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Ujarassiortut Kalaallit Nunaanni Misissuisoqarfiat
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Organic geochemistry of oil-impregnated cores from the Marraat-1 well, Nuussuaq, West Greenland – comparison with surface samples

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Field work and drilling on the Nuussuaq peninsula, West Greenland in August 1993 revealed the existence of live oil seeping into vesicular Paleocene lavas. The oil plugs most available porosity in two fault-bounded zones that can be traced more than 1 km along strike and several hundreds of metres across strike and furthermore was confirmed in the core of the uppermost 90 m of a 448 m deep borehole.

Based on organic geochemical data (extraction, class separation, GC, GC/MS, and carbon isotopes) from core and from surface samples collected in the vicinity of the drill site the depositional environment and thermal history of the inferred source rock, and the post-migration history of degradation have been interpreted.

From bulk compositions the degradation of the oil is interpreted as varying from very limited to moderate, with a composition varying from solid bitumen to heavy crude oil. Steranes, terpanes, and linear isoprenoids are unaffected by degradation in all samples and show remarkably constant ratios. *N*-alkanes are always present but are partly degraded in some of the samples. However, this pattern does not correlate with the degree of degradation interpreted from the bulk composition. Therefore active replenishment into the structure is suggested, either from an underlying reservoir or by long distance migration from an actively generating source rock.

The source rock seems to be in the early part of the oil window, judging from the high contents of NSO's, low Ts/Tm values and high moretane contents and various biomarker ratios. Hopane isomerisation has reached equilibrium whereas 20S/20S+R sterane isomerisation ratios show values between 0.40 and 0.45. Calculated Methylphenanthrene Index (Average MPI1 = 0.40, average MPI2 = 0.31) further supports a low thermal maturity.

A number of characteristic fingerprints (high Sa/Ar, high wax, high CPI, high Pr/Ph (4-5), dominance of C29 steranes, low contents of tricyclics and extended hopanes, high contents of phenanthrenes and carbon isotope composition suggest that the oil-prone material in the source rock is terrestrial in origin but was deposited under marine conditions (C30 steranes are present). This is further substantiated by the high contents of bisnorlupane and oleanane which are typical for latest Cretaceous and Tertiary deltaic source rocks.

The implications of this significant discovery are very encouraging for future exploration offshore Labrador, West Greenland and in Melville Bugt since it for the first time demonstrates that a source rock capable of generating oil exists in the region and thereby challenges the 1970s' reputation of the area as being entirely gas-prone.

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INTRODUCTION

One of the serious problems in the hitherto rather negative evaluation of the exploration potential of the Labrador and West Greenland shelves has been the lack of oil-prone source rocks. Consequently, GGU's expeditions to the onshore part of the Cretaceous-Tertiary sedimentary basin in the Disko-Nuussuaq-Svartenhuk Halvø area of West Greenland aimed primarily at studying the sedimentology, stratigraphy and organic geochemistry of the marine succession in the hope of finding oil-prone source rocks and describing their distribution, thickness and generative potential (Christiansen *et al.*, 1992; Christiansen, 1993). Furthermore considerable time and effort was used to search for direct evidence of hydrocarbon generation such as oil and gas seepage, oil-impregnation or solid bitumen, since the ongoing source rock studies has only provided evidence of gas source rocks with the exception of a few thin resinite-rich coals (GGU unpublished data).

In West Greenland previous geologically-confirmed evidence of hydrocarbon generation has been restricted to two examples of highly coalified solid bitumens, one on the island of Qeqertarsuaq to the north of Uummannaq (Henderson, 1969) and one at Marraat Killiit on Nuussuaq (Pedersen, 1986, see also review by Christiansen, 1994). Evidence of gas generation, observed as bubbles in fountains or lakes in pingos on Nuussuaq, was mentioned by Henderson (1969) and Henderson *et al.* (1976). Furthermore various indications had been noted throughout many decades by the local population and by people travelling in West Greenland (see Mikkelsen, 1954, 1993).

Near the end of the 1992 field season a significant oil-impregnation was discovered by Asger K. Pedersen and Søren Hansen from the Geological Museum, University of Copenhagen during a study the lowermost part of the Tertiary volcanics in the Marraat area on the south-west coast of Nuussuaq (Fig. 1). This discovery was only a few kilometres from the previously described locality with coalified solid bitumen (Pedersen, 1986). However, in the new discovery it was very encouraging that analysis late in 1992 by extraction, gas chromatography, and GC/MS showed that the oil had only suffered minor degradation and no thermal alteration. Furthermore the biomarker distribution made it possible to interpret both the depositional environment, age and thermal maturity of the as yet untouched source rock.

Based on these encouraging results it was decided to carry out additional field work in 1993 in order to study the extent of the oil impregnation. Furthermore it was suggested that drilling should be carried out close to the discovery locality if appropriate equipment could be made available. The main goal was to penetrate the base of the volcanic succession and reach into the underlying sediments to demonstrate an oil-prone source rock or an oil reservoir. The field work took place in the period from Aug. 2-13, 1993. A drilling programme was carried out from Aug. 15-21, 1993 using a rig that had been used by the mining company Falconbridge Ltd. in their mineral exploration programme earlier during the summer. This was followed by a logging and geophysical programme from Oct. 22 - Nov. 2, 1993. The activities and preliminary results have been summarised by Christiansen *et al.* (1994) and details on the drilling programme are given in the well summary report by Dam & Christiansen (1994). The main results which are of importance for the present organic geochemical study can be summarised as follows:

* The exposed zone of oil-impregnation proved to be much more extensive than first recognised. So far the impregnation has been traced for more than 1.5 km along strike and more than 0.5 km across strike. The oil impregnation is recognized in two different fault blocks with volcanics dipping 15-20° to the east and separated by steeply dipping N-S faults (Fig. 1). In this area a number of vesicular lava tops are impregnated with oil, generally plugging most of the available porosity.

* The drilling penetrated 447.75 m of the volcanics without reaching into the underlying sediments. The core confirmed the encouraging results from the field work. A series of porous zones in the lavas down to a depth of 86 m contain liquid oil (Fig. 2) whereas the underlying lava flows, pillow lavas and hyaloclastites display poor porosity and permeability and only occasionally show traces of oil (Fig. 2).

* After completion of drilling it became evident that formation water and gas were liberated from the hole and a valve was mounted on top of the casing. After the logging programme formation fluids were sampled at 8 levels in the upper 86 m of the hole, in all cases giving highly saline water, probably originating from deep basinal

brines. Results from the analyses of gas and formation waters will be presented in a separate report when completed.

GEOLOGICAL SETTING

The volcanics (and the minor sediment exposures) in the Marraat area were mapped and studied in 1971 and 1972 by Gilroy Henderson (GGU unpublished map 1:10.000); results that were published by Henderson (1975) and compiled onto the GGU 1:100.000 map 70 V1N. The oil-impregnated lavas belong to the oldest part of the Vaigat Formation; a level deeper than that found on Disko and described lithostratigraphically by Pedersen (1985).

Structurally the Marraat area is rather complex being situated in the eastern margin of a major fracture zone system - the Itilli Fault zone, which is centred in the Itilli valley about 5 km to the north. The margin of the fault zone displays compressional features and a large number of dykes (up to 5-10% of the total rock volume is reached very locally) which represent several phases of dyke emplacement. Due to the heating effects of dykes and sills and a number of hydrothermal fields marked by an abundance of mineralized veins (Binzer & Karup-Møller, 1974; Karup-Møller, 1969) and possibly also deeper subsidence and higher uplift than other areas on Nuussuaq, the thermal maturity of the exposed sediments in the Itilli valley is high with vitrinite reflectance values between 2% and 3.5%. However, just a few kilometres east of the Itilli valley, the uppermost part of the exposed sediments found just beneath Tertiary hyaloclastites has a much lower thermal maturity (TAI: 2^{+}-3) (Nøhr-Hansen, 1993).

In the Marraat area the volcanics dip 15°-25° towards east (exactly 18.0° at the drill site) and the succession is cut by a number of N-S and NNW-SSE steeply dipping faults with a westerly downthrow (Henderson, 1975 Fig. 3). Several km farther to the north, northeast and east, the dips of the flow are lower (~5° to the E and SE), and in central Nuussuaq they are close to a horizontal position and the number of faults is much smaller.

The main oil-impregnation is found in vesicular flow tops within a series of subaerial basaltic lava flows (Fig. 1 and 2). These flows both include feldsparphyric and aphyric basalts affected by high-level magma chamber processes, and some of the lavas are contaminated basalts silica-enriched through the reaction with upper crustal rocks (L.M.

Larsen and A.K. Pedersen, unpublished). The lavas can be mapped out as a light brownish-weathering marker horizon and help to define the structures of the area. The marker horizon is underlain by subaerial picrite lavas and more olivine-poor basalts and by two units of hyaloclastite. Inferred from the outcrop pattern along the coast north of the first oil-discovery locality, the hyaloclastites have a thickness exceeding 300 m.

The extent of the oil-impregnation as presently known in surface exposures is indicated on Fig. 1, many individual thin zones have been traced along distances between from 20 to more than 100 m. The two main areas of oil-impregnation, in both cases hosted by the same marker flows but in two different fault blocks, are spaced apart by about 1.5 km. At the oil-discovery locality, the breccias are inferred to have a thickness of at least 300 m, and probably not more than 600 m. The boundary to the underlying sediments is only observed as a fault exposed along the coast but the general pattern in the terrain may be deduced from minor outcrops in the poorly exposed terrain east of the Itilli valley.

SAMPLES

The analysed surface samples have been collected at a number of different localities: 1) 200-300 west of drill site at the first oil-discovery locality (400888A, 400888B), 2) 500 m northwest of drill site (409159, 409162, 409163, 409167), and 3) 1.3 km northwest of drill site in a different fault block (401574, 401580) (Fig. 1). More samples are available for additional analysis.

The analysed core samples, all with the GGU sample no. 408001, were taken at the following depths: -01: 5.50 m, -02: 8.74 m, -03: 11.25 m, -04: 27.96 m, -05: 52.02 m, -06: 62.60 m, and -07: 82.20 m (Fig. 3). These seven core pieces were wrapped in alumina foil and transported back to Denmark as hand luggage before the drilling operation was completed.

ANALYTICAL METHODS

The samples were analysed at the source rock laboratory at the Geological Survey of Denmark and the procedure follows the description given by Christiansen *et al.* (1989) and Bojesen-Koefoed (1989).

The analytical programme includes extraction in a Soxtech apparatus with subsequent deasphalting and column separation into saturated and aromatic hydrocarbons and NSO compounds. The saturated and aromatic hydrocarbons were analysed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS).

Selected extracts from the cores were mailed to GEOLAB-NOR in Trondheim, Norway for measurements of the carbon isotope composition.

RESULTS

Extraction, bulk composition

Most of the samples yield very high amounts of extractable material with the exception of surface samples 409162 and 409163 and core piece -02. Data from these three samples should be checked carefully before used in any critical interpretation. Some of the extraction data from these samples fall outside the general pattern and they have been omitted in calculations whereas the GC/MS data looks similar to most other samples.

The extraction data show a distinct scatter suggesting large variations in degradation (Table 1, Fig. 3). The asphaltene content varies from 3.3% to more than 30% with an average of ~20% The asphaltene-free extracts show a high proportion of NSO compounds (25-76%, average ~45%) and a dominance of saturated hydrocarbons over aromatic hydrocarbons (~2.5) (Fig. 4). Compared to world-wide averages given by Tissot & Welte (1984) (see Table 1 and Fig. 3), the Marraat oil is strongly enriched in non-hydrocarbons and shows a slightly higher ratio of saturated to aromatic hydrocarbons.

Gas chromatography (GC) of saturated hydrocarbons

Due to the variation in distribution of *n*-alkanes and isoprenoids, annotated gas chromatograms for all of the samples are shown in Fig. 5. Based on the patterns recognised the samples can be tentatively divided into three main groups, where the *n*-alkanes show evidence of increasing degradation from A to C:

A) Most of the surface samples (with the exception of 409162) and a two of the core samples (-05, -06) show remarkably similar gas chromatograms with evidence of light end evaporation and degradation being intense for *n*-alknanes shorter than C16 and decreasing up to C20. Isoprenoids occur in low to moderate contents compared to *n*-alkanes in the same range, typically with Pr/*n*C17 between 0.4 and 0.6 and Ph/*n*-C18 between 0.1 and 0.2. The envelope of distribution is broad and maximises at C23 or C25. Generally the waxiness is high and a distinct and constant odd-even preference is noted whether calculated as CPI (1.14-1.17) or as Philippi values (1.33-1.44) (Table 2).

B) A number of samples (-02, -04, -07) have rather similar characteristics to those mentioned for group A, the main difference being higher relative contents of isoprenoids with Pr/*n*-C17 between 1 and 2 and some scatter in other calculated values.

C) Some samples (409162, -01, -03) show a pattern where isoprenoids and other compounds dominate over *n*-alkanes (Pr/*n*-C17 between 4 and 6). There are tendencies for minor humps of unresolved compounds around C20 and C30.

Based on especially group A) data it can be inferred that Pr/Ph ratios of the Marraat oil are remarkably constant with high values around 4 (Table 2, Fig. 6).

Based on all the above observations the original undegraded oil is presumed to show a very broad envelope of *n*-alkanes but with a distinct odd-even predominance and a high wax content.

Gas chromatography/mass spectrometry (GC/MS)

The distribution of biomarkers in the saturated fractions has been studied by using m/z 217 (and 218) mass fragmentograms for the steranes and the m/z 191 (and 177) for the terpanes. The distribution of aromatic steranes has been studied by using m/z 253 mass fragmentograms for the monoaromatic steranes and the m/z 231 mass fragmentograms for the triaromatic steranes. One of the least degraded samples (-07) has been analysed in scan mode.

Generally the terpanes occur in much higher concentrations than the steranes. Fig. 8 shows one example of the terpane and sterane distributions; some of the parameters providing information on thermal maturity and depositional environment are listed in Table 3 and 4; annotation key is found in Table 6.

Terpane distribution

The terpane distribution is remarkably constant from sample to sample suggesting that these compounds are unaffected by degradation and that all the oil originates from the same source rock and with no variation in thermal history.

The terpanes are dominated by pentacyclics (hopanes, moretanes and few other compounds), whereas the tricyclics only occur in very low concentrations. H30 is the most abundant hopane followed by H29 with constant H29/H30 ratios between 0.63 and 0.80. Both the H31 and H32 have reached equilibrium of isomerisation with 22S/22S + 22R values close to 0.6 (Table 3). The extended hopanes show rapidly decreasing contents with increasing carbon number.

Ts occurs in very low concentrations compared to Tm with Ts/Ts + Tm ratios between 0.13 and 0.23. The 17β Tm which usually only occurs in low maturity source rock extracts (prior to early generation) is recorded in all samples with Tm/Tm + 17β Tm ratios between 0.92 and 0.96.

Compared to most crude oils the concentration of moretanes is relatively high with ratios of αβ/βα + αβ between 0.82 and 0.87 (Table 4). Also the amounts of β β hopanes, which normally only occur in significant amounts in immature source rocks are remarkable with β β /α β + β α + β β ratios between 0.04 and 0.06.

The terpane distribution is very distinct due to high concentrations of two other relatively rare pentacyclic biomarkers, bisnorlupane and oleanane. The BNL/H30 and O/H30 ratios vary from 0.27 to 0.50 and from 0.28 to 0.46 respectively (Table 4).

Sterane distribution

The sterane distribution is also constant from sample to sample suggesting that these compounds are unaffected by degradation and confirming that the oil originates from the same source rock with little variation in thermal history.

Diasteranes occur in moderate amounts, slightly lower than regular steranes. The distribution of the steranes shows a distinct dominance of S29 isomers (59-76%) (Table 4). The small, but significant, concentration of S30 isomers (3-7%) should be noted. The steranes show almost equal amounts of S and R and αα and β β isomers (20S/20S + 20R between 0.41 and 0.53, equil. = 0.55; $\beta\beta/\beta\beta + \alpha\alpha$ between 0.43 and 0.77, equil. = 0.75; Table 3) suggesting that thermal equilibrium has not been reached.

Aromatic biomarkers

Only aromatic hydrocarbons from the seven core samples have been analysed (see example of total ion mass chromatogram in Fig. 7). Four of them (-04, -05, -06, and -07) are very similar and show a simple pattern, being dominated by C1-C3 alkylated naphtalenes, phenanthrene and methylphenanthrenes. The content of phenanthrene is between 20% and 37% of the total aromatic fraction, at least four times higher than any other single aromatic compound. The distribution of methylphenanthrenes is almost constant. The concentration of mono- and triaromatic steranes is very low.

Cores pieces -01 and -03 are completely different from all others and the chromatograms show a major unresolved hump with maximum between C14 and C16. The concentration of naphtalenes and phenanthrenes is low, almost absent in -03 and the relative content of phenanthrenes is different (enriched in β-type isomers, especially 9-methylphenanthrene). The content of mono- and triaromatic steranes is higher. Core piece -02 has a composition somewhat in between these two groups.

The calculated Methylphenanthrene Indices (see Radke, 1988) show low average values of MPI 1 = 0.40 and MPI 2 = 0.31 (see Table 3). If only data from the first group (-04, -05, -06, -07) are used the average values are even lower (MPI 1 = 0.32, MPI 2 = 0.29).

The distribution of monoaromatic steranes is constant from sample to sample. The distribution reflects the distribution of the normal non-aromatic steranes with dominance of C 29 monoaromatic steranes. Due to coelution (2-4 compounds in some peaks), quantification of individual isomers has not been attempted. C_{26-28}Tri /(C_{26-28}Tri + C_{27-29}Mono) is in most cases very low (0.1-0.3). Sample -06 is the only exception (0.5); however, this sample has a very low concentration of both mono- and triaromatic steranes.

All samples contain very low amounts of C21-22 monoaromatic and C20-21 triaromatic steranes. The relative amounts of these short chain triaromatic steranes usually increase with maturity. All maturity parameters based on aromatic steranes suggest low thermal maturity.

Carbon isotopes

The carbon isotope composition was analysed in 6 samples from the Marraat-1 well. In each sample 5 fractions were measured: total extract, saturated hydrocarbons, aromatic hydrocarbons, NSO's, and asphaltenes.

The samples are remarkably constant in composition suggesting that all the oil was derived from the same source rock. Especially the NSO and asphaltene fractions show a variation almost within analytical error (Table 5). The highest variation is found for the saturated hydrocarbons which could be a degradation effect due to removal of the light-end *n*-alkanes. A considerable variation in isotope composition with increasing carbon number has been described for both *n*-alkanes and isoprenoids in several oils analysed by Bjorøy *et al.* (1991).

The variation of the total extracts reflects the relative proportions of the individual fractions or even compounds (Bjorøy *et al.*, 1991). The Galimov type plots (Fig. 9) show a very typical pattern with the saturated hydrocarbons being the most ^{13}C depleted fraction and increasingly higher concentrations of ^{13}C in aromatics, and NSO's and asphaltenes (the two latter very close).

DISCUSSION

Based on the consistent results presented above it is possible to reach rather detailed conclusions on the origin and history of the Marraat oil, particularly concerning depositional environment of the source rock, the thermal history of the source rock, and degradation of the oil during migration, accumulation, leakage at or near the present surface.

These important factors are discussed in reverse order because it is important to distinguish first the degradational, and thereafter the thermal alteration before discussing the primary variation of source rock geochemistry.

Degradation of oil, variation

The GC and GC/MS data from the analysed samples clearly demonstrate that the degradation of the Marraat oil is so limited that biomarkers like steranes, terpanes and isoprenoids have not been affected. Therefore the level of degradation varies between 1 and 3 (of 9) using the scale of Volkman *et al.* (1983). Discussions on variations in degradation thus have to be based on bulk composition and distribution of *n*-alkanes relative to isoprenoids and distribution of aromatics.

The extraction data clearly demonstrate an enrichment of non-hydrocarbons in the order of 5-10 times compared to normal crude oils, depending on whether the calculation is based on asphaltene content alone or on total amount of non-hydrocarbons. One of the critical factors in evaluating these numbers is the processes of degradation; does enrichment take place by selective removal of hydrocarbons alone or are some of the non-hydrocarbon compounds generated from hydrocarbons by biodegradation? It is beyond the scope of the present report to contribute to this discussion but it should be noted that some authors accept generation of asphaltenes by bacteria. In the present case with very low temperatures near the surface, we have neglected these ideas, and it seems most likely that the degradation is due to water washing and evaporation.

Important for the calculation is the primary composition of the Marraat crude oil prior to degradation. Due to the low thermal maturity of the oil (see discussion below) rather high concentrations of non-hydrocarbons, especially of the NSO compounds, are to be expected. However, the bulk composition still provides evidence for an enrichment in the order of 3-5 times. This is in conflict with an interpretation based on the GC traces of the saturated hydrocarbons. In most cases these data provide evidence of a limited degradation that is not likely to be enriched the content of non-hydrocarbons significantly.

The distribution of the aromatics from the core suggests that the near surface core pieces [especially -01 (= 5.50 m) and -03 (= 11.25 m), but to some degree also -02 (= 8.74 m)] have lost specific aromatic compounds due to evaporation and water washing. Alkylnapthalenes are relatively water soluble and degrade easily, and consequently have been lost in these samples. Phenanthrene is more water soluble than methylphenanthrenes and β-type methylphenanthrenes (1 & 9-methylphenanthrene are the least water soluble (Radke, 1987)). Phenanthrene is more susceptible to degradation than the methylphenanthrenes, and it appears that the 9-isomer is more persistent than the others (Rowland *et al.*, 1986). Aromatic steranes are not affected at this level of degradation and have thus been concentrated in the near surface samples.

Replenishment of oil into structure?

The lack of correlation between some of the degradational parameters demonstrated in the previous section raises a number of questions: is this pattern due to analytical errors or uncertainties, mis- or overinterpretation of data, or is it caused by replenishment of fresh oil into the structure that mixes with previously degraded oil? Furthermore, since the present-day degradation processes are not known, is it mainly water washing and evaporation of lighter compounds or is there significant microbial activity by bacteria, yeast or fungi? Has there been degradation during transportation and storage?

Most of the analytical methods provide very consistent data, especially the GC/MS, carbon isotope and some of the GC parameters; this is clearly evident from the constant ratios of many parameters described. The main problem is the use of extraction data, which generally are not very reliable, especially in cases with a low extractability or high contents of asphaltenes. It is therefore not recommended that these values are used for a detailed ranking even though the measured high contents of non-hydrocarbons are undisputable.

It is clear therefore that the combination of very high contents of non-hydrocarbons and the undegraded pattern of *n*-alkanes in most samples as well as the lack of correlation of parameters suggest several phases of migration and degradation or even active replenishment. Furthermore, the distribution pattern of aromatics indicates that degradation, primarily by water washing and evaporation, is much more intense in the near-surface layers (0-~20 m) than deeper in the hole. This suggests that the degradation is taking place at present and therefore favours the replenishment model.

Only few alternative models may be suggested; one possibility is reservoir heterogeneity. It has been recorded in other areas that significant differences may exist in oil composition (e.g. in maturity parameters) between oils found in reservoir rocks with high and low porosity within the same field. This has been interpreted as the result of a complex filling history by e.g. Leythaeuser & Rückheim (1989). In the present case, where the biomarker distributions are remarkably constant, possible heterogeneities in bulk composition can only be explained as a better preservation of the oil in small pores where permeability is low compared to more degraded oil in larger vesicles with circulation of water. At present, however, there are no data available for testing such a hypothesis.

Thermal maturity of source rock

All the parameters which provide information on thermal maturity of the source rock are in accordance with a relatively low maturity corresponding to 'early oil generation' or 'the upper part of the oil window'. A low maturity accounts for the high contents of NSO compounds, the relatively high waxiness and the distinct CPI. Also the low Ts and high moretane content and the preservation of 17β Tm and β β hopanes are explained by a low thermal maturity.

Several of the maturity parameters can be applied for a more detailed maturity correlation relative to various definitions of hydrocarbon generation zones or equivalent R_o values for those more familiar with such values, or they can be empirically, but directly, related to data from offshore wells/onshore outcrops in West Greenland.

Empirically the sterane isomerisation values for the Marraat oil correspond to a vitrinite reflectance of ~0.65-0.70% (e.g. Waples & Machihara, 1990). The low MPI values correspond to even lower calculated vitrinite reflectances ~0.50-0.60% (Radke, 1988, R_c = 0.40 + 0.4 x MPI 1). However, MPI values are generally more reliable at higher maturities with R_o between 0.65 and 1.4%.

The recorded maturity parameters can be directly compared with measured values (using same parameters) from the Ikermiut-1 well, offshore West Greenland and the Upper Cretaceous-Lower Tertiary outcrops on the north coast of Nuussuaq, West Greenland (GGU unpublished data). In particular sterane isomerisation, hopane isomerisation, Ts/Ts+Tm and CPI values are applicable. In the Ikermiut-1 well shale cuttings from ~3200 m slow slightly lower maturities whereas cuttings from ~3500 m slow slightly higher maturity values. The previously measured vitrinite data, reported by Rolle (1985), show that this interval has rather scattered R_o values between 0.55% and 0.8%.

On the north coast of Nuussuaq the complete exposed section has a lower maturity than the Marraat oil. Based on the well defined maturity trend observed, a maturity corresponding to the Marraat oil is likely to be reached a few hundred of metres below sea level, probably within Campanian shales (GGU, unpublished data).

Compared to the many compilations of maturity data and oil generation, all data for the Marraat oil are in accordance with generation from a source rock in the middle of the early generation zone (=upper part of 'oil window') (see e.g. Mackenzie, 1984; Peters & Moldowan, 1993).

Comparison of normal oils generated during deep subsidence with hydrothermal oils

Hydrothermally generated oils have been described from many active spreading zones. The best described examples are from Gulf of California (Guaymas Basin); North-East Pacific (Eascanaba Trough); Mid-Atlantic Ridge, Red Sea (see a number of papers in Simoneit, 1991). In non-active hydrothermal zones oils, and in particular relics of oil (solid bitumens), are common in volcanic terrains and in some types of ore deposits.

The composition of hydrothermally generated oils and bitumens seems highly variable, even over small distances. The oils are mixtures of hydrocarbons generated over a wide range of thermal regimes - up to about 350°C. The generation is instantaneous (hundreds to thousands of years) compared to other geological events in general, and to normal oil generation in particular. The generation products are rapidly removed and there is a low preservation potential, and when reported the biodegradation varies strongly.

Most examples of hydrothermally generated oils show high contents of NSO's and asphaltenes, low ratios of saturated to aromatic hydrocarbons, hopane isomerisation close to or in equilibrium, relatively high ratios of moretanes to hopanes, sterane isomerisation has rarely reached equilibrium, and very low values of Ts/Ts+Tm. Residual immature biomarkers may be present (ββ-hopanes, hopenes and sterenes). In contrast to the low maturity parameters recorded from the saturated hydrocarbons in hydrothermal oils most aromatic maturity indicators in the hydrothermal oils show high values. MPI1 and MPI 2 are higher than in most crude oils, typically between 0.7 and 1.3 and compare to pyrolyzates (e.g. Clifton *et al.*, 1990; Kvenvolden & Simoneit, 1990; Simoneit *et al.*, 1990).

Although hydrothermal oils share a number of characteristics with low maturity oils such as in Marraat, there are also a number of significant differences that make it unlikely that the Marraat oil was hydrothermally generated. First of all there is amount (probably millions of barrels) and distribution (over several kilometres along strike, in two fault blocks) of oil with a remarkably constant composition atypical for hydrothermally generated oils. Secondly, the maturity parameters measured for the aromatic hydrocarbons are completely different. The Marraat oil shows low maturity values for both saturated and aromatic hydrocarbons, whereas hydrothermal oils show low values for saturated hydrocarbons (slow reaction) but high values for the aromatics, which react much more quickly during short, but hot, thermal alteration.

Depositional environment of source rock

General terrestrial fingerprints

The organic geochemistry of the Marraat oil suggests that the source rock is generally dominated by terrestrially derived material. However, there are significant differences to most types of coaly or lacustrine source rocks dominated by algal material (see e.g. Powell, 1986; Philp *et al*., 1989). Furthermore several specific biomarkers constrain the depositional environment or suggest other specific precursors for some of the organic material in the source rock (see following section).

The moderate to high ratio of saturated to aromatic hydrocarbons, the high Pr/Ph ratios, the high CPI and the relatively high waxiness all suggest a significant terrestrial input to the organic material in the source rock (see e.g. Connan & Cassou, 1980; Tissot & Welte, 1984; Moldowan *et al.* 1985 and many others). This is further substantiated by the biomarker distribution where the lack or low contents of tricyclic terpanes and extended hopanes and the complete dominance of C29 steranes are typical for terrestrially derived organic material (e.g. Moldowan *et al*., 1985; Waples & Machihara, 1990; Peters & Moldowan, 1993). The very low contents of Ts relative to Tm is not only due to the low thermal maturity but is also source dependent, typically low Ts values are recorded in terrestrial material and in oxygenised environments (e.g. Moldowan *et al*., 1986; Waples & Machihara, 1990).

The terrestrial fingerprint is confirmed by the isotope data. The bulk composition, now with $\delta\ ^{13}C$ values close to -26, before degradation probably with $\delta\ ^{13}C$ between -26.5 and -27, falls within one of the main modes of compositional ranges from world-wide oils (Chung *et al.*, 1992). Most other examples with similar isotope composition are from "deltaic oils of varying age", e.g. from Niger basin, Gulf of Mexico, Scotian basin (all Cretaceous or Tertiary). The composition, when combined with the Pr/Ph ratio from GC, is clearly separated from all carbonate oils, all Palaeozoic oils, most marine shales, and all young Tertiary (Miocene) oils (Fig. 10). The cross-plot of aromatic versus saturated hydrocarbons isotope composition has traditionally been applied to distinguish marine from terrestrial oils/source rocks (Sofer, 1984) but has also been questioned by a number of authors (e.g. Moldowan *et al.*, 1985). In the present case one sample plots on the line separating the two types, three fall in the terrestrial field and two in the marine field but close to the dividing line (Fig. 11).

Specific biomarkers

Some of the biomarkers present provide a basis for a more detailed interpretation of the depositional environment of the source rock and the precursors of the organic material in the source rock. This is especially the case with the C30 steranes, some of the aromatics, and in particular oleanane and bisnorlupane.

C30 steranes have been recorded in all samples in small but significant quantities (Table 3 and Fig. 8). The presence of these compounds is the most powerful parameter for identifying a contribution from marine organic matter (algae) to a source rock (Moldowan *et al.*, 1985; Peters *et al.*, 1986; Mello *et al.*, 1988; Peters & Moldowan, 1993). The highest contents seem to occur in open marine environments, lower contents in restricted, hypersaline or deltaic settings (Peters & Moldowan, 1993).

The two aromatic diterpenoids simonellite and retene and the sesquiterpenoid cadalene found in quite high concentrations in the one sample (-07) analysed in scan mode suggest an origin from conifer resins (e.g Simoneit *et al.*, 1986; Heppenheimer *et al.*, 1992).

Oleanane has been described in oils and source rocks from a number of basins, especially those dominated by latest Cretaceous to Tertiary deltaic sediments such as the Niger Delta (Ekweozor *et al.*, 1979a,b; Ekweozor & Udo, 1988), the Mahakam Delta, Indonesia (Mackenzie *et al.* 1982, Hoffman *et al.*, 1984; Schoell *et al.*, 1984), the Po Basin, Italy (Riva *et al.*, 1986), the Beaufort-Mackenzie Delta, Canada (Brooks 1986a,b; Curiale, 1991), the Gippsland Basin, Australia (Philp & Gilbert, 1986), and several basins offshore Brazil (Mello *et al.*, 1988). Other examples have been described from Tertiary sediments and oils in the Far East such as Northwest Palawan, Philippines, Indonesia, South China, West Irian, New Zealand (Curiale & Lin, 1991; Grantham *et al.*,1983). From these papers the following main conclusions can be drawn:

* Oleanane is virtually restricted to Tertiary sediments (and uppermost Cretaceous) or to oils generated from Tertiary (and uppermost Cretaceous) source rocks;

* Oleanane indicates a terrestrially influenced depositional environment, either non-marine, deltaic or prodeltaic settings.

* The precursor for oleanane seems to be higher plants; some angiosperms evolved in latest Cretaceous or earliest Tertiary.

Bisnorlupane is even more rare than oleanane in source rocks and oils, but when recognized, and checked carefully, it is often found together with oleanane. Bisnorlupane is observed in the m/z 191 chromatogram with a retention time almost the same as that of bisnorhopane. The two compounds should be distinguished by comparing the m/z 177 chromatogram where the signal from bisnorlupane is about 5 times stronger than for m/z 191, whereas it is about five times smaller for bisnorhopane (Philp, 1985).

Bisnorlupane was first described in mudstones from West Greenland and Gulf of Suez (Rullkötter *et al.*, 1982) and has also been reported from the Beaufort-Mackenzie Delta (Brooks, 1986a,b) and from Tertiary oil in Washington (Kvenvolden *et al.*, 1991). A number of other characteristics are typically noted in oleanane- and bisnorlupane-rich oils and source rock extracts (see many of the references mentioned above): high Pr/Ph, odd/even predominance, high wax, low amounts of steranes with a dominance of C29 steranes, few extended hopanes (C33-C35), compound X (C30 pentacyclic terpane), few tricyclics, often C24 tetracyclic; all these characteristics are typical features of so-called "non-marine oils". Compared to the Marraat oil there are so many similarities that the interpretation of the depositional environment of the source rock by analogy seems fully justified.

Distribution of source rock

Although the source rock of the Marraat oil has not been found, either in the field nor by drilling, knowledge from this organic geochemical study combined with ongoing sedimentological, stratigraphic and seismic studies of the West Greenland region provide some constraints on the distribution of the source rock and its present position. The general 'terrestrial fingerprint' suggesting a deltaic or a prodelta shale as a source rock is in accordance with the geological setting of central West Greenland throughout most of the Cretaceous and Tertiary and gives many possibilities for source rocks, both in time and space.

However, despite a very large and systematic sampling programme of dark marine shales on Nuussuaq and Svartenhuk Halvø (Christiansen *et al.*, 1992; Christiansen, 1993) with subsequent organic geochemical screening analysis, it has not been possible to document a significant oil-prone source rock (GGU unpublished data, several reports in preparation). A few samples, typically representing less than one metre-thick coal seams occasionally have a high generative potential (TOC: 40-60%, Hydrogen Index: 200-300). So far these samples have only been found on the north coast of Disko and the north coast of Nuussuaq, in both cases in the Upper Cretaceous Atane Formation.

A large number of outcrop samples from these coaly units, from various lacustrine shales, from the resin-rich coals on Hareøen and from the marine shales have been analysed by GC and GCMS. Oleanane has only been recorded in trace amounts in a few of the marine shales. Significant amounts of bisnorlupane have been recorded in several Paleocene marine shales (not of source rock quality and very immature) in the Tunorssuaq valley, in all cases in the uppermost part of the exposed section, less than 100 m below the base of the volcanics. These data and the general knowledge on oleanane and bisnorlupane make it unlikely that the source rock for the Marraat oil is exposed in central or northern Nuussuaq. It could, however, be situated immediately below the volcanics on western Nuussuaq or farther west in the offshore areas.

Based on the assumption that replenishment of oil is continuously taking place, there are two main models for the source rock of the Marraat oil: 1) direct migration from an actively generating source rock or 2) leakage from an underlying reservoir.

Using the first model, seismic data may provide further indications of the position of the source rock, mainly by looking for areas where reflectors close to the base of the Paleocene basalts are situated at a depth of ~3.5 km. Such an interpretation, based on a limited number of confidential seismic lines, is presently under completion. Using the second model, it is more difficult to postulate the position of the source rock, since it depends on whether active generation takes place or whether generation took place during deepest subsidence, probably shortly after the end of the volcanism. The erosion and uplift history of Nuussuaq are not known in any detail, but it is known from the distribution of marine sediments and subaqueous basalts that the region has been uplifted at least 1 km since the Early Tertiary. However, using this model it is possible that the source rock could have a position at a depth of 1-2 km below the present day surface. This can only be tested by drilling into the sediments underlying the volcanics in the Marraat area.

CONCLUSIONS

Based on the analytical data, results from field work and drilling, the following main conclusions can be drawn concerning the source rock and history of the oil discovered at Marraat:

* The source rock of the Marraat oil was deposited in an environment with a dominance of terrestrially derived organic matter but with marine influence. The source rock is probably a deltaic or prodeltaic shale of latest Cretaceous or Early Tertiary (Paleocene) age.

* The source rock has a low thermal maturity corresponding to the upper part of the oil window. Based on analogues this corresponds to a depth of ~3.5 km in the offshore region and a vitrinite reflectance of 0.65-0.7%.

- The degradation of the Marraat oil varies from very limited to moderate. It is suggested that there have been several phases of migration and degradation or continuously replenishment into the structure.

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Table 1. Extraction data

GGU No.	Extract[1]	Asph (%)	Sat (%)	Aro (%)	NSO (%)	Sat/Aro	HC/non-HC
400888A	9.0	19.6	n.a.	n.a.	n.a.	n.a.	n.a.
400888B	4.4	18.7	45.8	14.8	39.4	3.1	1.0
409159	3.6	31.2	13.6	10.2	76.3	1.3	0.2
409162	0.0	57.1	33.3	33.3	33.3	1.0	0.4
409163	0.1	42.9	16.7	16.7	66.7	1.0	0.2
409167	2.1	22.3	42.0	13.5	44.6	3.1	0.8
401574	6.5	15.6	37.3	15.7	47.1	2.4	0.8
401580	1.4	33.8	67.2	8.0	24.9	8.4	1.0
408001-01	n.a.	21.4	29.3	19.2	51.5	1.5	0.6
408001-02	n.a.	5.9	40.0	20.0	40.0	2.0	1.3
408001-03	n.a.	18.7	26.7	15.7	57.6	1.7	0.5
408001-04	n.a.	3.3	49.5	18.7	31.7	2.6	2.0
408001-05	n.a.	13.8	48.3	13.8	37.9	3.5	1.2
408001-06	n.a.	34.5	34.7	20.4	44.9	1.7	0.6
408001-07	n.a.	5.8	41.3	22.3	36.4	1.9	1.5

n.a.: not available

1: (mg SOM/g TOC)

Table 2. Gas chromatography data

GGU No.	Pr/Ph	Pr/*n*C17	Ph/*n*C18	Iso/*n*C	CPI	Philippi	Waxiness
400888A	4.27	0.92	0.19	0.28	1.14	1.36	0.18
400888B	4.17	1.05	0.22	0.28	1.14	1.36	0.20
409159	3.68	0.34	0.08	0.10	1.17	1.37	0.90
409162	3.66	6.05	8.21	0.83	1.24	1.59	0.10
409163	2.71	0.46	0.12	0.12	1.13	1.33	0.07
409167	4.23	0.45	0.08	0.10	1.15	1.37	0.46
401574	3.29	0.39	0.09	0.08	1.17	1.37	0.79
401580	4.66	0.56	0.09	0.14	1.16	1.44	0.22
408001-01	4.11	5.70	1.57	2.15	0.89	n.a.	0.00
408001-02	2.91	1.26	0.38	0.35	1.17	1.38	0.68
408001-03	3.05	3.84	3.28	2.14	1.24	1.49	0.00
408001-04	4.43	1.56	0.29	0.44	1.11	1.37	0.11
408001-05	4.15	0.43	0.09	0.13	1.12	1.37	0.11
408001-06	4.18	0.49	0.11	0.17	1.10	1.36	0.07
408001-07	4.70	1.02	0.21	0.33	1.07	1.32	0.03

n.a.: not available

Table 3. GC/MS data and GC data (aromatics) on thermal maturity

GGU No.	Ts/Ts +Tm	Tm/Tm +17β	H31 22S/22S +22R	H32 22S/22S +22R	H30 αβ/αβ +βα	H30 ββ/αβ+ βα+ββ	S29 20S/20S +20R	S29 ββ/αα +ββ	MPI-1	MPI-2
400888A	0.15	0.95	0.60	0.62	0.87	0.04	0.47	0.45	n.a.	n.a.
400888B	0.16	0.94	0.60	0.59	0.85	0.04	0.46	0.47	n.a.	n.a.
409159	0.19	0.94	0.57	0.57	0.84	0.06	0.45	0.51	n.a.	n.a.
409162	0.17	0.94	0.54	0.57	0.82	0.05	n.a.	n.a.	n.a.	n.a.
409163	0.23	0.96	0.57	0.61	0.84	0.05	0.46	0.48	n.a.	n.a.
409167	0.14	0.94	0.58	0.59	0.84	0.04	0.53	0.57	n.a.	n.a.
401574	0.14	0.95	0.57	0.58	0.84	0.05	0.43	0.48	n.a.	n.a.
401580	0.13	0.94	0.58	0.59	0.82	0.06	0.44	0.42	n.a.	n.a.
408001-01	0.14	0.94	0.58	0.55	0.84	0.06	0.41	0.44	0.30	0.30
408001-02	0.20	0.94	0.57	0.55	0.84	0.05	0.43	0.42	0.42	0.43
408001-03	0.17	0.94	0.56	0.56	0.83	0.06	0.40	0.46	0.84	0.31
408001-04	0.19	0.92	0.59	0.57	0.84	0.05	0.43	0.44	0.44	0.41
408001-05	0.16	0.93	0.58	0.58	0.85	0.05	0.45	0.45	0.21	0.18
408001-06	0.17	0.94	0.59	0.59	0.85	0.05	0.44	0.45	0.31	0.30
408001-07	0.15	0.95	0.58	0.57	0.85	0.05	0.42	0.43	0.31	0.28

n.a.: not available

Table 4. GC/MS data on depositional environment

GGU No.	BNL/H30	H29/H30	O/H30	S27	(%ααR) S28	S29	(ααR) S27/S29	(ααR) S30/SUM
400888A	0.62	0.80	0.43	14	16	70	0.20	0.05
400888B	0.62	0.77	0.35	18	16	66	0.28	0.06
409159	0.27	0.60	0.28	10	16	74	0.13	0.04
409162	0.24	0.79	0.24	n.a.	n.a.	n.a.	n.a.	n.a.
409163	0.47	0.85	0.31	20	21	59	0.35	0.05
409167	0.50	0.64	0.37	11	20	69	0.16	0.07
401574	0.35	0.63	0.28	11	15	74	0.15	0.04
401580	0.59	0.74	0.46	11	15	74	0.15	0.03
408001-01	0.50	0.70	0.44	11	15	74	0.15	0.03
408001-02	0.54	0.75	0.39	13	14	73	0.18	0.03
408001-03	0.38	0.69	0.38	11	13	76	0.15	0.03
408001-04	0.50	0.69	0.39	11	14	75	0.15	0.03
408001-05	0.44	0.67	0.31	11	14	75	0.15	0.03
408001-06	0.48	0.69	0.30	12	14	74	0.17	0.04
408001-07	0.52	0.68	0.40	11	15	74	0.15	0.03

n.a.: not available

Table 5. Carbon isotope data for total extracts and fractions

GGU No.	Extr.	Sat	Aro	NSO	Asph
408001-01	−26.41	−28.16	−26.18	−25.56	−25.66
408001-03	−26.11	−28.40	−26.66	−25.54	−25.79
408001-04	−26.39	−27.47	−26.75	−25.38	−25.65
408001-05	−26.20	−28.18	−26.40	−25.49	−25.59
408001-06	−25.80	−27.45	−26.31	−25.42	−25.54
408001-07	−25.49	−27.87	−26.30	−25.48	−25.57
Average	−26.07 ±0.36	−27.92 ±0.39	−26.43 ±0.22	−25.47 ±0.07	−25.63 ±0.09

Table 6. Compound assignment of terpanes and steranes (Figs 7 and 8, Tables 3 and 4)

Terpanes

Ts	C_{27}	18α(H)	trisnorneohopane	
Tm	C_{27}	17α(H)	trisnorneohopane	
17β	C_{27}	17β(H)	trisnorneohopane	
BSL	C_{28}	17α(H)	bisnorlupane	
H29	C_{29}	17β(H)	norhopane	
M29	C_{29}	17β(H), 21α(H)	normoretane	
0	C_{30}	18α(H)	oleanane	
αβ H30	C_{30}	17α(H), 21β(H)	hopane	
βα M30	C_{30}	17β(H), 21α(H)	moretane	
ββ H30	C_{30}	17β(H), 21β(H)	hopane	
H31	C_{31}	17α(H), 21β(H)	homohopanes	(22S + 22R)
H32	C_{32}	17α(H), 21β(H)	bishomohopanes	(22S + 22R)
H33	C_{33}	17α(H), 21β(H)	trishomohopanes	(22S + 22R)

Steranes

S27 ααR	C_{27}	5α(H),	14α(H),	17α(H)	sterane	(20R)
S28 ααR	C_{28}	5α(H),	14α(H),	17α(H)	sterane	(20R)
S29 ααR	C_{29}	5α(H),	14α(H),	17α(H)	sterane	(20R)
S30 ααR	C_{30}	5α(H),	14α(H),	17α(H)	sterane	(20R)
S29 ααS	C_{29}	5α(H),	14α(H),	17α(H)	sterane	(20S)
S29 ββR	C_{29}	5α(H),	14β(H),	17β(H)	sterane	(20R)
S29 ββS	C_{29}	5α(H),	14β(H),	17β(H)	sterane	(20S)

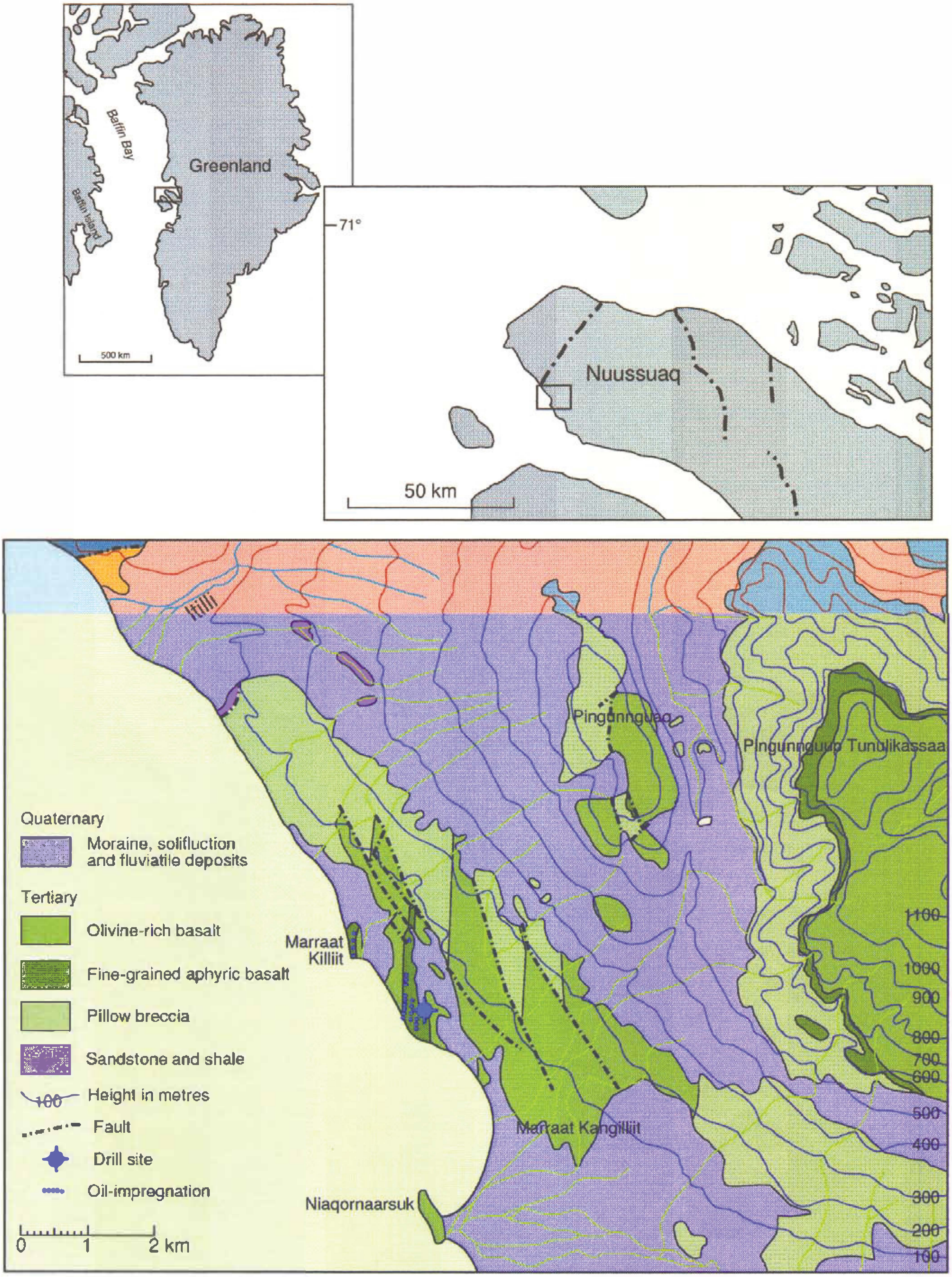

Fig. 1. Geological map of the Marraat area showing locations of drill site and oil-impregnation. Map based on Henderson (1975) and Christiansen (1994).

Marraat -1 core (GGU 408001)

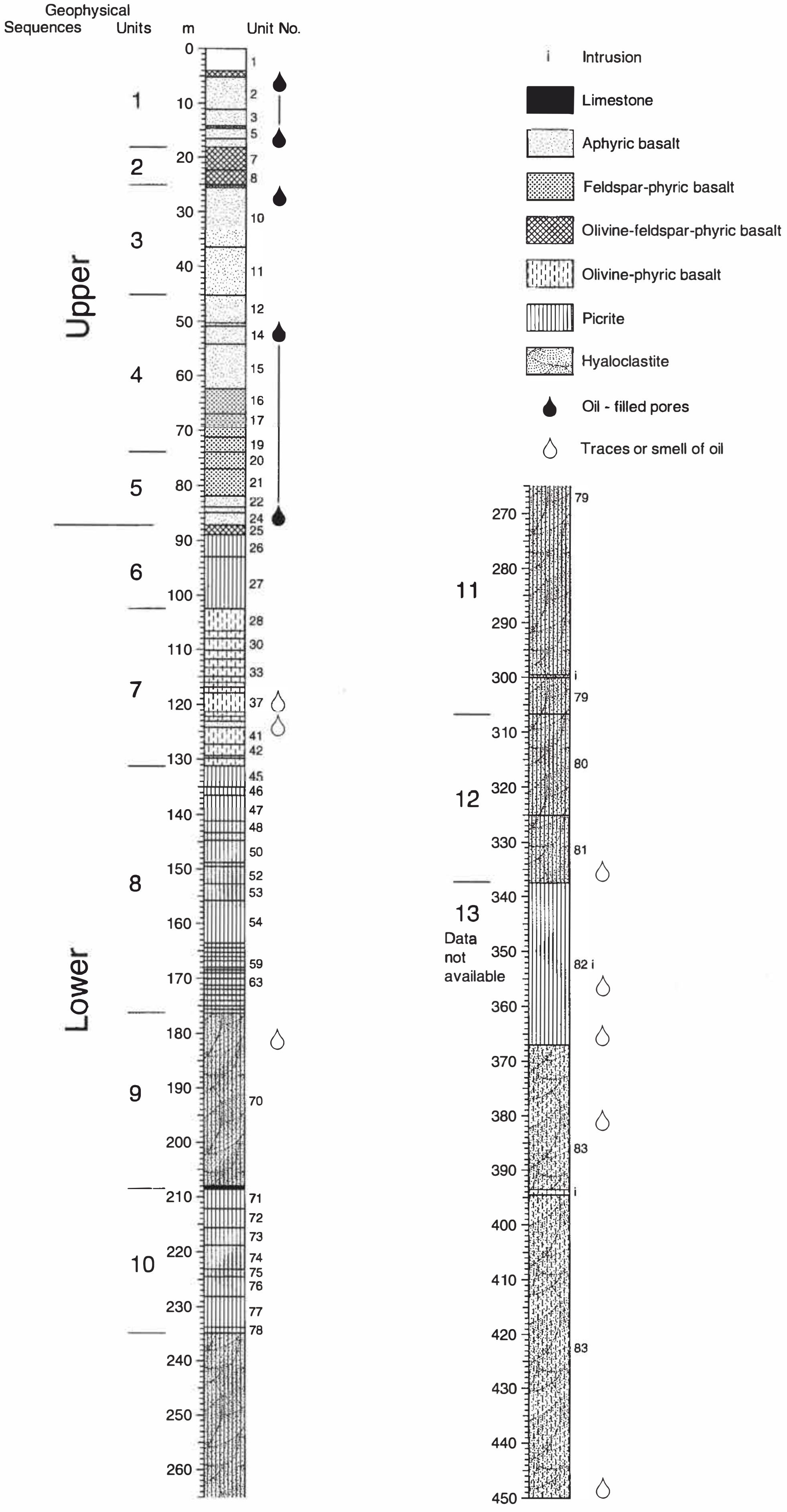

Fig. 2. Simplified stratigraphic and geophysical log of the Marraat- 1 core, based on Larsen & Pedersen (unpubl. data), and a geophysical formation evaluation of the borehole.

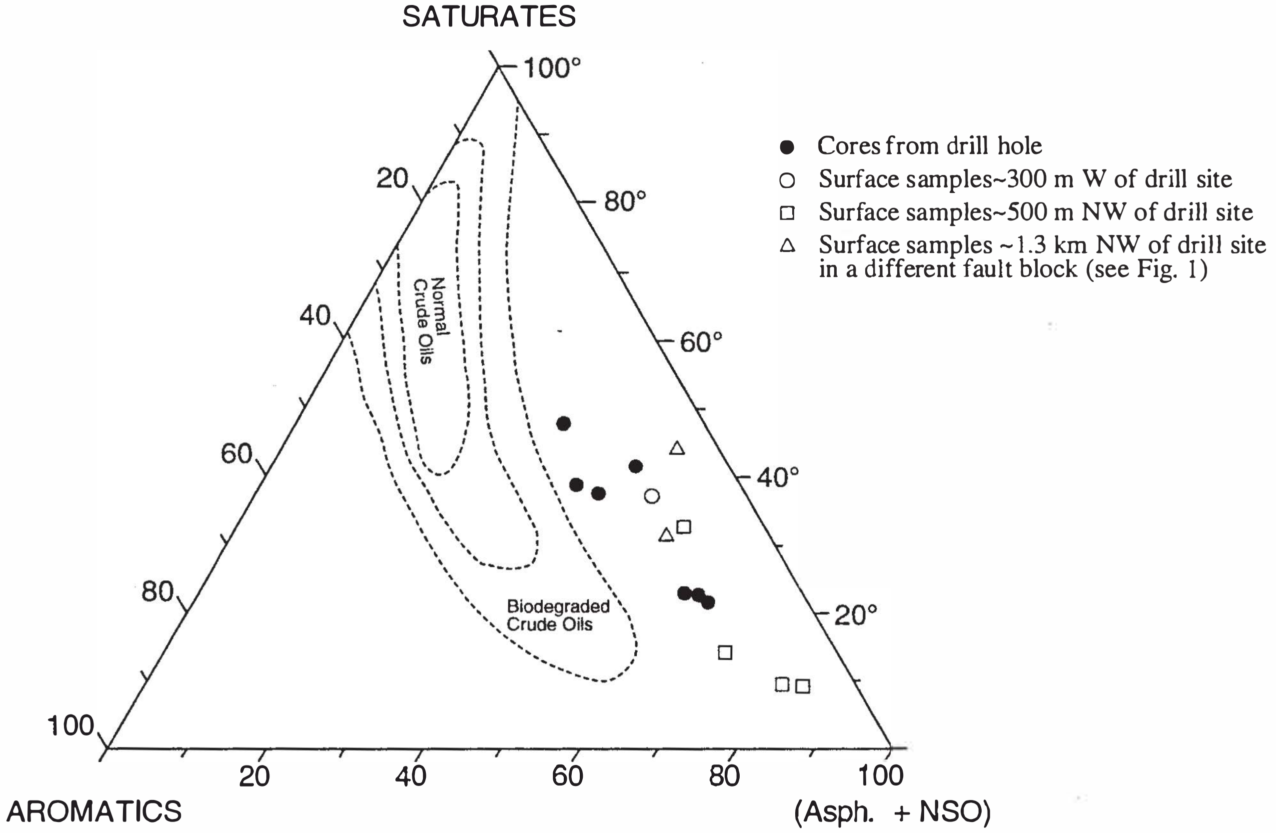

Fig. 3. Triangular diagram showing relative extract composition of saturated hydrocarbons (%), aromatic hydrocarbons (%) and NSO compounds + asphaltenes (%). The classification is adapted from Tissot & Welte (1984).

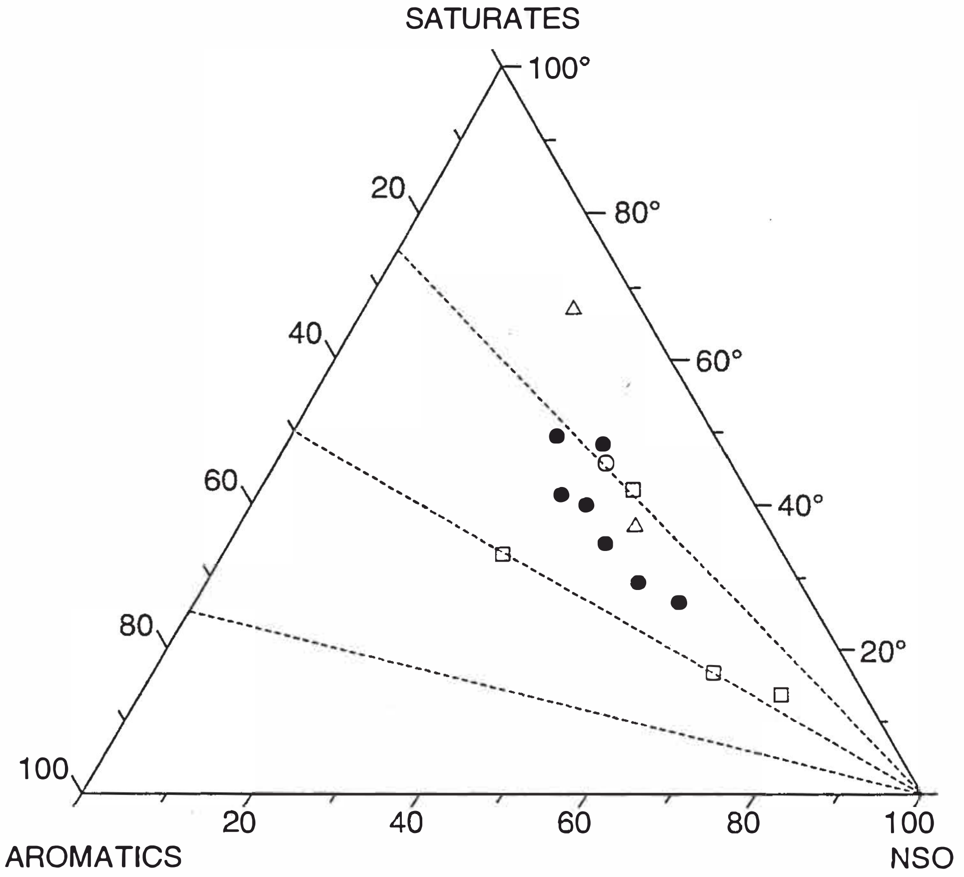

Fig. 4. Triangular diagram showing relative composition of asphaltene-free extracts; saturated hydrocarbons (%), aromatic hydrocarbons (%) and NSO compounds (%). Signatures like Fig. 3.

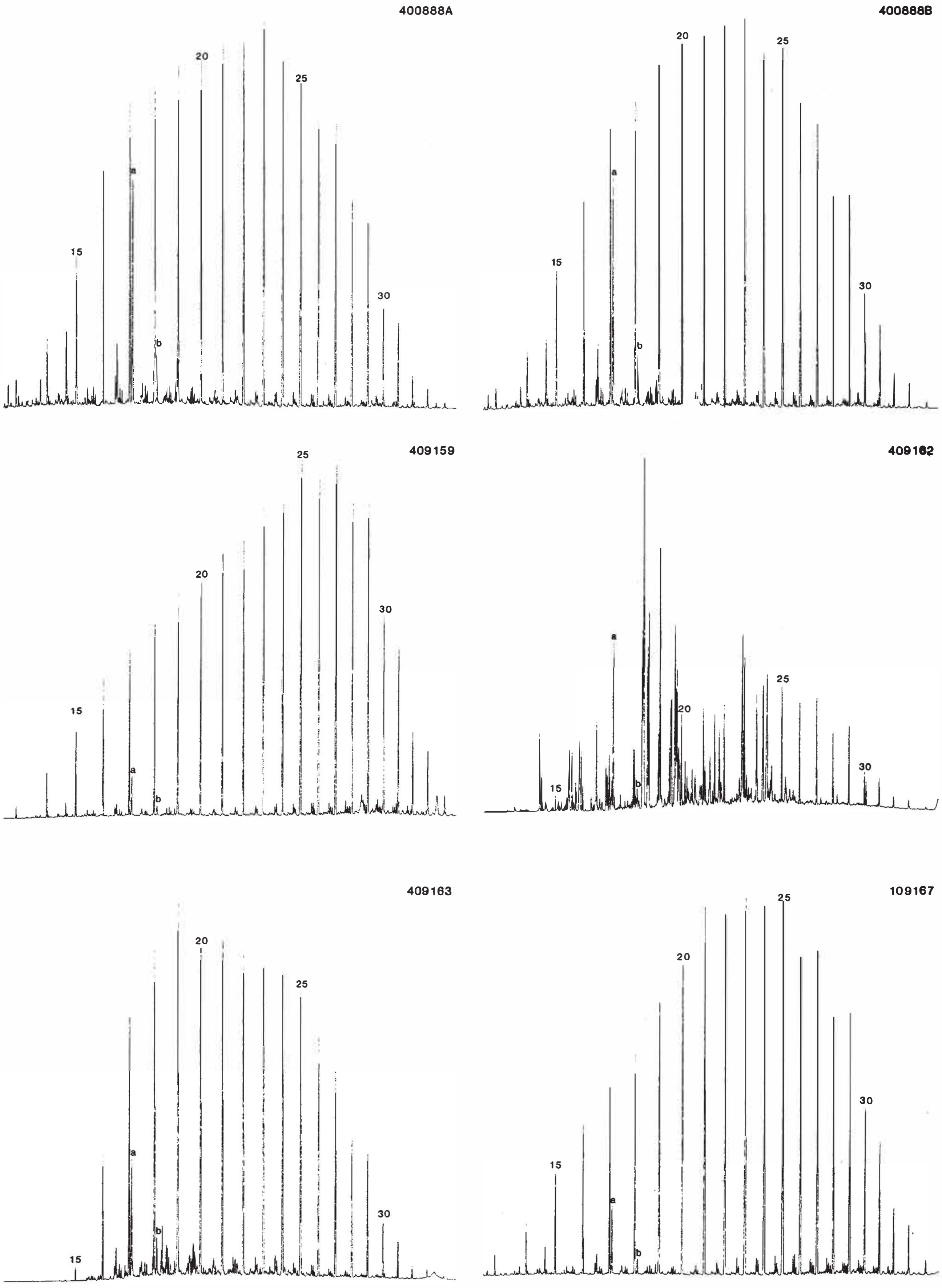

Fig. 5. Gas chromatograms of saturated hydrocarbons from all samples analysed. a: pristane, b: phytane, the numbers are *n*-alkane carbon numbers.

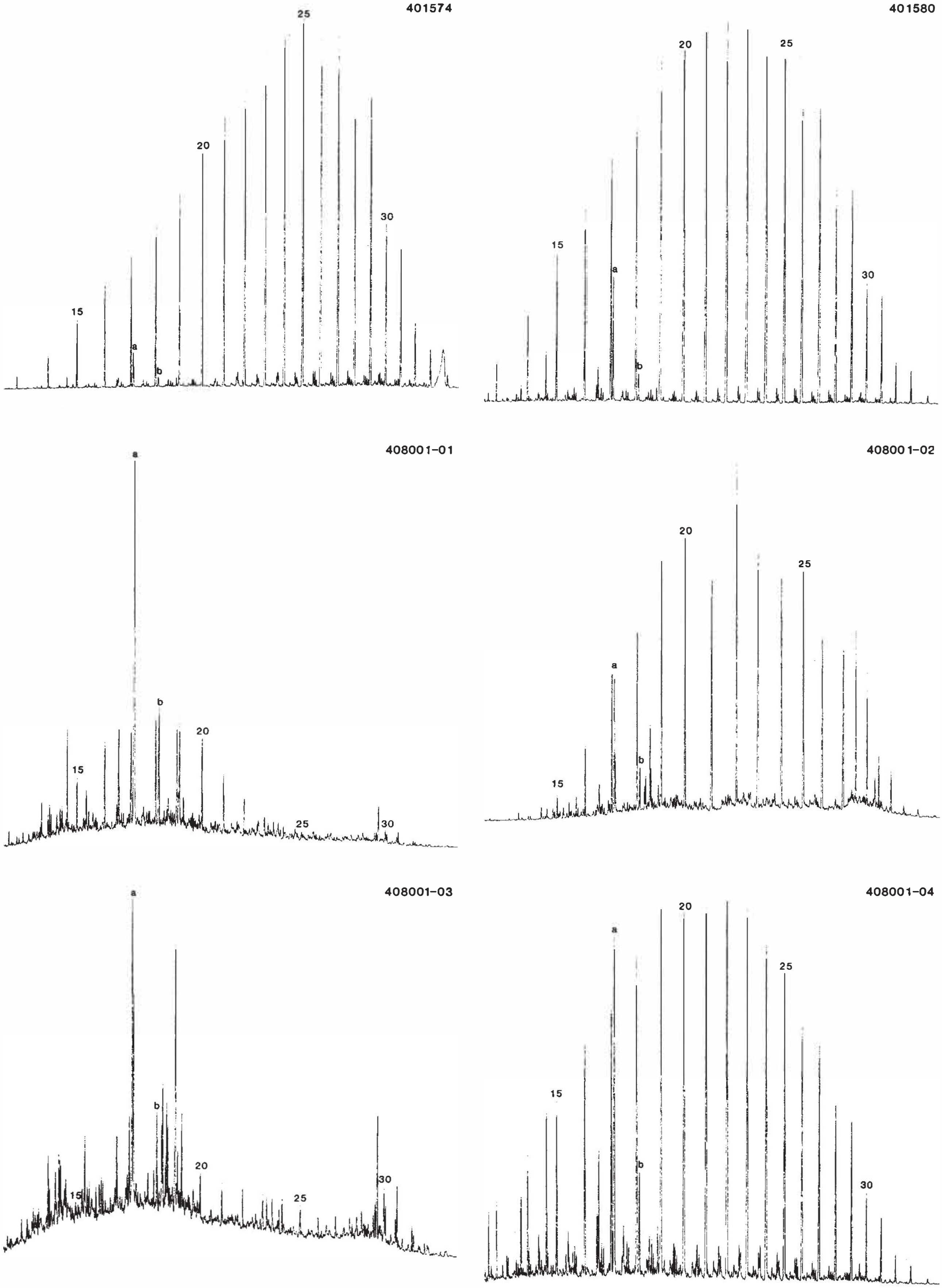

Fig. 5. continued.

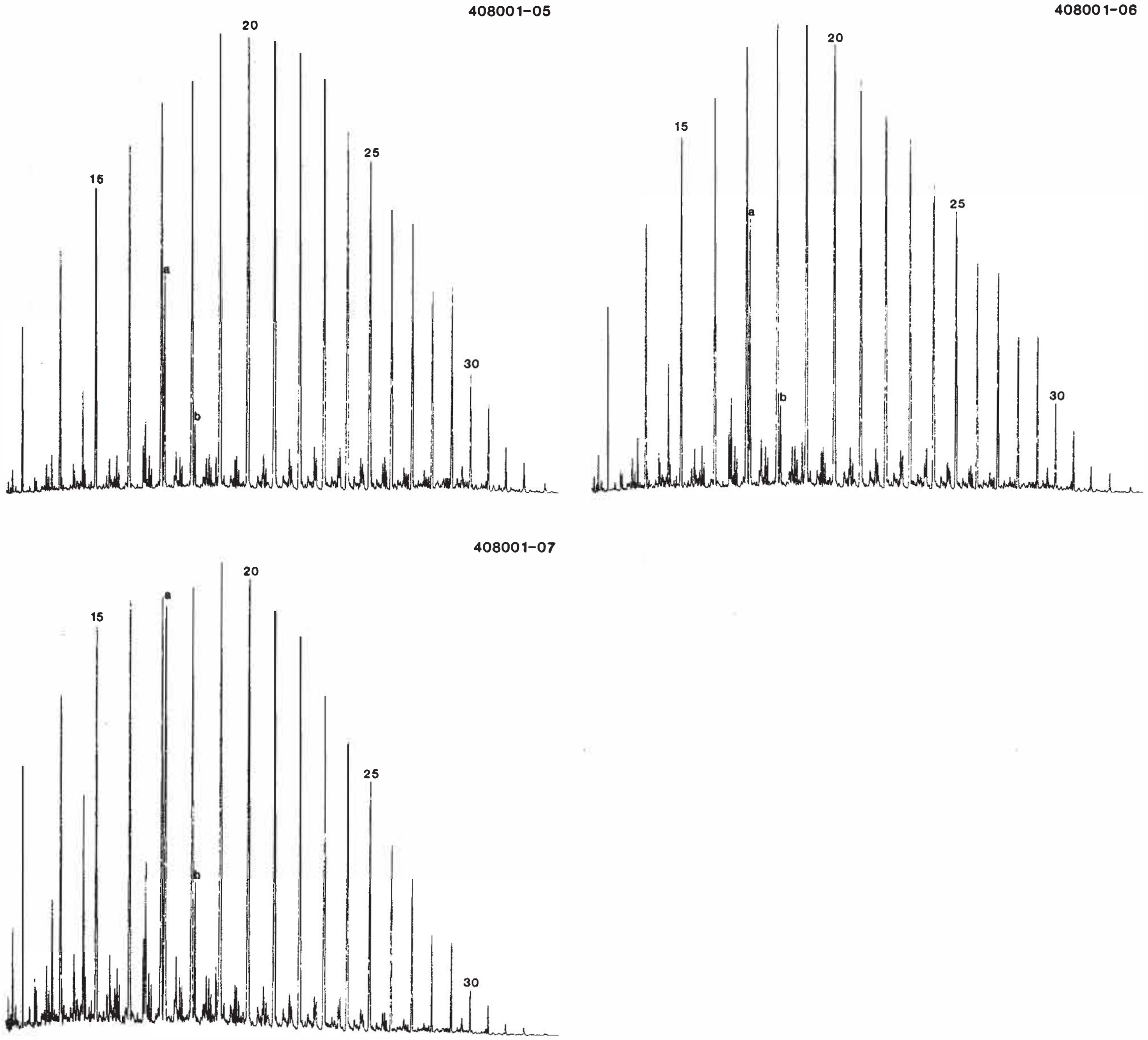

Fig. 5. continued.

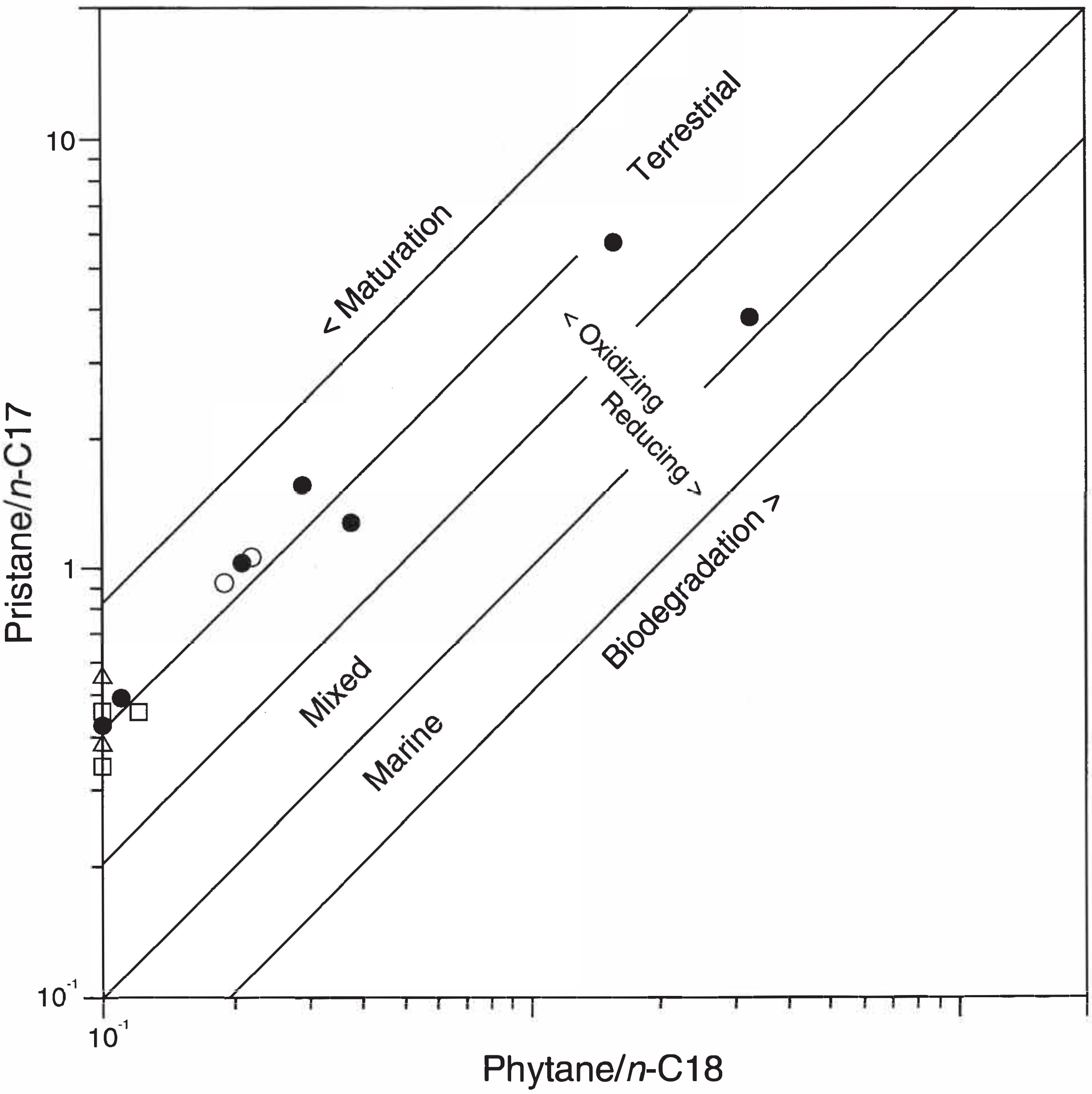

Fig. 6. Plot of Pr/*n*-C17 versus Ph/*n*-C18.

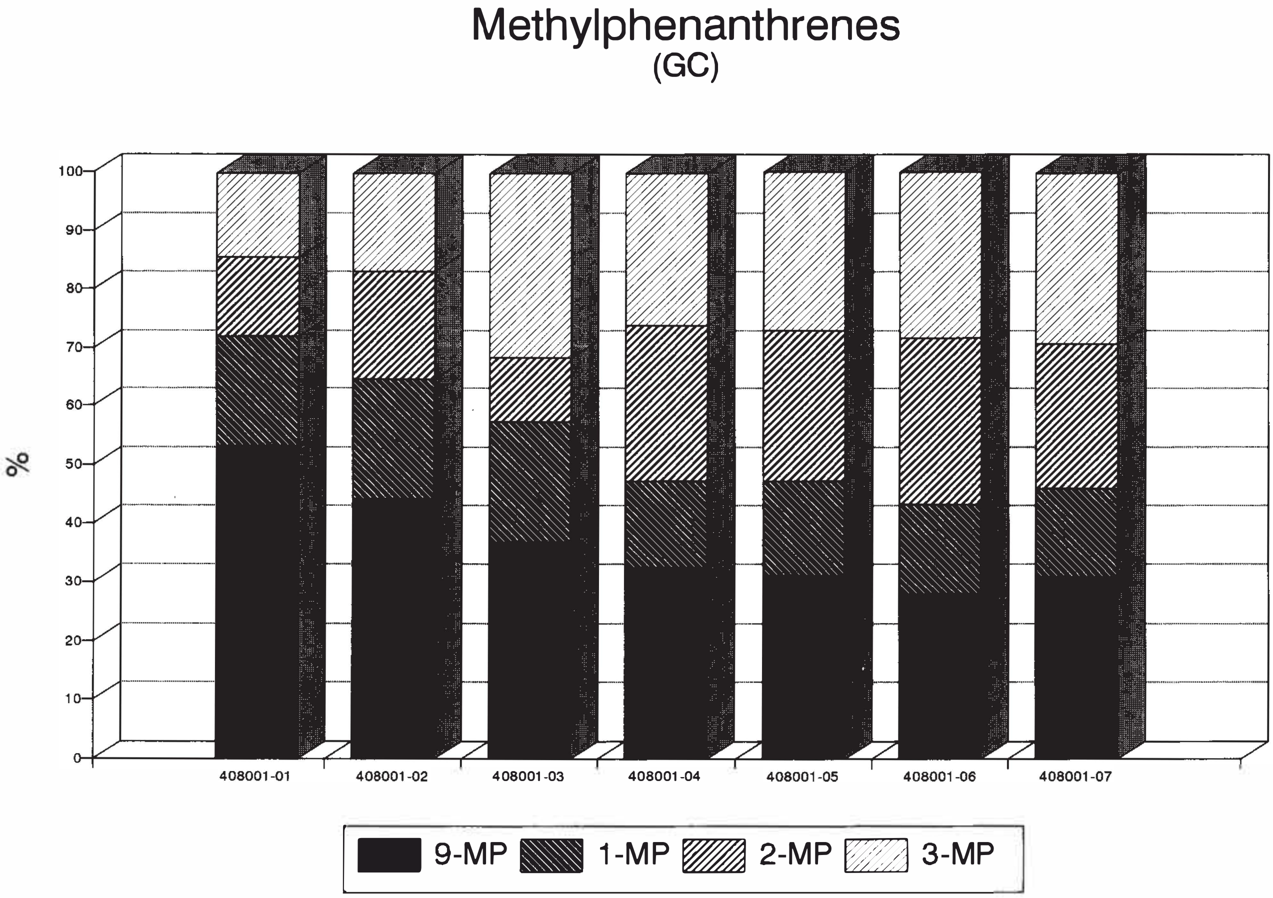

Fig. 7. Normalised distribution of methylphenanthrenes from the Marraat-1 core.

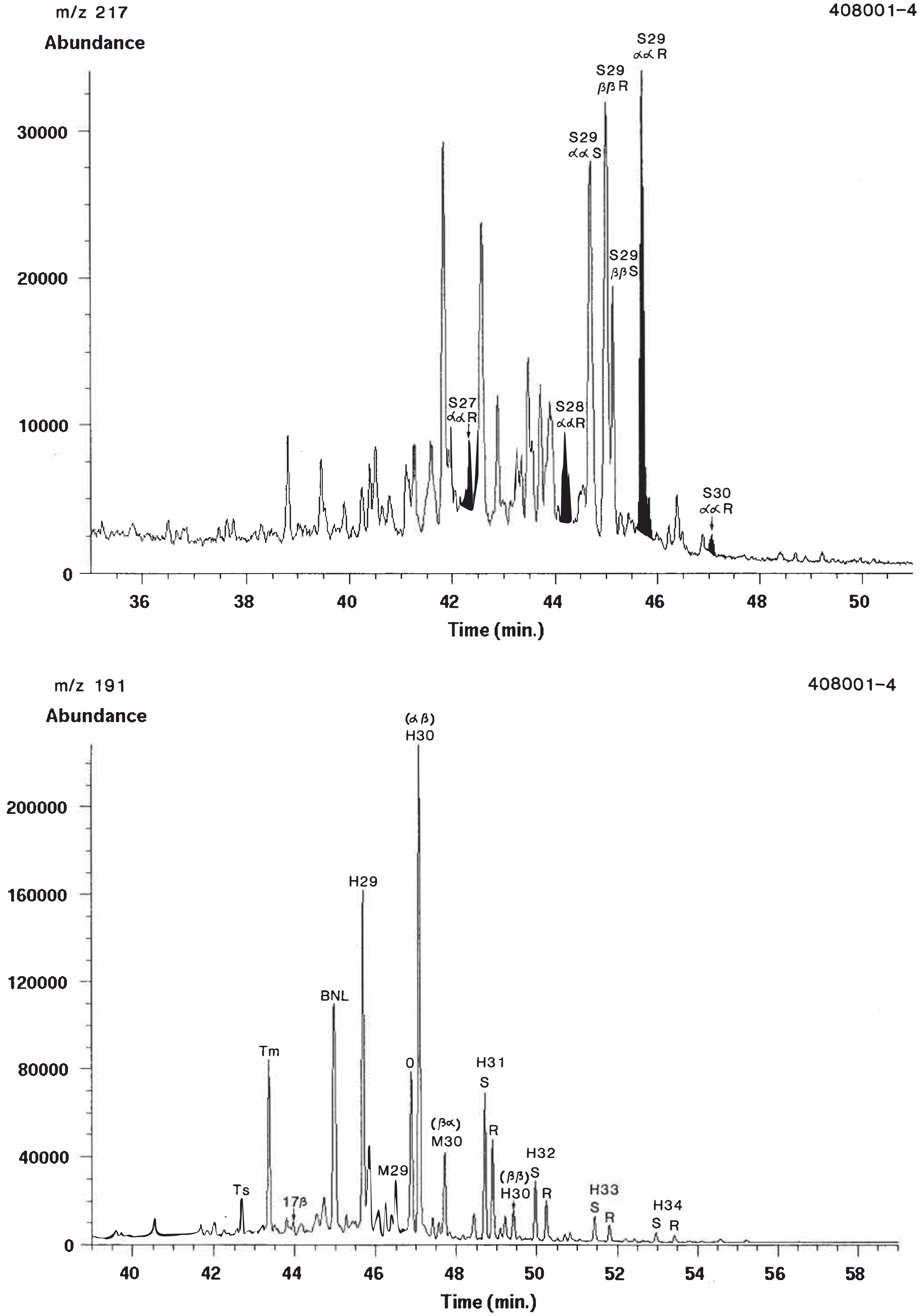

Fig. 8. Selected mass chromatograms of the terpanes (m/z 191) and steranes (m/z 217) from sample GGU 408001-04 (all other samples are very similar, see Tables 3 and 4. The compound assignment is explained in Table 6.

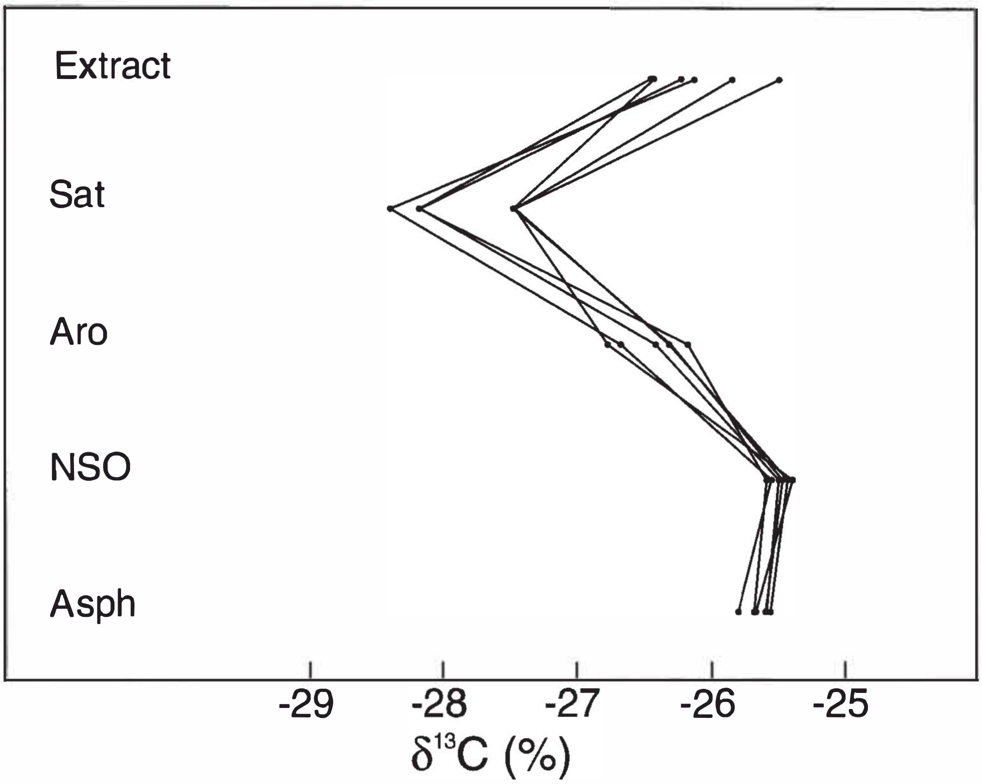

Fig. 9. Galimov-curves showing the isotope composition of total extract, saturated hydrocarbons, aromatic hydrocarbons, NSO compounds and asphaltenes for six core samples (408001-01, -03, -04, -05, -06, -07), see data in Table 5.

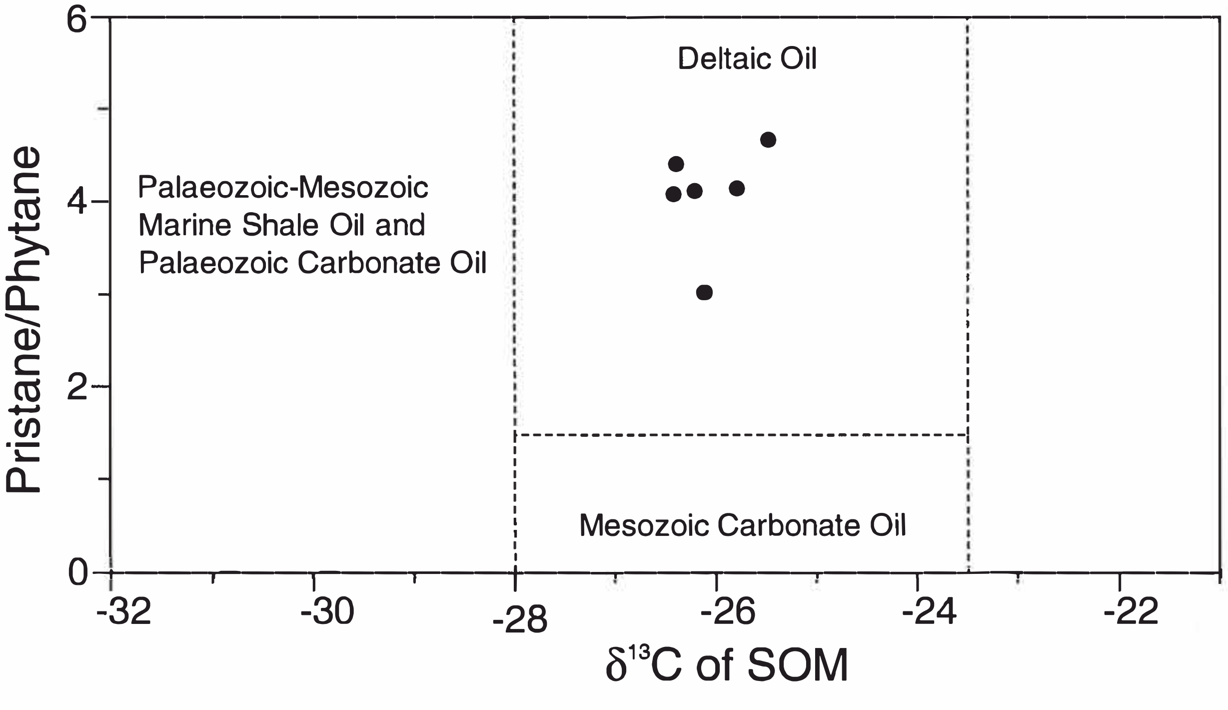

Fig. 10. Plot of C-isotope composition of total extract versus Pr/Ph with classification from Chung *et al.*(1992), see data in Table 5.

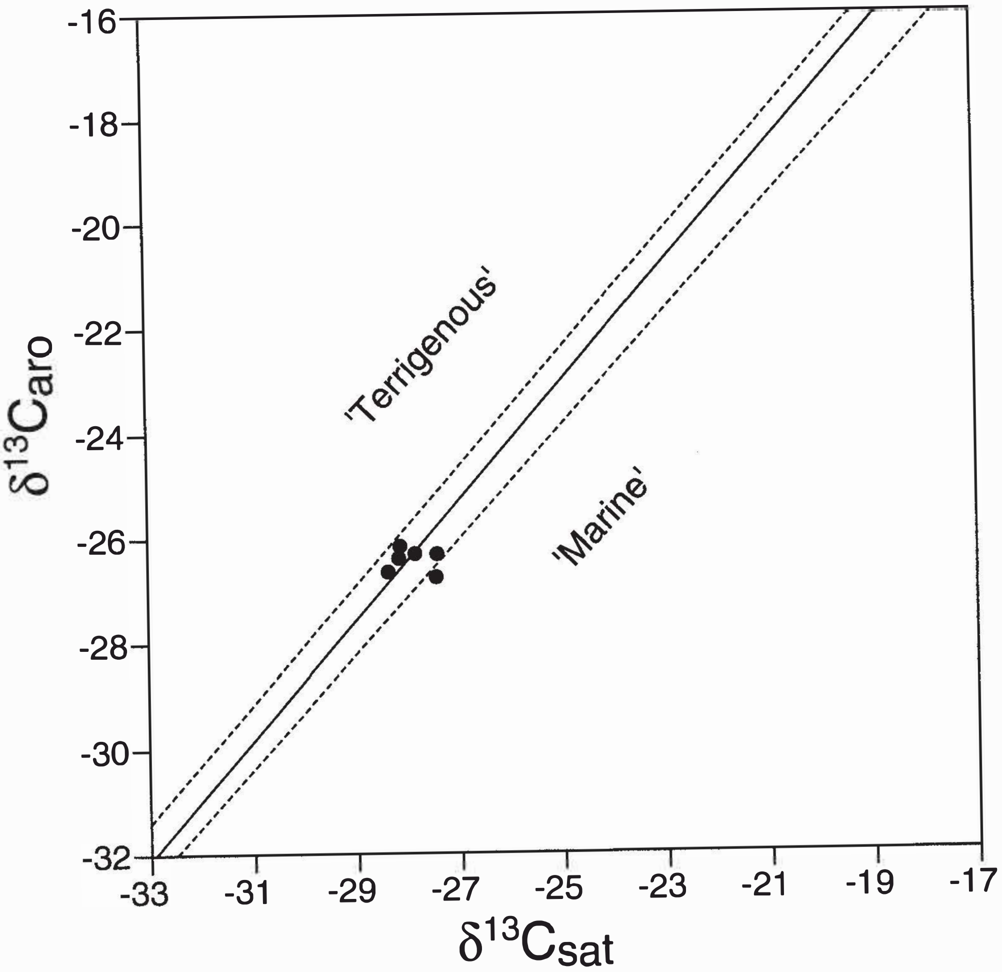

Fig.11. Plot of C-isotope composition of saturated hydrocarbons versus aromatic hydrocarbons with classification from Sofer (1984), see data in Table 5.

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