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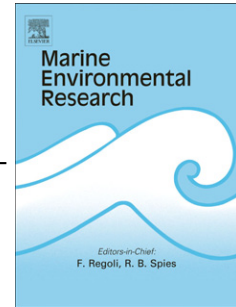
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1 **Petroleum-related hydrocarbons in deep and subsurface sediments from South-Western** 2 **Barents Sea**

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8 **Abstract**

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

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

23 **1. Introduction**

24 The Barents Sea continental shelf is rich in oil and gas resources. In the Norwegian sector, it
25 may contain 1199 million standard cubic meters of oil equivalents (Sm³ o.e.) according to the
26 latest estimates made by Norwegian Oil Directorate (NPD 2010). Most of this, 910 million
27 Sm³ o.e., are undiscovered resources (*ibid.*) The ongoing MAREANO program, a long-term,
28 multi-institutional Norwegian project aiming at extensive biological, geological and

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29 geochemical mapping of Norwegian continental shelf seabed, has recently provided detailed
30 geological and geochemical data on the composition of seabed sediments in South-Western
31 Barents Sea (MAREANO, 2010; Boitsov et al., 2009; Chand et al., 2009). The area of
32 Ingøydjupet, located some 80 km North-West of the coast of Norway, was found to contain a
33 pockmark field (depressions approximately 40–60 m in diameter and 6 m deep (Chand et al.,
34 2009)). Pockmarks are geological formations which may signify former or recent seepages of
35 hydrocarbon gas or fluids from formations below the sediment surface (e.g. Hovland and
36 Judd, 1988). Levels of predominantly petrogenic polycyclic aromatic hydrocarbons (PAH)
37 were found to increase in subsurface sediment layers (below 15 cm depth), also when
38 corrected for total organic carbon (TOC) levels (Boitsov et al., 2009). A local natural
39 petroleum source was suggested as a possible explanation (*ibid.*) This is not surprising in
40 view of the proximity of the Goliat oil field (see Fig. 2). According to Juntilla et al. (2010), in
41 other gravity cores of similar lengths taken within the area both Holocene and glaciomarine
42 sediments are encountered.

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

$$50 \text{ MPI-1} = 1.89(2\text{-MP} + 3\text{-MP}) / [P + 1.26(1\text{-MP} + 9\text{-MP})]$$

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

52 Aliphatic hydrocarbons (n-alkanes) may also serve as indicators of both genesis and thermal
53 maturity of organic matter (Peters et al., 2004). These compounds tend to be less specific than
54 PAH but several ratios can be useful, such as odd-to-even predominance index (OEP) and
55 pristane/phytane ratio (summarised by Commendatore et al., 2000). OEP is used to determine
56 maturity of organic matter, as odd-carbon-numbered alkanes dominate immature source rocks
57 ($\text{OEP} \gg 1$ or $\text{OEP} \ll 1$), while mature rocks have little or no carbon-number preference
58 ($\text{OEP} \cong 1$) (Peters et al., 2004). A high pristane/phytane ratio also indicates high thermal
59 maturity and may further be used to determine redox conditions in the source rock, $\text{Pr/Ph} < 1$
60 indicating anoxic and $\text{Pr/Ph} > 1$ indicating oxic conditions (Peters et al., 2004). An additional

61 parameter is isoprenoid/*n*-alkane ratio, which may be expressed as $K_{iso}=(Pr+Ph)/(C_{17}+C_{18})$,
62 which decreases with thermal maturity as more *n*-alkanes are generated from kerogen (Peters
63 et al., 2004).

64 Another, somewhat more reliable way of confirming petrogenic origin of hydrocarbons is to
65 analyse geochemical biomarkers specific for petroleum, such as hopanes, in the same
66 samples. Hopanes are aliphatic pentacyclic triterpanes formed in diagenetic processes and
67 abundant in oil. Precursors of hopanes, bacteriohopanols, are a part of bacterial membranes,
68 which is the reason for the ubiquitous nature of hopanoid-type compounds. They are found in
69 all sediments and have been referred to as the most abundant natural products on Earth
70 (Ourisson and Albrecht, 1992). Hopanes are strongly resistant to biodegradation and to
71 weathering otherwise, and are therefore definitive markers of the presence of oil, former or
72 current (Ourisson and Albrecht, 1992; Volkman et al., 1992; Prince et al., 1994; Peters et al.,
73 2004). For the same reason, they have been used as “natural internal standards” to measure
74 the degree of biodegradation (Prince et al., 1994). Stereoisomers of biological origin are
75 maturity-sensitive, degrading under thermal and pressure influence. Various maturity
76 parameters exist based on the relative abundances of two stereoisomers. One of them is T_s/T_m
77 ratio (“terpane stable to terpane maturable”, see Fig. 1), while another one is the ratio of the
78 biogenic precursor of these two terpanes, T_e (Fig.1), to their sum, $T_e/(T_s+T_m)$. These ratios
79 may provide information on the degree of transformation of organic matter (Seifert and
80 Moldowan, 1978; Farrimond et al., 1998). Another highly specific indicator of immature to
81 early oil generation is $22S/(22S+22R)$ isomerisation of homohopanes as C_{31} , giving
82 characteristic doublets in m/z 191 mass chromatograms (hopanograms) (Peters et al., 2004).
83 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
84 information on thermal maturity as $\beta\beta$ -hopanes (biohopanes) convert readily to $\alpha\beta$ - and $\beta\alpha$ -
85 configurations, and their high levels indicate low degree of maturity contrary to $\alpha\beta$ -hopanes
86 (Peters et al., 2004). A biomarker fingerprint (e.g. a hopanogram) may yield information on
87 the particular source and has been used to determine specific oils (e.g. Boehm et al, 2001;
88 Bartolomé et al., 2007; Saha et al., 2009). Due to a large number of isomers and low
89 biomarker levels in more recent sediments, GC-MS analysis of biomarkers requires a fine-
90 tuned analytical method and a thorough sample purification procedure. Several methods have
91 been described (Boonyatumanond et al., 2006; Zakaria et al., 2001). Other less specific
92 biomarkers, such as alkanes and PAH described above, may provide a confirmation of the

93 conclusions drawn from hopane analysis, and a combined analysis of various types of
94 biomarkers has been used to create an integrated approach to the study of the origin of
95 hydrocarbons in sediments (e.g. Yunker et al., 1995).

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

98 2. Methods

99 2.1. Sampling (UiT-NGU, IMR).

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

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

121 The shorter sediment cores were collected in 2009 by NGU and IMR during MAREANO
122 cruises in other areas of southwest Barents Sea and northeast Norwegian Sea, from
123 continental shelf (342 water depth) to the bottom of the continental slope (2220 m) (see Table

124 1). A multicorer was used to collect the samples at stations R406 and R488, whereas a
125 boxcorer was used at station R422. The cores were between 30 and 42 cm long, lithologically
126 homogenous, with low carbonate contents (Jensen et al., 2010; Jensen et al., 2011). The cores
127 were sliced onboard into 1 cm slices and kept frozen until the analyses. Prior to analyses, the
128 samples were air-dried. A detailed description of the samples taken for geochemical analyses
129 is given in Table 1, and the locations of the sampling stations are shown in Fig. 2.

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

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

133 *2.2. TOC, sulphur and grain size determination.*

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

140 Grain size analyses of total sediment were obtained from laser diffraction techniques (Coulter
141 LS 2000) (for details, see Xu, 2000, and references therein) and wet sieving. The Coulter LS
142 2000 measured the fractions from 0.4 µm to 2 mm while particles larger than 2 mm were
143 determined by wet sieving. Prior to each analysis, the samples were freeze-dried. The grain
144 size distribution is determined with respect to percent volume, with the assumption of
145 uniform density of the sample.

146 *2.3 Sample pre-treatment (extraction and cleanup, IMR)*

147 Air-dried samples were weighed (approximate weights are given in Table 1) and loaded in
148 ASE (Accelerated Solvent Extractor) cells together with diatomaceous earth. Internal standard,
149 isoadiantane-d₂ (100 ng, 100 µl hexane solution), was added to the mixture in the cells.
150 Conditions of ASE extraction on Dionex ASE300 apparatus were as follows: 2 cycles, 60%
151 flush volume, 150°C. Solvent used was 1:1 mixture of hexane and dichloromethane. Solvent
152 volume was reduced to 0.5 ml on a rotavap (room temperature) and copper added for sulphur
153 removal overnight. After further volume reduction, samples were cleaned-up on Bond Elute

154 silica SPE columns (3 cc, 500 mg), eluted with hexane. Final sample volume was 300 μ l
155 hexane solution.

156 2.4. Sample pre-treatment (sulphur removal and fractionation, VNIIO)

157 Sample extracts from the gravity core still contained traces of sulphur after sample pre-
158 treatment. These were therefore further cleaned-up on an activated copper column to remove
159 remaining sulphur. The solvent was removed by a rotavap ($T < 40^{\circ}\text{C}$). The samples were then
160 fractionated on silica gel to extract the methane-naphthenic and aromatic hydrocarbon
161 fractions.

162 2.5. GC-MS analysis (VNIIO)

163 Hydrocarbon fractions were analysed by GC-MS on a quadrupole Hewlett Packard
164 6850/5973 system. The analytical method described below has been certified in 2001 and
165 2005 by Russian State Standardization Service (Gosstandart), № POCC RU.0001. 512785 of
166 18.07.2001.

167 Alkanes, hopanes and steranes were analysed on the following system: GC capillary column
168 HP DB 30m x 0.25mm x 0.25 μm , stationary phase 5%phenyl-95%methylpolysiloxane.
169 Carrier gas was helium, flow rate 1,2 ml/min; injector temperature 320 $^{\circ}\text{C}$; oven temperature
170 gradient from 50 $^{\circ}\text{C}$ to 320 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C}/\text{min}$ and 7 min at 320 $^{\circ}\text{C}$; full scan detection at 50 to
171 500 m/z, 70 eV.

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

175 Polycyclic aromatic hydrocarbons (PAH) were analysed on the following system: GC
176 capillary column HP DB 30m x 0.25 mm x 0.25 μm , stationary phase 5%phenyl-
177 95%methylpolysiloxane. Carrier gas helium, flow rate 1.2 ml/min; injector temperature
178 290 $^{\circ}\text{C}$; oven temperature gradient from 60 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$, to 300 $^{\circ}$ at 10 $^{\circ}\text{C}/\text{min}$
179 and 5 min at 300 $^{\circ}\text{C}$; full scan detection at 50 to 500 m/z, 70 eV.

180 Parent PAH were analysed in selected ion monitoring mode (SIM) by ion masses m/z 128,
181 152, 154, 178, 192, 202, 206, 228, 252, 276 and 278. Alkylated PAH were analysed by
182 selective ion masses m/z 142, 156, 192, 206, 220, 216, 234 and 242.

183

184 3. Results and Discussion

185 3.1. *TOC and saturated hydrocarbons.*

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

191 Figure 3. The distribution of organic carbon (TOC) and total sulphur (total S) (a), the sum of
192 aliphatic hydrocarbons (b), and the distribution of low molecular weight (C_{14} - C_{19}) and high
193 molecular weight (C_{27} - C_{31}) n-alkanes normalised to TOC (c) versus depth in the gravity core
194 from station 06JM-12.

195 The average contents of saturated hydrocarbons in the core from station 06JM-12 (Fig. 3b),
196 1600 ng/g sediment, does not exceed the typical values of similar lithological varieties of the
197 West-Arctic continental shelf (Yunker et al., 1996; Dahle et al., 2006). A bimodal character
198 of alkane distribution (Fig. 4) indicates a mixed sapropel-humus composition of the original
199 organic matter (C_{14} - C_{19}/C_{14} - $C_{35} = 0.3$ average value). Odd-to-even predominance index
200 (OEP), which reflects the level of transformation of the humus part of organic matter (OM),
201 corresponds to the diagenetic stage of the transformation ($OEP_{27-31}=3.0$). In the case of low
202 molecular weight n-alkanes (C_{15} - C_{19}), OEP does not exceed 1, which may be due to their
203 selective degradation during early diagenesis (Grimalt and Allbaiger 1987; Venkatesan and
204 Kaplan, 1987)

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

207 At the same time, in three of the studied intervals of the core (20 – 22 cm, 135 – 137 cm, 222
208 – 224 cm), n-alkane distributions are anomalous. Absolute contents of saturated
209 hydrocarbons in these intervals increase 2- to 3-fold as compared to the rest of the samples
210 (Fig. 3b). When corrected for TOC contents, the increase is 3- to 6-fold (Fig. 3c). The
211 distribution of n-alkanes (Fig. 4) is also anomalous, with low molecular weight compounds
212 (C_{14} - C_{19}/C_{14} - $C_{35} = 0.8$) dominating, with a maximum at n- C_{16} .

213 The observed peculiarities in n-alkane distribution seem to indicate a pulsed influx of low
214 molecular weight hydrocarbons (C_{14} - C_{19}) to the sediments. This may be indicative of an
215 abrupt change in sedimentation conditions during a marine transgression and/or abrupt

216 increase in primary bioproductivity in the marine environment since these compounds are
217 markers of lipids of biotic origin (Venkatesan and Kaplan, 1987; Grimalt and Allbaiger,
218 1987; Petrova et al., 2010). However, this possibility does not seem plausible in view of the
219 lithological homogeneity of the sediment core and of the increase of anomalies when the data
220 are normalised to TOC. Alternatively, the increase in low molecular weight n-alkanes'
221 contents may indicate an input of petrogenic hydrocarbons. This fits well with the earlier
222 geochemical studies of the sediments from this region (Jensen et al., 2007), according to
223 which there is indicated a diffuse fluid flux of hydrocarbons from the bedrock. This facilitates
224 the formation of a wide pockmark area in the zone of unconsolidated fine-grained postglacial
225 deposits. The influence of deep fluids on the composition of OM/hydrocarbons seems quite
226 possible since this increase parallels a strong decrease in the hydrocarbons' odd-to-even
227 predominance index ($OEP_{C_{17}-C_{19}} < 1$) (Fig. 5a), which is typical for petroleum n-alkanes.

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

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

235 A comparison of the geochemical characteristics of the sediments from pockmark area station
236 06JM-12 with background sediments from various areas of South-Western Barents Sea also
237 contributed to the determination of the origin of the observed anomalies. Different
238 sedimentary facies are clearly reflected in n-alkane distribution in the samples from the
239 background areas. Thus, in samples from the continental shelf (station R422 BX90) the
240 distribution of n-alkanes is bimodal, with expressed maxima at C_{17} and $C_{27}-C_{31}$ (fig. 6a),
241 which is typical for organic matter of mixed sapropel-humus origin. Odd-and-even
242 predominance indices indicate the early diagenetic stage of transformation of OM ($OEP_{17} =$
243 $3.3 - 8.8$; $OEP_{27} = 2.5-3.5$).

244 Sediment samples from the pockmark area, originating from the same sea depth (420-440 m)
245 and core intervals (9-46 cm) as those from background areas, are in general similar in their
246 hydrocarbon composition (Fig. 6b) to the background samples. The origin of organic matter
247 is therefore also similar, a sapropel-humus one ($C_{14}-C_{19}/C_{20}-C_{35} = 0.35$, $OEP_{27} = 2.9$). An

248 exception is the sample from 21 cm depth. This sample exhibits a practically monomodal
249 distribution of n-alkanes with an clear maximum at C₁₆. The predomination of low molecular
250 weight hydrocarbons with a low OEP index ($C_{14}\text{-}C_{19}/C_{20}\text{-}C_{35} = 0.77$, $OEP_{17} = 0.7$) is a highly
251 specific signal of the presence of petroleum.

252 Figure 6. The distribution of n-alkanes in the sediments from the continental shelf (a) and the
253 pockmark area (b). Numbers for colored lines to the right in Figures 6a and -b are the
254 sampled depths in cm.

255 The distribution of saturated hydrocarbons observed in the core from station 06JM-12 is
256 different from those observed in the background sediment cores. In sediments from the
257 continental slope and its foot (Fig. 7 a, b), there is a consistent decrease with depth in the
258 amounts of the low molecular weight n-alkanes (C₁₅₋₁₉), products of transformation of lipids
259 of biotic origin, which actively degrade in the deep-water zone during sedimentation.
260 Correspondingly, an enrichment/contribution of OM with components of terrigenous origin
261 seen in Fig. 7a (humus OM) tied into persistent organomineral complexes within the
262 sediments takes place .

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

265 The nature of the observed anomaly was further studied by means of GC-MS analysis of the
266 non-specific groups of molecular markers. It is known that homological series of
267 alkylsubstituted cyclanes, e.g. n-alkylcyclohexanes, are a characteristic petroleum component
268 (Kashirtsev, 2003). At the same time, their presence is unlikely in Holocene-Quaternary
269 deposition in the marine environment. A comparison of mass-fragmentograms (Fig. 8) by the
270 characteristic fragment ion (m/z 83) has shown that n-alkylcyclohexanes are absent in the
271 background samples. In the samples from the pockmark area, on the other hand, it was the
272 same intervals that exhibited anomalies in n-alkane distribution, which were also enriched in
273 n-alkylcyclohexanes.

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

275 3.2. Cyclic hydrocarbons.

276 Cyclic hydrocarbons are represented in the gravity core 06 JM-012 mostly by triterpanes. An
277 interpretation of the distribution and composition of steranes in the samples was impossible
278 due to their low contents. However, a prevalence of hopanes over steranes may indicate a

279 significant role of microbiota in the formation of bacterial OM within the sediments (Peters
280 et al., 2004; Greenwood et al., 2006)

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

285 Figure 9. Hopanograms of the sediments from the core from the pockmark area (a) and from
286 the background samples (b).

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

293 Figure 10. Triterpane distribution in the sediment core from station 06JM-12.

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

309 communities (Innes et al., 1998). This suggestion is indirectly confirmed by the similar trends
310 in distributions of n-alkanes (Fig. 5a) and hopanes (Fig. 10).

311 On the other hand, the surface sediments from the pockmark area are enriched in geohopanes
312 ($\alpha\beta$ - and $\beta\alpha$ -hopanes) of considerable thermal maturity ($(22S/22S+22R) C_{31} = 0,70$). This
313 may be due to ancient pre-Quaternary source rock contributing to the sediments due to
314 erosion (Yunker et al., 1996) or the migration of thermally mature petroleum hydrocarbons
315 into the surface sediments. Their input into the surface Quaternary sediments may occur both
316 by means of sub-aquatic or continental erosion and by means of migration of deep fluids, as
317 for example leading to venting through the sediment surface and the formation of mud
318 volcanoes (Lein et al, 1999).

319 3.3. *Polycyclic aromatic hydrocarbons (PAH).*

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

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

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

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

342 The values of Methylphenanthrene Index (MPI 1), an indicator of thermal maturity of OM,
343 reach substantial values (up to 0.8), characteristic for hydrocarbons at the stage of
344 mesocatagenesis (MC₁-MC₂). The values of this parameter decrease down the core, which is
345 probably related to the ratio between ancient and Holocene-Quaternary deposits in the
346 sediments. However, there are three points of sharp deviation from the general trend, at the
347 same depths as where the anomalies in hydrocarbon composition have been noted (21 cm,
348 136 cm, 223 cm), as described above. The significant decrease of MPI 1 observed in these
349 samples points towards a considerable change in OM/hydrocarbon composition, namely to an
350 input of significant amounts of weakly transformed, presumably biogenic, matter. As follows
351 from the plot shown in Fig. 12, this process is most apparent in the upper part of the core (21
352 cm). It is also here that the odd-to-even predominance index of low molecular n-alkanes
353 (OEP C₁₇₋₁₉) decreases sharply while the relative amounts of Te (22,29,30-trisnorhop-17(21)-
354 ene) increase (Fig. 12), which strongly supports the above-mentioned assumption.

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

357 4. Conclusions

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

362 It is notable that the sediments collected outside of the pockmarks field, both from the shelf
363 and from deepwater (continental slope and its foot) areas, exhibit similar and uniform values
364 of geochemical parameters indicating a common genesis and source of the original
365 sedimentary OM. The slight differences observed between these samples are in accordance
366 with existing knowledge on diagenetic transformation of bottom sediment OM in continental
367 shelf and deeper sediments (Degens and Mopper, 1976; Yunker et al., 1995; Fahl and Stein,
368 1999; Yamamoto et al., 2008; Petrova et al; 2010).

369 At the same time, comparison of various geochemical parameters of the shelf sediments from
370 within a pockmark area and from without (background samples) clearly indicates the

371 differences in the genesis and the level of transformation of OM. These differences hold for
372 the whole sediment core, although they are manifested strongest at certain specific intervals,
373 denoted as “anomalies” (Table 2). Thus, pockmark area sediments have a higher relative
374 content and a higher level of transformation of low molecular weight n-alkanes (C_{17}/C_{27} ;
375 OEP C_{17-19}) at these horizons. A number of indicators point towards a higher level of thermal
376 maturity of OM in these samples ($22S/22S+22R C_{31}$; MPI 1). At the same time they have
377 higher contents of biogenic terpenoids, e.g. hopenes.

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

380 The observed combination of parameters may be explained by migration of the hydrocarbon
381 fluid from deep strata, occurring in a pulsed manner and creating conditions favourable for
382 intensive development of specific microbiota *in situ*. As the nutrient substrate is exhausted,
383 and under the influence of diagenetic processes, the microbial activity is reduced, which is
384 manifested in the levelling off of the geochemical parameters down the core.

385 Figure 13. A star-plot diagram showing the distinction between pockmark and background
386 sediments.

387

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- We study geochemical biomarkers, as hopanes, in sediments from the Barents Sea.
- An area with pockmarks has a special hydrocarbon composition of sediments.
- The genesis of organic matter there seems to be petrogenic.
- The level of transformation and of thermal maturity of organic matter is high.
- This may be explained by migration of the hydrocarbon fluid from deep strata.

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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

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

Location	Shelf station R422BX90 mean	Pockmark mean	Pockmark anomaly	Parameter
Ratios				
C₁₄₋₁₉/C₂₀₋₃₅	0.39	0.35	0.77	Genesis indicator
C₁₇/C₂₇	1.68	1.34	7.49	Genesis indicator
Pr/Ph	0.98	1.66	1.59	Facial /Genesis indicator
OEP C₁₇₋₁₉	5.04	1.04	0.74	Thermal maturity indicator
Ts/Tm	0.45	0.17	nd	Thermal maturity indicator
22S/22S+22R C₃₁	0.31	0.65	0.59	Thermal maturity indicator
aβ/(aβ+βa) C₃₀	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

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

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

Figure 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.

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

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

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

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

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

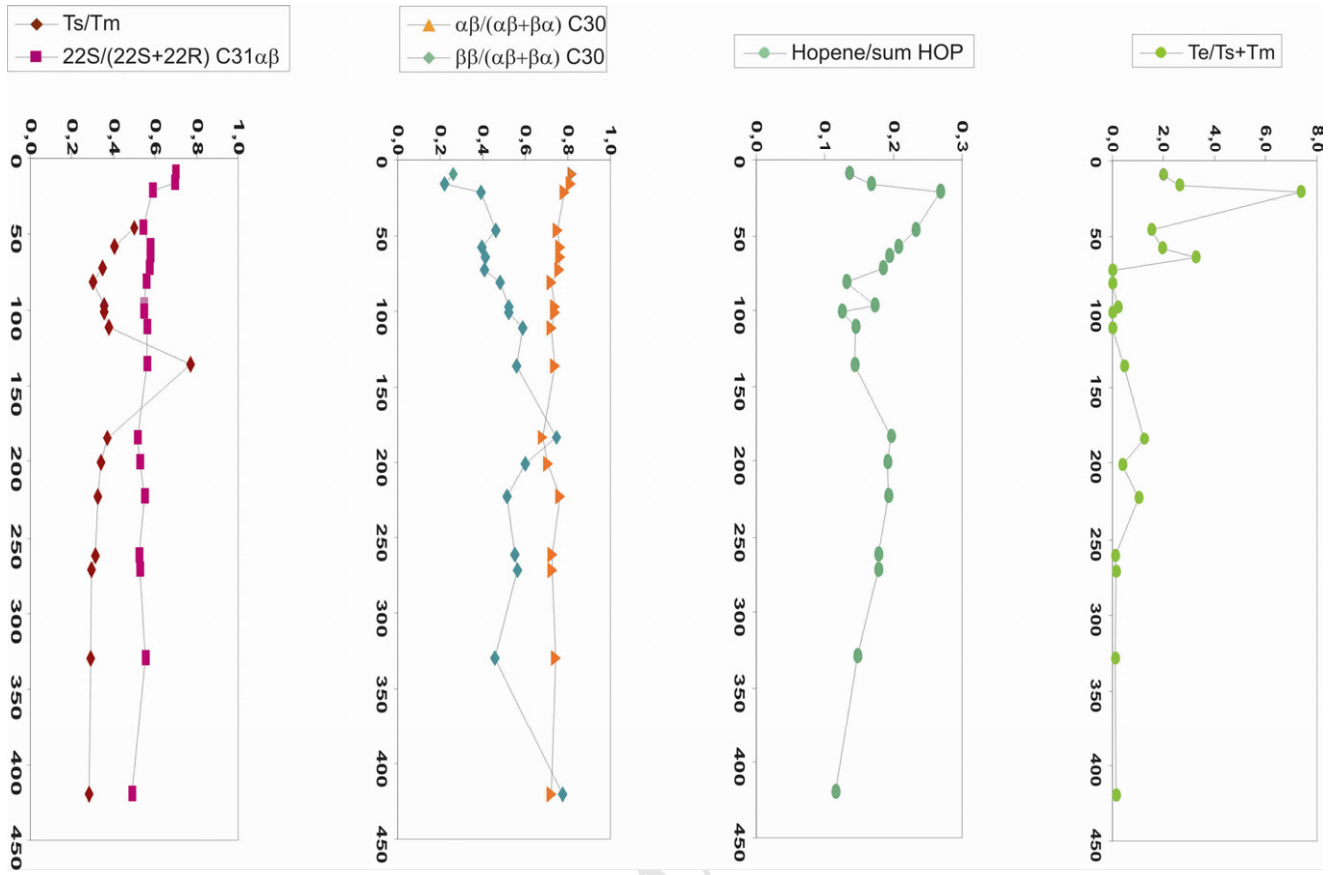
Figure 9. Hopanograms of the sediments from the core from the pockmark area (a) and from the background samples (b).

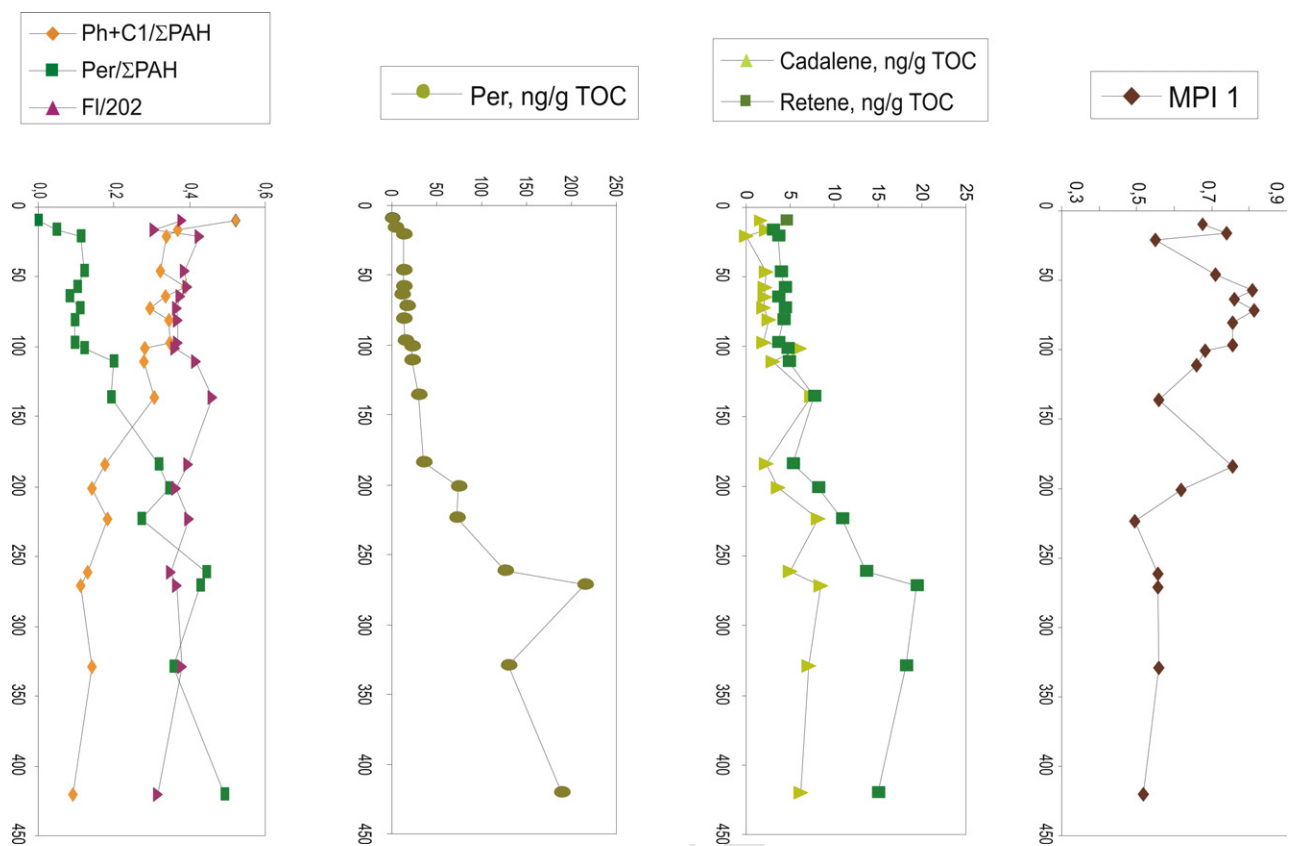
Figure 10. Triterpane distribution in the sediment core from station 06JM-12.

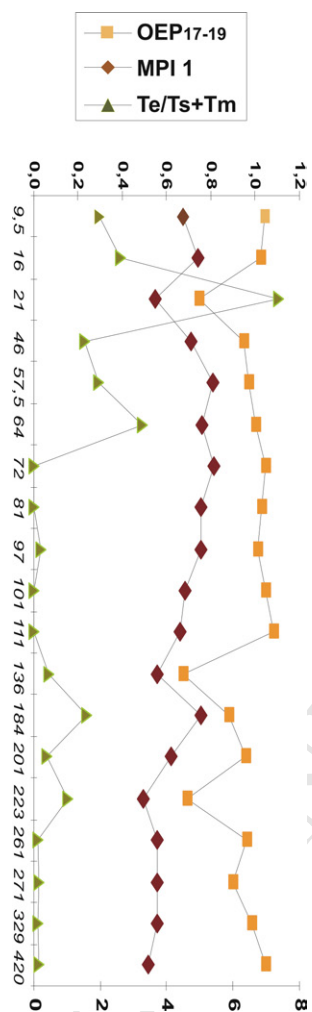
Figure 11. The distribution of PAH in the core from station 06JM-12. Ph: Phenanthrene; Per: Perylene; Fl: Fluoranthene; MPI 1: Methylphenanthrene Index.

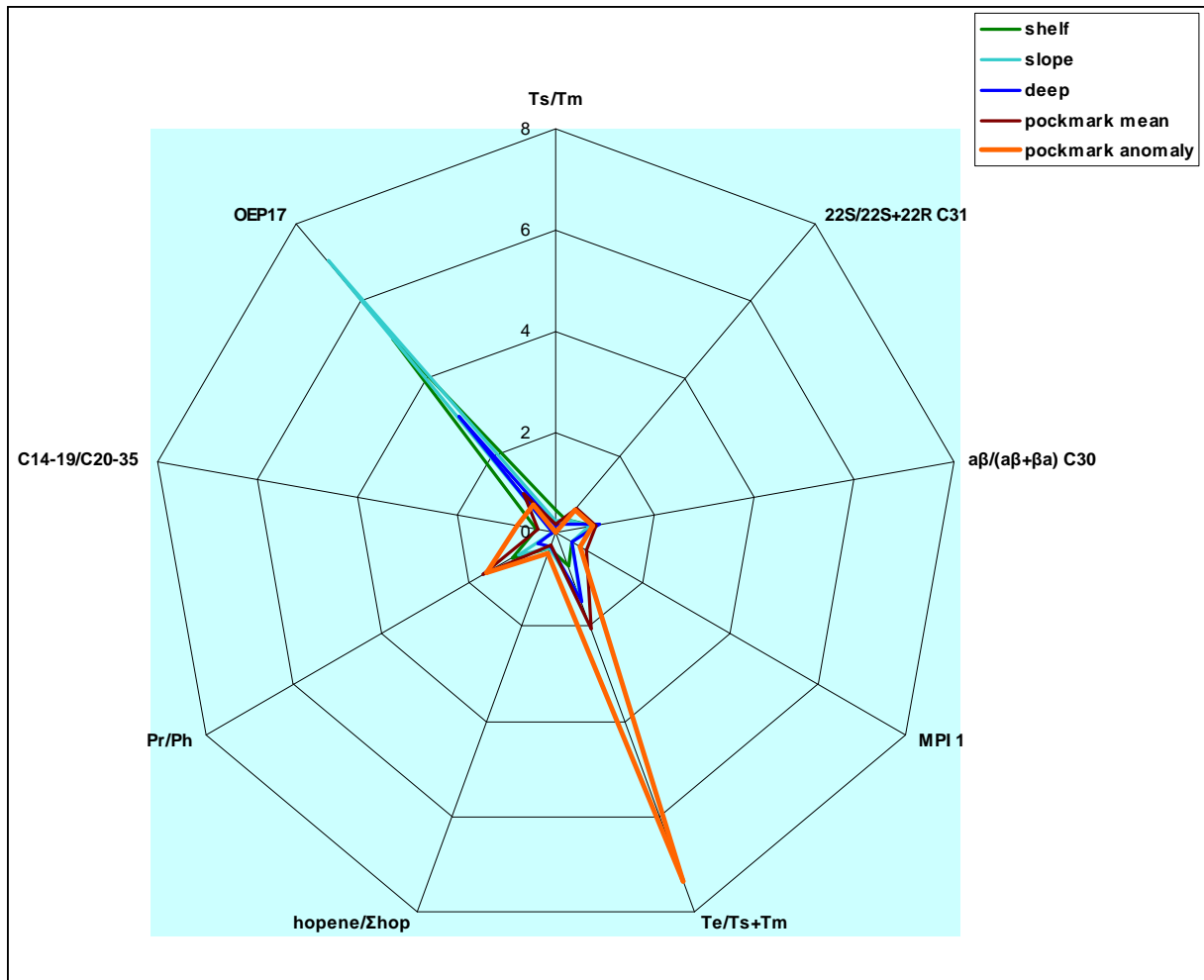
Figure 12. A comparative characterisation of n-alkanes, triterpanes and MPI 1 (PAH) in the core from station 06JM-12.

Figure 13. A star-plot diagram showing the distinction between pockmark and background sediments.

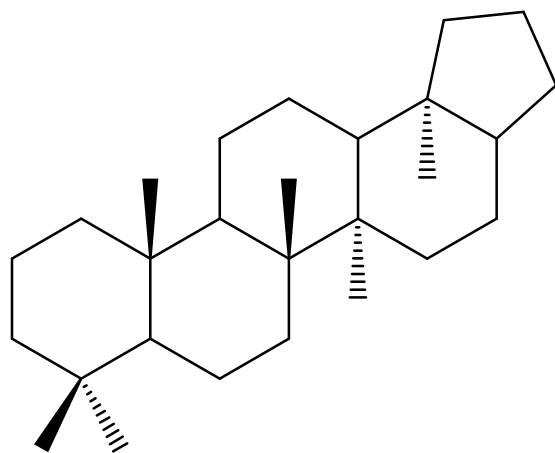




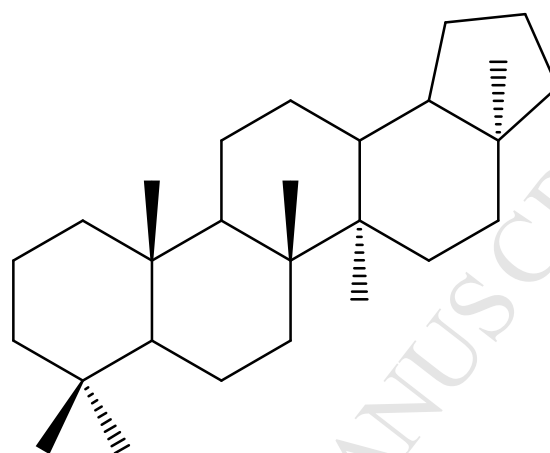




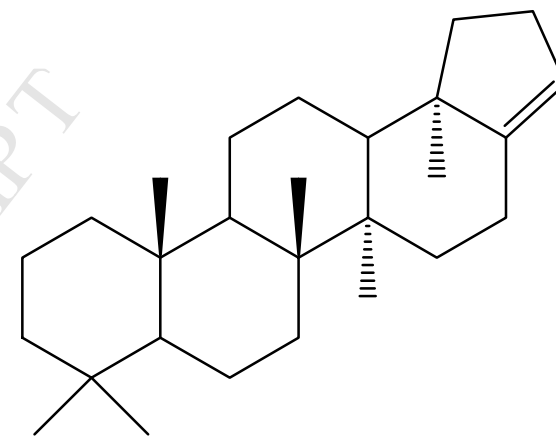
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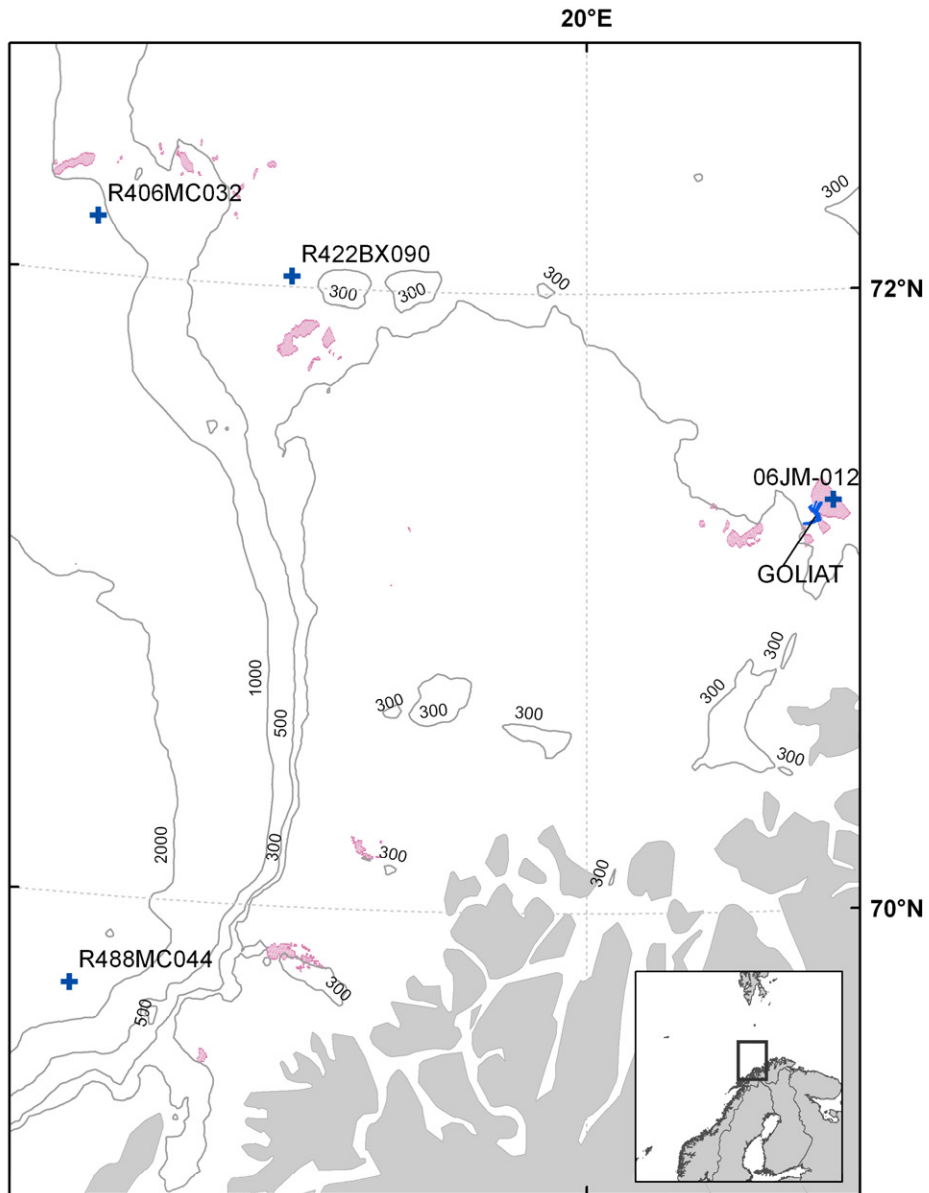
T_m
("Terpane maturable")

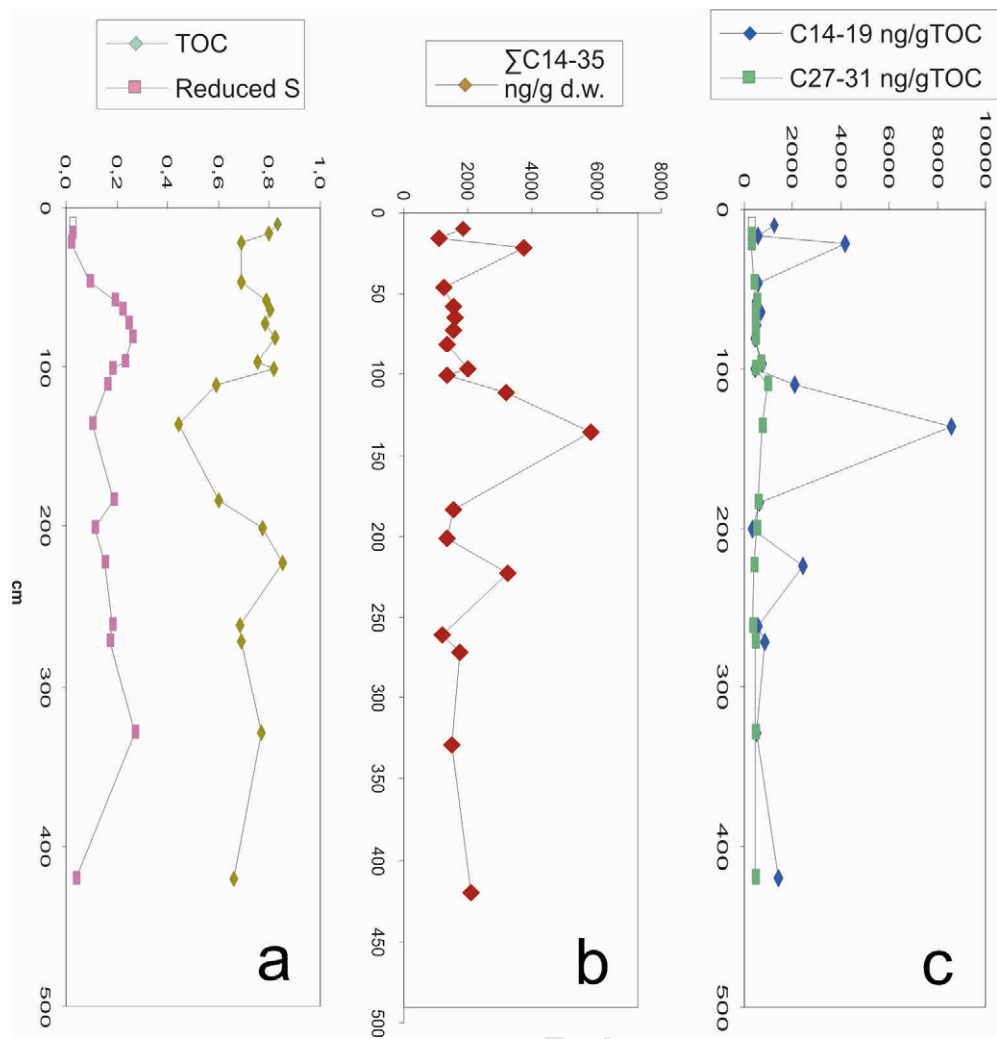


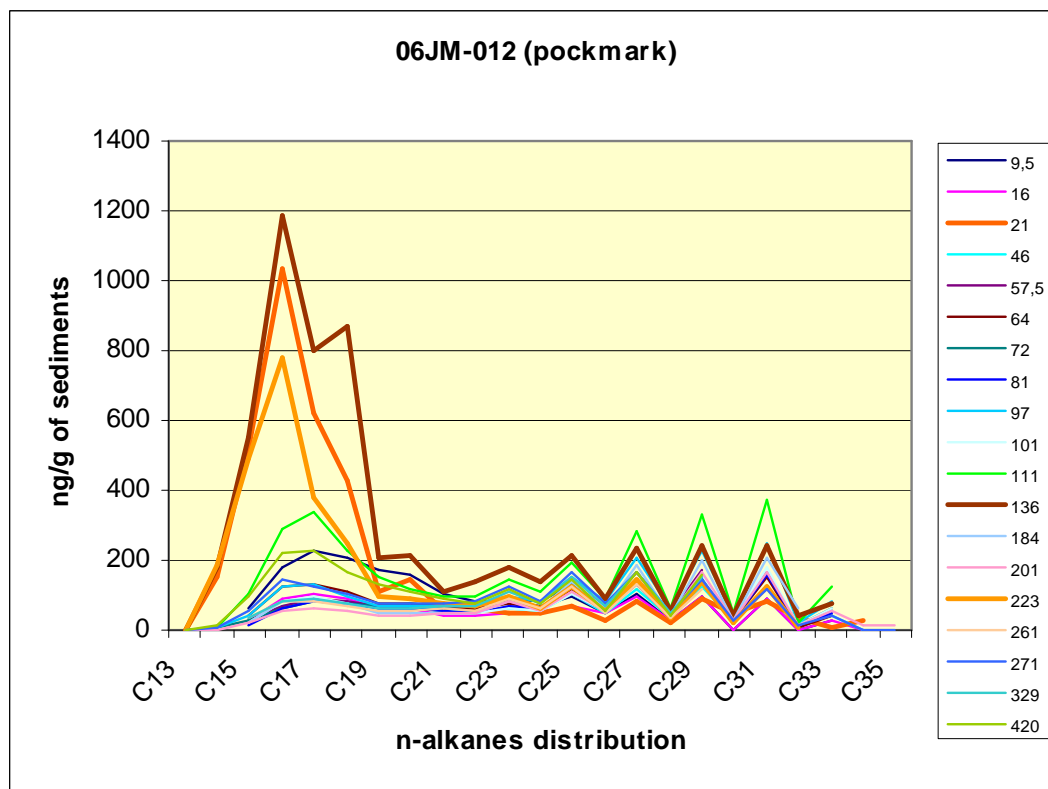
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("Terpane stable")

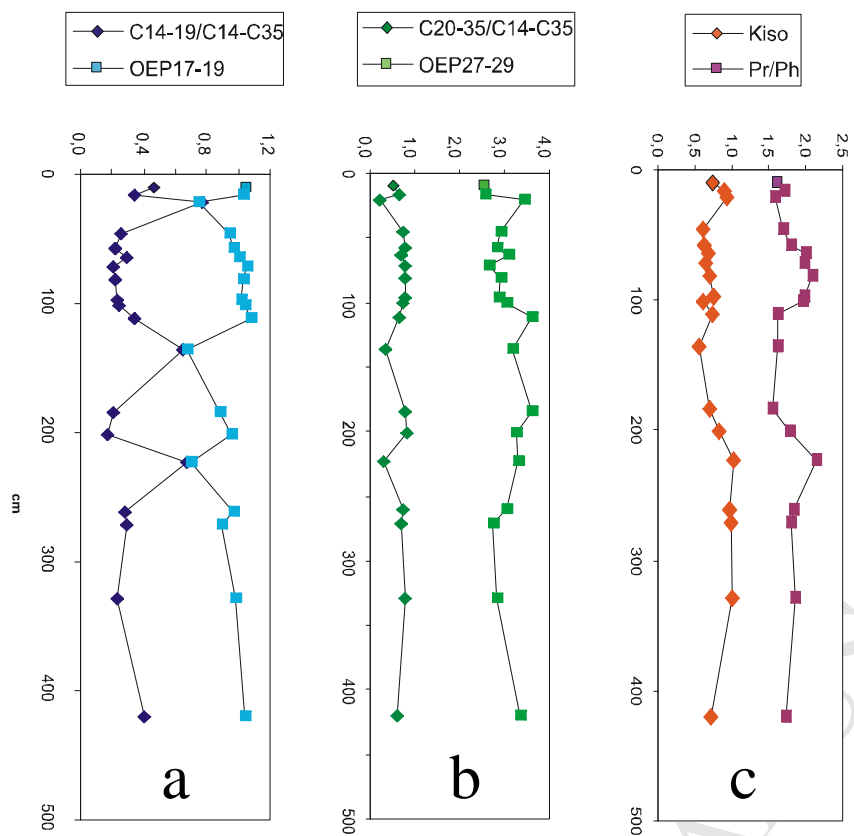


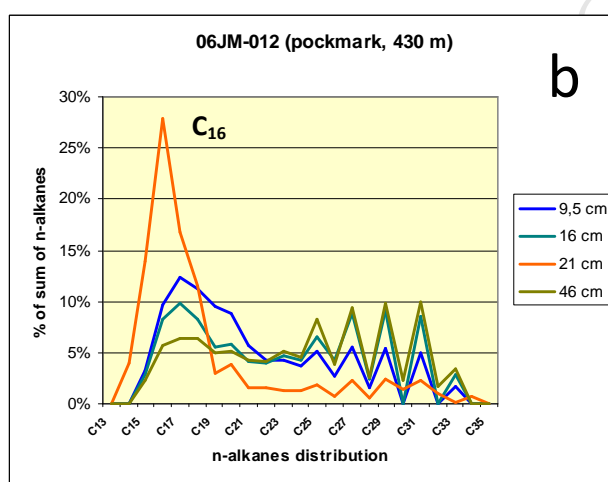
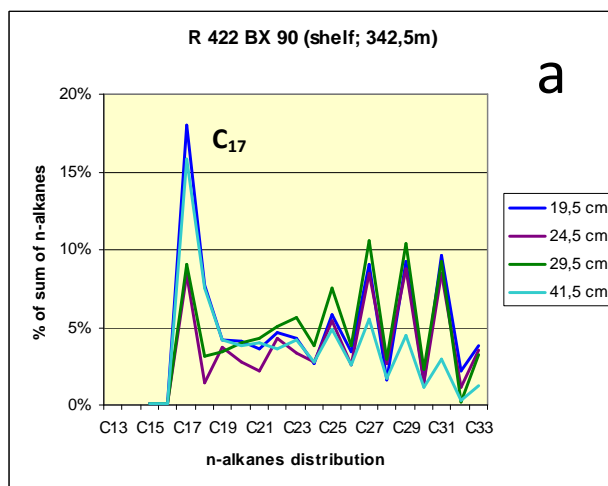
T_e

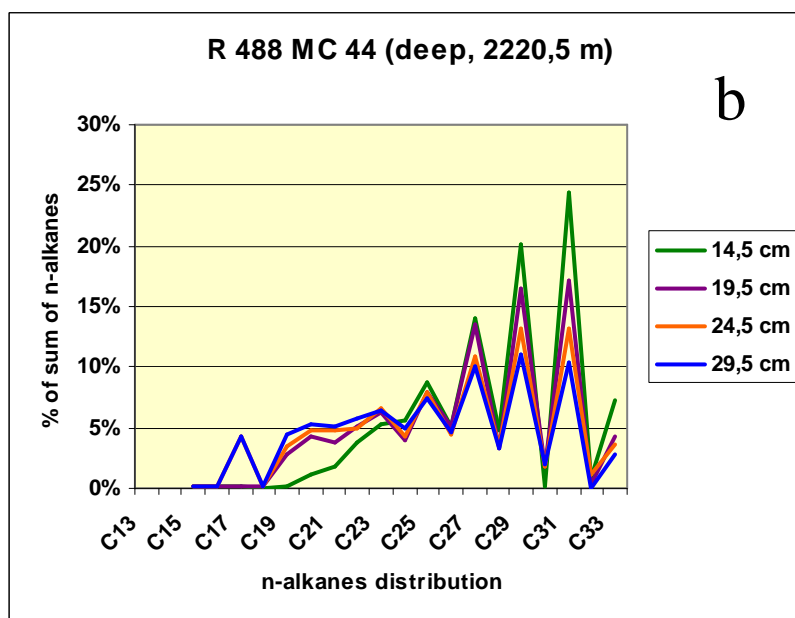
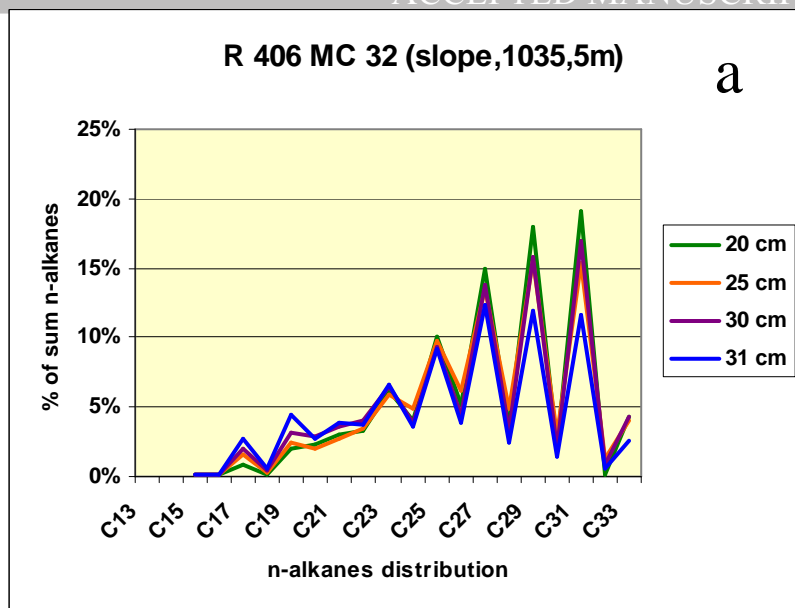




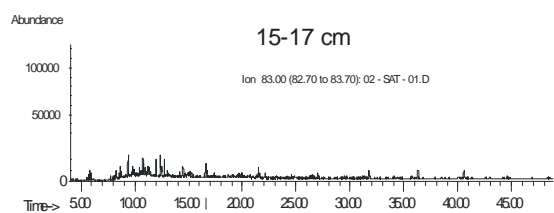




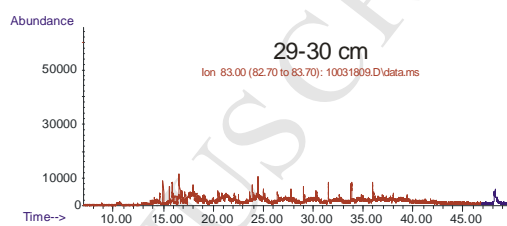
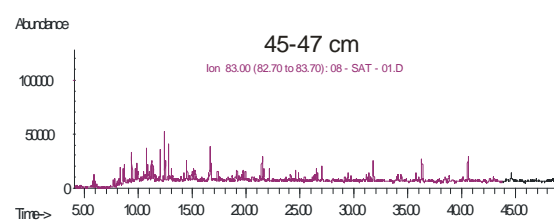
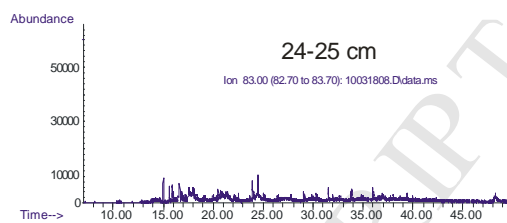
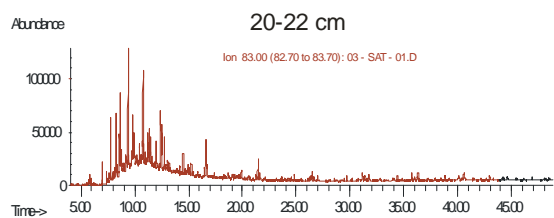
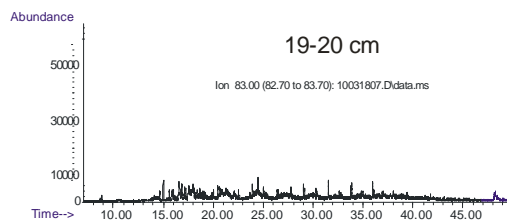




06 JM-012 (pockmark, 430 m)



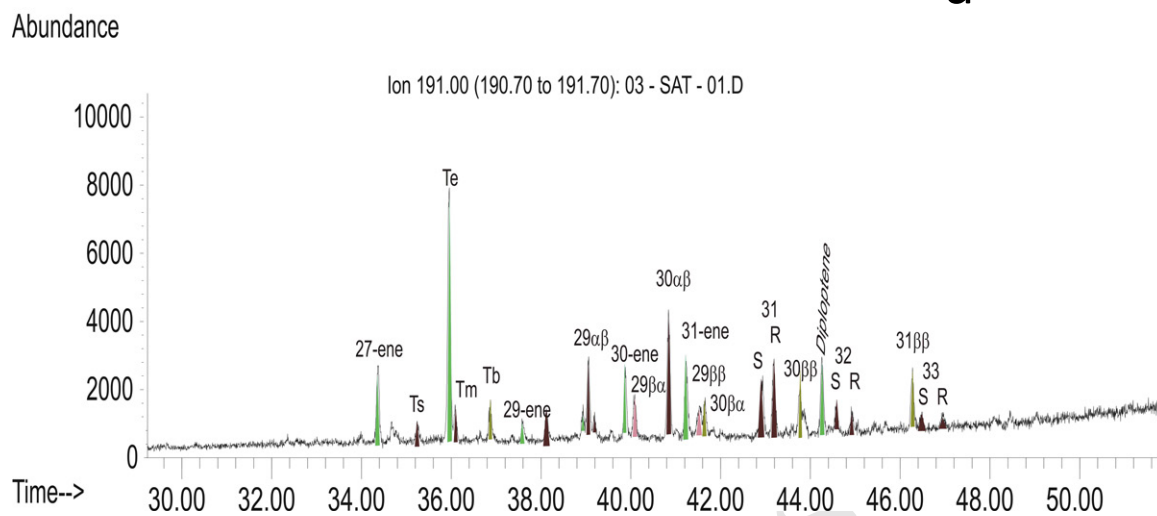
R422 BX 90 (shelf; 342,5m)



06 JM-012 (pockmark, 430 m)

20-22 cm

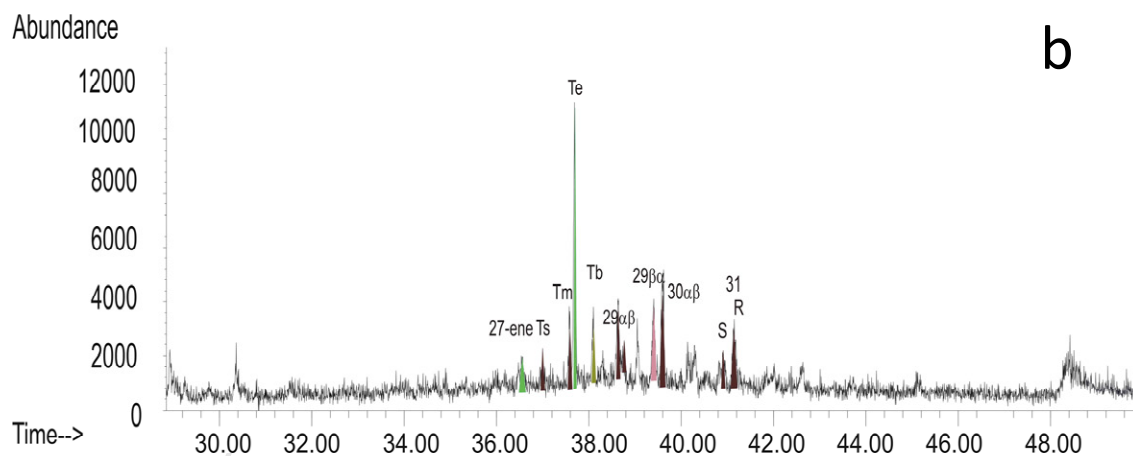
a



R422 BX 90 (shelf; 342,5m)

19-20 cm

Ion 191.00 (190.70 to 191.70): 10031807.D\data.ms



b