-20	20
					No data	24-25	20
					No data	29-30	20
					No data	34-35	20
					No data	41-42	20
R488 MC044	October 2009	69°42.89′	15°11.94′	2220	Sandy silt	14-15	20
					Sandy silt	19-20	20
					Sandy silt	24-25	20
					Sandy silt	29-30	20

Fig. 2. The positions of the sampling stations. Pink fields indicate pockmark locations while coloured fields indicate Goliat oil field.

2.2. TOC, sulphur and grain size determination.

One set of sediment sub-samples was analysed for weight percentages (wt. %) of total organic carbon (TOC). For the TOC analyses, aliquots (~200 mg) of the samples were treated with 10 % (volume) hydrochloric acid (HCl) at 60ºC to remove carbonate, and then washed with distilled water to remove HCl. We caution the reader that the possible loss of organic material by acid leaching is not taken into account. The samples were dried overnight (50ºC) and then analysed using a LECO CS 244 analyser.

Grain size analyses of total sediment were obtained from laser diffraction techniques (Coulter LS 2000) (for details, see Xu, 2000, and references therein) and wet sieving. The Coulter LS 2000 measured the fractions from 0.4 μm to 2 mm while particles larger than 2 mm were determined by wet sieving. Prior to each analysis, the samples were freeze-dried. The grain size distribution is determined with respect to percent volume, with the assumption of uniform density of the sample.

2.3 Sample pre-treatment (extraction and cleanup, IMR)

Air-dried samples were weighed (approximate weights are given in Table 1) and loaded in ASE (Acclerated Solvent Extractor) cells together with diatomaceous earth. Internal standard, isoadiantane-d_2 (100 ng, 100 μl hexane solution), was added to the mixture in the cells. Conditions of ASE extraction on Dionex ASE300 apparatus were as follows: 2 cycles, 60% flush volume, 150°C. Solvent used was 1:1 mixture of hexane and dichloromethane. Solvent volume was reduced to 0.5 ml on a rotavap (room temperature) and copper added for sulphur removal overnight. After further volume reduction, samples were cleaned-up on Bond Elute silica SPE columns (3 cc, 500 mg), eluted with hexane. Final sample volume was 300 μl hexane solution.

2.4. Sample pre-treatment (sulphur removal and fractionation, VNIIO)

Sample extracts from the gravity core still contained traces of sulphur after sample pre-treatment. These were therefore further cleaned-up on an activated copper column to remove remaining sulphur. The solvent was removed by a rotavap (T<40ºC). The samples were then fractionated on silica gel to extract the methane-naphthenic and aromatic hydrocarbon fractions.

2.5. GC-MS analysis (VNIIO)

Hydrocarbon fractions were analysed by GC-MS on a quadrupole Hewlett Packard 6850/5973 system. The analytical method described below has been certified in 2001 and 2005 by Russian State Standardization Service (Gosstandart), № POCC RU.0001. 512785 of 18.07.2001.

Alkanes, hopanes and steranes were analysed on the following system: GC capillary column HP DB 30m x 0.25mm x 0.25 μm, stationary phase 5%phenyl-95%methylpolysiloxane. Carrier gas was helium, flow rate 1,2 ml/min; injector temperature 320 ºC; oven temperature gradient from 50º C to 320º C at 3º C/min and 7 min at 320º C; full scan detection at 50 to 500 m/z, 70 eV.

Saturated hydrocarbons (n-alkanes, isoprenoids) were analysed in selected ion monitoring mode (SIM) by ion mass m/z 71 (cyclic hydrocarbons), m/z 191 (hopanes) and m/z 217, 218 (steranes).

Polycyclic aromatic hydrocarbons (PAH) were analysed on the following system: GC capillary column HP DB 30m x 0.25 mm x 0.25 μm, stationary phase 5%phenyl-

95%methylpolysiloxane. Carrier gas helium, flow rate 1.2 ml/min; injector temperature 290ºC; oven temperature gradient from 60º C to 200º C at 20º C/min, to 300º at 10º C/min and 5 min at 300º C; full scan detection at 50 to 500 m/z, 70 eV.

Parent PAH were analysed in selected ion monitoring mode (SIM) by ion masses m/z 128, 152, 154, 178, 192, 202, 206, 228, 252, 276 and 278. Alkylated PAH were analysed by selective ion masses m/z 142, 156, 192, 206, 220, 216, 234 and 242.

3. Results and Discussion

3.1. *TOC and saturated hydrocarbons.*

The distribution of total organic carbon (TOC) in the gravity core from station 06JM-12 in Ingøydjupet is shown in Fig. 3a and ranges from 0.4 to 0.8 % throughout the core. The content and distribution of total sulphur (TS) in the core is probably caused by the change in diagenetic conditions in the sediments, from oxidative conditions in the surface layer (8-47 cm) to reducing conditions (below 55 cm), see Fig. 3a.
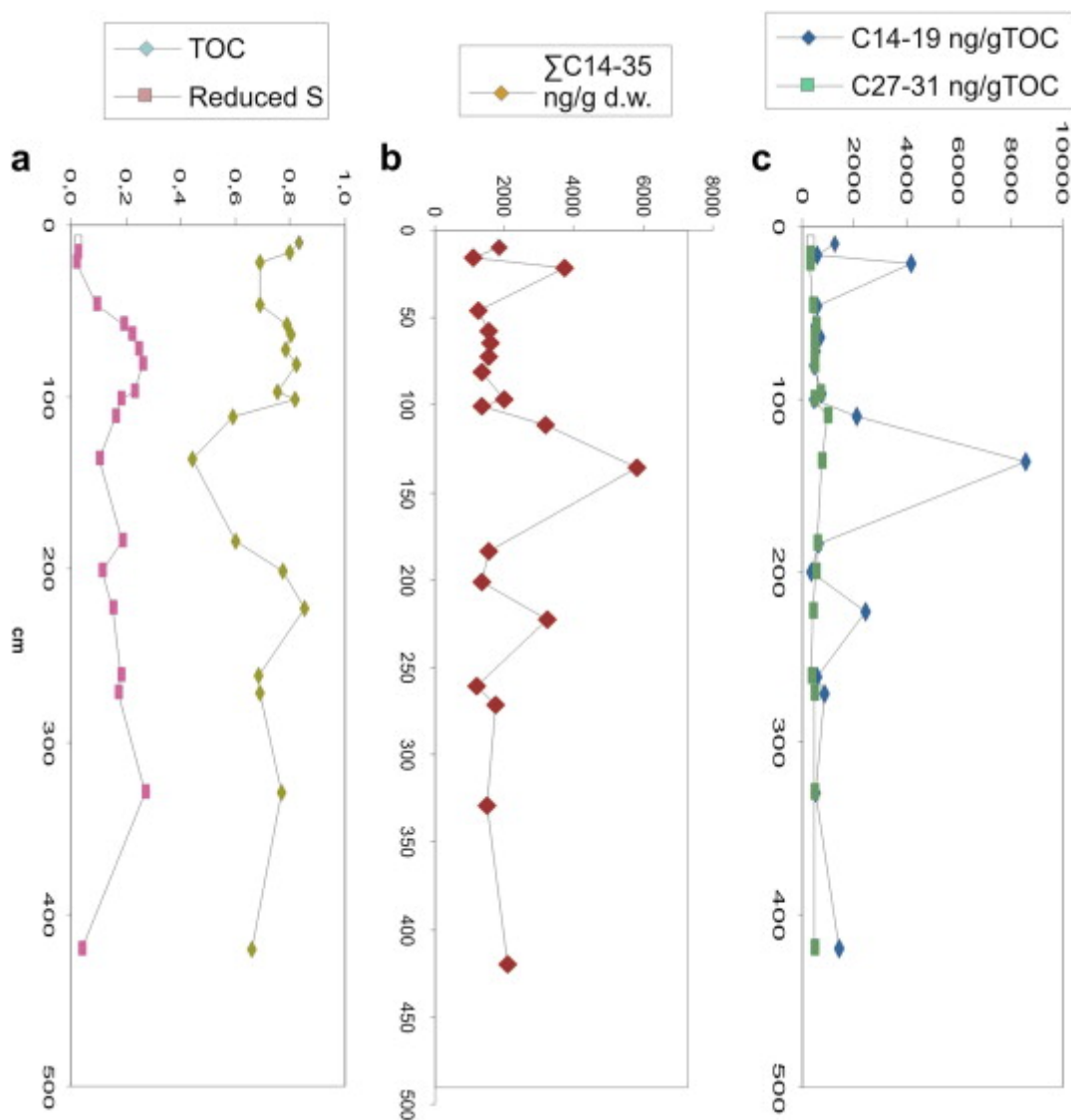

Fig. 3. The distribution of organic carbon (TOC) and/total sulphur (total S) (a), the sum of aliphatic hydrocarbons (b), and the distribution of low molecular weight (C14–C19) and high molecular weight (C27–C31) n-alkanes normalised to TOC (c) versus depth in the gravity core from station 06JM-12.

The average contents of saturated hydrocarbons in the core from station 06JM-12 (Fig. 3b), 1600 ng/g sediment, does not exceed the typical values of similar lithological varieties of the West-Arctic continental shelf (Yunker et al., 1996; Dahle et al., 2006). A bimodal character of alkane distribution (Fig. 4) indicates a mixed sapropel-humus composition of the original organic matter (C_{14}-C_{19}/C_{14}-C_{35} = 0.3 average value). Odd-to-even predominance index (OEP), which reflects the level of transformation of the humus part of organic matter (OM), corresponds to the diagenetic stage of the transformation (OEP_{27-31}=3.0). In the case of low molecular weight n-alkanes (C_{15}-C_{19}), OEP does not exceed 1, which may be due to their selective degradation during early diagenesis (Grimalt and Allbaiger 1987; Venkatesan and Kaplan, 1987)
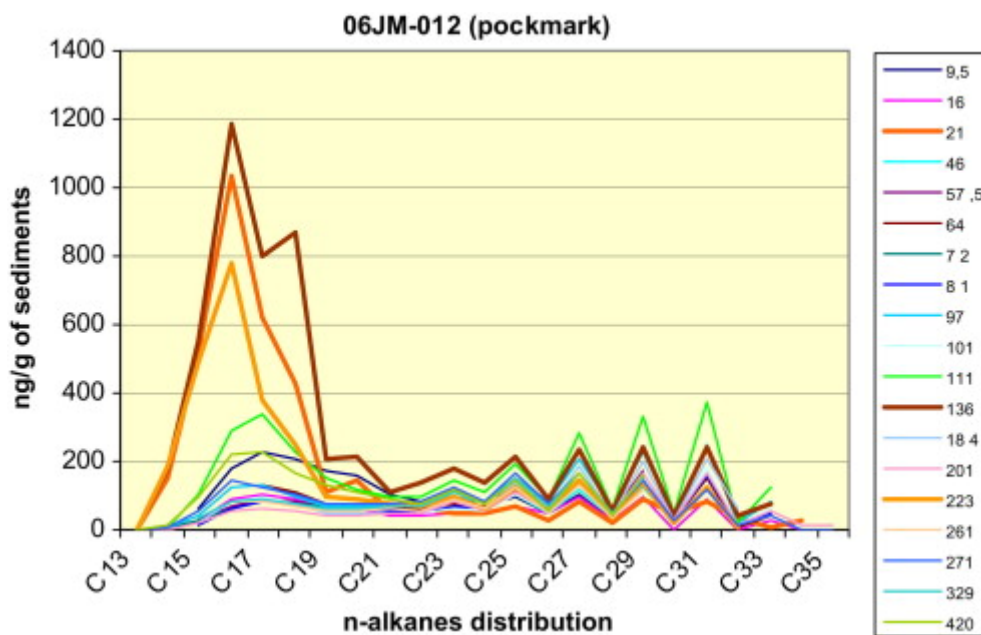

Fig. 4. N-alkane distribution in the gravity core from station 06 JM-012. Numbers for coloured lines to the right are the sampled depths in cm.

At the same time, in three of the studied intervals of the core (20 – 22 cm, 135 – 137 cm, 222 – 224 cm), n-alkane distributions are anomalous. Absolute contents of saturated hydrocarbons in these intervals increase 2- to 3-fold as compared to the rest of the samples (Fig. 3b). When corrected for TOC contents, the increase is 3- to 6-fold (Fig. 3c). The distribution of n-alkanes (Fig. 4) is also anomalous, with low molecular weight compounds (C_{14}-C_{19}/C_{14}-C_{35} = 0.8) dominating, with a maximum at n-C_{16}.

The observed peculiarities in n-alkane distribution seem to indicate a pulsed influx of low molecular weight hydrocarbons (C_{14}-C_{19}) to the sediments. This may be indicative of an abrupt change in sedimentation conditions during a marine transgression and/or abrupt increase in primary bioproductivity in the marine environment since these compounds are markers of lipids of biotic origin (Venkatesan and Kaplan, 1987; Grimalt and Allbaiger, 1987; Petrova et al., 2010). However, this possibility does not seem plausible in view of the lithological homogeneity of the sediment core and of the increase of anomalies when the data are normalised to TOC. Alternatively, the increase in low molecular weight n-alkanes' contents may indicate an input of petrogenic hydrocarbons. This fits well with the earlier geochemical studies of the sediments from this region (Jensen et al., 2007), according to which there is indicated a diffuse fluid flux of hydrocarbons from the bedrock. This facilitates

the formation of a wide pockmark area in the zone of unconsolidated fine-grained postglacial deposits. The influence of deep fluids on the composition of OM/hydrocarbons seems quite possible since this increase parallels a strong decrease in the hydrocarbons' odd-to-even predominance index (OEP C_{17}-C_{19} < 1) (Fig. 5a), which is typical for petroleum n-alkanes.

The distribution of alkane markers of terrestrial vegetation (C_{27}-C_{31}, Fig. 5b) experiences no significant changes in the sediment core, and the value of OEP>2,5 corresponds to an insignificant (diagenetic) degree of transformation. The type of distribution and the ratios of isoprenoids (Pr/Ph, Kiso=(Pr+Ph)/(C_{17}+C_{18}), Fig. 5c) seem to be determined by the background and are weakly influenced by the petrogenic constituent.
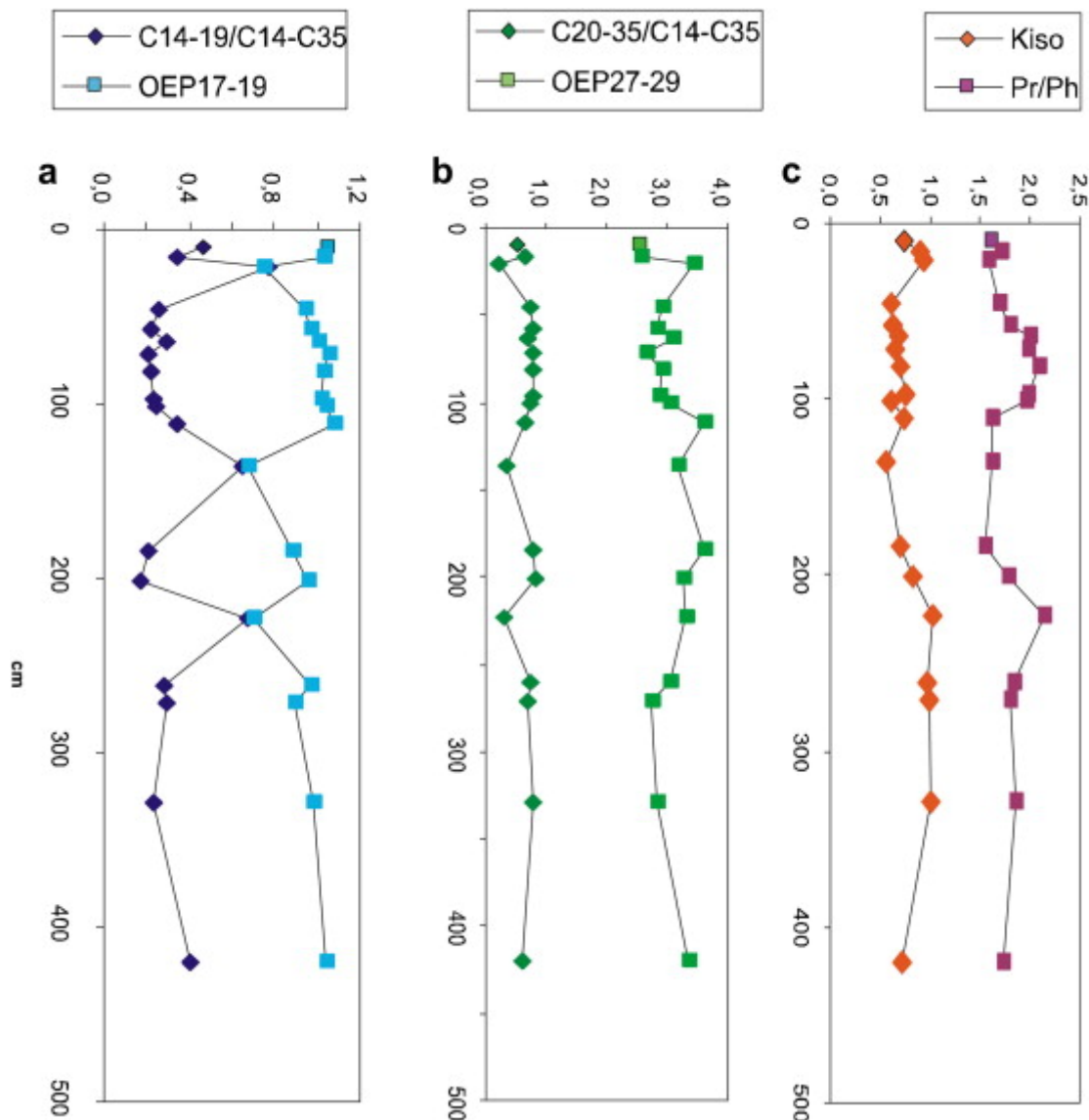

Fig. 5. Ratios of low molecular weight n-alkanes (a), high molecular weight n-alkanes (b) and isoprenoids (c) in the gravity core from station 06 JM-012.

A comparison of the geochemical characteristics of the sediments from pockmark area station 06JM-12 with background sediments from various areas of South-Western Barents Sea also contributed to the determination of the origin of the observed anomalies. Different

sedimentary facies are clearly reflected in n-alkane distribution in the samples from the background areas. Thus, in samples from the continental shelf (station R422 BX90) the distribution of n-alkanes is bimodal, with expressed maxima at C_{17} and C_{27}-C_{31} (fig. 6a), which is typical for organic matter of mixed sapropel-humus origin. Odd-and-even predominance indices indicate the early diagenetic stage of transformation of OM (OEP$_{17}$ = 3.3 -8.8; OEP$_{27}$ = 2.5-3.5).

Sediment samples from the pockmark area, originating from the same sea depth (420-440 m) and core intervals (9-46 cm) as those from background areas, are in general similar in their hydrocarbon composition (Fig. 6b) to the background samples. The origin of organic matter is therefore also similar, a sapropel-humus one (C_{14}-C_{19}/C_{20}-C_{35} = 0.35, OEP$_{27}$ = 2.9). An exception is the sample from 21 cm depth. This sample exhibits a practically monomodal distribution of n-alkanes with an clear maximum at C_{16}. The predomination of low molecular weight hydrocarbons with a low OEP index (C_{14}-C_{19}/C_{20}-C_{35} = 0.77, OEP$_{17}$ = 0.7) is a highly specific signal of the presence of petroleum.
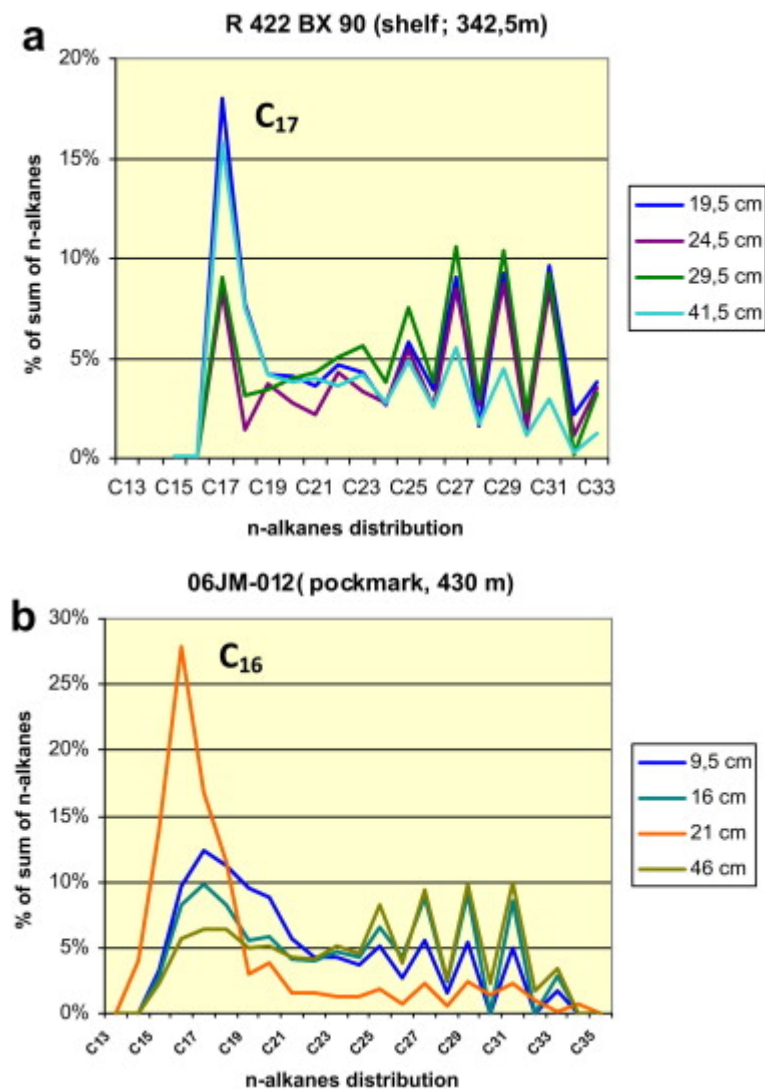

Fig. 6. The distribution of n-alkanes in the sediments from the continental shelf (a) and the pockmark area (b). Numbers for coloured lines to the right in a and b are the sampled depths in cm.

The distribution of saturated hydrocarbons observed in the core from station 06JM-12 is different from those observed in the background sediment cores. In sediments from the continental slope and its foot (Fig. 7 a, b), there is a consistent decrease with depth in the amounts of the low molecular weight n-alkanes (C_{15-19}), products of transformation of lipids of biotic origin, which actively degrade in the deep-water zone during sedimentation. Correspondingly, an enrichment/contribution of OM with components of terrigenous origin seen in Fig. 7a (humus OM) tied into persistent organomineral complexes within the sediments takes place.
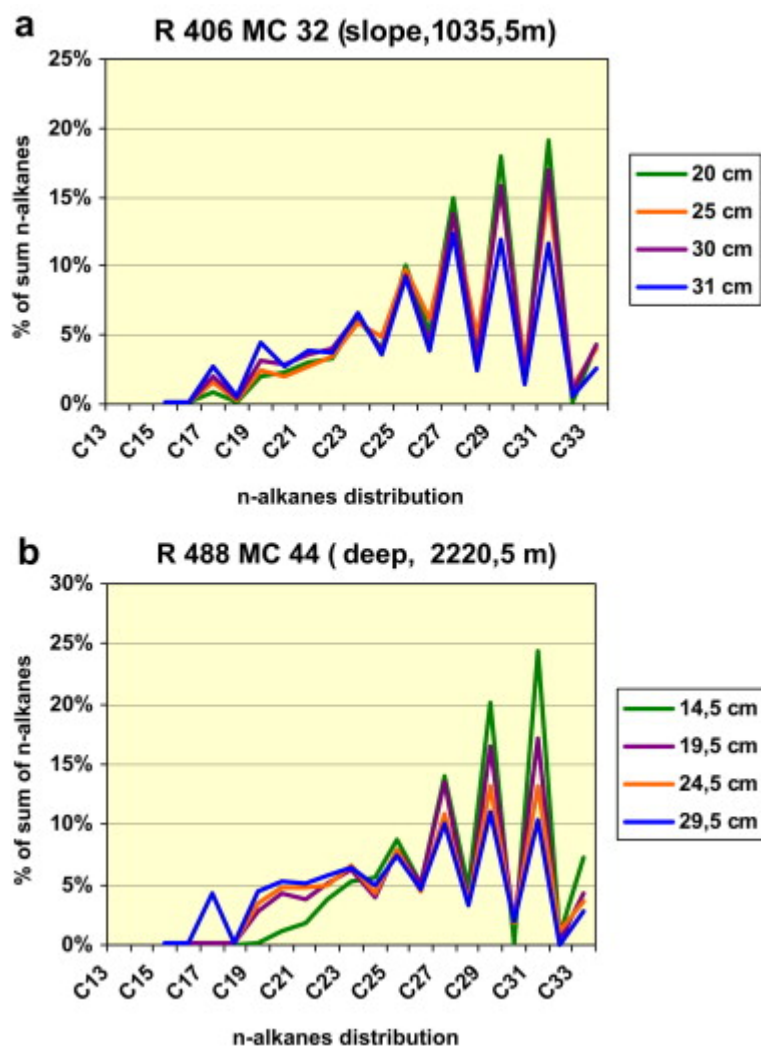

Fig. 7. N-alkane distribution in the sediments from the continental slope and its foot. Numbers for coloured lines to the right are the sampled depths in cm.

The nature of the observed anomaly was further studied by means of GC-MS analysis of the non-specific groups of molecular markers. It is known that homological series of alkylsubstituted cyclanes, e.g. n-alkylcyclohexanes, are a characteristic petroleum component (Kashirtsev, 2003). At the same time, their presence is unlikely in Holocene-Quaternary deposition in the marine environment. A comparison of mass-fragmentograms (Fig. 8) by the characteristic fragment ion (m/z 83) has shown that n-alkylcyclohexanes are absent in the background samples. In the samples from the pockmark area, on the other

hand, it was the same intervals that exhibited anomalies in n-alkane distribution, which were also enriched in n-alkylcyclohexanes.
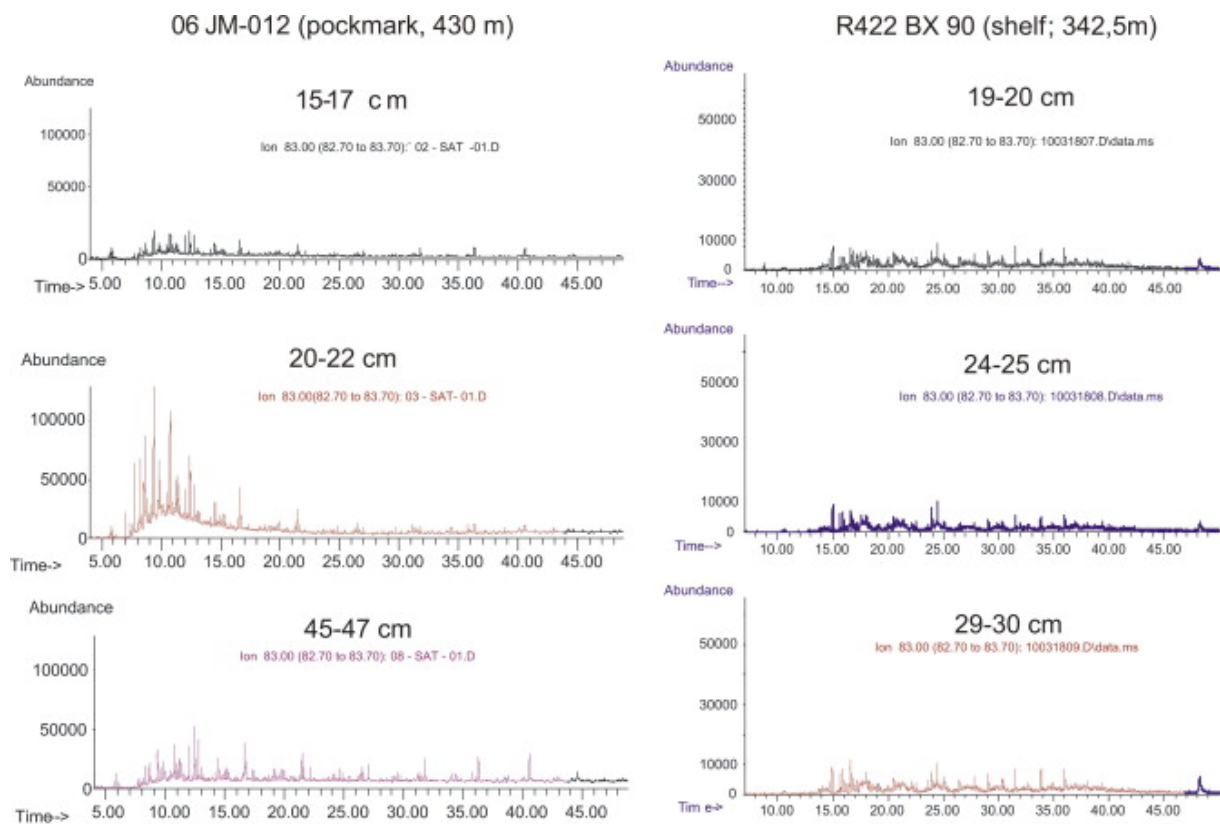

Fig. 8. Mass-fragmentograms of n-alkylcyclohexanes distributions in various samples.

3.2. *Cyclic hydrocarbons.*

Cyclic hydrocarbons are represented in the gravity core 06 JM-012 mostly by triterpanes. An interpretation of the distribution and composition of steranes in the samples was impossible due to their low contents. However, a prevalence of hopanes over steranes may indicate a significant role of microbiota in the formation of bacterial OM within the sediments (Peters et al., 2004; Greenwood et al., 2006)

Triterpanes in the sediments from the pockmark area are represented by a wide spectrum of compounds (Fig. 9). Comparing to the similar facies and intervals of the cores from background areas, hopenes and $\beta\beta$-hopanes play a more significant role in these samples, which is typical for weakly transformed OM.
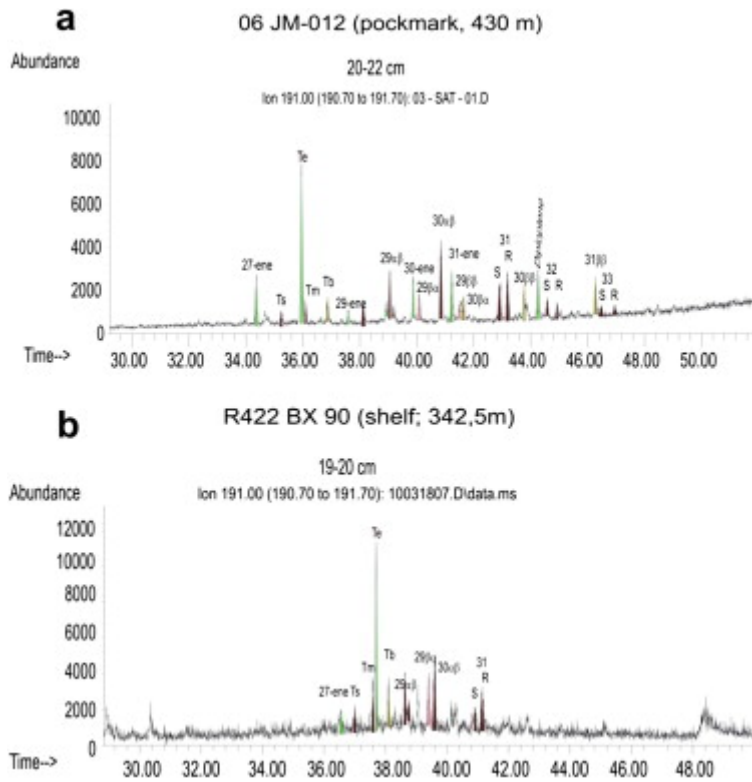
Fig. 9. Hopanograms of the sediments from the core from the pockmark area (a) and from the background samples (b).

At the same time, thermal maturity indices (Ts/Tm, $22S/(22S+22R)C_{31}$) (see Fig. 10) both have wide ranges (0.8-0.77 and 0.49-0.70 respectively), indicating the presence of sediment material containing thermally transformed organic matter (in the mesocatagenetic stage). These results are not contradictory, since the composition of triterpanes in the studied sediment core may be formed by various sources, including re-deposited, deeply transformed material of continental source rocks.
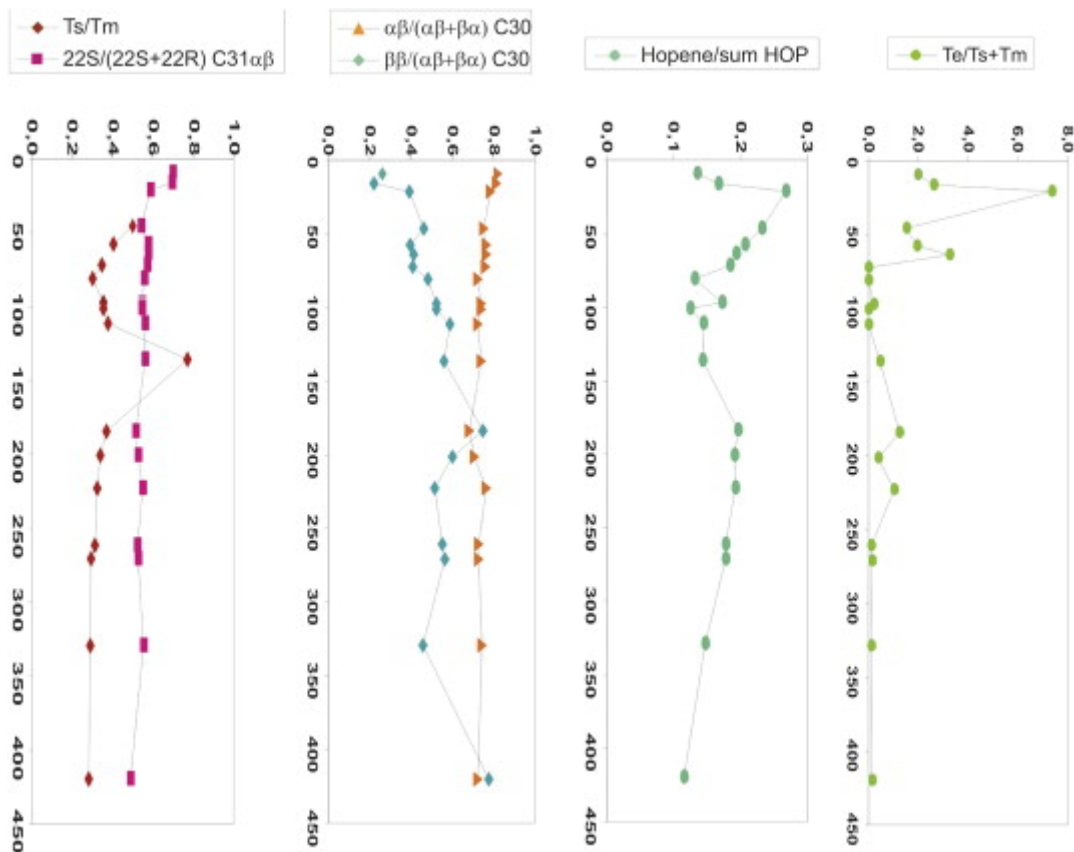
Fig. 10. Triterpane distribution in the sediment core from station 06JM-12.

The general trend in the change of the hopane composition towards deeper layers of the core reflects a decrease in the level of thermal maturity of hydrocarbons and of organic matter in general (Fig. 10). This follows from the reverse trends in the ratios of hopane C_{30} epimers, ($\alpha\beta/(\alpha\beta+\beta\alpha)$ C_{30}, $\beta\beta/(\alpha\beta+\beta\alpha)$ C_{30}). The contents of biohopane ($\beta\beta$) increase towards deeper layers of the core. This may be due to the decreasing role of mature re-deposited source rocks in sedimentation processes or as a result of petroleum hydrocarbons having migrated into specific intervals with higher permeability than the adjacent denser sediments. Besides, *in situ* diagenetic processes should also lead to an increase in the contents of transformation products of biogenic precursors of hopanes, hopanols (via hopenes and biohopanes). This fits well to the character of relative hopene distribution in general, and that of the specific hopene, C_{27} - 22,29,30-trisnorhop-17(21)-ene (Te, see Fig. 1), in the group of trisnorhopanes, for which it is the biogenic precursor (Fig. 10). This does not exclude the possibility of petrogenic hydrocarbons influx to the sediments. On the contrary, an increase in the levels of microbial life products in the sediments (in particular, biohopanols and therefore hopenes) may be due to the presence of an extra food source for hydrocarbon-oxidating bacterial communities (Innes et al., 1998). This suggestion is indirectly confirmed by the similar trends in distributions of n-alkanes (Fig. 5a) and hopenes (Fig. 10).

On the other hand, the surface sediments from the pockmark area are enriched in geohopanes ($\alpha\beta$- and $\beta\alpha$-hopanes) of considerable thermal maturity ((22S/22S+22R) C_{31} = 0,70). This may be due to ancient pre-Quaternary source rock contributing to the sediments due to erosion (Yunker et al., 1996) or the migration of thermally mature petroleum

hydrocarbons into the surface sediments. Their input into the surface Quaternary sediments may occur both by means of sub-aquatic or continental erosion and by means of migration of deep fluids, as for example leading to venting through the sediment surface and the formation of mud volcanoes (Lein et al, 1999).

3.3.   *Polycyclic aromatic hydrocarbons (PAH).*

The character of PAH distribution in the core from station 06JM-12 indicates the dominant role of natural (biogenic and/or petrogenic) sources. Thus, the Fl/202 ratio, varying weakly along the core, has the average value of 0.38 and does not exceed 0.46, which means an insignificant contribution of pyrogenic components (Fig. 11) (Yunker et al, 2002).

The distribution of such typical aromatic biomarkers as retene, cadalene and perylene (Fig. 11), genetically related to terrestrial higher plants, clearly shows the trend in the processes of transformation of original organic matter under reducing diagenetic conditions. The increase of the relative (Per/∑PAH) and absolute (ng/g TOC) contents of these compounds in the depth of the core is due to their diagenetic formation, by means of transformation of their biogenic precursors such as quinine pigments, di- and sesquiterpenoids. (Bouloubassi and Saliot,1993; Peters et al., 2004)

Unlike the trends found for biogenic PAH, the relative increase in the amounts of petrogenic PAH (such as phenanthrene and its alkylated homologues) is observed in the upper part of the core (Fig. 11), reaching more than 50% of total PAH levels. This may be due to a more intensive input of hydrocarbon source rocks to the sediments. However, it may also be possible that the input and selective accumulation of low-molecular weight PAH occurs due to a vertical migration of hydrocarbons as part of fluids from deeper strata, typical for oil- and gas-enriched areas, e.g. the Goliat oil-field within Ingøydjupet. The latter suggestion seems to be consistent with the fact that the studied core originates from the area with pockmarks.
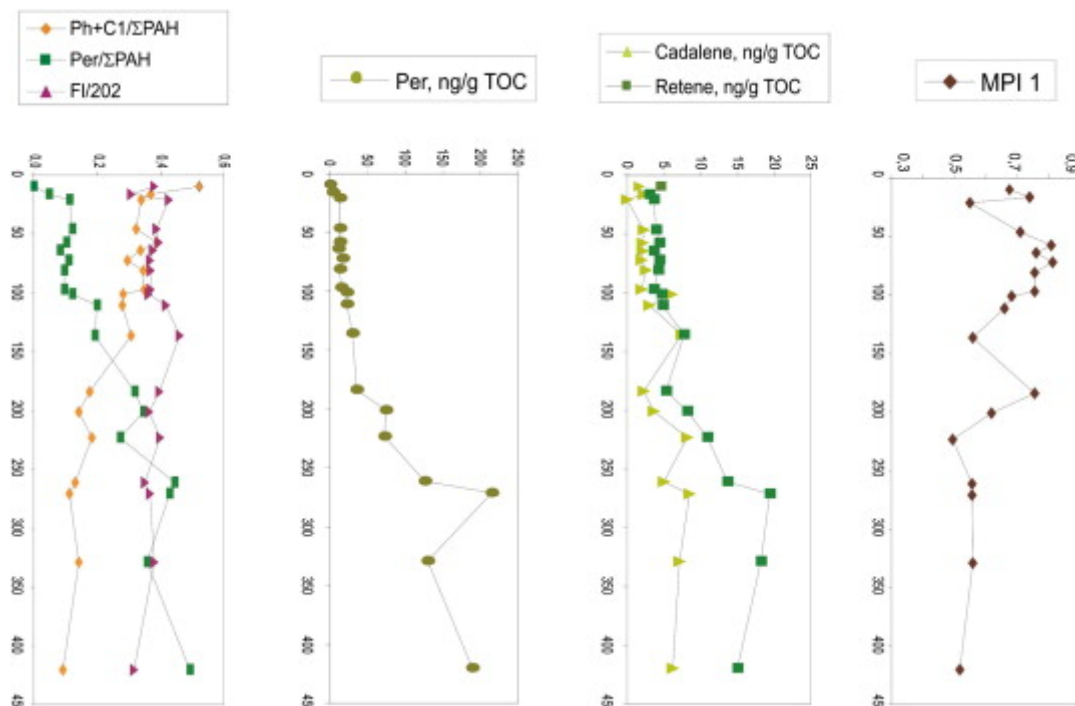

Fig. 11. The distribution of PAH in the core from station 06JM-12. Ph: Phenanthrene; Per: Perylene; Fl: Fluoranthene; MPI-1: Methylphenanthrene Index.

The values of Methylphenanthrene Index (MPI 1), an indicator of thermal maturity of OM, reach substantial values (up to 0.8), characteristic for hydrocarbons at the stage of mesocatagenesis (MC_1-MC_2). The values of this parameter decrease down the core, which is probably related to the ratio between ancient and Holocene-Quaternary deposits in the sediments. However, there are three points of sharp deviation from the general trend, at the same depths as where the anomalies in hydrocarbon composition have been noted (21 cm, 136 cm, 223 cm), as described above. The significant decrease of MPI 1 observed in these samples points towards a considerable change in OM/hydrocarbon composition, namely to an input of significant amounts of weakly transformed, presumably biogenic, matter. As follows from the plot shown in Fig. 12, this process is most apparent in the upper part of the core (21 cm). It is also here that the odd-to-even predominance index of low molecular n-alkanes (OEP C_{17-19}) decreases sharply while the relative amounts of Te (22,29,30-trisnorhop-17(21)-ene) increase (Fig. 12), which strongly supports the above-mentioned assumption.
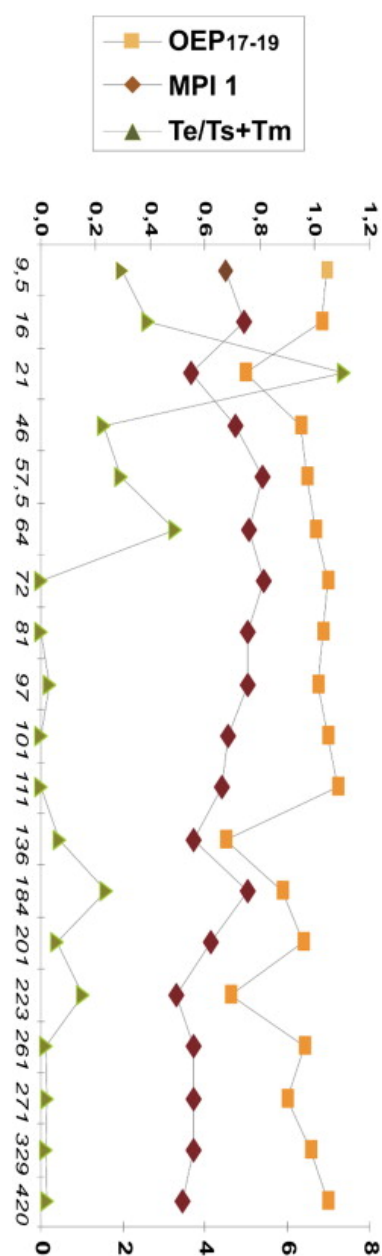

Fig. 12. A comparative characterisation of n-alkanes, triterpanes and MPI-1 (PAH) in the core from station 06JM-12.

4. Conclusions

A composite geochemical analysis of Holocene-Quaternary sediments from the area of pockmarks and their comparison with background sediments of South-Western Barents Sea have shown clear differences in the composition and distribution of hydrocarbon molecular markers in these sediments (Fig. 13).

It is notable that the sediments collected outside of the pockmarks field, both from the shelf and from deepwater (continental slope and its foot) areas, exhibit similar and uniform values of geochemical parameters indicating a common genesis and source of the original sedimentary OM. The slight differences observed between these samples are in accordance with existing knowledge on diagenetic transformation of bottom sediment OM in continental shelf and deeper sediments (Degens and Mopper, 1976; Yunker et al., 1995; Fahl and Stein, 1999; Yamamoto et al., 2008; Petrova et al; 2010).

At the same time, comparison of various geochemical parameters of the shelf sediments from within a pockmark area and from without (background samples) clearly indicates the differences in the genesis and the level of transformation of OM. These differences hold for the whole sediment core, although they are manifested strongest at certain specific intervals, denoted as "anomalies" (Table 2). Thus, pockmark area sediments have a higher relative content and a higher level of transformation of low molecular weight n-alkanes (C_{17}/C_{27}; OEP C_{17-19}) at these horizons. A number of indicators point towards a higher level of thermal maturity of OM in these samples (22S/22S+22R C_{31}; MPI 1). At the same time they have higher contents of biogenic terpenoids, e.g. hopenes.

Table 2. Various organic geochemical parameters indicating the origin and maturity of organic matter in the studied sediments.

Location Ratios	Shelf station R422BX90 mean	Pockmark mean	Pockmark anomaly	Parameter
C_{14-19}/C_{20-35}	0.39	0.35	0.77	Genesis indicator
C_{17}/C_{27}	1.68	1.34	7.49	Genesis indicator
Pr/Ph	0.98	1.66	1.59	Facial /Genesis indicator
OEP C_{17-19}	5. 04	1.04	0.74	Thermal maturity indicator
Ts/Tm	0.45	0.17	nd	Thermal maturity indicator
22S/22S+22R C_{31}	0.31	0.65	0.59	Thermal maturity indicator
$a\beta/(a\beta+\beta a)$ C_{30}	0.75	0.79	0.73	Thermal maturity indicator
Te/Ts+Tm	0.69	2.03	7.36	Relative biogenic indicator
hopene/Σhop	0.34	0.24	0.46	Thermal maturity indicator
MPI 1	0.39	0.71	0.55	Thermal maturity indicator

The observed combination of parameters may be explained by migration of the hydrocarbon fluid from deep strata, occurring in a pulsed manner and creating conditions favourable for

intensive development of specific microbiota *in situ*. As the nutrient substrate is exhausted, and under the influence of diagenetic processes, the microbial activity is reduced, which is manifested in the levelling off of the geochemical parameters down the core.
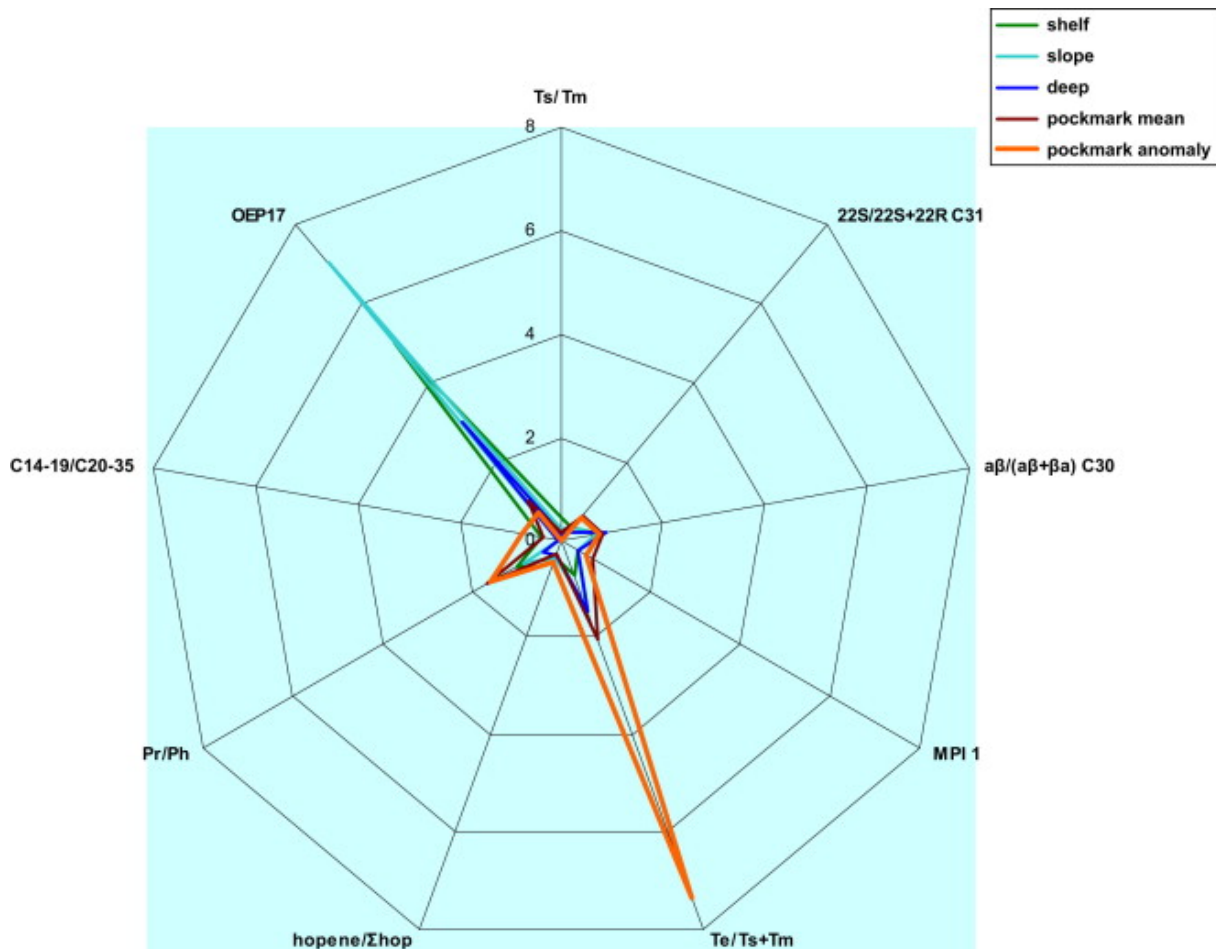

Fig. 13. A star–plot diagram showing the distinction between pockmark and background sediments.

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