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

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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.

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 metres 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 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:

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

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

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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≅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 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, αβ/(αβ+βα) C_{30} and ββ/(αβ+βα) C_{30}, provide information on thermal maturity as ββ-hopanes (biohopanes) convert readily to αβ- and βα-configurations, and their high levels indicate low degree of maturity contrary to αβ-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). 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.

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 60 °C 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
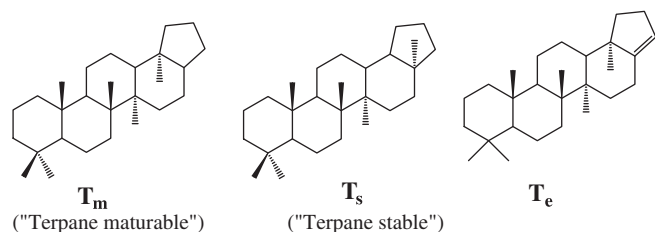

Fig. 1. Chemical structures of 22,29,30-trisnor-17α-hopane (T_m), 22,29,30-trisnor-18α-hopane (T_s), and 22,29,30-trisnorhop-17(21)-ene (T_e).